

Lithiated cobaltates for lithium-ion batteries

Structure, morphology and electrochemistry of oxides grown by solid-state reaction, wet chemistry and film deposition

C. Julien^{*}, S. Gastro-Garcia

*Laboratoire des Milieux Désordonnés et Hétérogènes, UMR 7603, Université Pierre et Marie Curie,
4 place Jussieu, case 86, 75252 Paris Cedex 05, France*

Received 21 June 2000; accepted 6 January 2001

Abstract

We present the structural (XRD and Raman) and electrochemical properties of various oxides of the cobaltate family (with the α -NaFeO₂-type structure) grown by solid-state reaction, wet chemistry and film deposition techniques. It is shown that synthesis greatly affects the electrochemistry and cycle life characteristics of these layer structured cathode materials. HT-LiCoO₂, LT-LiCoO₂, doped LiCo_{1-y}Al_yO₂ and LiCoO₂ films are investigated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cobaltate; Lithium-ion battery; Solid-state reaction

1. Introduction

Compounds with the α -NaFeO₂-type structure (R₃m) are widely studied in search of their structural stability and improved electrochemical performance for cathode materials in rechargeable lithium-ion batteries [1–5]. Physicochemical properties of LiCoO₂ can be summarized as follows. (i) Open circuit voltages of 3.5–4.5 V for Li_x-CoO₂//Li cells are consistent with the oxidizing power of the Co⁴⁺/Co³⁺ couple. (ii) The high Li⁺-ion mobility is relative to the spacing between oxygen layers facing the Li layers and the high electron affinity of the low-spin Co(IV)/Co(III) couple, which makes the oxygen layers strongly polarizable toward the cobalt layers. (iii) Some limitations due to its expensive technology, toxicity, cycle life failure, and coexistence of two phases are a debatable subject in using Li_xCoO₂, i.e. a critical composition in terms of cycle life failure seems to be at about $x = 1/2$, at which a monoclinic phase is observed. (iv) When the Li//LiCoO₂ cell is cycled over the limited composition range $0.5 < x < 1.0$, rechargeability and capacity retention are fairly good. The practical characteristics of LiCoO₂ as a cathode material also depend on extrinsic properties, such as particle size and electrode porosity, and hence on the growth method.

In this work, we present the structural and electrochemical properties of various oxides of the cobaltate family grown by solid-state reaction, wet chemistry and film deposition techniques. It is shown that synthesis greatly affects their electrochemistry and cycle life characteristics.

2. Synthesis and structure of cathode materials

High-temperature samples of LiCo_{1-y}Al_yO₂ were synthesized by direct reaction of LiOH, γ -LiAlO₂, and Co₃O₄. The homogenous mixture of the powders were packed in a shallow ceramic boat and heat treated at 450°C (melting point of LiOH) for 8 h under a flow of oxygen. Lithium cobaltate powders were also synthesized by wet chemistry method according to the sol-gel procedure reported elsewhere [6,7]. Pulsed laser deposited (PLD) LiCoO₂ films were grown onto silicon wafers from targets which were a mixture of LiCoO₂ powder and variable amounts of Li₂O additive ($0 \leq z \leq 15\%$). Thin-film deposition was performed in an oxygen atmosphere ($50 \leq P(\text{O}_2) \leq 300$ mTorr) at different substrate temperatures from RT to 300°C [8].

XRD patterns of LiCoO₂ and LiCo_{1-y}Al_yO₂ microcrystalline powders prepared by wet chemistry with a calcination at 800°C for 4 h in air indicate a pure phase. They are dominated by a strong Bragg peak located at ca. $2\theta = 19^\circ$ and Bragg peaks with medium intensity at 36 and 44°. Considering the intensity and position of the Bragg peaks, it is

^{*} Corresponding author. Tel.: +33-144-274-561; fax: +33-144-274-512.
E-mail address: cjul@ccr.jussieu.fr (C. Julien).

well known that patterns of the rhombohedral unit cell ($R\bar{3}m$ space group) can be indexed in the hexagonal system. Unit-cell parameters are $a_{\text{hex}} = 2.83 \text{ \AA}$ and $c_{\text{hex}} = 14.09 \text{ \AA}$ for LiCoO_2 . Powders exhibit XRD patterns with quite well-defined doublets (0 0 6, 1 0 2) and (1 0 8, 1 1 0) when calcined at 800°C for 4 h. The c/a ratio ($c/a = 4.98$) was different from the critical value 4.90 and the splitting of the (0 0 6) and (1 0 2) as well as (1 0 8) and (1 1 0) diffraction lines indicate, as far as XRD measurements are concerned, the stabilization of the 2D structure and an ordered distribution of lithium and transition-metal ions in the lattice.

