

# Stoichiometry-controlled high-performance $\text{LiCoO}_2$ electrode materials prepared by a spray solution technique

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## Abstract

$\text{LiCoO}_2$  cathode materials have been prepared by a spray-drying technique. The stoichiometry of the materials, their morphology, and the phase composition and electrochemical performance have been studied. The effects of thermal annealing and decomposition processes on the structure are discussed in detail. The changes of Li content in materials were monitored by ICP spectrometry. It was established that the decomposition of the acetates at around  $450\text{ }^\circ\text{C}$  is a slurry-making process that compacts the powder. It was found that well lithiated samples with good life cycle and high capacity can be prepared using acetate precursors and a spray solution technique. The morphology, grain size and texturing can be controlled by the sintering time and temperature in combination with intermediate grinding.

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*Keywords:* Spray-dry method; Cathode materials;  $\text{LiCoO}_2$  phase

## 1. Introduction

Li-ion batteries are currently widely used in modern portable electronic devices because of their high output voltage and specific energy, long life cycle, and the absence of memory effects. On the large scale they also have great potential for electric vehicles and stationary energy storage systems. The  $\text{LiCoO}_2$  phase is still the commercially most used cathode electrode material, due to its high performance (120–140 mAh/g and a life cycle of about 300–500 cycles). The  $\text{LiCoO}_2$  compound was developed in the 1980's by Mizushima et al. [1]. The first attempts to obtain the phase involved application of the solid-state reaction method, and most of the investigations concerning the electrochemical properties, structure, crystal size and morphology, and thermal stability were made on the basis of such materials [2–6]. More attention is now paid to the stoichiometry of the products as well [7]. As the  $\text{LiCoO}_2$  phase is stable over a broad concentration range of Li it is essential to know the Li:Co stoichiometry in the final battery electrode materials. Recently, various advanced chemical processes, such as sol-gel, spray decomposition and precipitation, freeze-drying methods, water in oil emulsion process, etc., have been applied to prepare high quality active material [8–14]. Most of these solution-based techniques are able to produce

materials with better homogeneity and finer powder than the normal solid-state reaction method. There is still a need, however, for better understanding of the effects of the different factors on the morphology, chemical composition, and electrochemical performance, as well as on how to control them. The present paper attempts to fill the gap in knowledge concerning  $\text{LiCoO}_2$  materials prepared by the spray-drying technique.

## 2. Experimental procedures

The  $\text{LiCoO}_2$  materials were prepared by a spray-dry method using  $\text{Li}_2\text{CO}_3$  and a Co acetate water solution with an addition of acetic acid to facilitate the full dissolution of the  $\text{Li}_2\text{CO}_3$  and to obtain a clear solution. The Li and Co were in a stoichiometric ratio Li:Co = 1.04:1. A commercial Yamato GA32 unit was used for the spraying process. The inlet temperature was in the range of  $190\text{--}220\text{ }^\circ\text{C}$ , and the outlet temperature was kept between  $90\text{--}100\text{ }^\circ\text{C}$ . The sprayed precursors were sintered using either single or two-step reaction procedures. The single step includes direct heating to the sintering temperature, while the two-step process includes decomposing the acetate precursor at  $450\text{ }^\circ\text{C}$ , grinding the slurry obtained during the decomposition and direct heating from room temperature to the sintering temperature. The sintering was carried out in air for 12–20 h at temperatures in the range of  $800\text{--}900\text{ }^\circ\text{C}$ .

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The phase composition of the powders obtained was studied by X-ray diffraction analysis (XRD), and the morphology was observed by scanning electron microscopy (SEM). The spray-dried precursors were subjected to differential thermal analysis and thermogravimetric analysis (DTA and TGA). The final stoichiometry of the products was examined by inductively coupled plasma–optical emission spectrometry (ICP–OES). For electrochemical characterization, Li-ion cells were assembled, in which the synthesized  $\text{LiCoO}_2$  was used as a cathode material and graphite powder was used as an anode material. The 1 M

$\text{LiPF}_6$  in a 1:1 mixture with ethylene carbonate and dimethyl carbonate was used as the electrolyte.

