JOURNALOF

Ceramic Processing Research

# The production of LiCoO<sub>2</sub> cathode thick films for an all-solid-state microbattery

Seung-Tae Lee<sup>a</sup>, Hyeon-Ju Kim<sup>a</sup>, Seung-Don Choi<sup>b</sup> and Sung-Man Lee<sup>a,\*</sup>

<sup>a</sup>Deparment of Advanced Materials Science and Engineering, Kangwon National University, ChunCheon Kangwon-do 200-701, Koera

<sup>b</sup>Battery Research Institute, LG Chemical Limited Daejeon 305-380, Korea

Crack-free LiCoO<sub>2</sub> films with a thickness more than 10  $\mu$ m have been prepared by a sol-gel derived screen-printing process, using two different-sized LiCoO<sub>2</sub> powders (mean particle sizes: 6  $\mu$ m and 0.8  $\mu$ m). The slurry as a coating medium consists of LiCoO<sub>2</sub> powders and a LiCoO<sub>2</sub> sol-gel precursor solution, which gives a well-dispersed slurry with high powder content. The slurry is screen-printed onto a Pt-coated alumina and annealed at relatively low temperatures as in a conventional sol-gel process. The feasibility of applying the fabricated films as cathodes for lithium rechargeable batteries is demonstrated. No obvious cracking after cycling was observed. Excellent cyclability was obtained. The films prepared using fine grain powders are less porous than those made from large grain powders, which lead to a better Coulombic efficiency for electrodes using the former. It is suggested that the novel process is promising for fabricating LiCoO<sub>2</sub> thick films for potential applications in all-solid-state rechargeable lithium batteries.

Key words: LiCoO<sub>2</sub>, Thick films, Scrsceen printing, All-solid-state rechargeable lithium microbatteries.

## Introduction

Recently, considerable attention has been paid to the preparation of all-solid-state lithium-ion microbatteries as micro-power sources for microsystems such as microsensors and microelectronics.

Several transition metal oxides have been extensively studied as high-voltage cathode materials for rechargeable microbatteries. Among them, LiCoO<sub>2</sub> has been widely used as the cathode material due to the advantages of having a high specific capacity and long lifecycle. LiCoO<sub>2</sub> thin films have been prepared by various techniques such as RF sputtering [1-12], pulsed laser deposition [13, 14], and a sol-gel method [15-18]. The sol-gel method is an attractive thin-film synthesis process since it has many advantages such as easy and low cost preparation, good control of stoichiometry, and a high deposition rate. Nevertheless, it is known that the sol-gel method is not suitable for the preparation of thick films. In order to obtain crack-free thick films, multiple coating processes are necessary. Considering that the capacity of microbatteries is related to the thickness of the cathode film, cathode thick films should be prepared using a simple, efficient process. Recently, it has been reported that thick LiCoO<sub>2</sub> cathode films were able to be prepared by a screen printing method, in which fine LiCoO<sub>2</sub> crystalline particles were dispersed in a sol-gel precursor solution to form a uniform slurry, and the slurry was screen printed onto a substrate, followed by annealing at relatively low temperatures as in the conventional sol-gel process [19]. As a result, the procedure for attaining the required thickness will be simplified compared to the conventional sol-gel process.

The present study focuses on the effect of the  $LiCoO_2$  particle size on the electrochemical characteristics of thick  $LiCoO_2$  cathode films prepared by this screen printing technique.

#### Experimental

#### Preparation of thick films by screen printing

A slurry was made by mixing the  $LiCoO_2$ -producing sol with a  $LiCoO_2$  powder using a ball mill machine (pulverisette-7, Fritsch). To determine the weight ratio of the powder to precursor sol, the powder content is defined as follows:

Powder content (wt %)=P/(P+S)

where P is the weight of the  $LiCoO_2$  powders added and S the remaining  $LiCoO_2$  in the precursor sol after annealing. A powder content of 90% was used in this work. For the  $LiCoO_2$  precursor solution, lithium acetylacetonate ( $LiCH_3Co-CHCoCH_3$ ) and cobalt acetatetetrahydrate ( $Co(CH_3CO_2)_2$ · $4H_2O$ ) in the ratio Li/Co of 1:1 were used as solutes, and a mixture of 2-methoxyethanol and acetic acid as a solvent.

