

# Synthesis of ultrafine $\text{LiCoO}_2$ powders by the sol–gel method

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Ultrafine high-temperature (HT)  $\text{LiCoO}_2$  powders were synthesized by the sol–gel method using polyacrylic acid (PAA) as a chelating agent. The decomposition process of the gel precursor was examined to determine the crystallization temperature and the dependence of the physicochemical properties of HT- $\text{LiCoO}_2$  powders on the PAA quantity was extensively investigated. Polycrystalline HT- $\text{LiCoO}_2$  powders, composed of very uniformly sized ultrafine particulates with an average particle size of 30–50 nm and a specific surface area of  $2.3\text{--}17\text{ m}^2\text{ g}^{-1}$ , could be obtained at the lower calcination temperature of  $550^\circ\text{C}$  and the shorter calcination time of 1 h compared to the solid-state reaction.

## 1. Introduction

The layered oxides,  $\text{LiMO}_2$  ( $M=\text{Co}, \text{Ni}, \text{V}$ ), have been extensively studied as potential cathode materials of a lithium battery with high energy density [1–4]. Of these, the research on  $\text{LiCoO}_2$  has been more active than that on the other oxides because of the simplicity of preparing the material. In addition, much attention has recently focused on  $\text{LiCoO}_2$  as the most promising alternative cathode material for the molten carbonate fuel cell [5, 6].

$\text{LiCoO}_2$  powders are usually prepared by solid-state reaction which consists of grinding and calcination of hydroxides or carbonates such as  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Li}_2\text{CO}_3$  and  $\text{CoCO}_3$  [7, 8]. This method, however, has several disadvantages: inhomogeneity, irregular morphology, larger particle size (ranging from 5–10  $\mu\text{m}$ ) broader particle-size distribution, higher temperatures and longer periods of calcination. In order to achieve a larger current capacity and reliability of the battery, it is necessary to obtain submicron particles of uniform morphology with narrow size distribution and homogeneity. This is because the performance of the battery depends on packing density, specific surface area, and homogeneity of  $\text{LiCoO}_2$  powders [8, 9].

Several solution methods have been developed to enhance the physicochemical properties of the oxide powder system [10–13]. However, there have been few reports on the synthesis of  $\text{LiCoO}_2$  powders by the solution method. Recently, it has been reported that  $\text{LiCoO}_2$  powders could be synthesized by ultrasonic spray decomposition [14]. However, this

method requires a high calcination temperature,  $900^\circ\text{C}$ , and produces large-size particles. The sol–gel method, one of the solution methods, can produce highly reactive homogeneous powders. This simple method also has many advantages: good stoichiometric control and the production of active submicron-sized particles in a relatively shorter processing time at lower temperatures. Synthesis of  $\text{LiCoO}_2$  powders by the sol–gel method using polyacrylic acid (PAA) has not been reported so far.

In this study, ultrafine  $\text{LiCoO}_2$  powders were prepared by the sol–gel method using PAA as a chelating agent. The effects of the molar ratio of PAA to total metal ions on the physicochemical properties of  $\text{LiCoO}_2$  powders were extensively investigated.

## 2. Experimental procedure

$\text{LiCoO}_2$  powders were prepared according to the procedure shown in Fig. 1. A stoichiometric amount of lithium and cobalt nitrate salts with the cationic ratio of  $\text{Li}:\text{Co} = 1:1$  was dissolved in distilled water and mixed well with an aqueous solution of polyacrylic acid (PAA). PAA was used as a chelating agent in making a gel. Nitric acid was slowly added to this solution with constant stirring until a pH of 1–2 was achieved. The resultant solution was then evaporated at  $70\text{--}80^\circ\text{C}$  for 1 day until a transparent pink sol was obtained. To remove water in the sol, the pink transparent sol was heated at  $70\text{--}80^\circ\text{C}$  while being mechanically stirred with a magnetic stirrer. As the evaporation of water proceeded, the sol turned into