### 3. Results and discussion

To clarify the reaction mechanism of the  $\text{LiCoO}_2$  phase, a sprayed precursor was subjected to DTA and TGA analyses (Fig. 1). The DTA curve exhibits a few endothermic peaks at low temperature related to losses of absorbed and structural water. This interpretation is confirmed by the weight-loss

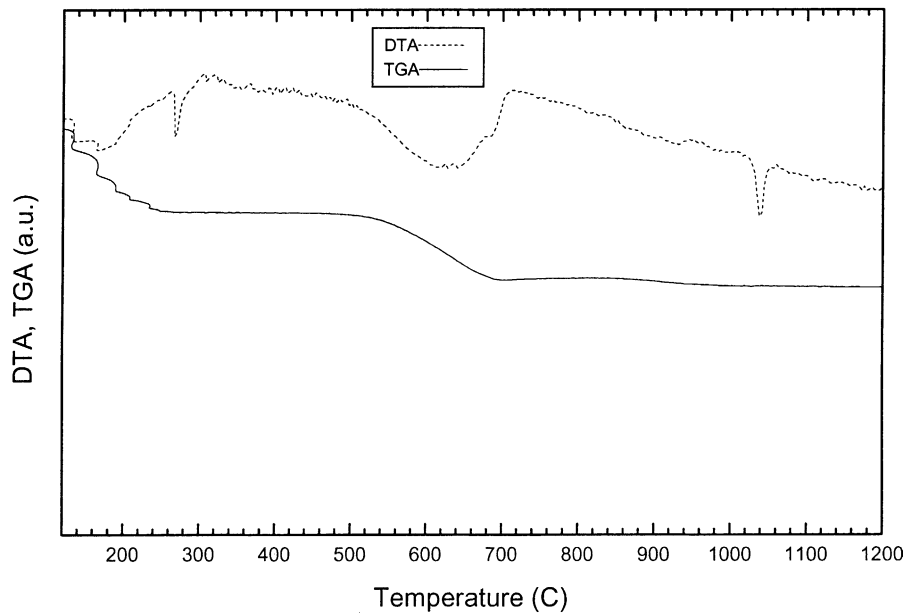


Fig. 1. The DTA–TGA curves of precursor formed by spray-drying method.

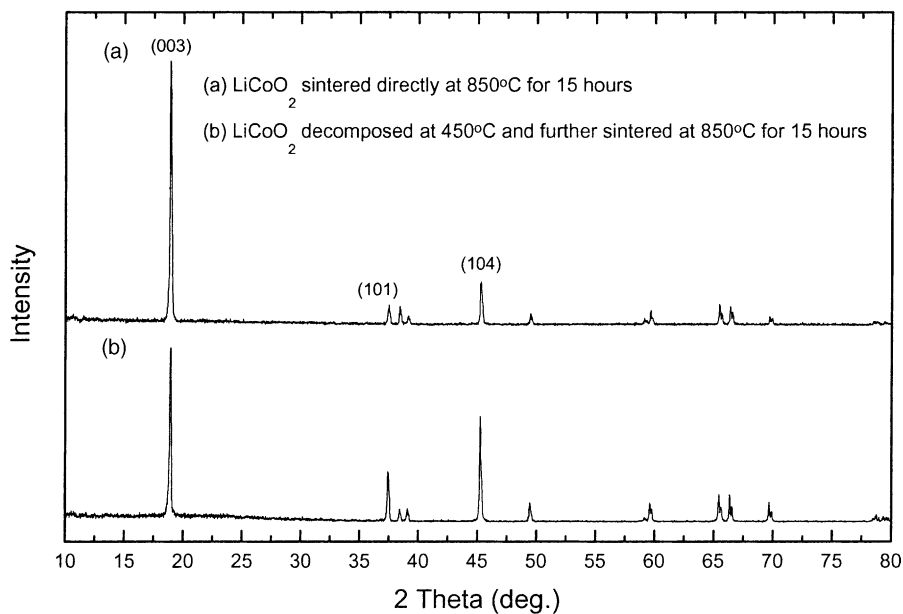


Fig. 2. The XRD patterns of  $\text{LiCoO}_2$  materials obtained by spray-drying technique. The effect of the sintering mode on the intensities  $I(0\ 0\ 3)$  and  $I(1\ 0\ 4)$  is demonstrated.

