

Fabrication and electrical properties of bulk textured LiCoO₂

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In order to study the orientation dependence of the electrical properties of layered structure cathode materials used in lithium-ion thin film microbatteries, a typical composition, LiCoO₂, has been hot-press sintered in bulk with strong crystallographic texture. Microstructural characterization using X-ray diffraction, scanning electron microscopy and Raman spectroscopy showed that the degree of LiCoO₂ texture depended upon the precise hot press conditions employed. There was a pronounced orientation of the polycrystalline LiCoO₂ *c*-axis in the pressing direction with a high Lotgering factor ($f = 0.96$) for sintering at 950°C. The pronounced texture led to a remarkable anisotropy in electronic conductivity between directions parallel ($\sigma_{//}$) and perpendicular (σ_{\perp}) to the pressing direction in the temperature range 190-400 K, with $\sigma_{\perp}/\sigma_{//} = 187$ at 300 K. The results suggest that texture can be used to tune not only the well-known electrochemical performance of all-solid-state lithium-ion thin film batteries, but also their electronic conductivity.

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I. Introduction

All-solid-state lithium-ion thin film microbatteries are used as micro-power sources in micro-sensors, micro-electronics and various miniaturised devices.¹ There are two major groups of cathode materials for thin film microbatteries: layered structure and olivine structured compounds, which are exemplified by LiCoO_2 and LiFePO_4 , respectively.² Electrochemical and electrical properties of layered cathode materials will depend strongly on the orientation of the crystal due to their anisotropic crystallographic structure. For example, thin film LiCoO_2 may exhibit a preferred crystallographic orientation dependent on the thickness of the film, and post-deposition annealing temperature and time.³⁻⁶ There have been investigations of the LiCoO_2 film electrochemical behaviour with crystallographic orientation since this behaviour relates directly to battery performance. The orientations with (110) and (101) planes parallel to the substrate are the most favourable for a high Li intercalation/deintercalation rate. In these orientations, the Li planes are aligned parallel to the direction of current.³⁻⁶

However, in addition to sufficiently rapid Li-ion self-diffusion kinetics, another pre-requisite property for high performance electrodes is a high electronic conductivity (σ) in order to minimize internal cell resistance and to support high rate capability.² Surprisingly, there are very few studies on the texture dependence of the electronic conductivity of layered cathode materials, which is of great significance when thin film microbatteries are considered. Takahashi *et al.*⁷ reported an anisotropic temperature dependence of the electronic conductivity in *single crystal* LiCoO_2 grown

by a flux method, with conductivities measured perpendicular (σ_a) and parallel (σ_c) to the c -axis having an anisotropy of $\sigma_a/\sigma_c \approx 500$ at 300 K. The temperature dependence of the in-plane conductivity (σ_a) suggested a variable range-hopping mechanism of conduction in the two-dimensional system. However in practice, thin film electrodes are composed of textured (preferred orientation) polycrystals. Systematic study of texture-electrical property relationships in these films is problematical because: (i) the films are usually made by physical vapour deposition, variable Li concentration often occurs^{5,8} and even small deviations in stoichiometry can produce large changes in electrical performance⁹ that partially or wholly obscure texture effects; and (ii) the texture cannot always be quantified by electron microscopy or X-ray diffraction based techniques because of low intensities and interference from the substrate.⁵ Therefore, we have developed an alternative processing route based on hot-press sintering that produces highly textured LiCoO₂ in bulk so that multiple samples in different orientations can be taken from the same polycrystalline sample with no change in composition. The microstructures and the dependence of the bulk electronic conductivity on the induced texture and temperature is then investigated. We do not propose that hot-press sintering is a viable route to thin film batteries, but show that under carefully controlled and novel bulk processing conditions, textured polycrystalline LiCoO₂ can be produced with control of chemistry and with remarkable electrical anisotropy of direct relevance to the understanding of thin film batteries.

