



# Charging of lithium cobalt oxide battery cathodes studied by means of magnetometry



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## ABSTRACT

The variation of the structural and electronic properties of  $\text{Li}_x\text{CoO}_2$  upon electrochemical Li-extraction was studied over wide range concentration of  $1 \geq x \geq 0.20$  by means of SQUID magnetometry. The ex-situ measurements performed for 13 different compositions were supplemented by operando measurements of the magnetic moment during repetitive electrochemical in-situ cycling of the Li-concentration. From the temperature-dependent measurements an effective magnetic susceptibility with Curie–Weiss behavior and an additional temperature-independent part due to Pauli and Van Vleck magnetism is derived. The increase of the temperature-independent susceptibility with Li-extraction reflects a concomitant increase of the electronic density of states and, in addition, indicates an Anderson-type of the occurring nonmetal–metal transition. The effective magnetic moment reveals that only a fraction of 30% of the charge is transferred to Co upon Li-extraction indicating a complex oxidation behavior involving oxygen. Exposure to ambient atmosphere gives rise to a complete oxidation of Co. The results on the structural variation with Li-concentration are compared with accompanying measurements by X-ray diffraction and by our recent defect studies by positron annihilation.

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## 1. Introduction

Due to the high technological relevance of  $\text{LiCoO}_2$  as cathode material of Li-ion batteries, much efforts are undertaken for better understanding the processes during charging on an atomistic scale. In addition to the regime of reversible Li de-/intercalation down to  $\text{Li}_{0.50}\text{CoO}_2$ , where the exact determination of the state of charge is still a challenging issue [1], also the processes underlying the performance loss when extracting more than 50% Li are of interest. A broad variety of characterization techniques is applied for this purpose, such as X-ray diffraction [2,3], nuclear magnetic resonance [4], X-ray photoelectron [5–7], or X-ray absorption [7] to mention only a few of them.

In addition to those techniques, magnetometry has proven as powerful tool since the magnetic moment of electrode materials is highly sensitive to structural phase changes, impurities, metallic/non-metallic transitions, and the oxidation state of the transition metal ions (see review by Chernova et al. [8]). In fact, the magnetic susceptibility changes by several 100% with Li de-/intercalation and, therefore, serves as sensitive fingerprint of the charging state. Over the last few years, various groups were concerned with magnetic measurements on  $\text{Li}_x\text{CoO}_2$  cathodes [4,7,9–22]. Studies over a certain range of concentrations

were performed by extracting Li either chemically or electrochemically: chemical Li extraction by Kellerman et al. [7] ( $0.98 \geq x \geq 0.60$ , 6 samples), Hertz et al. [9] ( $1 \geq x \geq 0.51$ , 9 samples), or Miyoshi et al. [10] ( $0.99 \geq x \geq 0.25$ , 6 samples), electrochemical Li extraction by Sugiyama et al. [11] ( $1 \geq x \geq 0.70$ , 3 samples), Mukai et al. [12] ( $1 \geq x \geq 0.10$ , 8 samples) or Motohashi et al. [13] ( $1 \geq x \geq 0$ , 9 samples).

In order to gain further detailed insight on the structural and electronic variation of  $\text{Li}_x\text{CoO}_2$  with Li-content  $x$ , the present work is devoted at in-depth study of SQUID magnetometry comprising more than a dozen different Li concentrations. Commercially applied cathode material was used for the present studies. All different sample compositions were characterized by XRD. A wide range concentration  $1 \geq x \geq 0.20$  was covered extending well beyond the limit of reversible charging,<sup>1</sup> and, in addition, the effect of exposure to ambient atmosphere was addressed. Compared to previous studies, particular emphasis was laid on minimizing the background signal of the magnetometer sample holder and, moreover, applying a procedure for proper subtraction of any residual background signal so that the magnetic susceptibility exclusively from the  $\text{Li}_x\text{CoO}_2$  samples could be determined. The results on the structural variation with Li-concentration are compared with

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<sup>1</sup> The terminology reversibility limit used here and in the following refers to the long term reversibility, for which a Li extraction beyond  $x = 0.50$  has to be avoided.

recent defect studies by positron annihilation performed by our group on the very same type of  $\text{Li}_x\text{CoO}_2$ -samples [23].

