

Structural and electrochemical characteristics of LiCoO₂ powders prepared by mechanical alloying

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Owing to the high synthesizing temperature (above 800°C), the LiCoO₂ (so-called HT-LiCoO₂) powder for lithium ion battery has some disadvantages such as broader particle size distribution, longer reaction time and higher processing cost [1-2]. To overcome these disadvantages, there have been many researches on the method of synthesizing HT-LiCoO₂. Recently, the mechanical alloying, which also referred to as high energy ball milling, reactive milling, mechanochemical synthesis etc., has also been recommended for a useful technique to synthesize transition metal oxides for lithium ion battery [3-4].

In our previous work [5], we also showed that well-ordered HT-LiCoO₂ could be synthesized by mechanical alloying of hydroxides (LiOH·H₂O and Co(OH)₂) and subsequent firing at relatively low temperature and times. In this work, details of structural characteristics and electrochemical performances of LiCoO₂ powders prepared by mechanical alloying were discussed.

The LiCoO₂ precursors were synthesized by optimized mechanical alloying conditions using a shaker type ball miller (SPEX 8000D) from starting materials of LiOH·H₂O and Co(OH)₂ powders. SEM, BET, XRD, Rietveld method were used to analyze the morphology and crystalline structure of ball milled precursors and/or subsequent fired powders. The electrochemical performances were evaluated using two-electrode cells with lithium metal foil as a negative electrode. The electrolyte was 1M LiPF₆ in a 1:1 mixture of ethylene carbonate and dimethyl carbonate (EC/DMC). The electrochemical cycle tests were performed between 3.0 and 4.2V at ambient temperature (26±2°C) using an automatic galvanostatic charge-discharge unit (Maccor series 4000) at various constant current, C/x (x=2, 5, 10, 40). To investigate the chemical diffusivity and kinetics of Li transportation, galvanostatic intermittent titration technique (GITT) and cyclic voltammetry (CV) experiments were performed using three-electrode cells.

Fig.1 shows the phase evolution of the mechanically alloyed precursors upon firing temperature. With increasing temperature, only the crystallinity of the single phase LiCoO₂ was increased and well ordered HT-LiCoO₂ phase could be obtained at 600°C only for 2h. Fig.2 shows typical charge-discharge curves for a mechanically alloyed and fired LiCoO₂ cycled at a constant current density of C/10 rate. The LiCoO₂ prepared by mechanical alloying showed the maximum discharge capacity of 152 mAh/g (at C/40 rate) and no phase transition from hexagonal to monoclinic during cycling. Details of structural and electrochemical characteristics will be presented and discussed.

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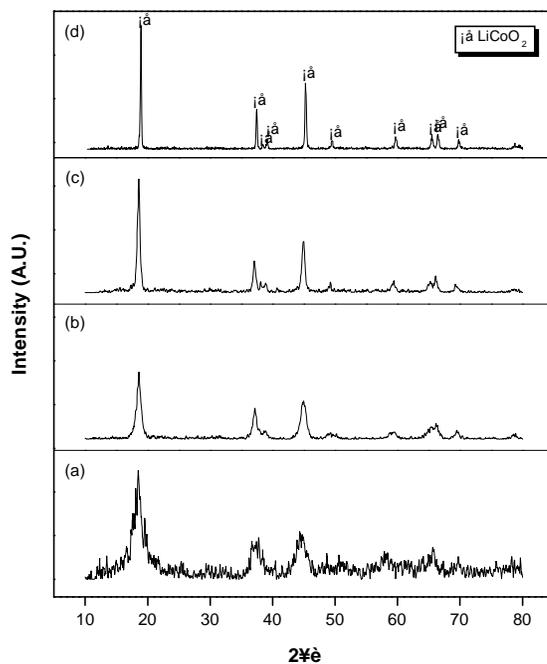
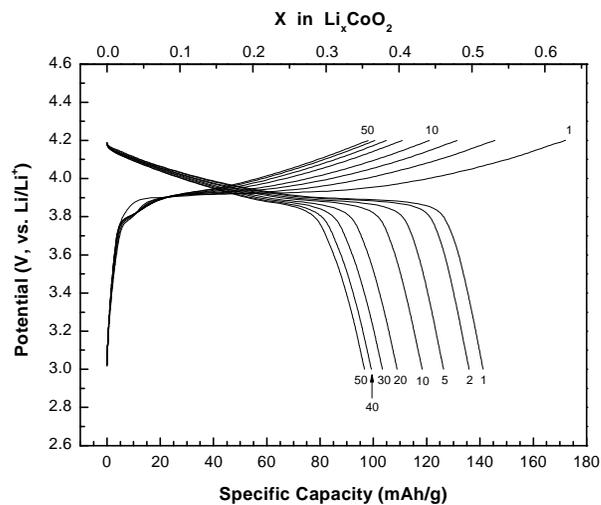


Fig.1 XRD patterns of mechanically alloyed precursors after firing at various temperatures for 2 h in air.



(a) As ball milled (b) 300°C (c) 450°C (d) 600°C

Fig.2 Charge-discharge curves for mechanically alloyed and fired LiCoO₂ cycled between 3.0 and 4.2V at a C/10 rate (27.4 mA/g).