

Microwave synthesis of LiCoO₂ cathode materials

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Abstract

LiCoO₂ is synthesized by microwave heating. It has high capacity and good cycleability. The advantages of microwave synthesis are: (i) the calcination process is very fast; (ii) the synthesized powders have small and uniform grains; (iv) the synthesis temperature can be lower, and (iv) the lithium oxide loss is smaller. © 1997 Elsevier Science S.A.

Keywords: Cathode materials; Microwave synthesis; Lithium

1. Introduction

In the past few years, there has been a growing interest in heating and sintering of ceramics by microwave energy. It was applied widely to produce superconductors, ferro-electric ceramics, carbides, nitrides, etc. [1–4], because of its great flexibility for thermal treatment which influences the microstructure of the materials. Microwave heating has the potential for overcoming problems encountered in conventional processes. Since the energy is absorbed directly by the bulk of the heated object, rather than being conducted from the outside, uniform and rapid heating can be achieved within a short time and at a temperature lower or much lower than normally required. When the heating rate is high, materials will pass through the lower-temperature regime where surface diffusion is more rapidly, and the small-grained microstructure occurs at high temperatures when grain boundary and lattice diffusion predominate over surface diffusion [5]. The time available for grain growth is substantially shortened in this process, and a uniform, fine and dense microstructure can, therefore, be achieved by using microwave energy sintering. Moreover, energy consumption and processing time are reduced significantly.

LiCoO₂ is currently used as a cathode material in commercial high-energy density lithium-ion batteries. In addition, it is also a promising cathode material in molten carbonate fuel cells [6,7]. It is a compound with a layered rock-salt structure in which the Li⁺ and Co³⁺ ions are situated in alternate planes (111) of the cubic rock-salt structure. This (111) ordering introduces a slight distortion of the lattice to

hexagonal symmetry (space group is $R\bar{3}m$) with cell constants $a=2.816 \text{ \AA}$ and $c=14.08 \text{ \AA}$ [8]. LiCoO₂ electrode materials are usually synthesized by prolonged heating of lithium and cobalt oxides, or their carbonates or nitrates, both at high temperatures (800–900 °C) and at low temperature (400 °C) [9,10]. However, there is no report yet on the fast synthesis of LiCoO₂.

The objective of this work is to investigate the effect of microwave energy synthesis on the structure and electrochemical properties of LiCoO₂. This paper reports the results of X-ray diffraction, scanning electron microscopy (SEM), and electrochemical discharge of LiCoO₂ synthesized by microwave energy.

2. Experimental

LiCH₃COO·2H₂O and Co(CH₃COO)₂·4H₂O were used as the starting materials and the starting Li:Co atomic ratio was 1:1. They were dissolved in de-ionized water and milled at 60 °C for 24 h. After drying at 120 °C for 24 h, the powder was calcined at 400 °C for 5 h to burn out the organic substances. Then pellets were pressed and submitted to microwave calcination.

The microwave calcination was conducted in air with a 2.45 GHz microwave setup shown in Fig. 1. The pellets were placed in mullite refractories, heated at temperatures ranging from 600 to 900 °C for 10 min. A single-mode microwave heating device was used in this experiment. The magnetron and associated control system can generate a maximum of 1 kW microwave power continuously. The temperature was

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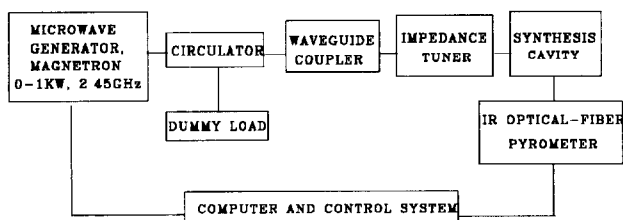


Fig. 1. Schematic diagram of microwave synthesizing system.

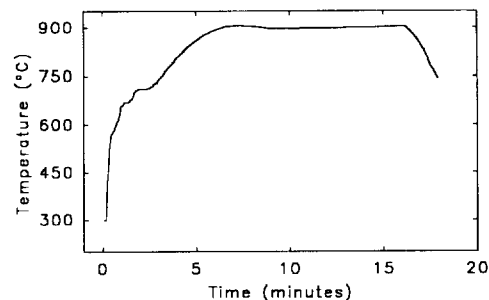


Fig. 2. Temperature profile of microwave heating of LiCoO_2 .

measured with an infrared optical-fiber pyrometer connected to a computer.

