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Published in:
Electrochimica Acta

DOI:
[10.1016/j.electacta.2019.135012](https://doi.org/10.1016/j.electacta.2019.135012)

Published: 10/12/2019

Document Version
Peer reviewed version

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Please cite the original version:
Lahtinen, K., Rauhala, T., Räsänen, S., Rautama, E., & Kallio, T. (2019). The effect of synthesis modifications on the lithium cobalt oxide using commercial precursors. *Electrochimica Acta*, 327, [135012].
<https://doi.org/10.1016/j.electacta.2019.135012>

The effect of synthesis modifications on the lithium cobalt oxide using commercial precursors

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Highlights

- The performances of stoichiometric, Li-rich and Mg-Ti doped LiCoO₂ are compared
- Ti in Mg-Ti doped LiCoO₂ lowers Co valence state, enhancing the conductivity
- Synthesis ratio Li/Co=1.05 vs. 1.005 causes poorer crystallinity and cycle life
- The capacity retention of Mg-Ti doped LiCoO₂ is 89% after 1000 cycles at C/2

Abstract

In this work, the effects of modifications in the synthesis Li/Co/dopant concentrations on the performance and cycle life of lithium cobalt oxide are investigated to learn how different modification methods work in relation to each other and to provide data for up-to-date commercial interest. The LiCoO₂ materials are prepared using the same precursors and synthesis process to ensure the comparability. The electrochemical characterizations are performed in both half-cells and LiCoO₂/graphite pouch cells. The Mg-Ti doped LiCoO₂ shows superior performance compared to stoichiometric and over-lithiated LiCoO₂. The Mg-Ti doped sample shows 89 % capacity retention after 1000 cycles in 3.0–4.2 V and 80% capacity retention after 240 cycles in 3.0–4.4 V in LiCoO₂/graphite pouch cell. The better rate capability is attributed to Ti doping reducing the Co valence in LiCoO₂, making it more metallic and conductive. The longer cycle life of the doped LiCoO₂, in turn, is attributed to a better structural stability caused mainly by

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Mg doping. This is also reflected in a smaller increase in the charge transfer impedance during cycling. In contrast, the Li doping increases the material impedance and thus decreases the cycle life of the material.

Graphical abstract

Key-words

Li-ion battery, LiCoO₂, Doping, Cycle life, Conductivity

1. Introduction

Since the commercialization of Li-ion batteries in 1991 [1], lithium cobalt oxide (LiCoO_2) has been used as a positive electrode material. Even now, a few decades later, it is still one of the most used materials in Li-ion batteries in portable applications as it exhibits relatively high theoretical capacity (274 mAh g^{-1} , approximately 160 mAh g^{-1} can be utilized), high charge/discharge potential and low self-discharge rate. [2,3] Because of its wide use, LiCoO_2 has been investigated extensively to improve its performance. [2,4] Nowadays, however, new advanced technologies require more power than ever. To keep up with the power demand, the potential range during cycling should be increased. This, however, introduces challenges for the material durability.

LiCoO_2 is a layered lithium-transition metal oxide crystallizing in the space group of $R\bar{3}m$. The structure consists of CoO_2 -layers stacked along the c -axis direction, and these layers are separated by layers of lithium ions. In order to enhance the electrochemical performance and stability of LiCoO_2 , several methods for modifying this material structure have been investigated in the past. These methods include e.g. doping, varying the Li/Co ratio of the material, and varying the LiCoO_2 particle size or morphology. Although LiCoO_2 and its modifications have already been investigated widely, the above-mentioned methods, involving the substitution of cobalt, have not been compared previously, to our knowledge. In addition, many of these studies have been carried out using potentials only up to $4.3 \text{ V vs. Li/Li}^+$ while the LiCoO_2 potential reaches higher values in many of the state-of-the-art commercial applications. In commercial perspective, it is not only important to understand how effective the different modification methods are but also how effective they are compared to each other.

It has been typical for the battery manufactures to buy the active material precursors instead of active materials, as this way they can tailor their material for a specific application. During the LiCoO_2 synthesis, the properties of the materials are determined by e.g. the Li/Co stoichiometry and the possible dopants. LiCoO_2 is typically doped with metals such as Al [5–7], Mg [7–13], Ti [14,15] and Zr [16,17]. In addition, cheaper and more environmentally friendly Mn and Ni are commonly used to replace Co atoms. Doping has been found to cause many changes depending on the used dopant material and its amount: It can stabilize the crystal structure [7–11,18], reduce the positive electrode dissolution in the electrolyte [4,19] or enhance the electric conductivity [4,17,20,21]. For example, Mg has been reported to enhance the LiCoO_2 cycle life [8,9,11] and Ti the rate capability properties [14,15]. Doping can also affect the microstructure and the morphology of the material [5,14,15]. In cases like these, the interpretation of the effects caused by the doping can be complicated, because it is difficult to identify if the improvement in electrochemical properties is induced by the doping or by the particle structure. [4] While single element doping has been the topic of countless investigations, doping LiCoO_2 with multiple elements is still a relatively new topic. [9,17,22–24]. To the knowledge of the authors, dual Mg-Ti doping of LiCoO_2 has previously been reported only by Zhang *et al.* [24], who, however, only investigated the material in half-cells.