A particular issue of the present studies pertains the comparison with accompanying operando SQUID measurements of the susceptibility variation of  $\text{Li}_x\text{CoO}_2$  upon reversible electrochemical cycling the Li-content. Operando measurements by means of an electrochemical cell operated in a SQUID magnetometer [24] open up the possibility to monitor charging-induced variations of the magnetic moments continuously and during repetitive cycles. Initial results on this novel technique are communicated elsewhere [25].

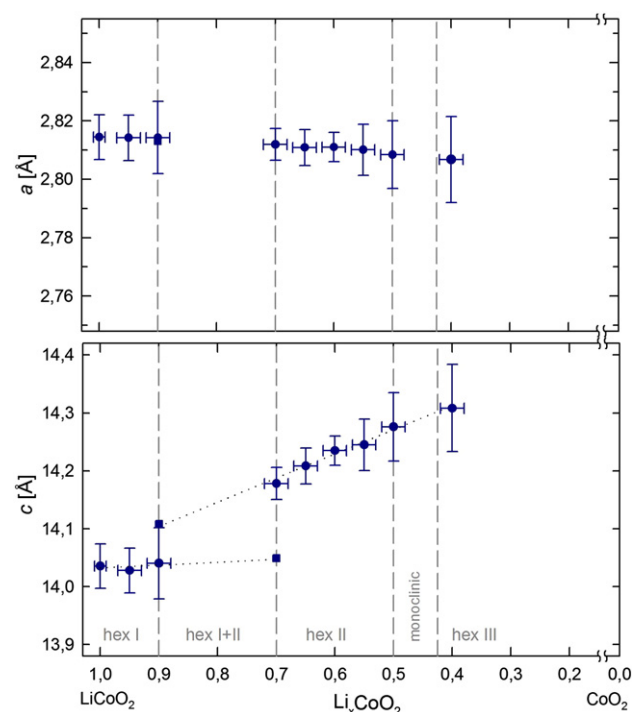
## 2. Experimental

The  $\text{LiCoO}_2$  samples were prepared in the same way as commercially used ones. A mixture containing 88 wt% of  $\text{LiCoO}_2$  particles, 7 wt% carbon black (Super P) as conducting agent and 5 wt% binder (poly(vinylidene difluoride hexafluoropropylene copolymer)) was dissolved in NMP (*N*-Methyl-2-pyrrolidone). Subsequently, the slurry was coated on aluminum foils (thickness of 0.25 mm), pre-dried at 333 K in air, followed by a 24 h heat treatment at 353 K in vacuum ( $10^{-3}$  mbar). On each sample foil with a diameter of 12 mm, active cathode material of about 35 mg was deposited.

The lithium extraction was performed electrochemically in a Maccor Series 4000 battery tester. The  $\text{LiCoO}_2$  cathodes were mounted as working electrode into a 3-electrode test cell (Swagelok-T-cell), separated from the metallic lithium foil counter and reference electrode by a non-woven polypropylene separator (Freudenberg FS2190). A mixture of ethylene carbonate and ethyl methyl carbonate (volume ratio EC/EMC 3:7) was used as electrolyte with 2 wt% vinylene carbonate and 1 M  $\text{LiPF}_6$  as conducting salt. After a 12 h rest, the Li ions were extracted to a predefined Li concentration  $x$  in the  $\text{Li}_x\text{CoO}_2$  cathodes. The chosen constant current density of  $13.5 \mu\text{A cm}^{-2}$  corresponds to a C-rate of 0.005 (complete Li-extraction in 200 h). The charging time for a pre-defined Li concentration  $x$  in the range of  $1 \geq x \geq 0.20$  was determined using a theoretical specific charge capacity of 274 mAh/g for complete lithium extraction. After the lithium extraction, the cathodes were dismantled, rinsed with diethyl carbonate to remove the electrolyte, and finally dried in a vacuum ( $10^{-3}$  mbar) at 353 K for 24 h. In total 13 different compositions were prepared. Reproducibility was tested by comparing each two samples of identical compositions for a few selected compositions.