peaks in the TGA curve. In the region of 500–700 °C a large endothermic peak exists and a corresponding weight loss is observed. They are both associated with full decomposition of the precursor and a chemical reaction between the Li and Co oxides, which leads to the formation of the high temperature (HT) hexagonal  $\text{LiCoO}_2$  phase. In fact, the XRD also confirms that this phase already exists above 600 °C. The next endothermic peak in the DTA curve is at 1020 °C corresponding to the melting stage, and there are no other peaks at higher temperatures. The behavior of the TGA curve is very important and has to be emphasized. Between 700–850 °C there is no weight loss, and above 850 °C the TGA curve goes down very slowly and steadily until the end of the analyzed tem-

perature range. This constant weight loss was attributed to Li evaporation on interpretation, which was substantiated in the range of 850–900 °C. To analyze the DTA–TGA information correctly we must note that the behavior of the TGA curve will be affected by the heating rate, which was 10 °C/min in our case. During the actual sintering the material remains at elevated temperatures much longer, which contributes to more intensive Li evaporation.

We found that any type of sintering in the temperature range of 800–900 °C and for sintering times of 10–20 h in air leads to the formation of single phase material when the initial stoichiometry  $\text{Li}:\text{Co} = 1.04:1$  is maintained in the sprayed solution. The XRD pattern of the sintered  $\text{LiCoO}_2$