On the other hand, the effect of the Li/Co ratio has not been investigated as widely as the doping. In lithium-poor materials ($\text{Li/Co} < 1$), the shortage of lithium causes the repulsions between CoO_2 -layers to increase, which leads to an increase in the lattice parameter c . This increases e.g. the Li-ion conductivity of the material, which in turn leads to better cycling properties. [3,25,26] In the case of lithium-rich materials ($\text{Li/Co} > 1$), the excess lithium ions replace some of the cobalt ions in the CoO_2 -layers, and the formed charge deficit is compensated with oxygen vacancies [27] or oxidation of Co^{3+} to Co^{4+} [28]. In other words, the excess lithium behaves similarly to dopants, and therefore the lithium-rich materials could be

called Li-doped materials. In their work, Imanishi et al. [29] reported that the excess Li enhances both the specific capacity and the electrochemical efficiency of the material.

In this study, the electrochemical performance of LiCoO_2 materials with small amount of stoichiometric cobalt replaced with either Li or Mg-Ti doping in the synthesis are compared. The materials are prepared using the same precursors and the same synthesis process, in order to ensure the comparability of the materials. The structure and the morphology of the materials are investigated as well, in order to understand the differences in the electrochemical behaviour under low and high voltage range operation. The electrochemical tests are done using an earlier customary maximum potential of 4.3 V vs. Li/Li^+ and a higher potential of 4.5 V vs. Li/Li^+ to provide data of interest to commercial applications today. In addition, to the knowledge of the authors, the behaviour of Mg-Ti doped LiCoO_2 in LiCoO_2 /graphite pouch cell is reported for the first time.

2. Experimental

The precursors and the three LiCoO_2 materials were provided by Freeport Cobalt. The LiCoO_2 samples are denoted as $\text{LiCoO}_2(\text{S})$, $\text{LiCoO}_2(\text{R})$ and $\text{LiCoO}_2(\text{D})$ referring to the stoichiometrically synthesized, over-lithiated and doped materials, respectively. The LiCoO_2s were synthesized *via* a solid-state synthesis at 1020 °C in a muffle furnace (Carbolite, CWF1200) using Co_3O_4 and Li_2CO_3 as precursors, and 0.2 mol% TiO_2 and 0.5 mol% $\text{Mg}(\text{OH})_2$ for doping. The dopant concentrations were chosen based on earlier optimization. The Li/Co ratio of the Li_2CO_3 and Co_3O_4 precursors for the synthesis were 1.005, 1.050 and 1.005 for $\text{LiCoO}_2(\text{S})$, $\text{LiCoO}_2(\text{R})$ and $\text{LiCoO}_2(\text{D})$, respectively. After the synthesis, the materials were ground and sieved through 325 mesh screen. The products were analysed with a Thermo iCAP6500 inductively coupled plasma optical emission spectrometer (ICP-OES).

The crystal structures were characterized by means of X-ray diffraction (XRD) with a PANalytical X'Pert Pro MPD Alpha-1 diffractometer using Cu $K_{\alpha 1}$ -radiation with a wavelength of 0.15406 nm. The measurements were done in a 2θ range of 10–90° with steps of 0.026°. Pulse height discrimination (PHD) range of 42–100 % was used to prevent the fluorescence of cobalt from disturbing the measurement. A double aberration corrected JEOL JEM-2200FS microscope was used to perform the Electron Energy Loss Spectroscopy (EELS) measurements. The vibration characteristics of the LiCoO_2 materials were analysed *via* Raman spectrometer (Horiba, LabRAM HR) using a 514.5 nm (50 mW) argon ion laser as a source of excitation in the range of 100–1900 cm^{-1} . The particle size and morphology of the materials were studied with scanning electron microscope (SEM, Zeiss Sigma VP, secondary electrons). To ensure the conductivity of the investigated powders for the SEM analysis, they were coated with platinum by sputtering. BET measurements were done using Monosorb MS-22 analyser with 70/30 He/ N_2 gas. Tap density was measured using jolting volumeter (JEL STAV II, ASRM B 527/EN ISO 3953 standard).

The preparation of the LiCoO_2 electrodes began by forming an active material containing slurry. The slurry contained 60 wt-% of solids, of which 95 wt-% was LiCoO_2 material, 2 wt-% carbon black (Timcal Super C65) and 3 wt-% PVDF (Solvay, Solef 5130). N-methyl-2-pyrrolidone, (NMP, BASF, Life Science) was used as a solvent, and the solution was mixed with a dispergator (Dispermat, VMA-Getzmann GMBH-D-51580 Reichshof) with 500 rpm. The homogeneous electrode slurries were then coated on an aluminium foil using a wet thickness of 90–100 μm to obtain a loading of 7.7–8.0 mg cm^{-2} . The electrode foils were dried in a fume hood overnight, and then at 80 °C oven for 4 hours. After this, electrodes were cut and calendered with a pressure of 3250 kg cm^{-2} . The electrode diameter was 14 mm for half-cells and 18 mm for three-electrode cells. Finally, the electrodes were dried under vacuum at 110 °C overnight and transferred into an argon-filled glovebox (Jacomex, oxygen and water vapour levels below 1 ppm).

