

# Studies of electrochemical properties of lithium cobalt oxide

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## Abstract

The electrochemical characteristics of high-temperature (HT) LiCoO<sub>2</sub> (900 °C) and low-temperature (LT) LiCoO<sub>2</sub> (450 °C) were studied. From cyclic voltammetry results, lithium intercalating into LT-LiCoO<sub>2</sub> generates two current peaks at 3.8 and 3.3 V, respectively, which is contrast to the intercalation of lithium into HT-LiCoO<sub>2</sub>. The resistance of lithium extraction is smaller than that of lithium insertion. The diffusion coefficients of Li<sup>+</sup> ions in LiCoO<sub>2</sub> have an order of 10<sup>-9</sup> cm<sup>2</sup>/s.

**Keywords:** Lithium intercalation; Lithium; Cobalt oxide

## 1. Introduction

LiCoO<sub>2</sub> is a member of the series LiMO<sub>2</sub> (M=V, Co and Ni), which have been studied extensively for their possible use as insertion electrodes in lithium batteries [1,2]. LiCoO<sub>2</sub>, so far, is the only cathode material showing promising performances in commercial wound-type lithium-ion batteries. Low-temperature (LT) LiCoO<sub>2</sub> has been synthesized recently [2], and has a different structure from high-temperature HT-LiCoO<sub>2</sub>. In this paper, the electrochemical properties of LiCoO<sub>2</sub> synthesized at 900 and 450 °C have been studied with cyclic voltammetry and a.c. impedance techniques.

## 2. Experimental

HT-LiCoO<sub>2</sub> was prepared by heating a stoichiometric mixture of Li<sub>2</sub>CO<sub>3</sub> and CoCO<sub>3</sub> at 900 °C. Initially, the powders were thoroughly mixed in hexane and then dried at 120 °C. LT-LiCoO<sub>2</sub> was prepared by the same procedure, but heated at 450 °C. The electrochemical characteristics of LiCoO<sub>2</sub> were determined in a three-electrode electrochemical cell, in which fresh lithium functioned as reference and counter electrodes, respectively. Cyclic voltammetry and a.c. impedance experiments were carried out in 1 M LiClO<sub>4</sub> propylene carbonate–dimethyl carbonate (1:1) with potentiostat and frequency analyzer Solartron 1286/1260. Cells were

assembled in a dry box, and the water content in the electrolyte is less than 20 ppm.

## 3. Results and discussion

The cyclic voltammetry (CV) results of HT-LiCoO<sub>2</sub> at a scan rate of 0.5 mV/s are given in Fig. 1; it reveals that the lithium insertion and extraction reactions are both one-step processes. No peak current was observed during the lithium extraction process, but a broad peak was observed around 3.5–3.6 V during the lithium

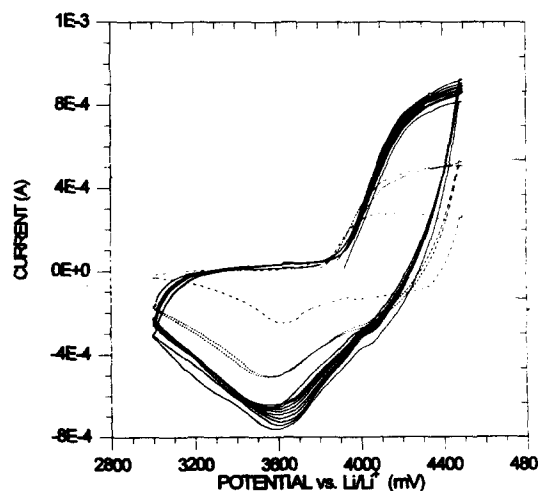


Fig. 1. Cyclic voltammetry of high-temperature at various scan rates: (—) 0.5 mV/s; (---) 0.3 mV/s, and (----) 0.1 mV/s.

insertion process. The cycling capacities per sweep can be obtained by integrating current with sweep time. Its cycling efficiencies are almost 100%, while the decay of the CV peak current is not fast. The CV peak current at various scan rates has been collected and shown in Fig. 2. The anodic and cathodic CV peak currents have a linear relationship with square root of scan rates, but the straight lines are not passing through the origin point. The anodic slope is larger than the cathode slope, which means that reaction resistance of lithium extraction is smaller than that of lithium insertion.

CV results of LT-LiCoO<sub>2</sub> at a scan rate of 0.5 mV/s are shown in Fig. 3; LT-LiCoO<sub>2</sub> has different electrochemical characteristics from HT-LiCoO<sub>2</sub>. The CV current peaks of LT-LiCoO<sub>2</sub> are sharp for both anodic and cathodic processes. There are two peaks observed during the lithium insertion process, and one peak

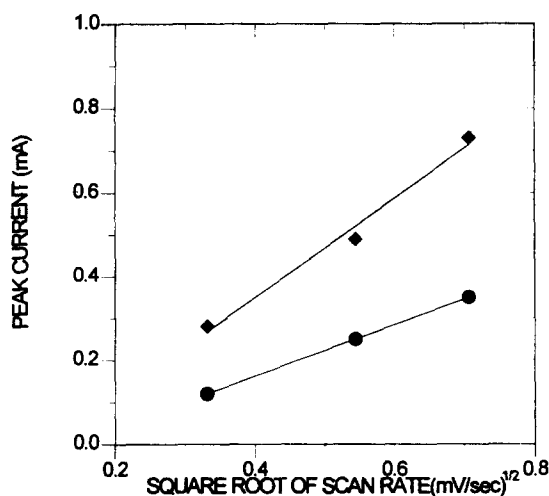


Fig. 2. (♦) Anodic and (●) cathodic cyclic voltammetry peak current of high-temperature LiCoO<sub>2</sub>.