II. Experimental procedure

Powdered LiCoO_2 (Sigma-Aldrich Company Ltd) with stated purity of 99.8% was ball milled for 72h and then sieved to under $250\mu\text{m}$. The powders were consolidated in a graphite die and sintered at a controlled temperature for 5h under a uniaxial applied pressure of 20MPa. Three sintering temperatures of $900\pm 5^\circ\text{C}$, $950\pm 5^\circ\text{C}$ and $970\pm 5^\circ\text{C}$ were studied. The resulting discs were cut into thin bars with the long axis either parallel or perpendicular to the hot press direction. In order to remove any residual carbon picked up from the graphite die, the bars were annealed at 750°C for 10h in air. The relative density measured by Archimedes immersion was 96.9%, 96.0% and 97.2% for the samples sintered at 900°C , 950°C and 970°C respectively. X-ray diffraction (XRD) using $\text{Cu } K_\alpha$ radiation was performed at room temperature in a Siemens D5000 diffractometer. The microstructures of the ceramic samples were analyzed in a scanning electron microscope (SEM; JEOL 840A). The mole ratio of Li and Co was examined by inductively coupled plasma (ICP) emission spectroscopy (Perkin-Elmer OPTIMA 3000DV). Raman spectra were recorded using a Horiba Labram Aramis imaging confocal Raman microscope. Electronic conductivity was measured parallel ($\sigma_{//}$) and perpendicular (σ_{\perp}) to the pressing direction in the temperature range 190-400 K using a Quantum Design Physical Property Measurement System (PPMS-14T). A four-probe arrangement was used with gold electrodes deposited by thermal evaporation on opposite end faces of the bar and point contact electrodes along the length of the bars.

III. Results and discussion

(1) Microstructural characterization of textured LiCoO_2

XRD patterns from the LiCoO₂ ceramic surfaces perpendicular to the pressing direction sintered at three different temperatures are shown in Fig. 1, and are compared with a pattern from the randomly oriented as-supplied powder. The diffraction peaks were matched and indexed according to the diffraction data of pure LiCoO₂ (JCPDF No. 44-145). The materials were all single-phase within the sensitivity of the technique. For the powdered sample, the highest intensity reflection was (003) followed by (101) and (104) reflections [Fig. 1(a)], while for all the pressed LiCoO₂ with the surface perpendicular to the pressing direction, the intensities of (003) reflection were much higher than all of other reflections indicating the development of texture along the *c*-axis of the LiCoO₂ lattice. However, the three highest intensity reflections for each hot press temperature were different: (003), (006) and (104) for 900°C [Fig. 1(b)]; (003), (006) and (00 12) for 950°C [Fig. 1(c)]; and (003), (104) and (006) for 970°C [Fig. 1(e)]. The strongest texture developed at 950°C with a preferred orientation of the type (00*l*) where *l* = 3, 6, 9, 12, only. In comparison with the powder and LiCoO₂ sintered at 950°C with the surface perpendicular to the pressing direction, LiCoO₂ sintered at 950°C with the surface parallel to the pressing direction showed an increased intensity of (101) and (104) reflections, and a decreased (003) reflection intensity [Fig. 1(d)].

The degree of texture can be estimated using the Lotgering factor *f* which was determined using the XRD data in the range 2θ = 15°–85° according to:¹⁰

$$f = (p - p_0) / (1 - p_0) \quad (1)$$

where $p = \sum_l I(00l) / \sum_{hkl} I(hkl)$, $\sum_l I(00l)$ and $\sum_{hkl} I(hkl)$ were the sums of the intensities of (00*l*) and (*hkl*) reflections respectively, and *p*₀ is the value of *p* for a

randomly oriented sample, taken in this study as the as-supplied powder. The f values for LiCoO_2 sintered at 900°C , 950°C and 970°C were 0.61, 0.96, and 0.51 respectively.