XRD patterns of LiCoO_2 films grown onto Si wafer maintained at $T_s = 300^\circ\text{C}$ in $P(\text{O}_2) = 100 \text{ mTorr}$ using a target without Li_2O additive display the presence of cobalt oxide impurities. As the amount of Li_2O increased in the target, the XRD patterns develop features expected for the regular layered phase. They are indexed using the $R\bar{3}m$ space group. Highly textured (0 0 3) films were obtained when a target with 15% Li_2O was used. The polycrystalline layered phase in LiCoO_2 films appears upon increasing the substrate temperature up to 300°C in oxygen partial pressure $P(\text{O}_2) = 50 \text{ mTorr}$ using a lithium-rich target [8].

Nano-domain formation and change in cation ordering has been observed by local probes such as FTIR and Raman scattering (RS) spectroscopy, that are complementary tools for XRD [9,10]. As an example, the polarized RS spectra of LiCoO_2 films deposited onto Si maintained at 300°C in oxygen partial pressure $P(\text{O}_2) = 50 \text{ mTorr}$ is shown in Fig. 1. Besides the Raman-active mode of the Si wafer (centered at 521 cm^{-1}) the experimental RS data consist of a series of broad bands located between 400 and 700 cm^{-1} . The RS peak positions at 484 and 594 cm^{-1} of PLD LiCoO_2 films are in good agreement with those reported for the LiCoO_2 crystal. The vibrational signature of the LiCoO_2 matches well with the two allowed Raman modes. The peak located at 693 cm^{-1} indicates the presence of Co_3O_4 impurities in the film. The formation of Co_3O_4 is related to lithium loss during the deposition process. To compensate this loss we have prepared films from lithium-rich targets including addition of 5–15% of Li_2O . The corresponding

spectra display a substantial decrease of the peak at 693 cm^{-1} indicating the vanish of Co_3O_4 species upon addition of Li_2O . The optimum amount of Li_2O to compensate the lithium loss lies between 10 and 15%.

3. Electrochemistry

In the potential domain 3.0–4.5 V, the charge–discharge curves correspond to the voltage profiles characteristics associated with lithium occupation of octahedral sites, in agreement with previous works [11,12]. However, low-temperature synthesized LiCoO_2 cathode materials show a lower potential for lithium deintercalation–intercalation than the HT-materials prepared at 800°C . The voltage profile of the cell with carboxylic acid-assisted cathode exhibits a potential slightly lower than for HT-synthesized compound. This is due to the different crystallographic texture and morphology of these two materials. It should be remarked that the fully intercalated phase is not recovered during the first discharge. This could be probably assigned to a kinetic problem especially as the phase Li_xCoO_2 is a poor electronic conductor. These studies also demonstrate that the LT-cathode yields significantly superior capacities (150 mAh/g) compared to HT-cathode when discharged to a cut-off voltage of 2.8 V. The improved performance of the LT- LiCoO_2 cell is evident due to the single-phase formation in the entire length of charge–discharge.

Fig. 2a shows the first charge–discharge curves for $\text{Li//LiCo}_{0.8}\text{Al}_{0.2}\text{O}_2$ cell operated between 2.5 and 4.4 V. The open-circuit voltage of freshly assembled cells were 2.80 to 2.95 V. Replacing a small amount of Co demonstrates higher voltage than the LiCoO_2 electrode and slightly decreases the cell capacity. At the cut-off voltage of 4.4 V, the charge gravimetric capacity of the $\text{Li//LiCo}_{0.95}\text{Al}_{0.05}\text{O}_2$ cell is ca. 150 mAh/g , which is a value similar to that delivered by LiCoO_2 cathode. This capacity decrease is more severe when cathode materials $\text{LiCo}_{1-y}\text{Al}_y\text{O}_2$ with $y > 0.10$ were used. A specific gravimetric capacity of 110 mAh/g was obtained for an $\text{Li//LiCo}_{0.75}\text{Al}_{0.25}\text{O}_2$ cell. The cells containing $\text{LiCo}_{1-y}\text{Al}_y\text{O}_2$ positive electrodes were on average 80% efficient when compared to their expected theoretical capacities. The trends for the Al^{3+} doped materials showed that lower capacities were obtained with an increase in y . This is consistent with the theoretical values, for which a decrease in capacity is expected with an increase in dopant level. The results showed that the cell using the $\text{LiCo}_{0.80}\text{Al}_{0.20}\text{O}_2$ powders performed slightly better than the other ones. This means that for Al^{3+} dopant, the optimum dopant level for gravimetric capacity and life cycle ability would be approximately $y = 0.20$. No reason could be given for such a trend. However, the average voltage of the charge characteristics of the $\text{Li//LiCo}_{1-y}\text{Al}_y\text{O}_2$ cells appears to be higher than that of Li//LiCoO_2 cells. The rechargeability of the $\text{Li//LiCo}_{1-y}\text{Al}_y\text{O}_2$ cells seems better than LiCoO_2 because the lack of the two-phase behavior in the high voltage region.