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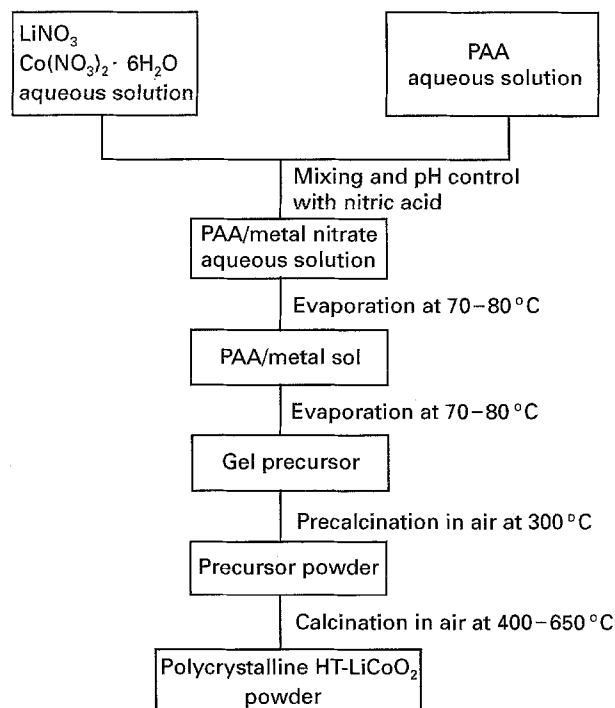


Figure 1 Flowsheet of the procedure preparing polycrystalline HT-LiCoO<sub>2</sub> powders by the sol-gel method.

a viscous transparent pink gel. For the preparation of the gel precursor with different molar ratios of PAA to total metal ions, the same procedure was repeated. The molar ratios of PAA to total metal ions were 0.5, 1, 1.5, and 2. The obtained gel precursor was decomposed at 300 °C for 1 h in air to eliminate organic contents. The decomposed powders (referred to as precursor powders) were further heated to 400–650 °C to obtain single-phase polycrystalline LiCoO<sub>2</sub> powders.

The thermal decomposition behaviour of the gel precursor was examined by thermogravimetry (TG) and differential thermal analysis (DTA). Powder X-ray diffraction (XRD) with CuK<sub>α</sub> radiation was used to identify the crystalline phase of the material calcined at various temperatures. The specific surface area of the powders was determined by the BET method with nitrogen adsorption. The particle morphology was also examined using scanning electron microscopy (SEM).

### 3. Results and discussion

The pink transparent gel could be formed for various ratios of PAA to total metal ions tested in this study. The transparency of the gel indicates that its composition was homogeneous. It is believed that the carboxylic groups on the PAA could form a chemical bond between the cations and polymeric chains, and these mixtures developed extremely viscous polymeric resins as they gelled [15].

Fig. 2 shows the TG and DTA results of the gel precursor prepared with an equal molar ratio of PAA to total metal ions. The weight loss of the gel precursor terminated at 380 °C and two discrete weight-loss regions occurred at 40–180 °C and 180–380 °C. The

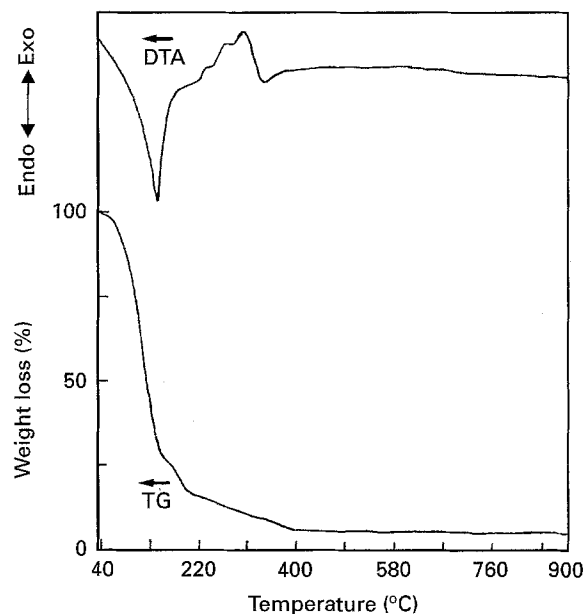


Figure 2 Thermogravimetric and differential thermal analyses of the gel precursors at an air flow rate of 40 cm<sup>3</sup> min<sup>-1</sup> and a heating rate of 5 °C min<sup>-1</sup>.

