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## On really stoichiometric LiCoO<sub>2</sub>

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### Abstract

The <sup>7</sup>Li NMR T1 relaxation time is shown to be a very severe criterion for determining the stoichiometry of LiCoO<sub>2</sub>. When Co<sub>3</sub>O<sub>4</sub> containing minimum impurity level of paramagnetic ions such as Fe or Ni is used as starting material (together with Li<sub>2</sub>CO<sub>3</sub>), a T1 value as long as 18 s is obtained but this requires a rather long thermal treatment for complete elimination of excess Li. Such highly stoichiometric Li<sub>1</sub>CoO<sub>2</sub> exhibits a rather early insulator to metal transition upon Li deintercalation. Magnetic susceptibility and specific heat capacity investigations show the exclusive presence of diamagnetic LS Co<sup>3+</sup>.

### Introduction

LiCoO<sub>2</sub> has been the subject of quite a lot of investigations, as reviewed by Antolini (1). Being still the most common positive electrode material for Li-ion batteries, it is quite significant that some aspects of its structure or properties are still under debate. Close similarity of its structure with the Na based cobaltites that presently receive considerable attention for their thermoelectric behaviour (2, 3) also makes LiCoO<sub>2</sub> a material of particular interest.

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We have previously concluded from Li NMR based studies of deintercalated  $\text{Li}_x\text{CoO}_2$  samples that the two-phase region occurring upon deintercalation from  $\text{LiCoO}_2$  for the  $0.75 \leq x \leq 0.94$  range is driven by a first order Mott transition from localized spin hole due to (LS)  $\text{Co}^{4+}$  ions for  $0.94 < x$  to delocalized electrons with metallic-like conduction for  $x < 0.75$  (4, 5). Recent magnetic measurements and muon spin relaxation studies of  $\text{Li}_x\text{CoO}_2$  by Mukai et al. are globally in agreement with this picture but also reveal more intriguing behaviour particularly in the temperature dependence of these properties which still lacks a comprehensive explanation (6). A very recent paper by Hertz et al (7) states that  $\text{Co}^{4+}$  ions are HS at the beginning of deintercalation but this conclusion is based on a miscalculation of the effective moments. Actually, the experimental susceptibility data reported by these authors rather well support our picture recalled above (with LS  $\text{Co}^{4+}$  ions).

We had also concluded some time ago that excess Li in lithium cobalt oxide can be accommodated in substitution for cobalt in the 3b site of the R-3m  $\alpha$   $\text{NaFeO}_2$ -type structure (O3-type oxygen packing, alternate layers of edge-sharing  $\text{CoO}_6$  and  $\text{LiO}_6$  octahedra), and that cobalt ions remain at the 3+ oxidation state via the creation of oxygen vacancies (8, 9). These defects lead to the existence of intermediate spin  $\text{Co}^{3+}$  ions, and prevent the macroscopic electron delocalization that leads to the two-phase behaviour in the stoichiometric compound. Thus a continuous solid solution upon deintercalation is obtained for Li-overstoichiometric “ $\text{LiCoO}_2$ ” (that should be written as  $\text{Li}_{1+t}\text{Co}_{1-t}\text{O}_{2-t}$  with t in the range of 0.04). This paramagnetic defect in  $\text{Li}_{1+t}\text{Co}_{1-t}\text{O}_{2-t}$  leads to a rather complex set of additional  $^7\text{Li}$  NMR signals whose assignment has not been achieved yet. Li NMR thus provides the most appropriate criterion for the characterization of Li-stoichiometry in lithium cobalt oxide. Hertz et al (7) also state from effective moment calculations that excess Li in  $\text{LiCoO}_2$  leads to the presence of HS  $\text{Co}^{4+}$ , but again their calculations are mistaken and their data are actually in good agreement with our hypothesis.

In this paper, we report further investigation of the synthesis and characterization of (really) stoichiometric  $\text{Li}_1\text{CoO}_2$ .

## Experimental

### *Materials preparation*

*Precursor:*  $\text{Co}_3\text{O}_4$  was prepared by thermal decomposition of either  $\text{CoCO}_3$  (Alpha Aesar) or  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich ACS reagent, containing less than 10 mg/kg of Fe, Ni, or Cu and less than 20mg/kg of Mn). The former is called “standard  $\text{Co}_3\text{O}_4$ ” and the latter “Co-pure  $\text{Co}_3\text{O}_4$ ” in the following. Only  $\text{Co}_3\text{O}_4$  was identified in their XRD patterns in either case.