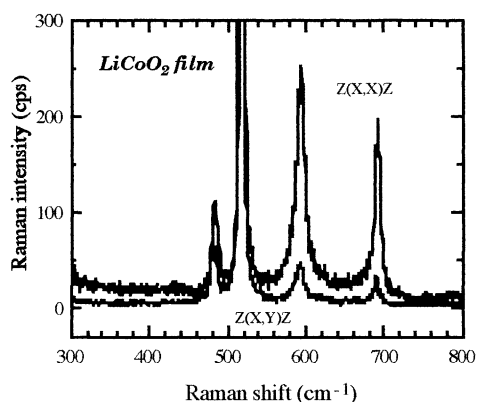


Fig. 1. Polarized RS spectra of LiCoO_2 film grown by PLD method. Peaks around 700 cm^{-1} are attributed to the presence of Co_3O_4 impurities.

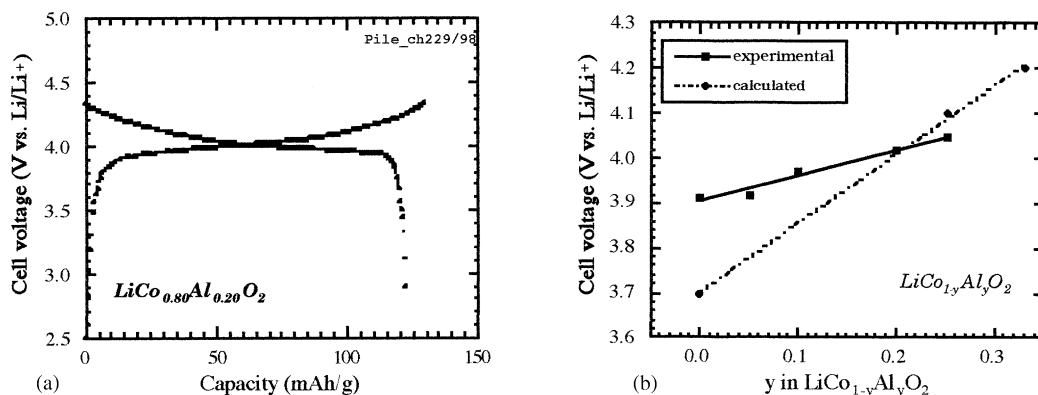


Fig. 2. (a) Charge–discharge profile of a Li//LiCo_{0.8}Al_{0.2}O₂ cell made with an aluminum doped material. (b) Variation in the cell voltage as a function of the Al substitution in LiCo_{1-y}Al_yO₂.

During the first discharge about 10 mAh/g capacity is irreversible for all the cathodes. It is suggested that the fully charge state appears when Li ions cannot be extracted from the host matrix because no electrons are removed from either Al³⁺ or Co⁴⁺. Fig. 2b displays the plot of the average cell voltage as a function of the Al content in LiCo_{1-y}Al_yO₂. Obviously, adding Al increases the lithium intercalation voltage. Experimental data from Li//LiCo_{1-y}Al_yO₂ cells are compared with values calculated by Ceder et al. [13] assuming an active role of oxygen anion in the electrochemical potential. The authors suggest that the amount of electron transfer to oxygen occurring upon Li intercalation correlates strongly with the cell voltages.

LiCoO₂ films grown onto silicon wafers maintained at 300°C were used as cathode materials and tested in lithium microbatteries with 1 M LiClO₄ in propylene carbonate as electrolyte. Cyclic voltammetry (CV) measurements show two sets of well-defined current peaks observed in the CV diagram corresponding to the oxidation and reduction reactions; they are located at 3.72 and 3.61 V for the LiCoO₂ film. These peaks are slightly shifted toward lower potentials for films grown at lower substrate temperature. These CV features are associated with the redox process of Co³⁺ to Co⁴⁺ and vice-versa, when lithium is extracted from, and inserted into the Li_xCoO₂ phase. The redox couple with a mid-peak potential of about 3.66 V is considered to be a single-phase insertion–deinsertion reaction of lithium ions in LiCoO₂. Fig. 3 shows the typical charge–discharge curves of Li//LiCoO₂ cells using pulsed-laser deposited films grown at substrate temperature in the range 25 ≤ T_s ≤ 300°C. Electrochemical measurements were carried out at a rate C/100 in the potential range 1.5–4.2 V; as such, the voltage profile should provide a close approximation to the open-circuit voltage (OCV). From these results, we may make some general remarks, that are (i) an initial voltage about 2.15 V versus Li/Li⁺ was measured for a fresh cell using a PLD LiCoO₂ film deposited at T_s = 300°C, which is lower to that recorded on the cell using crystalline cathode, (ii) the cell voltage curves display the typical profile currently observed for Li_xCoO₂ cathodes, (iii) the cell voltage is