Fig. 2 shows SEM images of fractured cross-section surfaces parallel to the pressing direction for all the sintering temperatures. There are dramatic differences in terms of the morphology and alignment of grains. As shown in Fig. 2(a), the microstructure sintered at 900°C exhibited a mixture of plate-like grains aligned to the pressing direction and equiaxed grains with dimensions of $1\sim 3\ \mu\text{m}$. In contrast, LiCoO_2 sintered at 950°C displayed almost all plate-like grains in which the short axis was aligned strongly to the pressing direction [Fig. 2(b)]. Most of the equiaxed grains were consumed during the growth of these plate-like grains. The average plate-like LiCoO_2 grain size sintered at 950°C ($15\ \mu\text{m}$ length and $4\ \mu\text{m}$ thickness) was much larger than that sintered at 900°C ($7\ \mu\text{m}$ length and $1.5\ \mu\text{m}$ thickness). Aligned plate-like LiCoO_2 grains remained when sintered at 970°C , as shown in Fig. 2(c). However, when compared with 950°C , the anisotropy in grain aspect ratio decreased at 970°C because of the development of coarser more equiaxed grains. Overall, the variation in the Lotgering factor f could be readily correlated to the development of elongated grains of increasing aspect ratio, with the highest value of f at 950°C corresponding to well-aligned and uniform plate-like grains. There was no systematic variation in micro-porosity in a particular direction and no measureable change in density for the three temperatures presented here.

The presence of the Co_3O_4 in LiCoO_2 is often encountered because of evaporation loss of Li during elevated temperature processing.^{5,8} Co_3O_4 has high electronic conductivity¹¹ that could affect subsequent electrical measurements. The Li/Co atomic

ratio obtained by ICP for LiCoO_2 sintered at 950°C was 0.98 and close to stoichiometry. Raman spectroscopy was also used to examine further the 950°C hot-pressed texture and possible impurity effects since it is more sensitive to minority phases that may be below the detection limit in XRD. Fig. 3 shows Raman spectra from the polished surface of textured LiCoO_2 sintered at 950°C both perpendicular and parallel to the pressing direction. The spectra showed two Raman active modes at 488 and 597 cm^{-1} assigned as E_g and A_{1g} respectively, which characterized layered LiCoO_2 .⁸ The absence of Co_3O_4 impurity phase was evidenced by the absence of any peak at 690 cm^{-1} .⁵ The intensity ratio I_{597}/I_{488} increased with the degree of c -axis orientation: 0.72 for the surface parallel to the pressing direction and 1.58 for the surface perpendicular to the pressing direction, and in agreement with similar measurements of LiCoO_2 thin films.⁵

(2) The effect of texture on the electronic conductivity of polycrystalline LiCoO_2

Fig. 4 shows the temperature dependence of the electronic conductivity of the LiCoO_2 bars sintered at 950°C . The strong dependence with temperature evidenced thermally activated semi-conducting behaviour in both orientations, and there was strong, nearly temperature-independent electronic conductivity anisotropy. The conductivity in the temperature range 190-400 K did not strictly obey often-assumed Arrhenius-type behaviour, as shown in the inset of Fig. 4. The LiCoO_2 electronic conductivities at 300K were $1.68 \times 10^{-3}\text{ S/cm}$ for σ_{\perp} and $8.97 \times 10^{-6}\text{ S/cm}$ for σ_{\parallel} . The anisotropy of conductivity $\sigma_{\perp}/\sigma_{\parallel}$ was 187 at 300 K and clearly indicated that the main conduction path was along the a - b plane, as previously reported for *single crystal* LiCoO_2 .⁷

However, similar behaviour has not been reported previously for *textured polycrystalline* LiCoO₂.

LiCoO₂ conductivity is provided by the variable-range hopping (VRH) mechanism arising from the localized Co-3d electrons in the valance band.¹² According to the VRH theory of conduction:

$$\sigma \propto \exp[-(T_0/T)]^{1/(d+1)} \quad (2)$$

where d is the dimension of the conduction path and T_0 is the Mott characteristic temperature.¹³ The σ_{\perp} data from the a - b plane were best-fitted to Equation (2) using a least-squares regression that yielded $d = 2.94$ with a regression coefficient $R^2 = 0.99993$. For comparison, if it was assumed $d = 3$ or $d = 2$, then $R^2 = 0.99991$ and 0.98471 , respectively. Fig. 4 shows the close fit to Equation (2) for $d = 3$. Given the very high degree of texture, it is at first slightly surprising that conduction in the highly aligned a - b plane should be suggested to be 3-dimensional, particularly since the a - b plane electronic conductivity in single crystal LiCoO₂ is reported as 2-dimensional with $d = 2$.⁷ An immediate explanation for the different dimensionality of a - b plane conduction in single ($d = 2$) and polycrystalline ($d = 3$) LiCoO₂ might implicate the role of grain boundaries, or the non-perfect alignment of the a - b plane in the textured polycrystalline material. However, there are at least two other reports of $d = 3$ for *single crystal* CuAlO₂¹⁴ and LiVO₂¹⁵ both of which have a similar layered structure and belong to the same space group as LiCoO₂. Therefore, grain boundaries alone may not be the only important consideration in explaining anisotropic conduction behaviour in polycrystalline materials of this type. Although the XRD and Raman data in Figures 1 and 3 suggested there was close control of stoichiometry, we