The LiCoO_2 electrodes for the half-cell measurements were assembled to Hohsen 2016 coin cells cases. A 0.75 mm thick lithium metal foil (Alfa Aesar) was used as a counter electrode and 1 M lithium

hexafluorophosphate (LiPF_6) dissolved in 1:1 ethylene carbonate (EC):dimethyl carbonate (DMC) solution (BASF, LP30) was used as an electrolyte. A glass fibre filter (Whatman GF/A, 0.26 mm) was used as a separator. Finally, the cells were left to stabilize for 24 hours before electrochemical testing. Half-cells were used for cyclic voltammetry (CV) and rate capability measurements.

The three-electrode cell measurements were conducted in commercial EL-CELL test cells. Lithium metal served both as the counter electrode and as the reference electrode. 1 M LiPF_6 in 1:1 EC:DMC was used as the electrolyte, and a 1.55 mm thick glass fibre separator (EL-CELL) was used. Three-electrode cells were used in the measurements for galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS).

In the pouch type full cells, graphite (Hitachi) was used as the negative electrode and the investigated LiCoO_2 materials as the positive electrode. The graphite slurry contained 92 wt-% graphite, 4 wt-% conductive carbon, and 4 w-% PVDF (Kureha), and it was coated on copper foil with a loading of 6.0–7.2 mg cm^{-2} . The LiCoO_2 slurry had the same composition as in the half-cell tests, but the electrode loading was slightly higher, being 11.0–14.5 mg cm^{-2} . The size of the graphite electrode was 65 mm x 48 mm, the LiCoO_2 electrode 61 mm x 44 mm and the separator 68 mm x 48 mm. The cells contained one negative electrode-positive electrode pair. The electrolyte was 1 M LiPF_6 in 25:70:5 EC:diethylene carbonate (DEC):propylene carbonate (PC) solution with 1 mol% vinylene carbonate (VC) and 1 mol% 1,3-propane sultone (PS) doping (Golden Light Hi-Tech Energy Storage Materials, JR-02). The pouch cells were used for cycle life and EIS tests.

CV was measured with an Autolab potentiostat (PGSTAT302N) using Nova software. CVs were recorded within a voltage range 3.0–4.5 V using scan rates 0.02 mV s^{-1} and 0.05 mV s^{-1} . Three cycles per both scan rates were measured. The galvanostatic measurements were done with a Neware battery cycler. Rate capabilities of the half-cells were measured in voltage ranges of 3.0–4.3 V and 3.0–4.5 V by varying

discharge C-rates from 0.2 C to 5.0 C and keeping the charge C-rate constant at 0.2 C. Theoretical capacity of 160 mAh g⁻¹ was used to calculate the C-rates in both the voltage ranges. At least three parallel measurements were carried out to ensure the repeatability of the results. The three-electrode measurements were done in the potential range of 3.0–4.5 V vs. Li/Li⁺.

GITT measurements were also done using a potential range of 3.0–4.5 V vs. Li/Li⁺. The measurement itself consisted of current steps conducted with 0.05 C, the step duration being 30 min, which corresponded to 2.5 % change in state of charge (SoC). A low current was used to keep the overpotentials as small as possible. After each current step, the cell was stabilized for 2 hours and then the open circuit potential (OCP) was recorded. Measurements were conducted for x in Li _{x} CoO₂ at $0.65 < x < 0.75$ (corresponding approximately to SoC of 30–65 %). The diffusion coefficients were then calculated using the following equation [30].

$$D = \frac{4}{\pi} \left(\frac{iV_m}{z_A F S} \right)^2 \left[\frac{\left(\frac{dE}{d\delta} \right)}{\left(\frac{dE}{d\sqrt{t}} \right)} \right]^2 \quad t \ll \frac{l^2}{D} \quad (1)$$

where i is the current, V_m is the molar volume of the active material, z_A is the charge number, F is the Faraday's constant, S is the electrode/electrolyte contact area estimated from the BET results and l is the diffusion length, for example the radius of a particle. $dE/d\delta$ corresponds to the dependence of the electrode potential (E) on stoichiometry of the inserted atoms (δ). $dE/d\sqrt{t}$ in turn corresponds to the slope of a plotted figure of electrode potential versus square root of time (t). [30–32]

Cycle lives of the pouch cells were measured in voltage ranges of 3.0–4.2 V and 3.0–4.4 V by cycling with a C-rate of 0.5 C. After every 50th cycle, the cells were cycled once with a C-rate of 0.1 C and an EIS measurement was performed for the cells at a SoC of 50%. The C-rates were determined by cycling the cells once with 4 mA in the beginning of the cycle aging, and the capacity of the cell was determined from

the data. The cycling was continued until the capacity dropped below 80 % of the initial capacity or until 1000 cycles were reached.