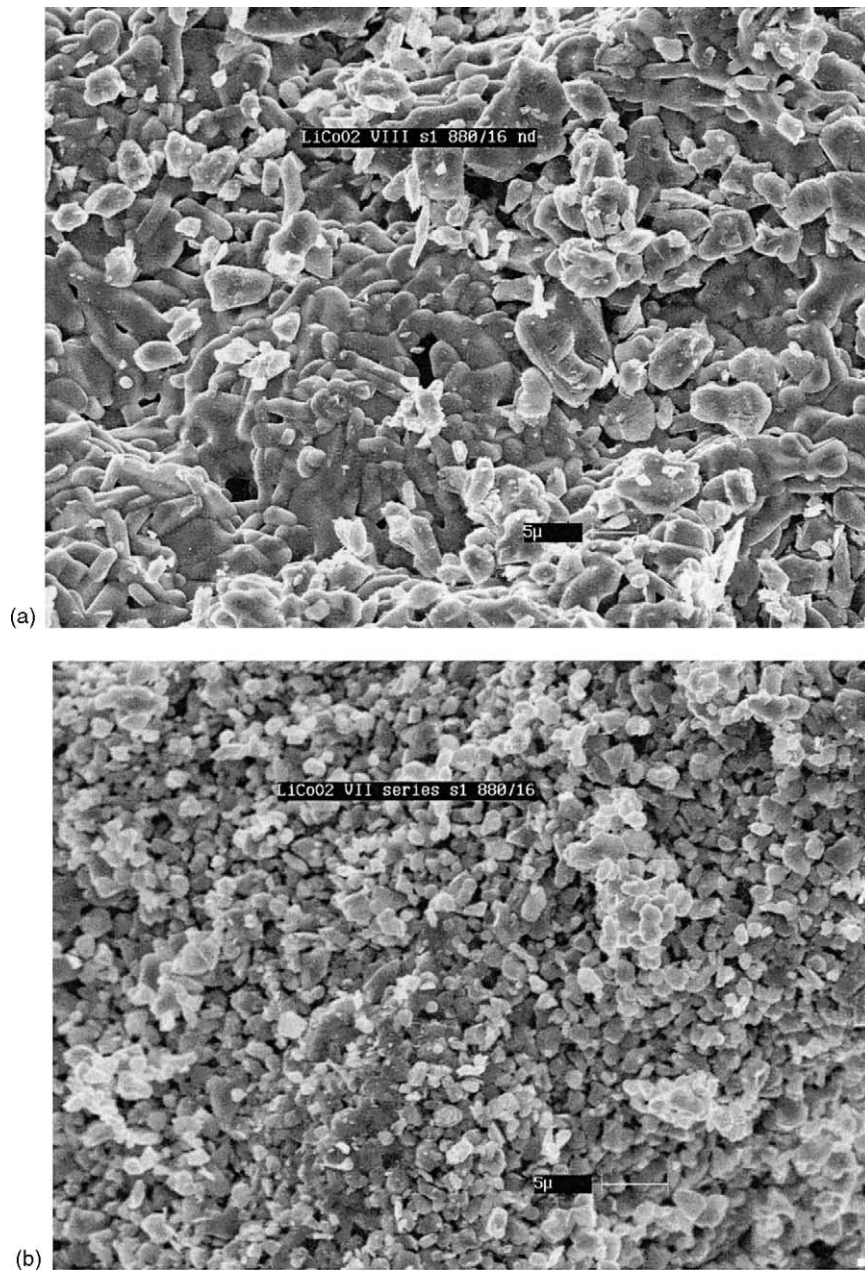


Fig. 3. SEM photograph of  $\text{LiCoO}_2$  material: (a) made using one-step sintering (880 °C for 20 h) and (b) prepared via two-step sintering at the same reaction temperature and time.

phase, however, is affected by the decomposition of the sprayed precursors, which is a slurry-making process that compacts the powder. The XRD patterns differ with respect to the ratio of the  $I(0\ 0\ 3)/I(1\ 0\ 4)$  peaks (Fig. 2). If direct sintering above 800 °C was applied, we observed a very high  $I(0\ 0\ 3)/I(1\ 0\ 4)$  XRD peak ratio of around 5:1 (Fig. 2a). This ratio is around 2:1 or less for  $\text{LiCoO}_2$  phase prepared in the conventional way. We obtained a similar ratio to that found in the commercial  $\text{LiCoO}_2$  by applying precursor decomposition at 450 °C followed by grinding and sintering at above 800 °C (Fig. 2b). The (1 0 1) peak intensity is suppressed if direct sintering is applied.

In the literature, the higher ratio is generally accepted as an indication for strongly ordered structure, while a low ratio is indicating the presence of structural defects in the crystal structure due to various reasons [13,14]. For instance, when Co cations are misplaced in the octahedral sites of the Li layers the ratio decreases. Similar effects could be observed if the  $\text{LiCoO}_2$  phase is Li deficient. The value of the  $I(0\ 0\ 3)/I(1\ 0\ 4)$  ratio also increases at higher temperatures because the disorder of Li and Co cations is suppressed at elevated temperatures [14]. In spray-dried materials, the very high ratio may be due to some preferred orientation of the grains. When direct sintering at above 800 °C is applied, the SEM photograph shows that this process facilitates fast crystal growth (Fig. 3a). The typical grain dimensions are around 10  $\mu\text{m}$ . The shape is plate-like, and most of the grains stick together. In the case of two-step sintering, the material is decomposed and ground before the final sintering. The grains remain smaller with the size mainly between 3 and 6  $\mu\text{m}$ , despite the fact that the same sintering temperature and times were applied (Fig. 3b). Therefore, special attention has to be paid when the  $I(0\ 0\ 3)/I(1\ 0\ 4)$  ratio is used as an indicator for defect free

Table 1

ICP results for the Li concentration and Li:Co atomic ratio in single-step sintered sprayed dried materials and in commercial powders

	Li (wt.%)	Li:Co (atomic ratio)
Sprayed precursor	10.90	1.04:1
Sample 1 (850 °C/15 h)	10.73	1.03:1
Sample 2 (880 °C/15 h)	10.66	1.02:1
Sample 3 (900 °C/15 h)	10.43	1.00:1
Commercial $\text{LiCoO}_2$ (OMG)	10.38	0.99:1
Commercial $\text{LiCoO}_2$ (Belgium)	10.39	0.99:1

structure, because in some cases, applying specific reaction methods, other factors, such as the preferred orientation may also affect the ratio. It is also useful to take into account the fact that the application of multi-step sintering and intermediate grinding allows us to control the morphology and crystal shape, as well as the reaction temperature and time.