tentatively suggest that even very minor changes in composition may have a role in the apparent mechanism of electron conduction.

Although the present study focused on bulk LiCoO_2 rather than thin films, it is reasonable to expect similar anisotropic electronic conductivity in textured cathode thin films with layered structure. As stated before, studies of LiCoO_2 films preferred orientations and electrochemical behaviour showed that the (110) and (101) orientations are most favourable for a high Li intercalation/deintercalation rate, whereas the (003) orientation is unfavourable.³ The present study suggests that from the viewpoint of previously unstudied electrical properties, polycrystalline layered structure cathode thin films with orientations further away from the c -axis (or close to the a - b -axis), offer the best performance for thin film batteries because they exhibit much higher electronic conductivity. A key deduction from our results is that polycrystalline layered structure cathode thin films with orientations close to the a - b -axis are highly desirable not only from the viewpoint of the associated well-known improvement in electrochemical behaviour, but also from that of electronic conductivity with particular ramifications in thin film microbatteries.

IV. Conclusions

An anisotropic electronic conductivity in polycrystalline cathode materials of lithium ion batteries with layered structure has been demonstrated through one typical compound, LiCoO_2 . Bulk polycrystalline LiCoO_2 has been fabricated with deliberately induced crystallographic texture by hot-press sintering. LiCoO_2 sintered at 950°C has a plate-like microstructure with a strong orientation of the c -axis in the

pressing direction and a high Lotgering factor of $f=0.96$, with a two-order of magnitude anisotropy in the electronic conductivity ($\sigma_{\perp}/\sigma_{\parallel}$) and the main conduction path within the a - b plane in the range 190-400K. Our results suggest that texture can be used to tune not only the well-known electrochemical performance of all-solid-state lithium-ion thin film batteries, but also their electrical properties.

References

¹ J. B. Bates, N. J. Dudney, B. Neudecker, A. Ueda, and C. D. Evans, "Thin-Film Lithium and Lithium-Ion Batteries," *Solid State Ionics.*, **135** [1-4] 33-45 (2000).

² M. S. Whittingham, "Lithium Batteries and Cathode Materials," *Chem. Rev.*, **104** [10] 4271-302 (2004).

³ J. B. Bates, N. J. Dudney, B. J. Neudecker, F. X. Hart, H. P. Jun, S. A. Hackney, "Preferred Orientation of Polycrystalline LiCoO₂ Films," *J. Electrochem. Soc.*, **147** [1] 59-70 (2000).

⁴ J. Xie, N. Imanishi, T. Matsumura, A. Hirano, Y. Takeda, O. Yamamoto, "Orientation Dependence of Li-ion Diffusion Kinetics in LiCoO₂ Thin Films Prepared by RF Magnetron Sputtering," *Solid State Ionics.*, **179** [9-10] 362-70 (2008).

⁵ Y. Iriyama, M. Inaba, T. Abe, Z. Ogumi, "Preparation of c -axis Oriented Thin Films of LiCoO₂ by Pulsed Laser Deposition and Their Electrochemical Properties," *J. Power Sources.*, **94** [2] 175-82 (2001).

⁶ P. J. Bouwman, B. A. Boukamp, H. J. M. Bouwmeester and P. H. L. Notten, "Structure-Related Intercalation Behaviour of LiCoO₂ Films," *Solid State Ionics.*, **152-153** 181-88 (2002).

⁷ Y. Takahashi, Y. Gotoh, J. Akimoto, S. Mizuta, K. Tokiwa, and T. Watanabe, "Anisotropic Electrical Conductivity in LiCoO₂ Single Crystal," *J. Solid State Chem.*, **164** [1] 1-4 (2002).