EIS measurements were done with an Autolab potentiostat (PGSTAT302N) using *FRA* software. Frequency ranges of 100 kHz–10 mHz and 100 Hz–10 mHz for pouch cells and three-electrode cells, respectively, are reported. The frequency range of the three-electrode cell setup was chosen based on the frequency range of the charge transfer resistance semicircle in the pouch cell results. An alternating potential amplitude was set to 5 mV. All measurements were done at the open circuit voltage (OCV) corresponding to a SoC of 50 % determined at the beginning of the cell cycling. The OCVs were 3.82–3.83 V for the cells cycled in the smaller voltage range, and 3.86–3.87 V for the larger voltage range cells. Number of frequencies was set to 60. The measurements were made at room temperature of 21–23 °C.

3. Results and discussion

3.1. Powder analysis

In addition to the inherent electrochemical properties of LiCoO_2 , its surface and crystal structure affect its performance. Therefore, the structure, morphology and chemical composition of the studied LiCoO_2 materials were investigated with XRD, EELS, Raman spectroscopy, SEM, BET and ICP-OES. The ICP-OES results are presented in Table 1. The elemental analysis shows that the Li/Co ratios for the materials are (in respect to full presence of Co) lower than the original ratios used in the synthesis. This was expected, and it is caused by the loss of lithium during the synthesis. Similarly, the Ti and Mg concentrations are slightly lower in the ICP-OES results. The expected relation is retained, i.e. the $\text{LiCoO}_2(\text{R})$ sample contains more lithium than the other samples.

Table 1. The compositional synthesis parameters and the LiCoO₂ composition from ICP-OES.

	LiCoO ₂ (S)	LiCoO ₂ (R)	LiCoO ₂ (D)
Li/Co ratio, synthesis	1.005	1.050	1.005
Li/Co ratio, product	0.97	1.00	0.98
Product formula	Li _{0.99} Co _{1.02} O ₂	Li _{0.99} Co _{0.98} O ₂	Li _{0.96} Mg _{0.005} Ti _{0.002} Co _{0.98} O ₂
Amount of dopants, synthesis (Mg/Ti, mol%)	-	-	0.50/0.20
Amount of dopants, product (Mg/Ti, mol%)	-	-	0.46/0.18

The powder XRD and EELS patterns of the studied LiCoO₂ materials are presented in Fig. 1. Based on the XRD data, all the samples have well-defined, crystallized structure, and the patterns of the LiCoO₂ materials correspond well to the hexagonal lithium cobalt oxide. Crystalline impurities are not observed. Especially the patterns of LiCoO₂(S) and LiCoO₂(R) are very similar to each other, although it seems that LiCoO₂(S) might be more well-crystallized based on the larger intensity of the LiCoO₂(S) peaks. Slight broadening of the peaks is observed for LiCoO₂(D) which indicates the presence of doping, and is in agreement with the observations by Eom *et al.* [33] In addition, the broadening also suggests that the crystallite size of LiCoO₂(D) could be slightly smaller compared to those of LiCoO₂(S) and LiCoO₂(R). The average of the full widths at half maximum (FWHM) for the four largest symmetrical peaks are presented in the supplementary data, Table S1.

Fig. 1. a) XRD diffractograms of the investigated materials and their Miller indices in $R\bar{3}m$, b) EELS spectra of Cobalt L-edge.

Lattice parameters given in Table 2 were determined for each pattern using the Rietveld refinement method and the program *Fullprof* [34]. The initial structural model was adapted from the work by Mustafa *et al.* [35]. The results show that the lattice parameter a is similar for all the LiCoO₂ materials. On the other hand, differences in the lattice parameter c are observed. LiCoO₂(S) and LiCoO₂(R) have yet similar values, but LiCoO₂(D) has a slightly larger lattice parameter c , which is attributed to the doping, as the ionic radii of Mg²⁺ (0.72 Å) and Ti⁴⁺ (0.61 Å) are larger than that of low-spin Co³⁺ (0.55 Å) [36]. Similar results have also been reported earlier [18,37].

Table 2. Selected structural parameters of the studied LiCoO₂ samples extracted from Rietveld refinement together with their goodness-of-fit values (R_{wp} , R_{Bragg} , χ^2).

	LiCoO ₂ (S)	LiCoO ₂ (R)	LiCoO ₂ (D)
a (Å)	2.8162(1)	2.8165(1)	2.8161(1)
c (Å)	14.053(1)	14.0530(1)	14.0615(1)
z	0.242(4)	0.2339(5)	0.238(4)
R_{wp} (%)	5.99	5.76	5.88
R_{Bragg} (%)	11.2	8.64	10.3
χ²	6.10	5.32	4.54

Space group R-3m (#166), hexag. setting. Li at 3a (0,0,0), Co at 3b (0,0,½), O at 6c (0,0,z).

To find an explanation for the above-observed results, local disorder of the cations involved was studied, within the limits of XRD scattering resolution. The possibility of Mg to replace a part of the lithium, and therefore to reduce the cobalt valence towards +2, would not be surprising owing to their well-known diagonal relationship due to similar size and charge density. Some studies have demonstrated [11,38] that the distribution on Li site is related to the synthesis conditions; the lower the temperature, the higher the amount of Mg on Li site. Our attempts to refine the occupancies of Li, Mg and Co freely under well-defined constraints did not result in physically meaningful values. However, 10 manually defined combinations of possible distribution levels were tested. Based on the goodness-of-fit indicators, the lowest values were gained when *ca.* 20 % of the total amount of the added Mg (0.1 mol-% in compound stoichiometry) locates on the slightly unoccupied Li site. This lowered the R_{Bragg} by 0.9 %. It must be noted that these results do not represent the best reliability by means of statistics, X-ray scattering factor limitations (especially Li) and the extremely small quantities of dopants (Mg and Ti). For the same reason, the attempts to distinguish whether some of Li in any of the samples would be positioned at the cobalt site were unsuccessful.