Magnetic susceptibility measurements were performed in a temperature range between 300 and 8 K (field cooling) at a constant magnetic field of 10 kOe, using a superconducting quantum interference device (SQUID: Quantum Design MPMS-XL-7). To enable a precise determination of the magnetic susceptibility of the  $\text{Li}_x\text{CoO}_2$  samples, a sample holder with minimized contribution to the magnetic signal was designed. The samples were placed in the middle of a 14 cm long polyolefin tube (diameter 3.2 mm). For this purpose the  $\text{Li}_x\text{CoO}_2$ -coated Al-foils were folded in such a way that they remained fixed at the pre-defined position. The polyolefin tube was mounted into an NMR-tube (Wilma 505-PS-7) which was closed with a teflon plug and hermetically sealed with epoxy resin. An appropriate tube length was chosen to ensure that the tube extended well beyond the SQUID pickup coils during the measurement scan. In this way it was guaranteed that the tubes do not contribute to the measured magnetic moment, similar as described for long homogenous substrates by Manios et al. [26].

In order to subtract the magnetic signals caused by the aluminum substrate and the 12 wt% additives (carbon black and polymer binder), the temperature-dependent susceptibility was measured for both the plain Al substrate and the Al substrate coated with polymer binder and carbon in the same volume ratio as for the  $\text{LiCoO}_2$ -samples. By means of these magnetic data along with the molar weights of all components, a precise correction of the background signal of each sample could be achieved. Sample preparation, handling and transfer into the SQUID device were carried out under protective Ar-atmosphere. Since the magnetic measurements were performed under He-atmosphere,



**Fig. 1.** Lattice parameters  $a$  and  $c$  of the three hexagonal phases deduced from XRD of  $\text{Li}_x\text{CoO}_2$  in dependence of Li concentration  $x$ . For  $\text{Li}_{0.45}\text{CoO}_2$ , a monoclinic phase was observed. Minor traces of the monoclinic phase were already observed for  $\text{Li}_{0.50}\text{CoO}_2$ . The data points (■) were obtained from the shoulders of the 003-peaks (see text). The dotted lines are guides for the eyes.

inert gas conditions prevail during the whole procedure up to the end of the magnetic measurements.

After the magnetic measurements, the samples were structurally characterized by X-ray diffractometry using a Bruker D8 Advance diffractometer in Bragg-Brentano geometry with  $\text{Cu-K}\alpha$ -radiation. The experimental procedure for operando measurements of the magnetic susceptibility on identically prepared  $\text{LiCoO}_2$  sample material is described elsewhere [25].

## 3. Sample characterization

The XRD measurements on  $\text{Li}_x\text{CoO}_2$  cathodes revealed three rhombohedral phases ( $R\bar{3}m$ ) and one monoclinic phase in the studied range  $1.0 \geq x \geq 0.40$  of Li concentrations. Following the procedure in literature, the XRD data of the rhombohedral structure are analyzed according to a hexagonal phase [2,3].

In Fig. 1, the lattice parameters  $a$  and  $c$  corresponding to a hexagonal unit cell are displayed as a function of Li-content  $x$ . For the first hexagonal phase (hex I) constant lattice parameters were found in the Li concentration range of  $1 \geq x \geq 0.90$ .

For the second hexagonal phase (hex II), a slight decrease of the lattice parameter  $a$  and a linear increase of the  $c$  parameter occurs in the range  $0.70 \geq x \geq 0.50$  which reflects an increasing Coulomb repulsion of the anions upon Li-extraction, as reported in literature [2,4]. For  $x = 0.90$ , a shoulder in the (003) diffraction peak of the dominant hexagonal-I phase indicates a minor phase fraction, the  $c$ -parameter of which nicely fits to that of the hexagonal-II phase; likewise, for  $x = 0.70$  indication of a minor hexagonal-I phase is deduced from the (003)-peak of the dominant hexagonal-II phase (see blue squares in Fig. 1). This indicates that for  $0.90 \geq x \geq 0.70$  both hexagonal phases coexist.<sup>2</sup> Li extraction

<sup>2</sup> It should be noted that for  $\text{Li}_x\text{CoO}_2$  it is not possible to detect secondary phases at levels lower than 5% with XRD measurements [27]. Therefore the phase separation could start already at higher Li-contents as indicated by potentiostatic measurements in literature [22,27].

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