Two different-sized powders (Fig. 1) were used; powders made by classical solid-state synthesis (mean

<sup>\*</sup>Corresponding author: Tel:+82-33-250-6266

Fax: +82-33-242-6256

E-mail: smlee@kangwon.ac.kr

The production of LiCoO<sub>2</sub> cathode thick films for an all-solid-state microbattery



Fig. 1. SEM micrograph for (a) fine and (b) large grain powders used to prepare a slurry.

diameter 6  $\mu$ m) and powders with a small grain size (~0.8  $\mu$ m) prepared by a sol approach. The slurries thus prepared were screen printed onto platinum-coated alumina substrates. For some cases, prior to thick film deposition from a slurry, a thin film was spin-coated from a xerogel precursor solution on to the substrate as a buffer layer. The deposited thick films were preheated at 150 and 380 °C for 1h and then at 750 °C for 1h.

#### Characterization of the films

The microstructure and the thickness of the films were observed by a field emission scanning electron microscopy (FE-SEM). The electrochemical properties of the films as a cathode for Li-ion batteries were evaluated using a glass beaker-type cell. The cell consisted of a lithium metal foil as a counter electrode and a LiCoO<sub>2</sub> film as a working electrode. The electrolyte was 1M LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume, provided by Cheil Industries Inc. South Korea). The cells were galvanostatically charged and discharged at 100  $\mu$ Ah/cm<sup>2</sup>. All experiments, including cell assembly and electrochemical tests, were carried out in an Ar-filled glove box.

### **Results and Discussion**

Figure 2 shows SEM photographs of the surface and the cross-sectional view of the thick films derived from the slurry using the different-sized powders. A thickness greater than 10  $\mu$ m was easily achievable and thick, crack-free LiCoO<sub>2</sub> films were prepared. At this



**Fig. 2.** SEM micrographs of the surface (a, b) and the crosssectional view (c, d) of the thick films prepared by screen-printing with different-sized powders: (a), (c) fine grain powder (mean diameter:  $0.8 \mu$ m) and (b), (d) large grain powder (mean diameter:  $6 \mu$ m).

point, it is meaningful to note that thick  $LiCoO_2$  coatings using a standard sol-gel technique are achieved by depositing multiple coats, and it is difficult then to make crack-free films thicker than 10 µm [15].

From the SEM micrographs, it could be also seen that film prepared from fine grain powders was less porous than those formed from by larger grain powders.

Figure 3 shows the capacity of the LiCoO<sub>2</sub> films as a function of cycle number, cycled between 3.0 and 4.25 V. The capacity increases with the film thickness and a stable cycleability is maintained. One can see that the film electrodes formed from large grain powder shows a relatively large irreversible capacity loss during the first cycle, corresponding to a Coulombic efficiency of ~75% and the Coulombic efficiency gradually increases to ~85%. However, in the case of the film prepared using fine grain powder, a good Coulombic efficiency of ~85% was obtained in the first cycle and above 90% for subsequent cycles. The corresponding Coulombic efficiency of these samples is compared as a function of cycle number in Fig. 4. It is believed that the Coulombic efficiency during cycling could be related to the contact resistance between the LiCoO<sub>2</sub> film and the current collector on the substrate, and/or the defects in the film electrode such as porosity. From the present results, it seems that a slurry prepared using fine powders leads to a less porous film and an improved contact between the film and the current collector.

In order to enhance the contact, a  $\text{LiCoO}_2$  thin film was deposited on the substrate as a buffer layer by a sol-gel spin-coating method before the thick film deposition by screen printing. Using this approach, the Columbic efficiency of the film derived from the larger grain powder (6 µm) was improved as shown in Fig. 5. On the other hand, in the case of the film prepared using the fine grain powder (0.8 µm), the effect of the buffer layer on the Coulombic efficiency appeared to be small compared to that of the film with the larger



**Fig. 3.** The charge and discharge capacity of the  $\text{LiCoO}_2$  films as a function of cycle number: (a) 15 µm thick film derived from fine  $\text{LiCoO}_2$  powders (b) and (c) 22 µm and 6 µm thick films derived from large grain powders.

grain powders(data not shown here).

Figure 6 shows an SEM image of a  $\text{LiCoO}_2$  thick film (described in Fig. 1(a)) after 55 cycles. The surface of the film electrode after cycling is devoid of any cracks and the morphology of the film appears to be unchanged from that before cycling. One might expect that cracking in the cathode film structure and during cycling would lead to a short-circuit of all-solid-state cells fabricated with such cathodes [2] and would have



**Fig. 4.** Coulombic efficiency of electrodes described in Fig. 1 as a function of cycle number.



**Fig. 5.** The effect of the buffer layer on the Coulombic efficiency of a 6  $\mu$ m thick LiCoO<sub>2</sub> film derived from large grain powder.