*$\text{Li}_1\text{CoO}_2$ :*  $\text{Co}_3\text{O}_4$  and  $\text{Li}_2\text{CO}_3$  (Alpha Aesar) were mixed in stoichiometric amounts and first reacted for 12 h at  $600^\circ\text{C}$  under oxygen, and then the product was reground and heated at  $900^\circ\text{C}$  under oxygen for typically 15 days. Depending on the type of  $\text{Co}_3\text{O}_4$  used, these compounds are called “standard  $\text{Li}_1\text{CoO}_2$ ” or “Co-pure  $\text{Li}_1\text{CoO}_2$ ”.

### *XRD*

XRD patterns were recorded with a Philips X’Pert Pro powder diffractometer in the Bragg-Brentano geometry, using cobalt  $\text{K}\alpha$  radiation. Data collection was made in the  $10$ - $120^\circ$   $2\theta$  range with a  $0.0167^\circ$  step, using an X’Celerator detector (linear PSD covering 2.122 mm). Rietveld refinement was performed using a pseudo-Voigt peak shape as implemented in the Fullprof program (10).

### *NMR*

$^7\text{Li}$  MAS NMR spectra were recorded on a Bruker 300 Avance spectrometer at 116 MHz (7.05 T magnet), with a standard 2.5 mm Bruker MAS probe. A combination of single pulse and Hahn echo sequences was used in MAS conditions (30 kHz spinning speed). The single pulse sequence with  $t_{\pi/2} = 2.0 \mu\text{s}$  requires a first-order phasing process with a  $\sin x/x$  baseline correction due to the dead time of the spectrometer. The Hahn echo sequence [ $t_{\pi/2}-\tau_1-t_{\pi}-\tau_2$ ] was used to facilitate the phasing of all the signals and to ensure the observation of possible very wide signals which are lost during the receiver dead time, while refocusing the interactions with electron spins (11). The  $90^\circ$  pulse duration was equal to  $t_{\pi/2} = 2.0 \mu\text{s}$ . A recycle time of 100 seconds was used.

#### *Electrochemical cells*

$\text{Li}_1\text{CoO}_2$  was used either as a pressed pellet with no additive (for low rate galvanostatic intermittent titration (GITT) experiments) or mixed with 10% carbon black and 5% PTFE binder (for cycling experiments). The electrolyte was 1M  $\text{LiPF}_6$  in (EC/PC/DMC) and the negative electrode was metallic Li.

#### *Magnetic measurements*

Magnetic susceptibility was measured using a SQUID (Quantum Design MPMS) up to 5 T.

#### *Specific heat*

Heat capacity measurements were performed in a helium Quantum Design PPMS cryostat using the “ $2\text{-}\tau$  relaxation method” in the 1.8-300 K range under vacuum. The heat capacity is calculated by carefully subtracting a blank measurement, including both the contribution of the sample platform and of the grease used to attach the sample to the puck, from the total heat capacity measurement.

## Results and Discussion

### *XRD*

Rietveld refinement of both Co-Pure and standard  $\text{Li}_1\text{CoO}_2$  show the exclusive presence of  $\text{LiCoO}_2$  (R-3m) with rather good quality of fits, leading to the following cell parameters  $a = 2.8158(1) \text{ \AA}$  and  $c = 14.0508(1) \text{ \AA}$  and Oxygen position:  $z = 0.2600(2)$ , in very good agreement with literature (1).

In addition, XRD patterns recorded down to 4K did not show any change (other than the expected shifts of the lines due to cell contraction at low temperature).

### *NMR*

$^7\text{Li}$  MAS NMR characterization of standard  $\text{Li}_1\text{CoO}_2$ , as shown in Fig. 1 shows the absence of any additional signal but the usual - 0.5 ppm one for  $\text{Li}^+$  ions in the 3b site of stoichiometric  $\text{LiCoO}_2$ , containing only LS  $\text{Co}^{3+}$  ions, as expected for a stoichiometric compound (8).