The EELS results presented in Fig. 1(b) show the energy loss spectra for Cobalt L-edge. For the Cobalt L₃-edge, the energy losses are 780.2 eV, 780.0 eV and 779.4 eV, for LiCoO₂(S), LiCoO₂(R) and LiCoO₂(D),

respectively. For L_2 , the energy losses are 794.7 eV, 794.5 eV and 794.0 eV, in the same order. The L edges are caused by the electron transition from $2p_{3/2}$ orbital to $3d_{3/2}3d_{5/2}$ orbital and from $2p_{1/2}$ orbital to $3d_{3/2}$ orbital for L_3 and L_2 , respectively. The L-edge has been reported to be sensitive to the valence state of transition metals. [39–42] Based on Fig. 1, $\text{LiCoO}_2(\text{D})$ seems to have the L-edge at slightly lower energy loss. As the electrons in the 3d orbital screen the 2p orbital, their amount affects the 2p energy [39]. In other words, a higher valence causes a larger energy loss. Therefore, it can be deduced that the cobalt in $\text{LiCoO}_2(\text{D})$ has a slightly lower valence than the other two materials.

The valence state can be further analyzed by calculating the L_3/L_2 -edge intensity ratio. The L_3 and L_2 edge intensities are related to the unoccupied states of 3d orbital, and thus the intensity ratio can be used to indicate the differences in the valence state. In other words, the higher intensity ratio indicates a lower valence state. [39–41] In this work, the L_3/L_2 intensity ratio was calculated by the method reported by Wang *et al* [40], and values are 2.63, 2.72 and 2.99 for $\text{LiCoO}_2(\text{S})$, $\text{LiCoO}_2(\text{R})$ and $\text{LiCoO}_2(\text{D})$, respectively. As the intensity ratio for $\text{LiCoO}_2(\text{D})$ is clearly the highest, the result indicates lower valence state for cobalt in the doped LiCoO_2 . For a reference, Wang *et. al* [40] have reported the intensity ratio to be approximately 3.2 for Co_3O_4 (Co valence +2.67) and circa 2 for CoSi_2 (Co valence +4). Theoretically, cobalt in LiCoO_2 should have a valence state of +3. $\text{LiCoO}_2(\text{S})$ with the stoichiometric structure and the intensity ratio of 2.63 most likely resembles trivalent Co. However, as the L_3/L_2 edge intensity ratio of $\text{LiCoO}_2(\text{D})$ is quite close to the intensity ratio of Co_3O_4 , it is likely that some of the Co in $\text{LiCoO}_2(\text{D})$ is reduced to Co^{2+} . The cause for the reduced valence of $\text{LiCoO}_2(\text{D})$ is most likely the Ti doping, the higher valence of Ti (+4) causing the Co valence decrease. Based on the refining attempts, Mg doping is assumed to be located in both Li and Co sites, and therefore not affect the valence of Co.

Raman was used as an additional structural characterization method to see impurity phases possibly not visible by XRD. The Raman spectra of the studied LiCoO_2 materials are presented in the supplementary data, Fig. S1. All the three materials show the characteristic two bands of hexagonal LiCoO_2 at 485 cm^{-1}

and 595 cm^{-1} . Based on the work of Inaba *et al.* [43] and Julien *et al.* [44] the former band is attributed to O-Co-O bending vibrations (e_g) and the latter one to Co-O stretching (a_{1g}). The only extra band appears at 680 cm^{-1} , and it can be attributed to Co_3O_4 . Co_3O_4 was not detected in XRD, and the band intensity in the Raman spectra is low, which indicates that the Co_3O_4 content in the materials is very small. However, the existence of other impurities (within the detection limit of Raman), such as Li_2CO_3 , can be ruled out. The band positions are also the same for all the three LiCoO_2 materials.

In addition to the structural analysis, the morphology of the materials was analysed with SEM. The micrographs of the materials are presented in Fig. 2, and they display spherical or oval shaped LiCoO_2 particles with the average size for all three samples being approximately $16\text{ }\mu\text{m}$ in diameter. In addition, it can be observed that the particles have a fine structure: smaller primary particles cluster together to form the micrometre sized secondary particles. The primary particles are not clearly visible, and it appears that they have partly merged. Their size varies, but generally $\text{LiCoO}_2(\text{D})$ has the smallest primary particles and $\text{LiCoO}_2(\text{R})$ the largest. As the stoichiometric material has smaller primary particles than the over-lithiated material, it appears that the Li/Co-stoichiometry affects the primary morphology of LiCoO_2 . However, the effect of the doping on the microstructure appears to be larger than the Li/Co-stoichiometry. It should also be noted that the primary particle size does not affect the secondary particle size.

