

Electronic state of cobalt and oxygen ions in stoichiometric and nonstoichiometric $\text{Li}_{1+x}\text{CoO}_2$ before and after delithiation according to XPS and DRS

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Abstract

X-ray, IRS, XPS, EDRS and magnetic measurements were used to study $\text{Li}_{1+x}\text{CoO}_2$ ($0 < x \leq 0.1$) samples prepared by conventional ceramic method. It was shown that nonstoichiometric $\text{Li}_{1+x}\text{CoO}_2$ are characterized by homogeneous crystal structure with statistically distributed vacancies in the cobalt and oxygen layers and the increased Co–O bond covalency. The excess lithium results not in the reduction of Co^{3+} ions, but in the appearance of a new state of oxygen ions different from cell oxide, with higher value of binding energy (BE), i.e. with smaller electronic density. Acid treatment of $\text{Li}_{1+x}\text{CoO}_2$ leads to the appearance of delocalized (itinerant) electrons. The electronic state of cobalt ions does not change noticeably whereas the additional oxygen state increases significantly, thus, evidencing that oxygen ions do compensate for the charge upon chemical delithiation. The structure of nonstoichiometric samples appeared to be more stable upon this process. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

The cycling behavior of rechargeable lithium batteries strongly depends on the crystal and electronic structure of intercalation cathode materials. Traditionally, it has been accepted that in LiCoO_2 the valence state of the cobalt ions compensates for the charge on the intercalated lithium: $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$. The assumption was that the oxygen valence state is fixed at O^{2-} . Recently, Ceder et al. [1] have shown that the oxygen ions play the dominant role in accepting the incoming charge.

The authors [2] showed that the excess lithium in LiCoO_2 influences its electrochemical characteristics. They did not find any difference in the crystal structure of stoichiometric and nonstoichiometric samples. However, the electronic structure of nonstoichiometric $\text{Li}_{1+x}\text{CoO}_2$ was not investigated. The aim of the present study was a spectroscopic investigation of $\text{Li}_{1+x}\text{CoO}_2$ ($0 < x \leq 0.1$) before and after delithiation. Our attention was focused on the study of the electronic state of cobalt and oxygen ions.

2. Experimental

$\text{Li}_{1+x}\text{CoO}_2$ samples with $x = 0, 0.05$ and 0.1 were prepared starting from Li_2CO_3 and Co_3O_4 by conventional ceramic method at 800°C with slow cooling in air. The samples as-prepared were delithiated by aqua distillata with pH 5.5 and sulfuric acid solutions (0.1–1.0N) for 1 h. Then they were dried at 100°C in air.

The samples were investigated using X-ray powder diffraction (DRON-3.0 diffractometer, $\text{Cu K}\alpha$ irradiation), IR spectroscopy (Bruker FTIR spectrometer), electron diffuse reflectance spectroscopy (UV-VIS 4501 Shimadzu spectrophotometer), XPS (VG ESCALAB HP, $\text{Al K}\alpha$ irradiation) and magnetic measurements.

3. Results and discussion

3.1. Characterization of $\text{Li}_{1+x}\text{CoO}_2$ samples as-prepared

According to XRD, all obtained samples were homogeneous with the structure assigned to HT- LiCoO_2 [3]. The clear splitting of (0 0 6) and (0 1 2); (0 1 8) and (1 1 0)

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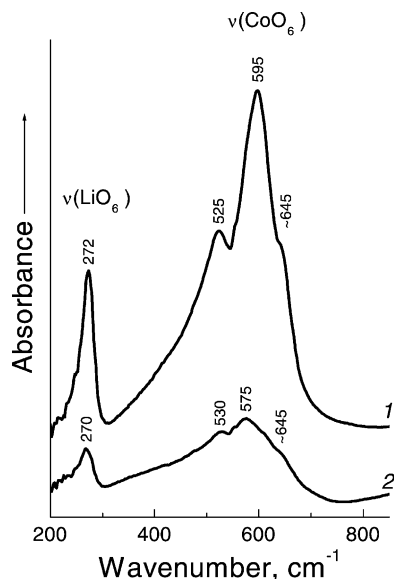
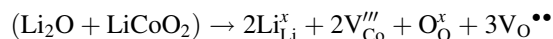