weight loss in the temperature range 40–180 °C corresponds to the removal of superficial and structural waters in the gel precursor, which is accompanied by an endothermic peak in the DTA curve at 135 °C. The weight loss in the temperature range 180–380 °C is associated with the combustion of inorganic and organic constituents in the gel precursor, such as nitrates and PAA, which occurs with exothermic peaks at 229, 251, and 277 °C in the DTA curve. The first exothermic peak at 229 °C appears to be due to the decomposition of nitrates. Similar behaviour was previously reported where nitrate decomposition in citrate-nitrate gels took place above approximately 200 °C [16]. The exothermic peaks at 251 and 277 °C can be considered to result from the decomposition of PAA, because the gel precursors are self burning, once ignited. This argument is supported by the observation that the gel precursors turned into fluffy dark brown powders after being calcined at 300 °C. Two exothermic peaks have also been observed by other investigators [17] during the thermal decomposition of La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> gel precursor using PAA as a gelling agent, although the order of the exothermic peak magnitudes was reversed. This reversal should be explained by the interaction difference between PAA and various metal ions. It is presumed that the last endothermic peak of the DTA curve at 340 °C corresponds to the crystallization of the LiCoO<sub>2</sub> phase.

Fig. 3 shows the X-ray diffraction (XRD) patterns for the gel-derived materials calcined at various temperatures for 1 h in air, where the molar ratio of PAA to total metal ions was 1.5. For the material calcined at 300 °C, impurity peaks as well as the LiCoO<sub>2</sub> phase were observed. When a material was calcined at 400 °C, a significant amount of LiCoO<sub>2</sub> phase and a small number of impurity peaks were detected. This is quite consistent with the DTA result which shows

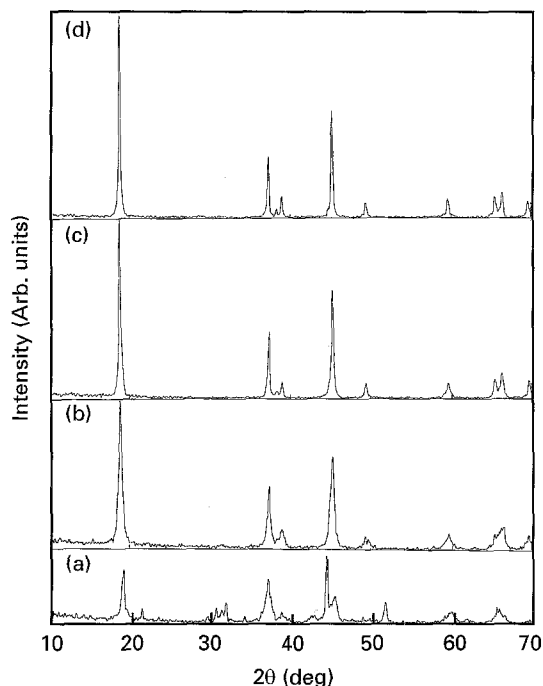


Figure 3 X-ray diffraction patterns of the gel-derived materials calcined at various temperatures: (a) 300 °C, (b) 400 °C, (c) 550 °C, and (d) 600 °C. The molar ratio of PAA to total metal ions was 1.5.

the crystallization peak at 340 °C. A single phase of high-temperature  $\text{LiCoO}_2$ , referred to as HT- $\text{LiCoO}_2$ , formed when the material was calcined at 550 °C. It took less than 1 h to attain full crystallinity. As the material was calcined at 600 °C, there was a slight increase in the characteristic peak intensities of HT- $\text{LiCoO}_2$  accompanied by sharpening of the peaks at  $2\theta = 38.35^\circ$  and  $59.5^\circ$ . This result strongly suggests that the sol-gel preparation method requires a much lower calcination temperature and shorter calcination time than the solid-state reaction where the calcination temperature is almost 900 °C and the calcination time is more than 24 h. This method is also superior to the ultrasonic spray decomposition method where the calcination temperature for HT- $\text{LiCoO}_2$  is around 900 °C. The use of PAA as a chelating agent greatly suppresses the formation of precipitates from which the heterogeneity stems, because the cross-linked gel may provide a more homogeneous mixing of the cations and lower tendency for segregation during calcination. Thereby, the fine mixture state of calcined materials with the homogeneous composition makes it possible to form a single phase of HT- $\text{LiCoO}_2$  under the mild conditions. This may be ascribed to the fact that the materials derived from the gel precursor are of atomic scale and homogeneously mixed with each other, and thus have high sinterability. Similar results have been observed, where the perovskite oxides were synthesized through the sol-gel method using PAA as a gelling agent at 500 and 600 °C for  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  and  $\text{LaCoO}_3$ , respectively [11, 17].

