CORRELATION BETWEEN STRUCTURE AND ELECTROCHEMICAL PROPERTIES OF LiCoO₂ ELECTRODES

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Abstract

LiCoO₂ powders were prepared by the Pechini process and characterized by X ray diffraction. Cyclic voltammograms of the composite electrodes showed a reversible redox process at 4.0V/3.85V and an irreversible redox process at 3.3V that disappears after thermal treatment at 500°C. The Rietveld method was used for the structural refinement of the LiCoO₂ powders obtained at different temperatures. The results showed the co-existence of the cubic LiCoO₂ (spinel) and rhombohedral LiCoO₂ (layered) structures when the material was obtained at 400°C and also showed that only the rhombohedral structure was obtained for LiCoO₂ after post thermal treatment at 600°C. The maximum energy capacity in the first discharge was 131 mAg⁻¹ for a composite electrode prepared with LiCoO₂ obtained after thermal treatment at 700°C.

Introduction

Lithium transition metal oxides, such as LiCoO₂, LiNiO₂ and LiMn₂O₄ have been extensively studied as cathode of the secondary lithium batteries due to their high output voltage and high specific energy [1].

LiCoO₂ can be classified in two types: LT-LiCoO₂ (low-temperature LiCoO₂) and HT-LiCoO₂ (high-temperature LiCoO₂). HT-LiCoO₂ has a layered-type (rhombohedral) structure with R3m symmetry. The lithium and the metal ions occupy alternate layers in octahedral sites between the cubic-close-packed oxygen planes [2]. On the other hand, the LT- LiCoO₂ is related
to a spinel-type structure (cubic structure) with Fd3m symmetry. Gummov et al. showed that LT-
LiCoO₂ has a structure similar to HT- LiCoO₂ with 6% of the cobalt ions in the lithium layer
using neutron diffraction data [2,3].

LiCoO₂ is known due to its preparation easiness when compared with other oxides. The
most used route is the solid-state reaction, however, a high temperature and a high heat treatment
time are necessary to prepare LiCoO₂ (900°C for 48h) [4]. Other methods such as sol-gel [5,6] ,
complex formation reaction [7], spray-drying synthesis [8], hydrothermal condition [9] and
mechanochemical synthesis have been used to synthesize LiCoO₂ [10].

The purpose of this paper is to synthesize LiCoO₂ by the Pechini method and analyze the
correlation between the oxide structure and the electrochemical response.

**Experimental**

The LiCoO₂ was prepared using the Pechini method by heating ethylene glycol to 60°C
with stirring and then adding to it the Co(NO₃)₂. Finally citric acid was added and the
temperature increased to 110°C. The resulting resin was thermally treated at 400°C, 500°C,
600°C and 700°C for 12 h and analyzed by X ray diffraction (XRD). Structural refinements were
performed by the Rietveld method. Composite electrodes were prepared with LiCoO₂ powders,
poly-vinylidene fluoride (PVDF) binder (Aldrich) and carbon black (Union Carbide) in the
85:5:10 %w/w ratio using dimethylformamide (DMF) (Merck) as solvent. This homogeneous
mixture was painted on platinum plates (1×0.5cm) and dried at 120°C for 24h in vacuum.

For the electrochemical cell, two lithium plates (2.0×1.0cm) were used as reference and
counter electrodes. The electrolytic solution was composed of ethylene carbonate (Carlo Erba)
and dimethylcarbonate (Aldrich) (1:1 v/v) and anhydrous lithium perchlorate (Aldrich) as support
electrolyte.

**Results and discussion**

Gummov et al. suggested, using Rietveld refinement with X ray diffraction data, that the
LiCoO₂ synthesized at low temperature (LT- LiCoO₂) has a structure spinel-like [11].
The structural evolution for LiCoO₂ obtained at different temperatures was evaluated by the Rietveld method with X-ray diffraction data. The structure with spinel-like character was considered in the refinements.

For the LT- LiCoO₂ obtained with post heat treatment at 400°C it was observed a good agreement with the coexistence between rhombohedral (layered) and cubic (spinel) structures. The results of the structural refinement indicate the existence of 14% w/w for spinel-like LiCoO₂ and 84% w/w for layered structure. At temperatures higher than 600°C only the layered structure was determined.

The cyclic voltammograms for composite electrodes based on LiCoO₂ obtained at different temperature are shown in Figure 1. The cyclic voltammograms show a reversible redox process at 4.0V/3.85V. This process is associated with Li⁺ deinsertion/insertion, respectively. Less pronounced peaks are also observed at 4.1V/4.0V, what is related to order/disorder phase transitions [12]. An irreversible process at 3.3V is observed for LiCoO₂ at 400°C. This process could be related to the spinel structure of the LiCoO₂, that presents Li⁺ deficiency and leads to the irreversible Li⁺ insertion process.

Temperature is the main parameter in the formation of either spinel or layered structures. The different structures therefore obtained influence the electrochemical properties of this material.

The energy capacity obtained at the first discharge shows a low value for the LiCoO₂ obtained at 400°C. With the increase of the temperature, the energy capacity increases due to the favorable layered structure. The maximum value of the energy capacity at the first discharge was observed for the LiCoO₂ obtained at 700°C (131 mAhg⁻¹), a value which is similar to the one for LiCoO₂ obtained by the conventional solid state method (137mAg⁻¹).
Figure 1: Cyclic voltammograms for composite electrodes based on LiCoO₂. a) 400°C, b) 500°C, c) 600°C, and d) 700°C. Scan rate = 1mVs⁻¹.

Conclusions

LiCoO₂ powders were synthesized by the Pechini method. It was observed the coexistence of the spinel and layered structures for the LiCoO₂ obtained at lower temperatures (400°C and 500°C). Only the layered structure was observed for the LiCoO₂ obtained at higher temperatures (600°C and 700°C).
The cyclic voltammograms show a reversible process at 4.0V/3.85V for all composite electrodes and an irreversible process at 3.3V for LiCoO$_2$ obtained at lower temperatures, that could be associated to the irreversible Li$^+$ insertion in the spinel structure.

The maximum energy capacity at the first discharge was 131 mAhg$^{-1}$ which is comparable with the value for the LiCoO$_2$ obtained by the conventional solid state method.

References