One of the most important factors when multi-element oxides containing volatile elements are to be sintered successfully is appropriate control of the final stoichiometry. Many papers, which deal with the structure and properties of the  $\text{LiCoO}_2$  phase do not take into account the Li:Co final ratio. Generally, it is assumed that the Li loss occurs above 900 °C. In [7], the most significant Li losses (above 15%) are observed at temperatures of 950 °C and higher. From our experiments, however, we have detected Li loss even at 850 °C, especially, in the case where the material is sintered for more than 10 h. ICP results for the Li concentration in different materials are given in Table 1. The results are compared with those of two industrial  $\text{LiCoO}_2$  powders. It is clearly seen that the Li content decreases from the initial

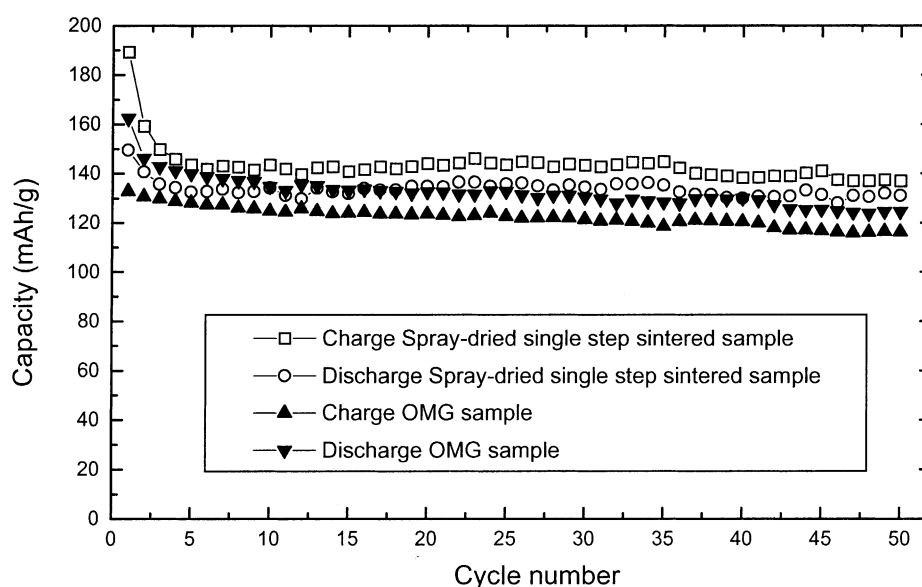


Fig. 4. Capacity and life cycle performance of single-step sintered  $\text{LiCoO}_2$  material (open symbols) and of commercial (OMG)  $\text{LiCoO}_2$  material (filled symbols). The charge–discharge current is 0.3 mA/g. The cycling potential range is 3.0–4.4 V.