Fig. 6. SEM image of 15  $\mu$ m thick LiCoO<sub>2</sub> film derived from fine powder after 55 cycles.

a deleterious effect on the interface stability between the cathode and the solid electrolyte films. Therefore, the present results, although preliminary in nature as obtained from the half-cell using a liquid electrolyte, are reflective of the potential of a thick  $LiCoO_2$  film prepared by a combined process of a sol-gel method and screen-printing as cathodes electrodes for all-solidstate rechargeable batteries.

Further investigation is ongoing to improve the microstructure of the films through controlling the content, size and dispersion of powders in the slurry, and the viscosity of the slurry. Hopefully this will further improve the electrochemical properties of the films for all-solid-state rechargeable lithium batteries.

## Conclusions

Crack-free LiCoO<sub>2</sub> thick films have been prepared by a screen-printing technique using a slurry consisting of fine LiCoO<sub>2</sub> powders and a LiCoO<sub>2</sub> sol-gel precursor solution. The fine particles and the sol-gel medium are bonded together during post-annealing at relatively low temperatures compared with the conventional sol-gel process. The thick films prepared using fine grain powders are less porous than those prepared from larger grain size powders. This seems to lead to better electrochemical properties as cathode electrodes for allsolid-state lithium rechargeable microbatteries. No obvious cracking during film fabrication and cycling was observed.

### Acknowledgments

This work was supported by the Korean Ministry of Science and Technology through the research program for "National Research Laboratory", and also supported, in part, by LG Chemical Ltd.

#### References

- 1. N.J. Dudney and Y.I. Jang, J. Power Sources 119-121 (2003) 300-304.
- 2. B. Wang, J.B. Bates, F.X. Hart, B.C. Sales, R.A. Zuhr, and

J.D. Robertson, J. Electrochem. Soc. 143 (1996) 3203-3213.

- J.K. Lee, S.J. Lee, H.K. Baik, H.Y. Lee, S.W. Jang, and S.M. Lee, Electrochem. Solid state Lett. 2 (1999) 512-515.
- J.F. Whitacre, W.C. West, and B.V. Ratnakumar, J. Power Sources 103 (2001) 134-139.
- J.B. Bates, N.J. Dudney, B.J. Neudecker, F.X. Hart, H.P. Jun, and S.A. Hackney, J. Electrochem. Soc. 147 (2000) 59-70.
- C.-L. Liao and K.-Z. Fung, J. Power Sources 128 (2004) 263-269.
- J. Pracharova, J. Pridal, J. Bludska, I. Jakubec, V. Vorlicek, Th. Dikonimos Makris, R. Giorgi, and L. Jastrabik, J. Power Sources 108 (2002) 204-212.
- C.N. Polo da Fonseca, J. Davalos, M. Kleinke, M.C.A Fantini, and A. Gorenstein, J. Power Sources 81-82 (1999) 575-580.
- P. Fragnaud, T. Brousse, and D.M. Schleich, J. Power Sources 63 (1996) 187-191.
- 10. W.S. Kim, J. Power Sources 134 (2004) 103-109.
- K.J. Rao, H. Benqlilou-Moudden, G. Couturier, P. Vinatier, and A. Levasseur, Mat. Res. Bull. 37 (2002) 1353-1367.
- Y.I. Jang, N.J. Dudney, D.A. Blom, and L.F. Allard, J. Power Sources 119-121 (2003) 295-299.
- M. Antaya, K. Cearns, J.S. Preston, J.N. Reamers, and J.R. Dahn, J. Appl. Phys. 76 (1994) 2799-2806.
- Y. Iriyama, M. Inaba, T. Abe, and Z. Ogumi, J. Power Sources 94 (2001) 175-182.
- M.K. Kim, H.T. Chung, Y.J. Park, J.G. Kim, J.T. Son, K.S. Park, and H.G. Kim, J. Power Sources 99 (2001) 34-40.
- Y.H. Rho, K. Kanamura, M. Fujisaki, J. Hamagami, S. Suda, and T. Umegaki, Solid state Ionics 151 (2002) 151-157.
- K. Kushida and K. Kuriyama, J. Cryst. Growth. 237-239 (2002) 612-615.
- J.P. Maranchi, A.F. Hepp, and P.N. Kumta, Mater Sci. Eng. B116 (2005) 327-340.
- S.T. Lee, S.W. Jeon, B.J. Yoo, S.D. Choi, H.J. Kim, and S.M. Lee, J. Power Sources 155 (2006)375-380.