⁸ M. Inaba, Y. Iriyama, Z. Ogumi, Y. Todzuka and A. Tasaka, "Raman Layered Rock-Salt LiCoO₂ and its Electrochemical Lithium Deintercalation," *J. Raman Spectrosc.*, **28** [8] 613-17 (1997).

⁹ M. Ménérier, I. Saadoune, S. Levasseur, C. Delmas, "The Insulator–Metal Transition upon Lithium Deintercalation from LiCoO₂: Electronic Properties and ⁷Li NMR Study," *J. Mater. Chem.*, **9** [5] 1135-40 (1999).

¹⁰ T. Takenaka and K. Sakata, "Grain Orientation and Electrical Properties of Hot-Forged $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Ceramics," *Jpn. J. Appl. Phys.*, **19** [1] 31-9 (1980).

¹¹ T. Tennakoon, G. Lindbergh, B. Bergman, "Performance of LiCoO_2 Cathode, Prepared Using the Pechini Method, in Molten Carbonate Fuel Cell," *J. Electrochem. Soc.* 144 [7] 2296-301 (1997).

¹² K. Kushida and K. Kuriyama, "Mott-Type Hopping Conduction in the Ordered and Disordered Phases of LiCoO_2 ," *Solid State Commun.*, **129** [8] 525-28 (2004).

¹³ B. Kramer and A. MacKinnon, "Localization: Theory and Experiment," *Rep. Prog. Phys.*, **56** [12] 1469-564 (1993).

¹⁴ M. S. Lee, T. Y. Kim, and D. Kim, "Anisotropic Electrical Conductivity of Delafossite-Type CuAlO_2 Laminar Crystal," *Appl. Phys. Lett.*, **79** [13] 2028-30 (2001).

¹⁵ H. Takei, M. Koike, K. Imai, H. Sawa, H. Kadowaki and Y. Iye, "Growth and Properties of Li-Deficient Lithium Vanadium Dioxide Single Crystal," *Mater. Res. Bull.*, **27** [5] 555-62 (1992).

Figure captions

Fig. 1. XRD patterns of LiCoO₂: (a) as-supplied powder; and hot pressed LiCoO₂ sintered at (b) 900°C with the surface perpendicular to the pressing direction; (c) 950°C with the surface perpendicular to the pressing direction; (d) 950°C with the surface parallel to the pressing direction; and (e) 970°C with the surface perpendicular to the pressing direction.

Fig. 2. SEM micrographs from the fractured cross-section surfaces of LiCoO₂ parallel to the pressing direction surface: sintered at (a) 900°C, (b) 950°C, and (c) 970°C.

Fig. 3. Raman spectra of textured LiCoO₂ sintered at 950°C with the polished surface (a) perpendicular and (b) parallel to the pressing direction.

Fig. 4. σ vs. $T^{-1/4}$ plots for the textured LiCoO₂ sintered at 950°C and measured parallel (σ_{\parallel}) and perpendicular (σ_{\perp}) to the pressing direction. Inset is on Arrhenius plots of σ vs. $1000/T$.