The specific surface areas and tap densities of the LiCoO_2 materials are presented in Table 3. The tap densities are similar and the BET measurements show that the materials also have similar specific surface areas. The latter is attributed to the spherical shape resulting in low surface to volume ratio (observed in Fig. 2) as well as the micrometre size of the secondary particles. It would also appear that although primary structure is observed, it does not affect the surface area very much. This supports the observation of the primary particles being merged together, leading to a low porosity of the particles. Therefore, it can be concluded that the primary particle size of the LiCoO_2 materials does not significantly affect their specific surface area or tap density, although the external appearance of the particles in the Fig. 2 might suggest

otherwise. In summary, the powder analysis indicates that although the materials have similar size and outer morphology, there are differences in the local crystal structure and the crystallite size.

Fig. 2. SEM images of the a) $\text{LiCoO}_2(\text{S})$, b) $\text{LiCoO}_2(\text{R})$ and c) $\text{LiCoO}_2(\text{D})$ powders.

Table 3. Properties of the LiCoO_2 samples.

	$\text{LiCoO}_2(\text{S})$	$\text{LiCoO}_2(\text{R})$	$\text{LiCoO}_2(\text{D})$
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	0.12	0.11	0.13
Tap density (g cm^{-3})	2.89	2.85	2.89

3.2. CV

The electrochemical behaviour of the studied LiCoO_2 materials was investigated by CV and the graphs of the $\text{LiCoO}_2(\text{S})$, $\text{LiCoO}_2(\text{R})$ and $\text{LiCoO}_2(\text{D})$ are presented in Fig. 3. The integrated peak areas corresponding to the sample capacities are similar (approximately 185 mAh g^{-1}) for all the samples at a slow scan rate of 0.02 mV s^{-1} , but at a scan rate of 0.05 mV s^{-1} , $\text{LiCoO}_2(\text{D})$ has clearly larger peak area (185 mAh g^{-1}) compared to the other two materials (177 mAh g^{-1} and 170 mAh g^{-1} for $\text{LiCoO}_2(\text{S})$ and $\text{LiCoO}_2(\text{R})$, respectively). This indicates that the rate capability properties of the $\text{LiCoO}_2(\text{D})$ are better than those of the other two materials and these are discussed more in the Chapter 3.3.

Fig. 3. Cyclic voltammograms of the $\text{LiCoO}_2(\text{S})$, $\text{LiCoO}_2(\text{R})$ and $\text{LiCoO}_2(\text{D})$ half-cells using scan rates of 0.02 mV s^{-1} (solid lines) and 0.05 mV s^{-1} (dashed lines). The first of the three cycles is presented for all the LiCoO_2 materials at both scan rates.

Three peaks during both the Li insertion and extraction scans are observed in the first cycle of scan rate 0.02 mV s^{-1} . In the first cycle of scan rate 0.05 mV s^{-1} , these three pairs of peaks are observed in the CV of $\text{LiCoO}_2(\text{D})$, but $\text{LiCoO}_2(\text{S})$ and $\text{LiCoO}_2(\text{R})$ both show only one pair of broad peaks with fine structure. The peak potential of the largest of the three peaks, observed in 0.02 mV s^{-1} Li extraction scans, is 3.96 V, 3.95 V and 3.97 V for $\text{LiCoO}_2(\text{S})$, $\text{LiCoO}_2(\text{R})$ and $\text{LiCoO}_2(\text{D})$, respectively. The corresponding peaks can be observed in the Li insertion scans as well, but the peak potentials are shifted to slightly lower values. The peaks are caused by the lithium deintercalation/intercalation reaction in the two-phase domain, in which a transformation between a semi-conducting phase and a metallic phase takes place [45]. During delithiation, $\text{LiCoO}_2(\text{D})$ shows a wider peak than the other two materials, but during lithiation $\text{LiCoO}_2(\text{R})$ and $\text{LiCoO}_2(\text{S})$ have wider peaks than $\text{LiCoO}_2(\text{D})$. This indicates that the resistance of the cells, especially the $\text{LiCoO}_2(\text{R})$ and $\text{LiCoO}_2(\text{S})$ cells, increases during the first Li extraction (charge). During the two subsequent cycles at 0.02 mV s^{-1} (reported in Supporting Information, Fig. S2), the peaks of $\text{LiCoO}_2(\text{S})$ and $\text{LiCoO}_2(\text{R})$ widen, decrease in height and their peak separation increases. It is possible that during the 0.02 mV s^{-1} scans, irreversible reactions occur in the cells, resulting in products that increase the cell resistance.