Fig. 1. IR spectra of LiCoO_2 (1) and $\text{Li}_{1.1}\text{CoO}_2$ (2).

reflections was observed; the c/a ratio was equal to 4.99. The absence of a weakening of (0 0 3) reflection intensity for nonstoichiometric samples excludes the presence of a noticeable amount of cobalt ions in the lithium layers. The unchangeable intensity ratio of (0 0 3) and (1 0 4) reflections shows the preservation of lithium and cobalt ions ordering. Calculation of cell parameters shows that Co–O bond length and an interlayer distance do not change noticeably with added lithium.

In the IR spectrum of the stoichiometric sample, two bands at 598 and 273 cm^{-1} , corresponding to $\nu(\text{CoO}_6)$ and $\nu(\text{LiO}_6)$, are present [4] (Fig. 1). For nonstoichiometric samples, the bands' intensity significantly decrease along with their broadening. This points to the heterogeneity of a close structural environment for cobalt and lithium ions

showing the formation of defects (vacancies) statistically distributed over the bulk:



The shift of $\nu(\text{CoO}_6)$ to lower frequencies points (or evidences) to increase of the Co–O bond covalency.

On the contrary, Co 2p XPS spectra of stoichiometric and nonstoichiometric samples are practically identical (Fig. 2). The position of the Co 2p_{3/2} line (780 eV) as well as the fine structure (the value of spin-orbital splitting, equal to 15 eV, and the presence of weak shake-up satellites) are characteristic of Co^{3+} ions in octahedral oxygen coordination [5,6]. The absence of additional lines in the Co 2p spectrum shows that the excess lithium does not lead to reduction of Co^{3+} to Co^{2+} .

The most discrepancy is observed in the O 1s spectra (Fig. 2). The O 1s lines consist of two components with the binding energy (BE) of 529.3 and 531.7 eV. The first peak, doubtless, is attributed to the cell oxygen in the perfect LiCoO_2 crystal structure. The nature of the second component should be discussed in details. It is known that surface admixtures of lithium and cobalt carbonate and hydroxide bring to the appearance of O 1s lines with close values of BE: 531.1–531.2 eV for LiOH and Li_2CO_3 [7], and 531.3 eV for $\text{Co}(\text{OH})_2$ [8]. However, the preparation conditions (synthesis temperature of $800\text{ }^\circ\text{C}$ in air, as well as the preliminary treatment at $450\text{ }^\circ\text{C}$ for 10 h in a vacuum inside a XPS spectrometer) allows exclusion the presence of surface lithium or cobalt hydroxides, and lithium peroxide. This oxygen state can be associated with surface carbonates for a stoichiometric sample since $[\text{O}]/[\text{C}]$ ratio for it is equal to 3. However, for stoichiometric samples, $[\text{O}]/[\text{C}]$ ratio is equal to 10, thus showing the formation of a new oxygen state, different from the cell oxide, with a higher value of BE, i.e. with smaller electronic density.

In DRS spectrum of the stoichiometric sample, two clear bands at $17,000\text{ cm}^{-1}$ (2.1 eV) and $29,000\text{ cm}^{-1}$ (3.6 eV)