Fig. 4 shows the dependence of the specific surface area of polycrystalline  $\text{LiCoO}_2$  powders on the calcination temperature when the molar ratio of PAA to total metal ions was 1.5 and the gel was calcined in air for 1 h. The specific surface area of the powders de-

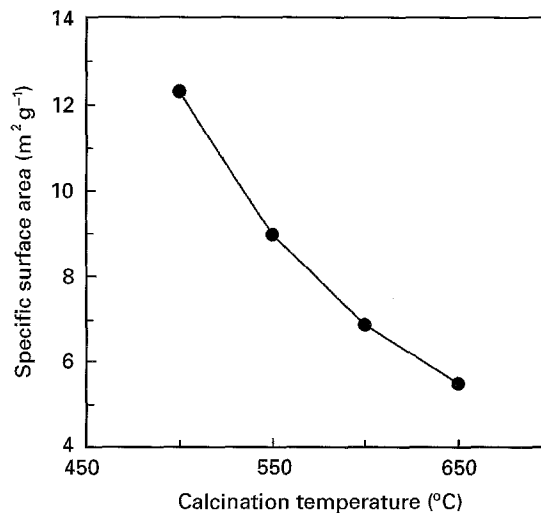


Figure 4 Dependence of the specific surface area of  $\text{LiCoO}_2$  on the calcination temperature when the molar ratio of PAA to total metal ions was 1.5.

creases linearly with increasing calcination temperature. The specific surface area of the powders prepared in this study is seen to be somewhat larger than that of the commercialized sample supplied by Cyprus Foote Mineral Co. ( $0.21 \text{ m}^2 \text{ g}^{-1}$ ). For example, the specific surface area of single-phase HT- $\text{LiCoO}_2$  powders calcined at 550 °C was  $8.97 \text{ m}^2 \text{ g}^{-1}$ , and it was 42 times larger than that of the commercial  $\text{LiCoO}_2$  powders. This clearly shows that, in the sol-gel process, lowering of the calcination temperature for the formation of the single HT- $\text{LiCoO}_2$  phase results in the production of larger surface-area oxides.

Fig. 5 shows the XRD patterns for the materials calcined at 600 °C for 1 h in air with various molar ratios of PAA to metal ions (0.5, 1, 1.5 and 2). It was confirmed from the XRD patterns that a polycrystalline HT- $\text{LiCoO}_2$  phase could be formed regardless of the molar ratio of PAA to total metal ions tested in this study. However, with increasing molar ratio of PAA to total metal ions, the crystallinity of the materials is seen to increase if we compare the magnitude of the peak intensities.

Fig. 6 shows the dependence of the specific surface area of the same materials as shown in Fig. 5 on the molar ratio of PAA to total metal ions. With increasing molar ratio the specific surface area is also seen to increase. For example, the specific surface area of the material with the molar ratio of 2 is  $17.42 \text{ m}^2 \text{ g}^{-1}$ , which is 83 times larger than that of the Cyprus Foote Mineral powders.