The absence of paramagnetic ions (like intermediate spin  $\text{Co}^{3+}$ ) was further characterized by measuring the T1 relaxation time, which is well known to be drastically decreased by even traces of electron spins in any compound. Using the inversion-recovery sequence on static samples, a fit of the magnetisation recovery with a single exponential was achieved, with an acceptable match. It is known that for quadrupolar nuclei such as  $^7\text{Li}$  ( $I = 3/2$ ), recovery of the magnetization is not necessarily single-exponential; however, it was shown that the quadrupolar contribution to the NMR lineshape of  $\text{LiCoO}_2$  is rather small (12), so that such a fit is considered to be significant to yield the T1 value. This leads to about 3.5 s

for such “standard” stoichiometric compounds. This is significantly shorter than the  $^7\text{Li}$  NMR T1 for Li carbonate, considered as model diamagnetic compounds (150 s) (13).

For Co-pure  $\text{Li}_1\text{CoO}_2$  (prepared with a long annealing from “Co-pure”  $\text{Co}_3\text{O}_4$ ), the NMR signal is strictly identical (no trace of additional signal) but the T1 measured (again with a satisfactory single exponential fit of the recovery) reaches 18 seconds, which we consider as a proof that virtually no electron spin is present in the compound. Clearly, the mere presence of trace paramagnetic impurities of most probably Ni and/or Fe originating from the starting “standard”  $\text{Co}_3\text{O}_4$  is enough to shorten the  $^7\text{Li}$  NMR T1 by one order of magnitude. The 18 s value obtained is indeed still shorter than for  $\text{Li}_2\text{O}$  or  $\text{Li}_2\text{CO}_3$  but the van Vleck paramagnetism of low spin  $\text{Co}^{3+}$  is anyway present; furthermore, the relaxation mechanisms can be different, and the absence of paramagnetic impurity is probably not absolute, even with the Co-pure  $\text{Co}_3\text{O}_4$ .

In the (quasi) absence of paramagnetic impurities, the value of T1 is a particularly severe criterion for the sample stoichiometry. Indeed, for compounds prepared in the same way with Co-pure  $\text{Co}_3\text{O}_4$  but with a final thermal treatment ranging from 1 to 15 days, the  $^7\text{Li}$  NMR spectrum obtained is strictly identical to that shown in Fig. 1, but the T1 value typically ranges between 1 and 18 seconds. Note that identical thermal treatments on different batches may lead to significantly different T1’s, but there is a clear trend that T1 increases with the thermal treatment duration, and the “maximum” value of 18 s can be guaranteed only for a 15 day thermal treatment in our experimental conditions (of course when using Co-pure  $\text{Co}_3\text{O}_4$  as starting material).

This suggests that, for shorter thermal treatments, the sample is not free from paramagnetic defects, that we assume are the sign of a slight tendency to Li-overstoichiometry in the form of IS  $\text{Co}^{3+}$ , in too small amount though to lead to observable extra peaks on the Li NMR spectrum. Since the reagents are used in nominally stoichiometric

amount, this is probably related to the fact that the  $\text{Co}_3\text{O}_4$  compound obtained by thermal decomposition of either cobalt nitrate or carbonate may not be pure, or may have some Co deficiency (14). Again, none of these facts could be evidenced by XRD, but let us emphasize again that T1 is extremely sensitive to the presence of paramagnetic defects. In order then to obtain a really stoichiometric compound, it is necessary to perform a very long annealing at  $900^\circ\text{C}$  under oxygen, which was already shown in (8) to lead to the formation of stoichiometric  $\text{LiCoO}_2$  by elimination of  $\text{Li}_2\text{O}$  from the overstoichiometric compound.

### *Electrochemical characteristics*

The electrochemical behaviour of such (very stoichiometric) standard  $\text{Li}_1\text{CoO}_2$  is shown as the first dynamic cycle at C/20 (one Li in 20 h) in Fig. 2, no significant difference being found with the “Co-pure” analogue. This galvanostatic cycling curve is significantly different (see insert in Fig. 2) from the one we reported earlier from an  $\text{LiCoO}_2$  sample that was considered as stoichiometric from the absence of detectable “additional”  $^7\text{Li}$  NMR signals (leading therefore to a spectrum identical to that presented in Fig. 1), but whose T1 had not been investigated (4). This compound had in any case not been annealed for a long time as explained in the present work, and can therefore in retrospect be considered to be slightly less stoichiometric than those of the present study. An “overshoot” is clearly observed for the (very stoichiometric)  $\text{Li}_1\text{CoO}_2$ , which originates from the fact that the pristine compound is a very bad electronic conductor (as containing only LS  $\text{Co}^{3+}$  ions), leading to a strong initial polarization of the electrochemical cell. When deintercalation starts, oxidation of Co induces a hopping-like hole conduction as shown in (4), which then allows this polarization to relax, leading to the observed characteristic behaviour. Fig. 2 also shows a particularly well defined feature for the monoclinic-distorted  $\text{Li}_{0.5}\text{CoO}_2$  composition, with two well apparent two-phase plateaus separating the distorted compound from the undistorted ones. Again, this is very well