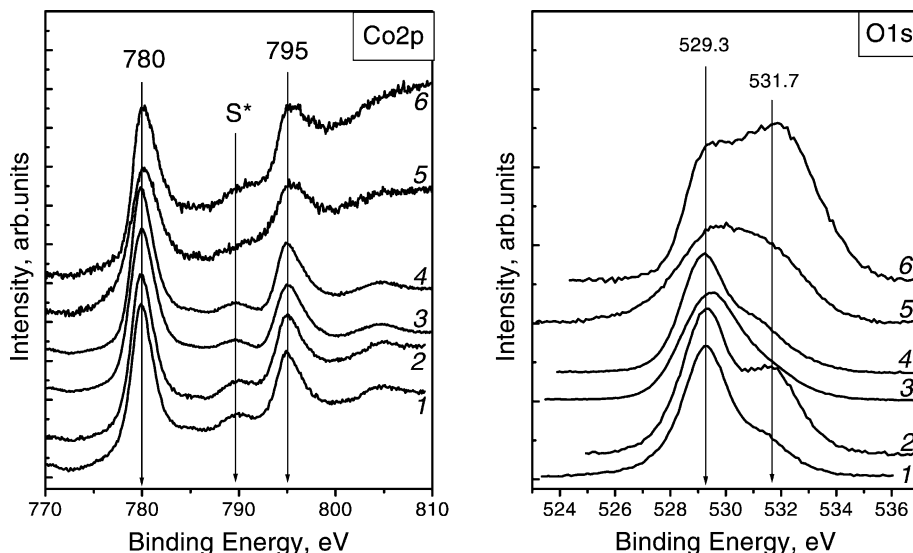


Fig. 2. Co 2p and O 1s spectra of: (1) LiCoO_2 ; (2) $\text{Li}_{1.1}\text{CoO}_2$; (3 and 4) samples 1 and 2 treated in water; (5 and 6) samples 1 and 2 treated in 1N H_2SO_4 .

Table 1
Magnetic measurements data

Sample	A_0 ($\text{cm}^3/\text{mol} \times 10^4$)	C ($\text{cm}^3 \text{K}/\text{mol}$)	θ (K)	$\text{Co}^{2+}/\text{Co}_{\text{tot}}$ (%)
LiCoO_2	1.02	0.000868	47	–
$\text{Li}_{1.05}\text{CoO}_2$	0.849	0.0309	–52	1.65
$\text{Li}_{1.10}\text{CoO}_2$	0.799	0.0382	–46	2.03

are observed. It is known that the main state of cobalt ions in LiCoO_2 is a low-spin octahedrally coordinated Co^{3+} ($t_{2g}^6 e_g^0$) with the ${}^1A_{1g}$ ground state. Thus, the DRS spectrum must exhibit two transitions to the ${}^1T_{1g}$ and ${}^1T_{2g}$ excited states [6]. According to the first principle calculations [9], the line with 2.1 eV must be assigned to an electron transition from Co 3d t_{2g} valence band (Fermi level) to Co 3d e_g^* conductive band. The second line with $E = 3.6$ eV is associated with charge-transfer from t_{1u} (mostly, O 2p orbital) to Co 3d e_g^* . In fact, XES shows that the splitting of the occupied Co 3d and O 2p orbitals is equal to 1.6 eV [10].

The excess lithium leads to decrease of d–d transition with $E = 2.1$ eV. The new band at 11,000–14,000 cm^{-1} arises, which can be associated with the appearance of admixture levels inside the band gap due to defect formation. The decrease of the charge transfer band intensity is a result of a decrease of the O 2p orbitals occupancy and an increase of the Co–O bond covalency.

According to magnetic measurements, the concentration of paramagnetic centers increases for nonstoichiometric samples. Magnetic susceptibility is well described by Curie–Weiss law (Table 1). The different sign of θ for stoichiometric and nonstoichiometric samples allows to suppose the different types of paramagnetic centers.

3.2. Characterization of water-treated samples

Chemical analysis shows that water treatment brings minor lithium extraction (Table 2). X-ray patterns as well as cell parameters did not change noticeably. The shape and the position of IR bands were unaltered, except a inessential

intensity growth. In XPS spectra of all samples, a slight decrease of Li 1s peak intensity is observed showing the process of partial lithium deintercalation. Simultaneously, insignificant broadening of Co 3p, Co 2p and O 1s lines takes place (Fig. 2). According to magnetic measurements, water treatment of the samples does not lead to noticeable change of their magnetic properties.

On the contrary, DRS spectra changed significantly (Fig. 3b). They are characterized by a decrease of the intensity of the d–d transition and by the shift of the charge transfer band to 32,000 cm^{-1} .