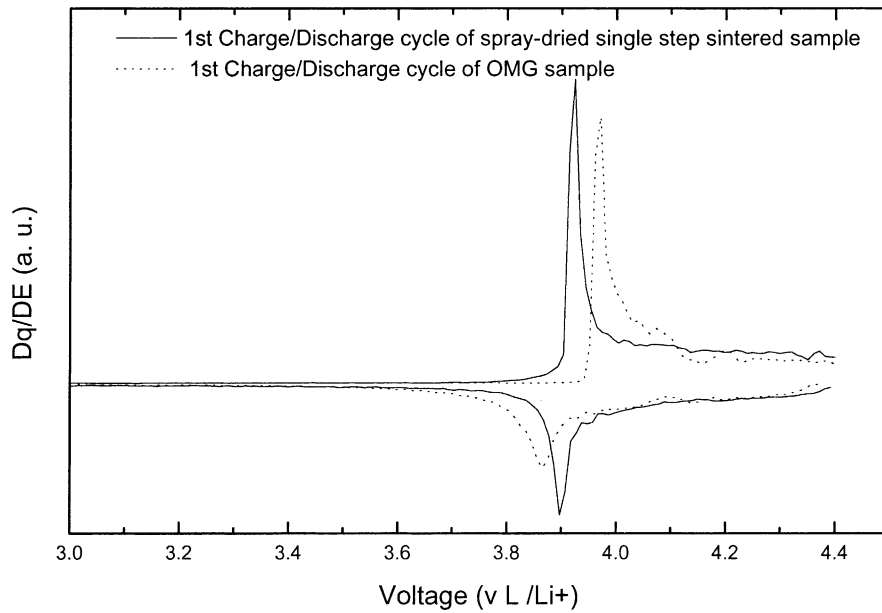


Fig. 5. Incremental capacity–voltage dependencies of single-step sintered spray-dried and commercial OMG  $\text{LiCoO}_2$  powders.

stoichiometry from 2 wt.% at 850 °C to around 5 wt.% at 900 °C, and this fact should be taken into account in order to get the correct Li:Co 1:1 stoichiometry. The analysis of the commercial  $\text{LiCoO}_2$  reveals a slight Li deficiency (around 1 wt.%) from the ideal stoichiometry. We have additionally found that the Li loss increases under similar sintering conditions if a higher Li excess is introduced in the initial precursor. In the case where a 10–20 wt.% excess of Li is applied in the initial material the Li loss reaches 4–10 wt.% for the temperature region of 850–900 °C which can be explained by the facilitated Li evaporation of the unreacted Li remaining in the system.

The electrochemical performance of  $\text{LiCoO}_2$  materials possessing a high  $I(0\ 0\ 3)/I(1\ 0\ 4)$  ratio were investigated with lab made coin cells. Typical capacity–life cycle dependences of single-step sintered and commercial OMG  $\text{LiCoO}_2$  powders are shown in Fig. 4. For the spray-dried sample, the capacity reaches 140 mAh/g, and its degradation after 50 cycles is below 10%. We believe that one of the reasons for these good results is the full lithiation of the samples. The possible presence of a preferred orientation could also contribute to the high electrochemical performance. The capacity of the OMG sample is around 130 mAh/g, and the degradation after 50 cycles is above

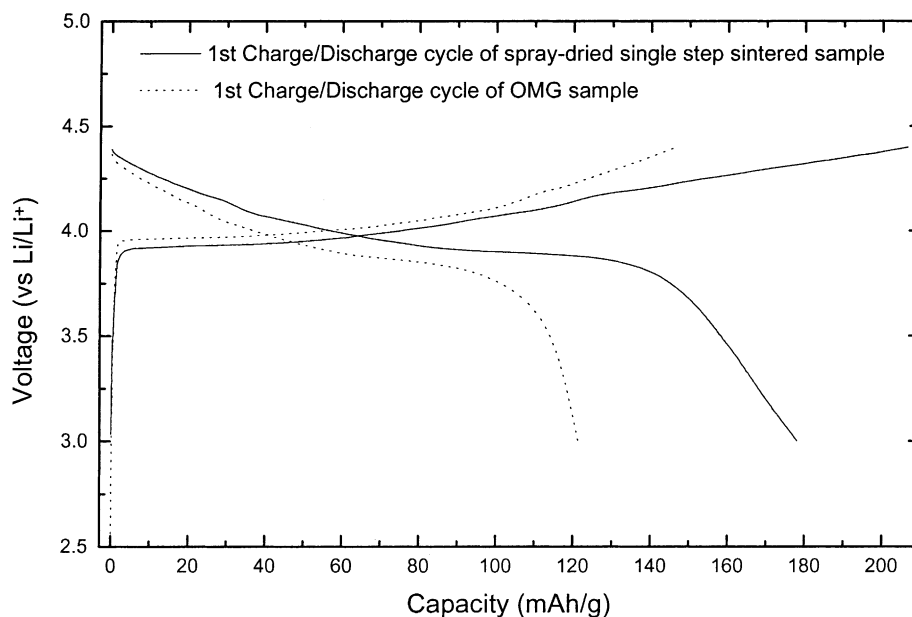


Fig. 6. First charge–discharge vs. capacity cycles of single-step sintered spray-dried and commercial OMG  $\text{LiCoO}_2$  powders.