X-ray diffraction data were obtained from a Rigaku DIMAX-YB powder diffractometer with $\text{Co K}\alpha$ radiation. The microstructure of the powders was observed using SEM. Lithium and cobalt concentrations in the LiCoO_2 samples were determined by atomic absorption spectroscopy.

The electrochemical characteristics of the samples were studied using a two-electrode electrochemical cell. The working electrode consisted of 10–20 mg of LiCoO_2 (80 wt.% by mass) with acetylene black (15 wt.%) and Teflon (5 wt.%). Pure-lithium foil is used as the counter electrode. The electrolyte used was 1 M LiPF_6 in 1:1 EC/DEC solution. The measurements of electrochemical capacity were carried out with an automatic charge/discharge instrument. Cells were charged and discharged at constant current (0.8 mA/cm^2).

3. Results and discussion

The results of microwave heating show that cobalt oxide and LiCoO_2 can absorb and couple with microwave radiation efficiently. Fig. 2 shows the temperature profile of the calcination of LiCoO_2 . The heating starts with a sharp increase in temperature at the beginning due to the absorption of microwaves by the cobalt oxide and LiCoO_2 . It costs only 3–5 min to reach the synthesis temperature from room temperature. Thus, the use of microwave energy for calcination has a great advantage in terms of time and energy saving. Moreover, by calcining in a short time using microwave energy, LiCoO_2 powders with fine and fairly uniform grains can be obtained,

as can be seen from the SEM micrograph (Fig. 3). The grain size is about 0.1–0.5 μm , which is 1/10 of that of LiCoO_2 made by conventional sintering, and particle coarsening is partly avoided, so the powder can be used as prepared without further milling.

Fig. 4 shows the X-ray diffraction patterns of the powder before (400°C), and after microwave heating for 10 min at 600, 700, 800, 850, and 900°C , respectively. Before microwave calcination, the sample consists of cobalt oxide and LiCoO_2 . But after microwave heating at 600 to 900°C , only LiCoO_2 is observed. It indicates that LiCoO_2 can be synthesized fast at lower temperatures by microwave energy. Comparing the X-ray diffraction peak of various samples, it can be seen that the diffraction lines are narrowing and the peak intensity increases with increasing synthesizing temperature, thus at higher temperatures it seems that a more perfect LiCoO_2 phase can be obtained. Table 1 lists the X-ray patterns of LiCoO_2 synthesized at 800°C by microwave energy ($a = 2.8159 \text{ \AA}$, $c = 14.0519 \text{ \AA}$). They are in very good agreement with those obtained from a conventionally calcined powder.

Another obvious feature observed from the experiment is that the lithium loss due to lithium oxide evaporation declines greatly in the case of microwave calcination. In the conventional calcination ($800\text{--}900^\circ\text{C}$, 5–30 h), the lithium loss is usually observed to be 20–30%. But according to the results of lithium and cobalt concentrations in microwave synthesized LiCoO_2 , Li:Co atomic ratios vary from the starting ratio 1:1 to 0.96:1 after being synthesized at 800°C by microwave

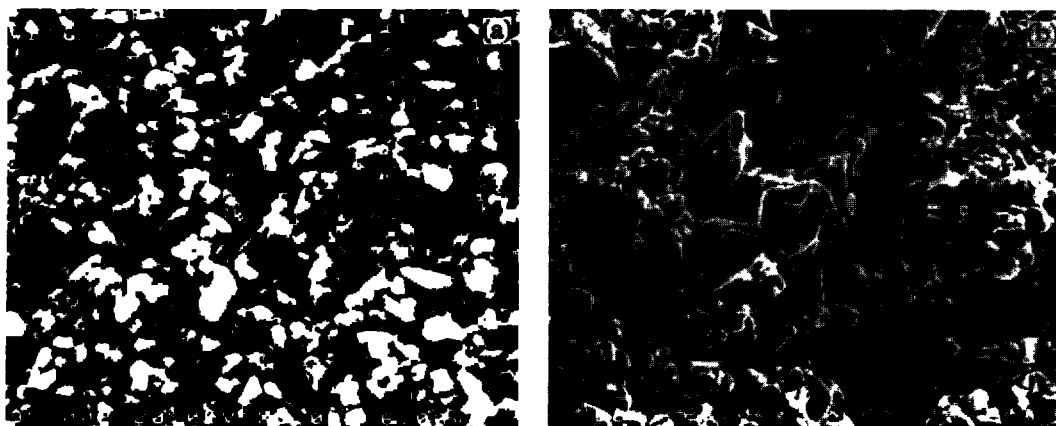


Fig. 3. Microstructure for LiCoO_2 synthesized by (a) microwave energy at 800°C for 10 min, (b) conventional solid reaction at 800°C for 5 h.