in line with the highly stoichiometric character of the compound, since we showed earlier that Li-overstoichiometry suppresses this voltage feature (8). Another apparent feature is that the very stoichiometric compound exhibits a better reversibility of the first cycle, which may again be related to the presence of the metallic  $\text{Li}_{0.75}\text{CoO}_2$  phase down to the very end of the discharge process.

Since the “overshoot” feature discussed above hinders proper observation of the two-phase domain in dynamic conditions, we ran GITT experiments on a pellet of standard  $\text{Li}_1\text{CoO}_2$  without additive, at very low rate and with a severe 0.1 mV/h voltage stability criterion for the relaxation periods. Fig. 3 shows a very strong overshoot at the onset of deintercalation; indeed, the absence of conducting agent enhances the effect of the appearance of electronic conductivity in the active material. Furthermore, it is clear that the two-phase domain indeed starts very early (the second deintercalation step corresponds to  $\text{Li}_{0.99}\text{CoO}_2$ ) for such “very stoichiometric” compound, as again compared with the characteristics of an  $\text{LiCoO}_2$  sample earlier considered as stoichiometric on the basis of the NMR signal, but whose T1 had not been determined (4). Again, this reinforces the argument that even a very small amount of structural defects induced by any slight amount of Li-overstoichiometry that can only be evidenced by measuring the Li NMR T1 relaxation time can hinder the long range electronic delocalization that prevails to the establishment of the two-phase domain.

It is also worth to compare the first cycle of our very stoichiometric  $\text{LiCoO}_2$  with that reported by Shao-Horn and co-workers for  $\text{AlPO}_4$ -coated  $\text{LiCoO}_2$  (15). These authors suggest that reaction of  $\text{AlPO}_4$  with initially slightly over-stoichiometric  $\text{LiCoO}_2$  leads to formation of  $\text{Li}_3\text{PO}_4$  and to stoichiometric  $\text{LiCoO}_2$ . Even though remaining Al seems to partly substitute for Co at the surface of  $\text{LiCoO}_2$ , its stoichiometric nature is fully confirmed by the close similarity of the charge curve of this coated compound with that of our very stoichiometric sample. One may therefore wonder whether the main beneficial effect of such coating is not

simply to render the  $\text{LiCoO}_2$  very stoichiometric by inducing the rapid loss of excess  $\text{Li}_2\text{O}$  at moderate temperature, which might make it more stable towards Co dissolution and thermal decomposition. Further cycling and thermal stability characterization of bare very stoichiometric  $\text{LiCoO}_2$  as obtained in the present paper should shed light on this aspect.

### *Magnetic susceptibility*

Magnetic susceptibility measurements for Co-pure  $\text{Li}_1\text{CoO}_2$  are shown in Fig 4 and 5. The magnetization versus field is linear at room temperature and quasi-linear at 5 K; with no hysteresis. The field cooled (FC) and zero field cooled (ZFC) susceptibility measurements at 1 T are pretty similar and show essentially a temperature independent magnetism, with some indication of local moments at low temperature. The susceptibility at room temperature is about  $90 \cdot 10^{-6}$  emu/mol, which is significantly lower than the value (about  $200 \cdot 10^{-6}$  emu/mol) reported earlier for a sample prepared from standard  $\text{Co}_3\text{O}_4$  and that was considered as stoichiometric based on the  $^7\text{Li}$  NMR signal but, as already mentioned above, without T1 characterization (8). The value obtained in Fig. 5 for the present (very stoichiometric) sample is fully consistent with the diamagnetic plus van Vleck contribution for low spin  $\text{Co}^{3+}$ , considering for the latter the value given for  $\text{Na}_1\text{CoO}_2$  ( $150 \cdot 10^{-6}$  emu/mol) by Lang et al. (16).