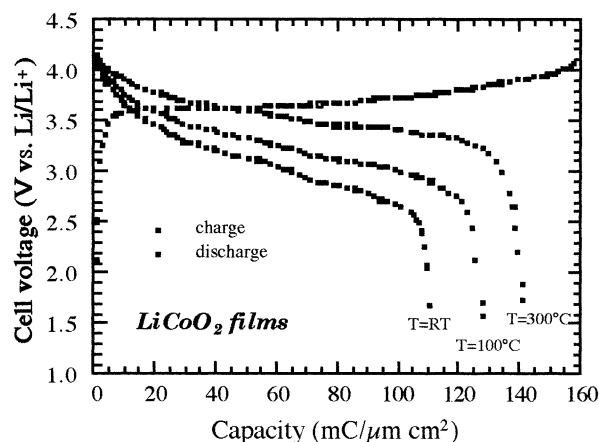


Fig. 3. Charge–discharge profiles of Li//LiCoO₂ cells with 1 M LiClO₄/PC electrolyte. PLD cathode films were grown onto silicon substrate at 25 ≤ T_s ≤ 300°C in P(O₂) = 50 mTorr.

a function of the structural arrangement in the film and thus depends on the substrate temperature. These potentials slightly increased for films grown at high substrate temperature. This is consistent with many literature data and ensures that at T_s = 300°C the material particles are electrochemically active.

4. Conclusion

Many advances have been made in battery technology in recent years; however, the practicality of systems is highly dependent upon the performance of positive electrodes. Despite the commercial success of LiCoO₂, many problems remain in the use of the lithiated cobaltates. The synthesis of new phases, i.e. preparation by *chimie douce*, cationic substitution show various physico-chemical properties associated with improvement of the cycle life of rechargeable lithium batteries. The LT-phases display lower voltage, which could prevent decomposition of the organic electrolyte, and submicron-sized particles, which enhanced the rate

capability. The relationship between crystallinity and electrochemical features has been clearly demonstrated for cathode materials prepared by film deposition technique.

Acknowledgements

The authors would like to thank Mr. M. Lemal for his careful work in performing the XRD measurements. Drs. L. Escobar-Alarcon and E. Haro-Poniatowski are acknowledged for the preparation of PLD films.

References

- [1] M.M. Thackeray, W.I.F. David, P.G. Bruce, J.B. Goodenough, *Mater. Res. Bull.* 18 (1983) 461.
- [2] T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, H. Komori, *Electrochim. Acta* 38 (1993) 1159.
- [3] M. Broussely, F. Pertion, P. Biensan, J.M. Bodet, J. Labat, A. Lecerf, C. Delmas, A. Rougier, J.P. Peres, *J. Power Sources* 54 (1995) 109.
- [4] D. Guyomard, J.M. Tarascon, *J. Electrochem. Soc.* 139 (1992) 937.
- [5] C. Delmas, I. Saadoune, *Solid State Ionics* 53–56 (1992) 370.
- [6] C. Julien, S.S. Michael, S. Ziolkiewicz, *Int. J. Inorg. Mater.* 1 (1999) 29.
- [7] D. Mazas-Brandariz, M.A. Senaris-Rodriguez, S. Castro-Garcia, M. Camacho-Lopez, C. Julien, *Ionics* 5 (1999) 345.
- [8] L. Escobar-Alarcon, E. Haro-Poniatowski, M. Massot, C. Julien, *Mater. Res. Soc. Symp. Proc.* 548 (1999) 223.
- [9] C. Julien, *Ionics* 5 (1999) 351.
- [10] C. Julien, G.A. Nazri, *Mater. Res. Soc. Symp. Proc.* 548 (1999) 79.
- [11] K. Ozawa, *Solid State Ionics* 69 (1994) 212.
- [12] C. Delmas, I. Saadoune, A. Rougier, *J. Power Sources* 43–44 (1993) 595.
- [13] G. Ceder, M.K. Aydinol, A.F. Kohan, *Comput. Mater. Sci.* 8 (1997) 161.