15%. Fig. 5 represents the incremental capacities versus voltage for both the materials. The main peaks in the charge and discharge curves for the sprayed sample are positioned at 3.92 and 3.90 V, respectively, while for the OMG sample they are at 3.97 and 3.86 V, respectively. The narrower charge–discharge voltage range, together with the lower charge and higher discharge values of the sprayed sample are an evidence for its better electrochemical performance compared to the commercial material. The charge–discharge versus capacity curves shown in Fig. 6 also confirm the better performance of the spray-dried  $\text{LiCoO}_2$  sample, which demonstrates larger plateaus and an extended capacity range compared to the commercial one.

#### 4. Conclusions

By using a spray-drying method and acetate precursors,  $\text{LiCoO}_2$  electrode materials were obtained that showed high electrochemical performance. The decomposition of the acetates at around 450 °C is a slurry-making process that compacts the powder. This process facilitates fast grain growth. If the precursors are heated directly to the sintering temperature, large plate-like grains are observed and high  $I(0\ 0\ 3)/I(1\ 0\ 4)$  ratios (around 5:1) are obtained. Decomposition at around 450 °C and further grinding followed by sintering lead to smaller ratios (2:1) and a smaller grain size, even if the same sintering temperature and time are applied. The ICP analysis shows that there is Li loss at temperatures between 850 °C and 900 °C, which should be taken into account if a desired stoichiometry is needed in the final product. The electrochemical performance of single-step sintered  $\text{LiCoO}_2$  is excellent, with a capacity of around 140 mAh/g and a remarkable life cycle showing capacity

losses below 10% for 50 cycles. These results are a consequence of the good lithiation of the samples and possibly of the presence of a preferred orientation in the structure.

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#### References

- [1] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, *Mater. Res. Bull.* 17 (1980) 783.
- [2] E. Antolini, M. Ferretti, *J. Solid State Chem.* 117 (1995) 1.
- [3] C.Y. Yao, T.H. Kao, C.H. Cheng, J.M. Chen, W.M. Hurng, *J. Power Sources* 54 (1995) 491.
- [4] S.P. Sheu, C.Y. Yao, J.M. Chen, Y.C. Chiou, *J. Power Sources* 68 (1997) 533.
- [5] E. Antolini, *Mater. Res. Bull.* 32 (1997) 9.
- [6] E. Antolini, *J. Eur. Ceram. Soc.* 18 (1998) 1405.
- [7] E. Antolini, *Int. J. Inorg. Mater.* 3 (2001) 721.
- [8] G.T.K. Fey, K.S. Chen, B.J. Hwang, Y.L. Lin, *J. Power Sources* 68 (1997) 519.
- [9] Y.-M. Chiang, Y.-I. Jang, H. Wang, B. Huang, D.R. Sadoway, P. Ye, *J. Electrochem. Soc.* 145 (1998) 887.
- [10] T.J. Boyle, D. Ingersoll, T.M. Alam, C.J. Tafuya, M.A. Rodriguez, K. Vanheusden, D.H. Doughty, *Chem. Mater.* 10 (1998) 2270.
- [11] Y.-K. Sun, *J. Power Sources* 83 (1999) 223.
- [12] Y. Li, C. Wan, Y. Wu, C. Jiang, Y. Zhu, *J. Power Sources* 85 (2000) 294.
- [13] K. Kanamura, A. Goto, R.Y. Ho, T. Umegaki, K. Toyoshima, K. Okada, Y. Hakuta, T. Adshiri, K. Arai, *Electrochem. Solid State Lett.* 3 (2000) 256.
- [14] C.H. Lu, P.-Y. Yeh, *J. Eur. Ceram. Soc.* 22 (2002) 673.