

AN AC IMPEDANCE SPECTROSCOPIC STUDY OF Li_xCoO_2 AT DIFFERENT TEMPERATURES

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For over ten years LiCoO_2 has been used as positive electrode material in commercial Lithium-ion batteries.¹ In spite of the large number of experimental and theoretical papers²⁻⁴ that appear regularly in the literature on LiCoO_2 and, in general, on the other members of the family $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$, a debate is still open on the electronic conductivity, electronic structure, phase transitions and on their effect and on the electrochemical performances. The literature data^{3, 5, 6} leave no doubts about the existence of a drastic change of the electronic conductivity occurring at the early stage of lithium deintercalation and caused by an insulator to metal transition. In the case of LiCoO_2 , the transition has been proposed to be responsible for the existence of a two phase region between the Li concentrations of $x = 0.93$ and $x = 0.75$.⁴ The drastic change in resistance caused by the insulator to metal transition must necessarily be reflected in the impedance dispersion. However, the high impedance values⁷ at the beginning of the deintercalation are either discarded on the assumption that the electrodes are blocking⁷ or attributed to the charge-transfer resistance. Hence, the effects of the insulator to metal transition are underestimated. This may have been favored also by the fact that the fully intercalated phase is believed to be difficult to restore during discharge after the first deintercalation.

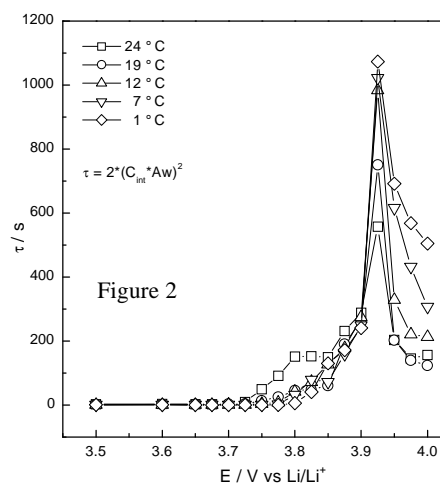
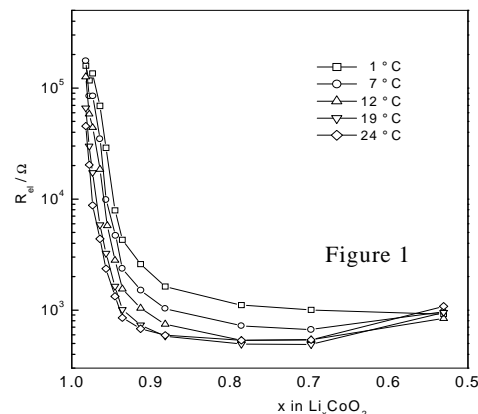
In recent papers⁸⁻¹⁰ the AC impedance of compounds of the series $\text{LiCo}_y\text{Ni}_{1-y}\text{O}_2$ have been studied with special attention to the ionic and electronic conductivity. It was found that the large variation in the conductivity in the x range between 1 and 0.9 is clearly reflected by the AC spectra also in cycled electrodes. The inclusion in the equivalent circuit of an element related to the electronic conductivity results in a more realistic picture of the physical phenomena occurring during the deintercalation process.

This paper presents an electrochemical impedance study (EIS) of LiCoO_2 electrodes at various temperatures. Particular attention has been paid to the study of the temperature dependence of spectral features in order to discriminate between thermally and not thermally activated physical properties.

Figure 1 shows the variation of the parameter, R_e , associated to the material electronic resistance, with x at the different temperatures, as deduced from the simulation. As may be seen R_e falls by about three order of magnitude over a narrow x range from $x \cong 1$ to $x \cong 0.9$. This is consistent with the trend already found for the compounds of the family⁸⁻¹⁰ $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$. The corresponding apparent conductivity, computed as reciprocal of R_e , resembles the one measured in situ using microarray electrodes.⁶

Fig. 2 shows the characteristic diffusion time τ that can be computed¹¹ from the values of the differential capacity and Warburg slope ($\tau = 2[Q_i A_w (dx/dE)^2]$)¹¹ as obtained by the fitting program. The characteristic

diffusion time is linked to the chemical diffusion D (cm^2/s) coefficient through the diffusion length (i.e. $\tau = l^2/D$). The curve shows that τ is maximum at each temperature in the proximity of the voltammetric peak.



- 1) S. Megahed and B. Scrosati, *J. Power Sources*, **51**, 79 (1994).
- 2) G. G. Amatucci, J. M. Tarascon, and I. Uchida, *J. Electrochem. Soc.*, **143**, 1114 (1996).
- 3) S. Levasseur, M. Ménétrier, E. Suard and C. Delmas, *Solid State Ionics*, **128**, 11 (2000).
- 4) A. Van der Ven, M. K. Aydinil, G. Ceder, K. Kresse, and J. Hafner, *Phys. Rev. B*, **58**, 2975 (1998).
- 5) J. Molenda, P. Wilk, and J. Marzec, *Solid State Ionics*, **119**, 19 (1999).
- 6) M. Nishizawa, S. Yamamura, T. Itoh, and I. Uchida, *Chem. Comm.* 1631(1998).
- 7) H. Sato, D. Takahaschi, T. Nishima, I. Uchida, *J. Power Sources*, **68**, 540 (1997).
- 8) F. Croce, F. Nobili, A. Deptula, W. Lada, R. Tossici, A. D'Epifanio, B. Scrosati, R. Marassi, *Electrochem. Comm.*, **1**, 605 (1999).
- 9) F. Nobili, R. Tossici, F. Croce, B. Scrosati, R. Marassi, *J. Power Sources*, **98**, 238 (2000).
- 10) F. Nobili, F. Croce, B. Scrosati, R. Marassi, *Chem. Mater.*, **13**, 1642 (2001)
- 11) M. D. Levi, G. Salitra, B. Markovsky, H. Teller, D. Aurbach, U. Heider, L. Heider, *J. Electrochem. Soc.*, **146**, 1279 (1999).

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