At the scan rate of 0.05 mV s^{-1} , the $\text{LiCoO}_2(\text{D})$ peak height and width increase compared to the 0.02 mV s^{-1} scan, and the peak potential of lithium extraction shifts to 3.99 V. The peaks for $\text{LiCoO}_2(\text{S})$ and $\text{LiCoO}_2(\text{R})$, however, decrease in height, and the width increases more than for $\text{LiCoO}_2(\text{D})$. In addition, the peak potential shifts to clearly higher potentials, being now 4.09 V for $\text{LiCoO}_2(\text{S})$ and 4.22 V for $\text{LiCoO}_2(\text{R})$. This further indicates that $\text{LiCoO}_2(\text{S})$ and $\text{LiCoO}_2(\text{R})$ have larger resistance, which induces larger overpotentials. This shows that doping stabilizes and possibly enhances the conductivity of $\text{LiCoO}_2(\text{D})$, and because of this its resistance does not increase as much as for the other two materials. This is further confirmed by the cycle life results presented in Chapter 3.5. It should also be noted that the resistance of $\text{LiCoO}_2(\text{R})$ is clearly larger than that of $\text{LiCoO}_2(\text{S})$. This is interesting, because the powders had very similar physical properties.

However, the difference could be explained by the slightly better crystallinity of $\text{LiCoO}_2(\text{S})$ which is seen as the enhanced XRD peak intensities.

The two smaller peaks at 4.05 V and 4.20 V in the CVs are visible for all the samples in the 0.02 mV s^{-1} scan. However, at 0.05 mV s^{-1} they are seen only for $\text{LiCoO}_2(\text{D})$, as the peaks of $\text{LiCoO}_2(\text{S})$ and $\text{LiCoO}_2(\text{R})$ have merged with the shifted main peak. These peaks do not shift notably with the scan rate, and they result from Li-ion ordering within the LiCoO_2 structures at Li_xCoO_2 $x \approx 0.5$. During delithiation, at the lower potential, rhombohedral symmetry is turned to monoclinic symmetry, and at the higher potential the monoclinic symmetry is turned back to rhombohedral [25,26]. During lithiation, the reactions occur to the opposite direction.

According to Levasseur *et al.* [46], 5 % Mg doping prevents the phase transitions in LiCoO_2 and the lack of structural changes stabilizes the structure. However, in Fig. 3, the phase transitions are observed for $\text{LiCoO}_2(\text{D})$. A plausible explanation for this is that during the high-temperature synthesis and doping processes, the Mg-Ti doping does not fully diffuse into the material, meaning they can cluster in the form of a layer of high Mg-Ti concentration LiCoO_2 on the grain boundaries or on the surfaces of the particles. In addition, it should be noted that the amount of doping used in this study is significantly lower (0.2 mol% Ti and 0.5 mol% Mg) than in the study by Levasseur *et al.* This can also explain the occurrence of the phase transition in the doped material. Furthermore, in the work by Liu *et al.* [9] the improved performance is attributed to the suppressed impedance growth of the Mg/Mn doped sample, not the suppressed phase transitions. This corresponds with our results, and the cell impedances will be further discussed in Chapter 3.6 that concentrates on the EIS results.

3.3. Rate capability in half-cells

The rate capability measurements were done with two different voltage ranges to compare the initial capacities and the capacity retention at increasing currents. Voltage range of 3.0–4.3 V corresponds to the range used traditionally in the Li-ion battery applications. Voltage range of 3.0–4.5 V, in turn, represents the widest range LiCoO₂ can be cycled in so that the cycle life is still acceptable [9]. The discharge curves of the LiCoO₂ material half-cells in voltage ranges of 3.0–4.3 V and 3.0–4.5 V are presented in Fig. 4. In addition, the 0.03 C, 0.1 C and 0.2 C charge curves as well as the end 0.2 C charge curves measured after the rate capability test are shown in the figure. The initial average specific discharge capacities of the materials at 0.03 C in the voltage range of 3.0–4.3 V are 160 mAh g⁻¹, 159 mAh g⁻¹ and 167 mAh g⁻¹ for LiCoO₂(S), LiCoO₂(R) and LiCoO₂(D), respectively. In the voltage range of 3.0–4.5 V, the average initial specific discharge capacities are 195 mAh g⁻¹, 193 mAh g⁻¹ and 204 mAh g⁻¹, in the same order. This means that in both the voltage ranges, the initial specific capacity of LiCoO₂(D) is slightly larger than those of the other two investigated materials. Overall, LiCoO₂(S) and LiCoO₂(R) have very similar initial capacities. The relation of specific discharge capacities and C-rates is presented in the supplementary data, Fig. S3.

Fig. 4. Discharge curves of the studied LiCoO_2 materials at C-rates of 0.03 C, 0.1 C, 0.2 C, 0.5 C, 1.0 C, 2.0 C, 4.0 C and 5.0 C. The charge curves at 0.03 C, 0.1 C and 0.2 C are also shown. a) $\text{LiCoO}_2(\text{S})$ in voltage range of 3.0–4.3 V, b) $\text{LiCoO}_2(\text{S})$ in 3.0–4.5 V, c) $\text{LiCoO}_2(\text{R})$ in 3.0–4.3 V, d) $\text{LiCoO}_2(\text{R})$ in 3.0–4.5 V, e) $\text{LiCoO}_2(\text{D})$ in 3.0–4.3 V, and f) $\text{LiCoO}_2(\text{D})$ in 3.0–4.5 V.