### *Specific heat*

Fig. 6 shows the specific heat capacity  $C_p$  of Co-pure  $\text{Li}_1\text{CoO}_2$  from 1.8 K to 300 K. Over the temperature range considered, the data can be fitted using a linear electronic contribution and a single Debye term for the network contribution as follows (17):

$$C_p(T) = \gamma_{\text{HT}} T + 9nR \left( \frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (\text{I})$$

The first term  $\gamma_{HT}$  represents the temperature-linear electronic contribution and the second term is the Debye-type contribution.  $R = 8.314 \text{ J/mol.K}$  is the molar gas constant,  $\theta$  is the Debye temperature and  $n$  is the number of atoms per mole ( $n = 4$ ). A decent agreement with the dataset was achieved with  $\gamma_{HT} = 0.0(1) \text{ J/mol.K}^2$  and  $\theta = 795(1) \text{ K}$  (Figure 6a)).

At temperatures below 10 K, the electronic contribution to the specific heat has been calculated using the Debye approximation  $C/T = \gamma + \beta(\theta)T^2$ . A linear fit to the data using this equation (Figure 6b)) gives  $\theta = 834(28) \text{ K}$  deduced from  $\beta(\theta) = 12\pi^4 nR / (5\theta^3)$  and  $\gamma = 4.5(2) \times 10^{-5} \text{ J/mol.K}^2$ . This latter is one order of magnitude lower than the value reported recently for a nominally stoichiometric  $\text{LiCoO}_2$  sample that was however assumed to contain a slight amount of Li excess (7).

The values of  $\gamma$  and  $\theta$  obtained in the high and low temperature domains are very close and suggest a good consistency of our calculations. The extremely small  $\gamma$  is in good agreement with the insulating behaviour of the non-magnetic  $\text{CoO}_2$  layers with LS  $\text{Co}^{3+}$  in (really) stoichiometric  $\text{Li}_1\text{CoO}_2$ .

## Conclusion

Really stoichiometric  $\text{Li}_1\text{CoO}_2$  is rather delicate to obtain, but can be. Its properties, including the Li NMR T1 relaxation time, are characteristic of the exclusive presence of diamagnetic LS  $\text{Co}^{3+}$  ions. The fact that a rather long annealing is required confirms that  $\text{LiCoO}_2$  has a propensity to accommodate excess Li when present during the synthesis, and that the inherently stable compound (in the absence of Li vapour pressure) is the stoichiometric compound. Simply, it takes some time even at  $900^\circ\text{C}$  for the excess Li to be eliminated in the form of  $\text{Li}_2\text{O}$  since this involves a redistribution of the Co-O bonds, and since this  $\text{Li}_2\text{O}$  needs to sublime.

Only when (virtually) no structural defects are present does the two-phase domain induced by macroscopic electronic delocalization upon Co oxidation start quite at the onset of Li deintercalation. Similarly, in this case, the voltage feature driven by Li/vacancy ordering for the  $\text{Li}_{0.5}\text{CoO}_2$  composition appears with unprecedented clarity. Particularly when no conducting agent is used (even with very low current density), the initial absence of any electronic conduction leads to a significant overshoot of the voltage at the very beginning of the first charge.

Such very stoichiometric  $\text{Li}_1\text{CoO}_2$  has been used for XPS investigation of the redox phenomena during deintercalation (18), and is currently used for EPR and muon-SR characterization to be reported elsewhere.

Acknowledgements:

The authors wish to thank Cathy Denage for technical assistance.