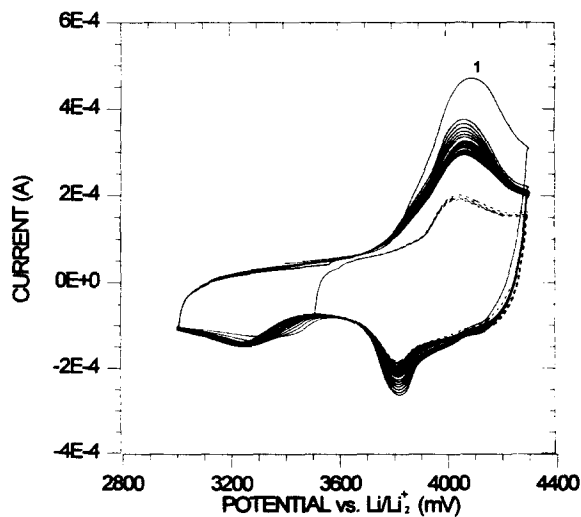


Fig. 3. Cyclic voltammetry of low-temperature LiCoO<sub>2</sub> at a scan rate of 0.5 mV/s.

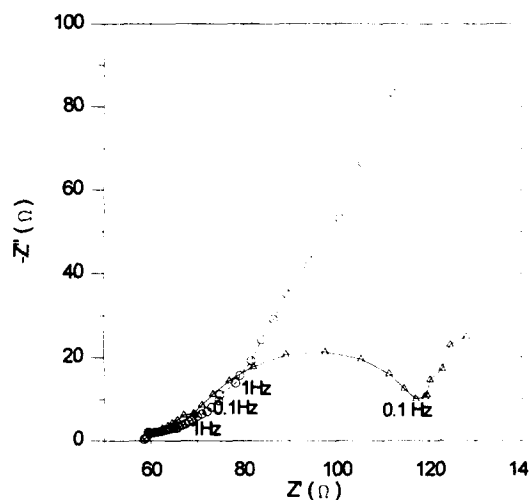


Fig. 4. A.c. impedance spectra of LiCoO<sub>2</sub>: (Δ) high-temperature LiCoO<sub>2</sub>, and (○) low-temperature LiCoO<sub>2</sub>.

observed during the lithium extraction process. The cycling efficiencies are 99%, and the decay of CV peak current is not significant. If controlled potential is swept only to 3.5 V, then the anodic peak current decreased and its capacity loss is 40%, which is equal to capacities contributed by lithium insertion at a lower potential.

Distinct a.c. impedance spectra at various  $x$  in Li<sub>1-x</sub>CoO<sub>2</sub> were obtained from a.c. impedance analyses. In general, two semi-circles and a constant phase angle in the low frequency region are observed in the spectra for HT-LiCoO<sub>2</sub>, as shown in Fig. 4. The high frequency semi-circle was regarded as film formation [3], and the charge-transfer process induces the low frequency semi-circle. For LT-LiCoO<sub>2</sub>, low frequency semi-circle is not easy to identify because of the constant phase angle of diffusion impedance is interacting with charge-transfer impedance. The diffusion coefficients of Li<sup>+</sup> ions moving into LiCoO<sub>2</sub> can be obtained with the method described by Ho et al. [4]. In our experimental results, diffusion coefficients of Li<sup>+</sup> ions in LT-LiCoO<sub>2</sub> are smaller than that of Li<sup>+</sup> ions into HT-LiCoO<sub>2</sub>, they changed slightly with the lithium content in the materials, and have an order of 10<sup>-9</sup> cm<sup>2</sup>/s.

#### 4. Conclusions

Lithium intercalating into LT-LiCoO<sub>2</sub> generates two CV peaks at 3.8 and 3.3 V, respectively, which is contrast to that of HT-LiCoO<sub>2</sub>. The reversibility of the sweep current for LT-LiCoO<sub>2</sub> is very well and its cycling efficiency is high during the sweeps. For HT-LiCoO<sub>2</sub>, reaction resistance of the Li<sup>+</sup> ion extraction is smaller than that of the Li<sup>+</sup> ion insertion. The diffusion coefficients of Li<sup>+</sup> ions in LT-LiCoO<sub>2</sub> are smaller than that in HT-LiCoO<sub>2</sub>, and have an order of 10<sup>-9</sup> cm<sup>2</sup>/s.

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