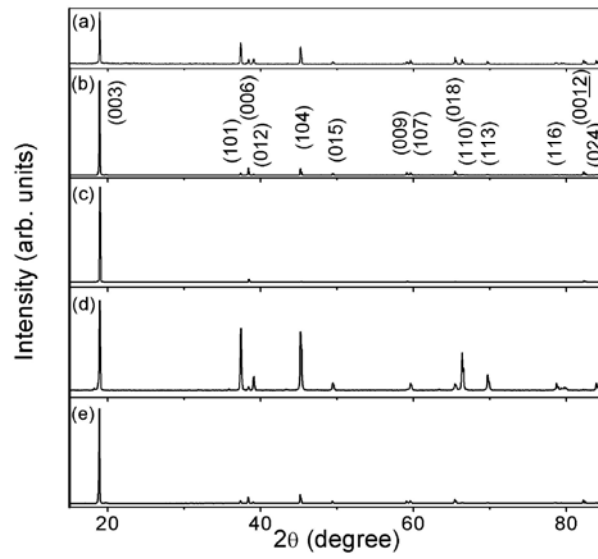


Fig. 1

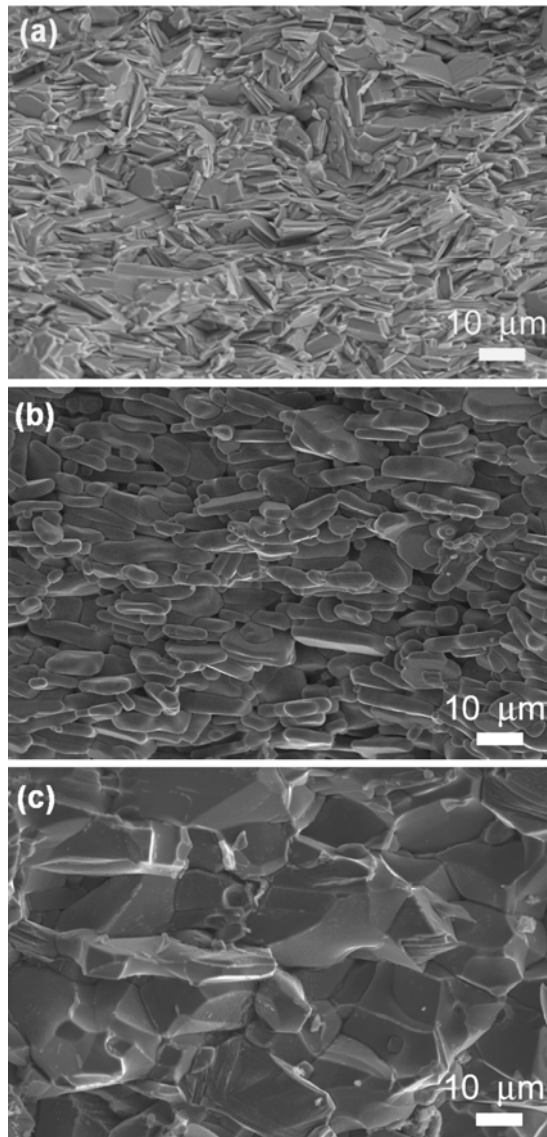


Fig. 2

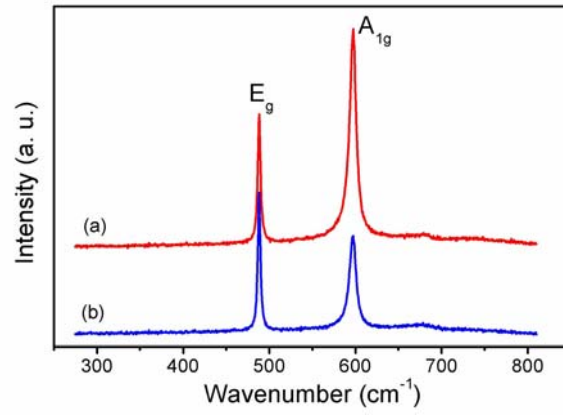


Fig. 3

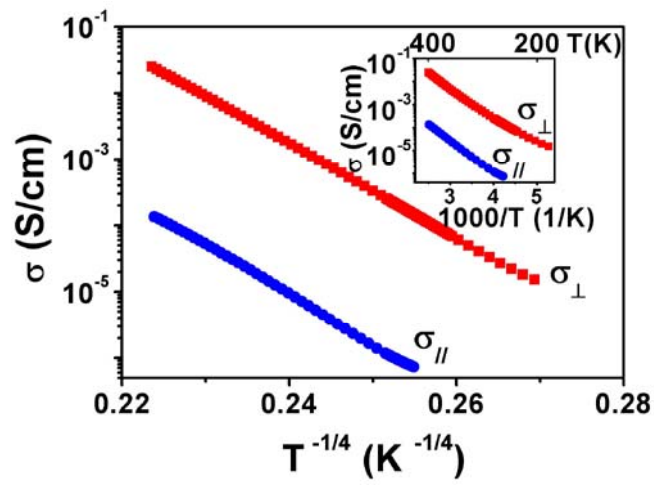


Fig. 4