## References

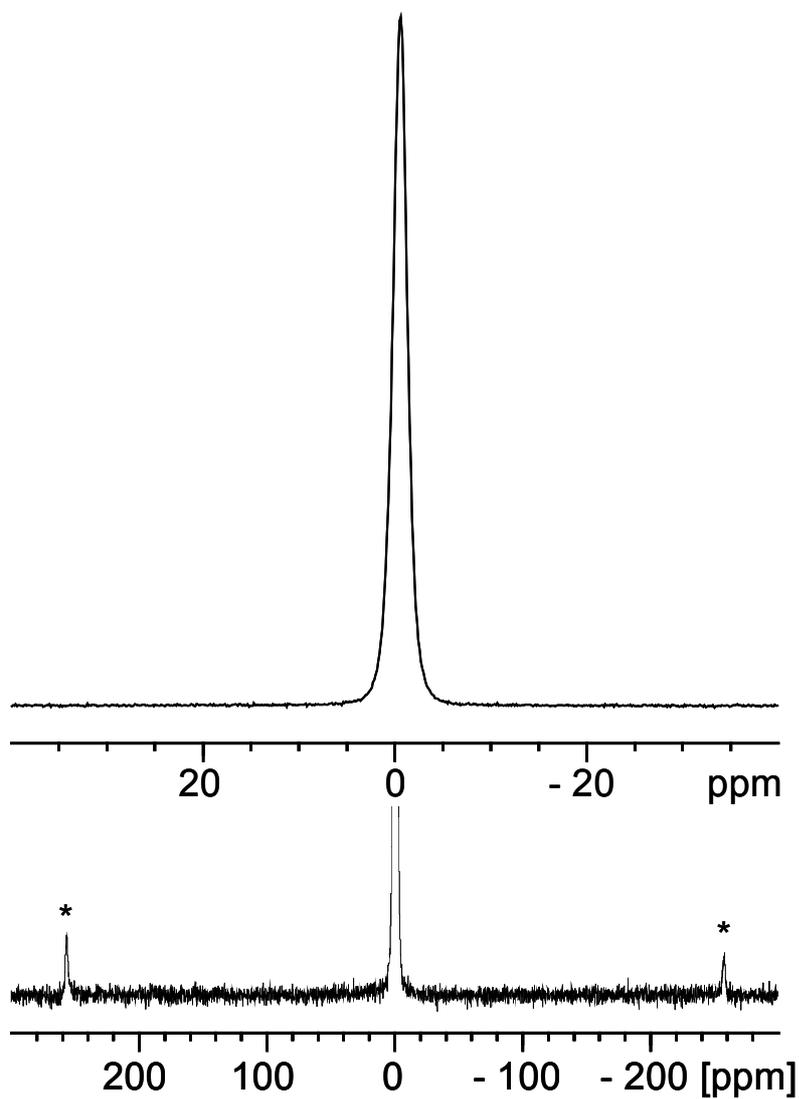


Figure 1:  ${}^7\text{Li}$  MAS NMR spectrum of standard  $\text{Li}_1\text{CoO}_2$  (116 MHz, spinning 30 kHz, synchronized echo). Top: full scale; bottom: 20 times expanded intensity scale (\*: spinning sidebands)

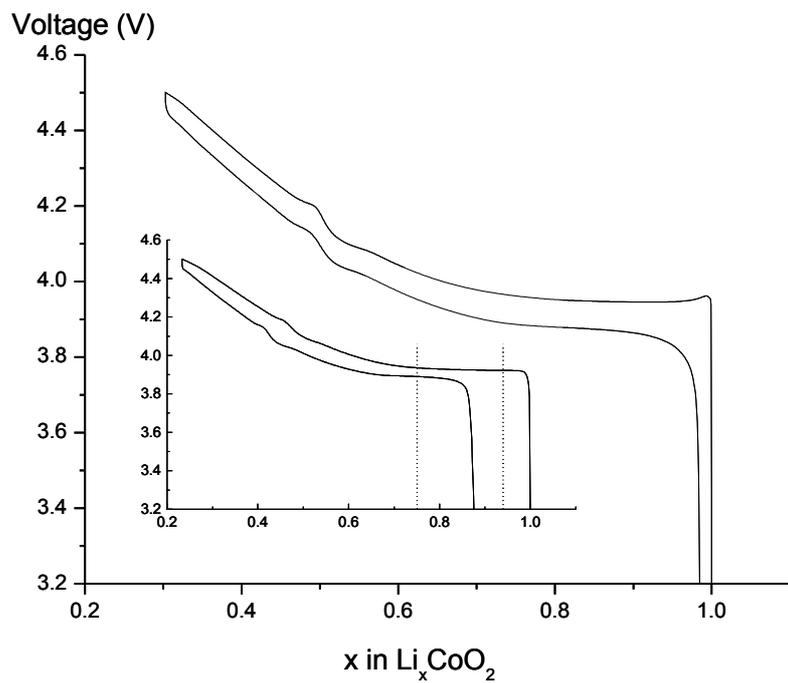


Figure 2: First dynamic galvanostatic charge-discharge cycle of a Li//( $\text{Li}_1\text{CoO}_2$ -carbon) cell (one Li in 20 h). Inset: comparison with an  $\text{LiCoO}_2$  earlier considered as stoichiometric from ref (4).