3.3. Characterization of acid-treated samples

After acid treatment, the chemical composition and the crystal and electronic structure of the samples profoundly changed. The composition of the solid phase was calculated based on the chemical analysis data of filtrates and is shown in Table 2. To simplify the analysis, atomic content of cobalt was accepted to be 1. It follows that lithium extraction is accompanied by extraction of Co^{2+} in solution. The degree of lithium extraction decreases for nonstoichiometric samples.

On the X-ray pattern of the stoichiometric sample, one can observe the broadening of reflections along with the weakening of their intensity. Some new reflections evidence the heterogeneity of the solid phase. Most probably, such a pattern represents a superposition of two hexagonal phases differing by c parameter. According to [11], it really occurs for $0.08 < x(\text{Li}_{1-x}\text{CoO}_2) < 0.24$, which correlates with our data (see Table 2). It is known that with the increasing of x , in vicinity of $x = 0.5$, a monoclinic distortion occurs. Up to this value the reaction is topotactical, then the structure undergoes a monoclinic transformation leading to its destruction.

On the contrary to stoichiometric LiCoO_2 , the nonstoichiometric samples remained structurally homogeneous. Note that no noticeable decrease of the X-ray reflection intensity, neither their broadening occurs. For all samples, the increase of the intercalation degree leads to the shift of

Table 2
Chemical analysis data of the $\text{Li}_{1+x}\text{CoO}_2$ samples treated in H_2O and H_2SO_4

Initial composition	Treatment	Li (percentage to theoretical)		Co (percentage to theoretical)		Li/Co in filtrate	Composition of solid phase after treatment
		In filtrate	In solid phase	In filtrate	In solid phase		
LiCoO_2	H_2O	0.8	99.2	–	100	–	$\text{Li}_{0.992}\text{CoO}_2$
	0.1N H_2SO_4	23.84	76.16	13.29	86.71	1.79	$\text{Li}_{0.878}\text{CoO}_2$
	1N H_2SO_4	52.42	47.58	33.37	66.63	1.57	$\text{Li}_{0.714}\text{CoO}_2$
$\text{Li}_{1.05}\text{CoO}_2$	H_2O	0.78	99.22	–	100	–	$\text{Li}_{1.042}\text{CoO}_2$
	0.1N H_2SO_4	22.78	77.22	12.53	87.47	1.91	$\text{Li}_{0.927}\text{CoO}_2$
	1N H_2SO_4	44.32	55.68	27.32	72.68	1.70	$\text{Li}_{0.804}\text{NiO}_2$
$\text{Li}_{1.1}\text{CoO}_2$	H_2O	2.97	97.03	–	100	–	$\text{Li}_{1.067}\text{CoO}_2$
	0.1N H_2SO_4	17.44	82.56	8.63	91.37	2.22	$\text{Li}_{0.994}\text{CoO}_2$
	1N H_2SO_4	39.37	60.63	24.13	75.87	1.79	$\text{Li}_{0.879}\text{CoO}_2$