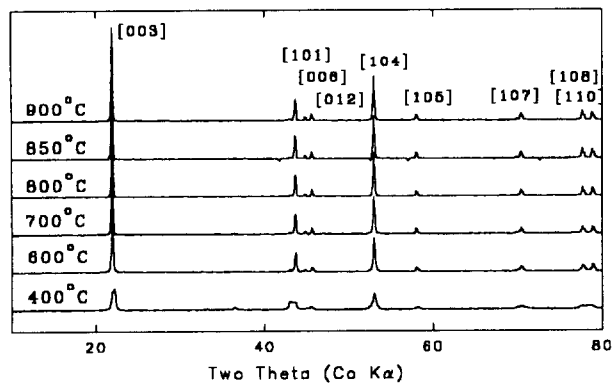


Fig. 4. X-ray diffraction patterns of LiCoO₂ precursor (400 °C precalcined), and after microwave heating for 10 min at 600, 700, 800, 850, and 900 °C.

Table 1

X-ray diffraction patterns of LiCoO₂ synthesized at 800 °C by microwave energy

<i>hkl</i>	<i>d_{calc}</i>	<i>d_{obs}</i>	<i>d</i> (JCPDS No. 160427)
0 0 3	4.68397	4.6915	4.68
1 0 1	2.40269	2.4038	2.401
0 0 6	2.34198	2.3434	2.346
0 1 2	2.30378	2.3053	2.302
1 0 4	2.00325	2.0036	2.001
0 1 5	1.84187	1.8420	1.841
0 0 9	1.56132	1.5614	
1 0 7	1.54985	1.5499	1.549
0 1 8	1.42526	1.4254	1.424
1 1 0	1.40793	1.4079	1.407
1 1 3	1.34833	1.3483	1.348
1 0 10	1.21752	1.2177	1.215
0 2 1	1.21474	1.2148	1.213
1 1 6	1.20666	1.2066	1.206
2 0 2	1.20134	1.2016	
0 0 12	1.17099	1.1708	1.169
0 2 4	1.15189	1.1518	1.151
0 1 11	1.13159	1.1316	1.130
2 0 5	1.11856	1.1184	1.118
1 1 9	1.04559	1.0454	1.045
0 2 7	1.04212	1.0421	1.041
2 0 8	1.00163	1.0016	1.001

energy, i.e. the lithium loss is only 4% during the microwave calcination. That value is much lower than that in the conventional calcination process. Therefore, the lithium concentration in LiCoO₂ can be easily controlled by microwave synthesis.

The lithium de-intercalation and intercalation behaviour of microwave synthesized LiCoO₂ were studied. As can be seen from Fig. 5, the precursor precalcined at 400 °C, displays two charge and discharge plateaus and the discharge capacity is only 60 mAh/g. Through microwave calcination, the capacity of LiCoO₂ increases greatly and reaches a maximum of 140 mAh/g when the synthesizing temperature is 800 °C. The voltage profiles are quite monotonous. The microwave

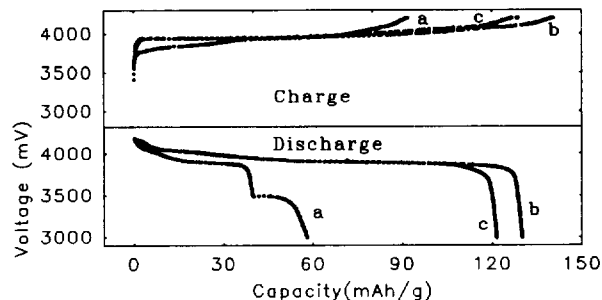


Fig. 5. Charge and discharge curves of Li/LiCoO₂ synthesized by microwave heating at different temperatures: (a) the precursor precalcined at 400 °C, (b) LiCoO₂ calcined at 800 °C, and (c) LiCoO₂ calcined at 900 °C

synthesized LiCoO₂ has a good cycleability. After 40 cycles, the capacity is still greater than 130 mAh/g, which is a rather good result for an Li/LiCoO₂ cell.

4. Conclusions

Pure and single-phase LiCoO₂ with fine and uniform grains can be synthesized fast by microwave calcination, and the lithium concentration can be controlled accurately. The obtained LiCoO₂ materials has high electrochemical capacity and good cycleability. All the results indicate that the microwave synthesis is a promising method for preparing LiCoO₂ cathode materials.

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