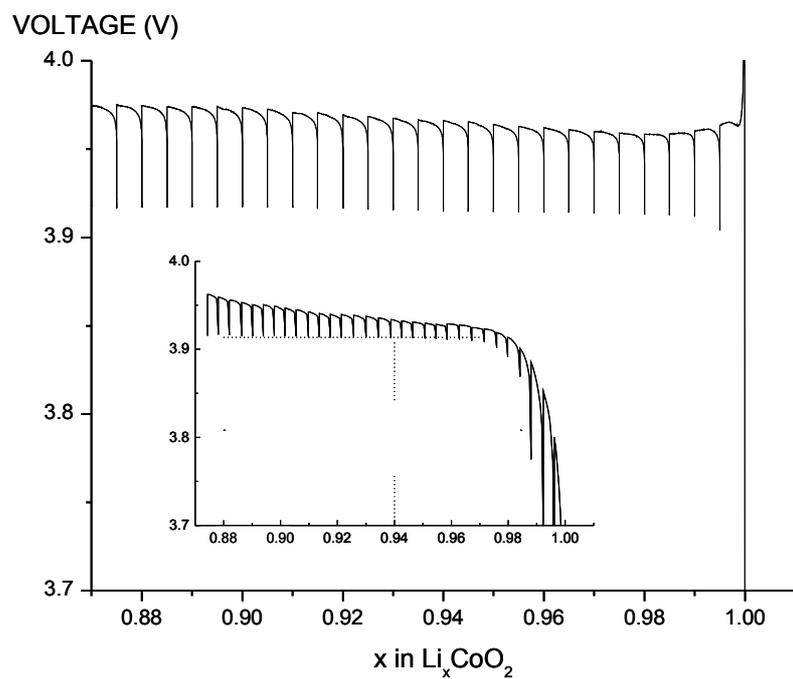


Figure 3: First GITT charge of a Li//standard  $\text{Li}_1\text{CoO}_2$  cell (120 min steps with one Li in 300 h, relaxation steps with 0.1 mV/h voltage stability). Insert: comparison with an  $\text{LiCoO}_2$  earlier considered as stoichiometric from ref (4).

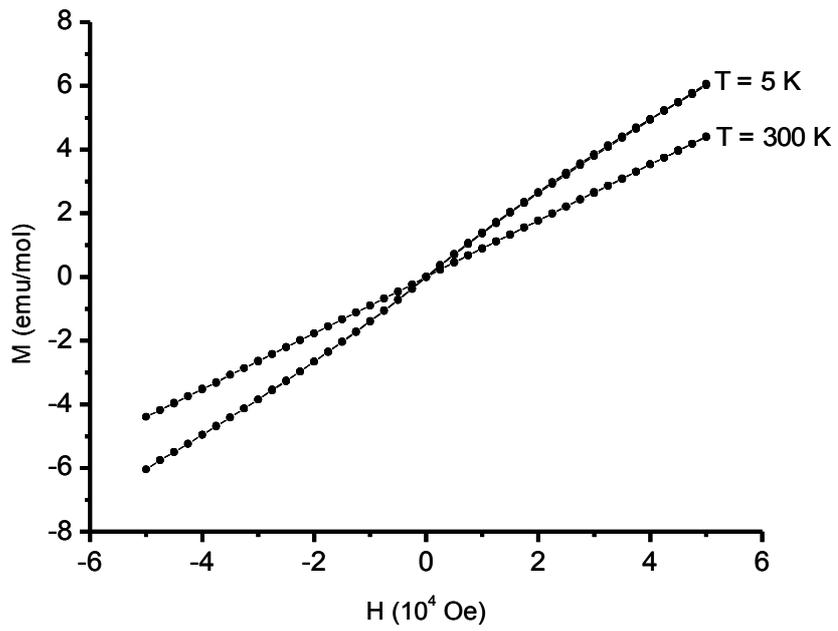


Figure 4: Magnetization vs. field for Co-Pure Li<sub>1</sub>CoO<sub>2</sub>.