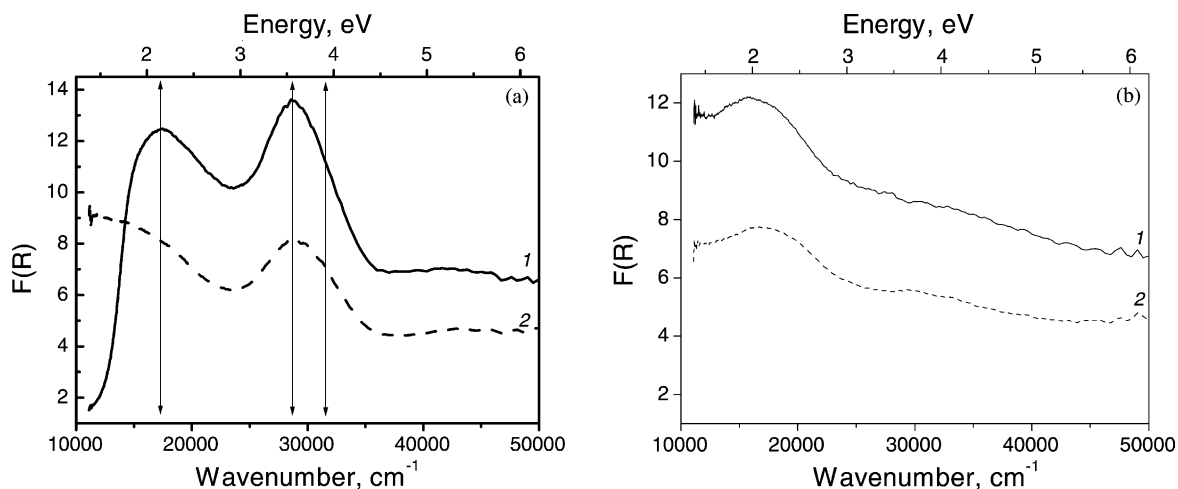


Fig. 3. (a) EDRS spectra of LiCoO_2 and $\text{Li}_{1-x}\text{CoO}_2$; (b) the same treated in 1N H_2SO_4 .

the (0 1 8) and (1 1 0) reflections in different sides, pointing to the decrease of a parameter (an approach of cobalt ions) and increase of c parameter (an increase of interlayer distance). The a/c ratio becomes higher than 5.

IR spectra of delithiated samples are characterized by disappearance of vibration structure, especially for nonstoichiometric samples. A sharp decrease (up to full disappearance) of the $\nu(\text{CoO}_6)$ and $\nu(\text{LiO}_6)$ bands is associated with the appearance of delocalized electrons. An increase of background for the stoichiometric sample in the 400–4000 cm^{-1} range is, probably, due to scattering irradiation. It should be noted that the bands of SO_4^{-2} groups are absent.

According to XPS, a significant decrease of Li 1s peak intensity is observed for all samples, pointing to the lithium deintercalation process. Simultaneously, non-uniform broadening of Co 3p and Co 2p lines occurs towards higher energies. This may be a result of rehybridization of the Co–O molecular orbitals [12–14], or an increase of effective charge on cobalt ions [5]. In the O 1s spectra, the intensity of the line with BE = 529.3 eV, corresponding to cell oxygen, decreases while the intensity of the line with BE = 531.7 eV increases (Fig. 2).

In DRS spectra of delithiated samples, the charge transfer band is absent whereas the band at 14,000–16,000 cm^{-1} becomes more intensive (Fig. 3b). The disappearance of a charge transfer band is connected with a decrease of the occupancy of O 2p oxygen orbitals. In fact, in the O 1s spectra, the line with higher BE is the most intensive. On the other hand, the presence of oxygen ions with smaller electronic density leads to formation of the σ^* unoccupied states in the conductive band (O 2p–Co 3d orbitals), localized by ~ 1.5 eV above Fermi level [14], that does brings to the appearance of an absorption band in the 14,000–16,000 cm^{-1} range. Thus, upon lithium deintercalation, a charge is compensated by the decrease of an electron density on oxygen ions and rehybridization of Co–O molecular orbitals. No noticeable charge change on cobalt ions occurs.

According to magnetic measurements, the concentration of paramagnetic centers in the acid-treated samples significantly increases.

4. Conclusion

Thus, as-prepared $\text{Li}_{1+x}\text{CoO}_2$ ($0 < x \leq 0.1$) samples are characterized by homogeneous crystal structure with statistically distributed vacancies in cobalt and oxygen layers and an increased Co–O bond covalency. The excess lithium results not in the reduction of Co^{3+} ions, but in the appearance of a new state of oxygen ions different from cell oxide, with higher value of binding energy, i.e. with smaller electronic density. The nonstoichiometric samples are characterized by the appearance of delocalized (itinerant) electrons, thus, pointing to profound changes in the LiCoO_2 electronic structure. Delocalization process increases upon the acid treatment of $\text{Li}_{1+x}\text{CoO}_2$. The electronic state of cobalt ions does not change noticeably whereas the additional oxygen state increases significantly, thus, evidencing that oxygen ions do compensate for the charge upon chemical delithiation. The structure of nonstoichiometric samples appeared to be more stable upon this process.

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