The reason why the crystallinity and the specific surface area of HT- $\text{LiCoO}_2$  powders increase with the quantity of PAA used can be explained as follows. From the DTA curve of the gel precursor in Fig. 2, it is seen that the exothermic peaks occur at 229, 251, and 277 °C, and the peaks at 251 and 277 °C correspond to the combustion of PAA. It is presumed that PAA not only works as a chelating agent but also provides the combustion heat required for synthesis of  $\text{LiCoO}_2$ . The greater the amount of PAA used in preparing the gel precursor, the more the cross-linked gel precursor

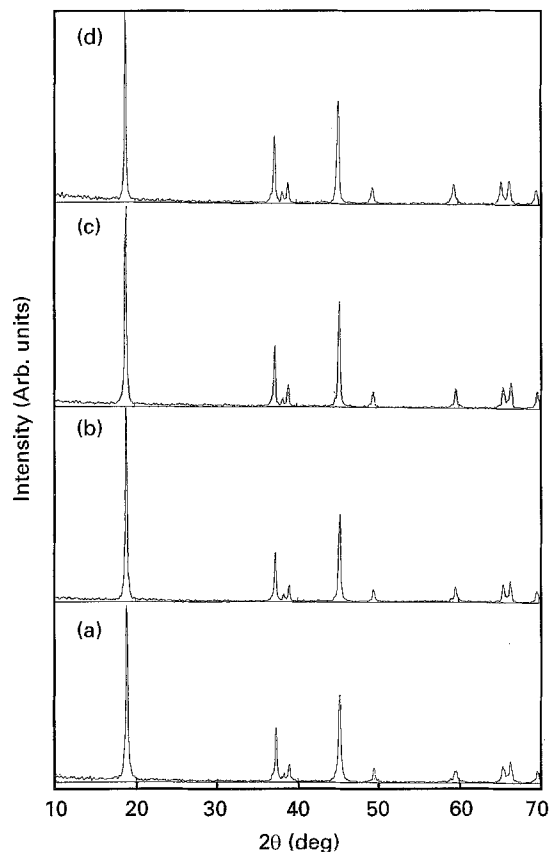


Figure 5 X-ray diffraction patterns of the gel-derived materials calcined at 600°C at various molar ratios of PAA to total metal ions: (a) 0.5, (b) 1.0, (c) 1.5, and (d) 2.0

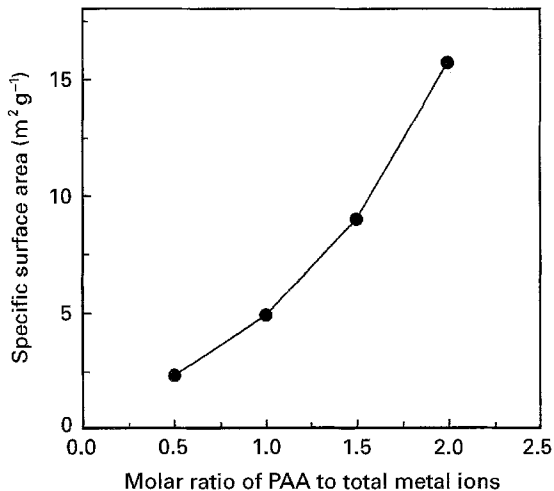


Figure 6 Dependence of the specific surface area of HT-LiCoO<sub>2</sub> powders calcined at 600°C on the molar ratios of PAA to total metal ions.

suppresses cation mobility and the greater the combustion heat which is generated from PAA, yielding the LiCoO<sub>2</sub> phase together with fluffy powders which result from many void volumes generated by CO and CO<sub>2</sub> during the thermal decomposition of PAA. This suggestion is supported by the observation that the materials are more puffed up after calcination of the gel precursor at the same calcination temperature with increasing the PAA content. Therefore, the increased combustion heat might be thought to increase the