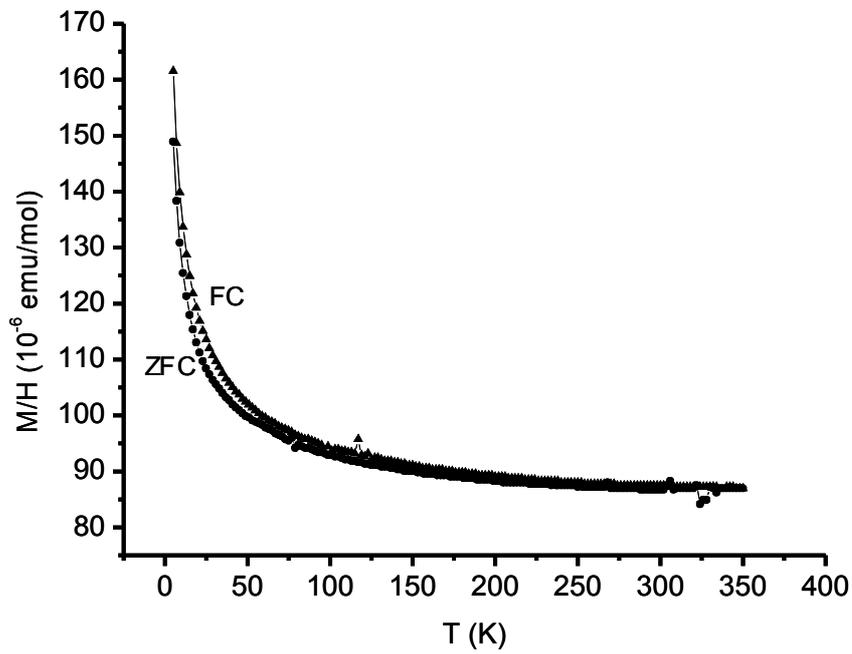


Figure 5: Susceptibility vs. temperature at 1 T for Co-pure  $\text{Li}_1\text{CoO}_2$  (no diamagnetic correction was done).

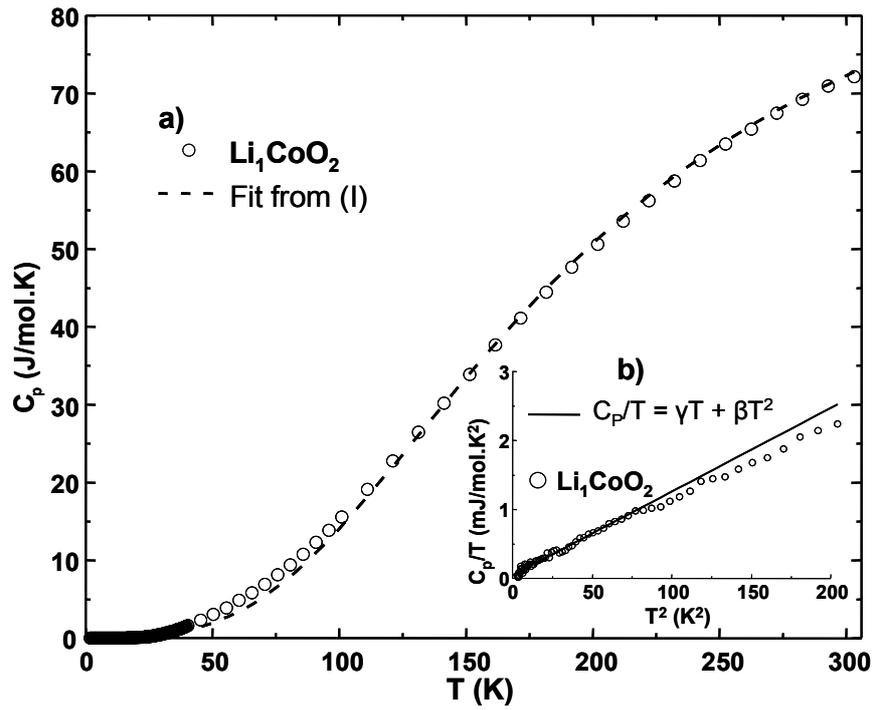


Figure 6: Specific heat data for Co-pure  $\text{Li}_1\text{CoO}_2$ . a) The dashed curve corresponds to the model described in (I). Panel b) represents the low-temperature dependence of  $C_p/T$  vs.  $T^2$ .