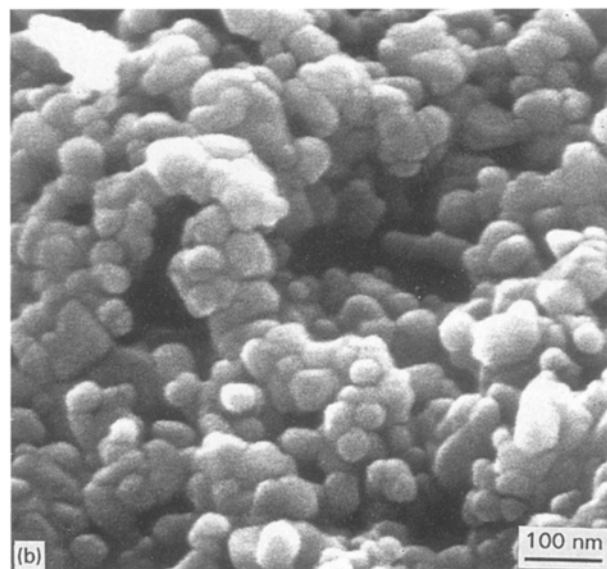
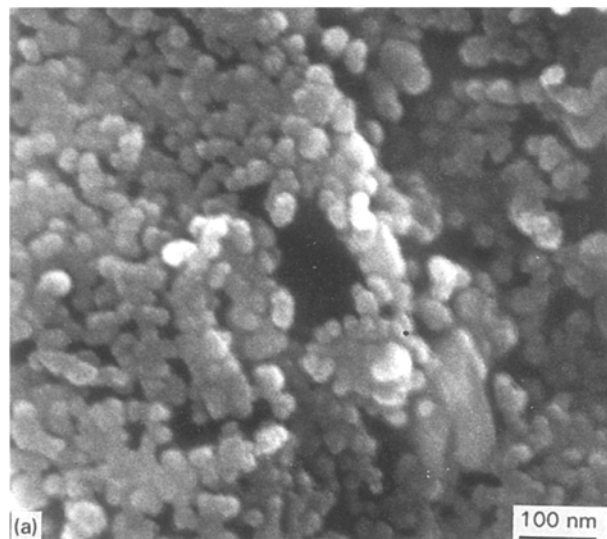


Figure 7 Scanning electron micrographs of the powders calcined at (a) 550°C and (b) 600°C.

crystallinity and the specific surface area of HT-LiCoO<sub>2</sub> powders on increasing the PAA quantity.

If too much PAA is used, a negative effect is produced by decreasing the partial pressure of oxygen from the increased amount of CO or CO<sub>2</sub> during the decomposition of PAA. However, if the PAA quantity is too small, the combustion heat becomes insufficient to yield the HT-LiCoO<sub>2</sub> phase [18]. But, the PAA quantity used in this study was out of this range and such a negative effect was not observed.

Fig. 7 shows scanning electron micrographs of the powders calcined at 550 and 600°C for 1 h in air when the molar ratio of PAA to metal ions was 1.0. The surface of the powders calcined at 550°C contains monodispersed spherical fine particulates with an average particle size of about 30 nm. When the precursor powders were heated at 600°C, it was observed that the particle size of the powders increased to about 50 nm with a fairly narrow particle-size distribution, although some agglomerations were observed. These particle sizes are 6–14 times smaller than those of perovskite-type La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> powders prepared by the same method [17].

The powders with ultrafine particles and large specific surface area could be one of the major factors influencing the electrochemical, magnetic, and mechanical properties of the material in the practical application as cathodes of lithium batteries and fuel cells. Although the physicochemical properties of HT-LiCoO<sub>2</sub> powders were investigated, and it was found that the powders prepared by the sol-gel method were superior to those prepared by the other methods, it will be necessary to study the electrochemical characteristics of the powders in the near future.

#### 4. Conclusions

Ultrafine LiCoO<sub>2</sub> powders were synthesized by the sol-gel method which consists of three steps: the formation of transparent sols from an aqueous solution of metal nitrate containing polyacrylic acid (PAA) as a chelating agent, formation of the gel precursor from sols, and its decomposition to the oxide powders. During the thermal decomposition of the gel precursor, crystallization began at 340 °C and pure polycrystalline HT-LiCoO<sub>2</sub> powders were obtained when the precursor was calcined at 550 °C for 1 h in air. This suggests that the sol-gel method requires a much lower calcination temperature and shorter calcination time than the solid-state reaction. When the molar ratio of PAA to total metal ions was increased, the crystallinity and the specific surface area of HT-LiCoO<sub>2</sub> powders increased. Polycrystalline HT-LiCoO<sub>2</sub> powders were found to be composed of very uniformly sized ultrafine particulates with an average particle size of 30–50 nm and a specific surface area of 2.3–17 m<sup>2</sup> g<sup>-1</sup>.

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