As can be seen in Fig. 4, the specific capacity decrease is rapid with the increase of the C-rate for $\text{LiCoO}_2(\text{S})$ and $\text{LiCoO}_2(\text{R})$, but significantly smaller for $\text{LiCoO}_2(\text{D})$. For all the materials, the decrease is faster in the higher voltage range of 3.0–4.5 V than in the lower voltage range of 3.0–4.3 V. For example, in the range from 3.0 V to 4.3 V, the specific discharge capacity of $\text{LiCoO}_2(\text{S})$ at 0.03 C is 160 mAh g^{-1} but at 0.2 C it has already dropped to 146 mAh g^{-1} , and at 4.0 C to only 12 mAh g^{-1} . In the range from 3.0 V to 4.5 V, the

specific discharge capacities are ~ 0 mAh g⁻¹ with 2.0 C and higher currents. LiCoO₂(R) has very similar rate capability properties to LiCoO₂(S). In contrast, for LiCoO₂(D) in 3.0–4.3 V the specific discharge capacity at 5.0 C is no less than 130 mAh g⁻¹, and in 3.0–4.5 V it is 135 mAh g⁻¹. The enhanced rate capability properties have earlier been attributed to the Ti doping [14,15], and this is most likely the case for LiCoO₂(D) as well. Based on the EELS results reported in Chapter 3.1, it seems that the Ti doping decreases the Co valence, increasing the amount of electrons in the orbital and making it more metallic. Consequently, its conductivity increases, resulting in enhanced rate capability properties of the doped LiCoO₂. Additionally, the smaller crystallite size might also affect the rate capability, as grain boundaries and smaller particle size ease the lithium diffusion in the material. Wilson et al. [47] have reported similar results.

If the 0.2 C capacities at the beginning and at the end of the rate capability measurement are compared, it is possible to obtain initial information about the cyclability of the material. The smaller the drop from the beginning 0.2 C capacity to the end 0.2 C capacity is, the better cyclability it indicates. Based on Fig. 4, the capacity drop is larger for LiCoO₂(R) than it is for LiCoO₂(S), which indicates that LiCoO₂(S) has a better cyclability. For LiCoO₂(D), the drop from the initial 0.2 C to the end 0.2 C discharge capacity is from 158 mAh g⁻¹ to 153 mAh g⁻¹ in the range of 3.0–4.3 V. In the range of 3.0–4.5 V, the drop is from 188 mAh g⁻¹ to 176 mAh g⁻¹. This indicates good cyclability for LiCoO₂(D). The cyclability of the materials is investigated further using LiCoO₂/graphite pouch cells in Chapter 3.5.

In addition to the decreasing specific capacity, the difference of charge and discharge voltages increases as the C-rate increases. This can be seen well in Fig. 4 indicating that polarization occurs in the cells, and that the polarization for LiCoO₂(R) is the largest, in agreement with the above-discussed CV results. This is further verified by the EIS results of the three-electrode cells presented in the supplementary data, Fig. S8, in which the charge transfer resistance of the LiCoO₂(R) increases the fastest during cycling. The increased polarization of the electrodes could possibly be caused by side reactions with the electrolyte [48].

In all the charge-discharge graphs of Fig. 4, the voltage plateau at 3.9 V caused by the two-phase domain can be clearly identified in the first cycles. In addition, the two smaller plateaus resulting from Li-ion ordering at 4.05 V and 4.20 V can be clearly seen in the cycling curves at currents of 0.03 C and 0.1 C. However, at higher currents, the plateaus disappear. When the charge curves presented in the supplementary data, Fig. S4 are examined, it is seen that the plateaus disappear even when the charge current is held constant at 0.2 C while the discharge current increases. Furthermore, the disappearance of the ordering plateaus is faster in the wider voltage window for LiCoO₂(S) and LiCoO₂(R). According to Xia *et al.* [49] and Reimers *et al.* [50] this ordering is sensitive to defects in the crystal structure. However, the disappearance of the plateaus could also result from an increased polarization induced by the increasing resistance in the cells, the overpotential covering the fine structure of the charge-discharge curves. All in all, although the exact explanation for the Li-ion ordering transitions and their disappearance cannot be given in this study, it can be concluded that LiCoO₂(D), for which the phase transitions remain visible the longest, has the best rate capability and cyclability properties.

3.4. GITT

The diffusion coefficients of Li-ions in the LiCoO₂ materials were estimated from GITT measurements to investigate if the Li-ion conductivities could explain the observed electrochemical differences. The potential curves of the measurement are presented in the supplementary data, Fig. S5. In addition, the cell potential is plotted as a function of square root of time, the slope thus corresponding to $dE/d\sqrt{t}$. The E vs. $\sqrt{t}$ curves can be found in the supplementary data, Fig. S6. The average values for diffusion coefficients for all three LiCoO₂ materials at discharge are presented in Fig. 5.

Fig. 5. Discharge Li diffusion coefficients determined from GITT-data at the SoC range of 35–65 %.

The diffusion coefficients are 10^{-13} – 10^{-11} cm²/s for all the studied materials. These are in good agreement with the values reported earlier in literature [51–53]. As can be seen from the Fig. 5, LiCoO₂(D) has slightly larger diffusion coefficients compared to the other two materials, and LiCoO₂(R) shows the smallest values. This result is consistent with the observations about the cobalt being more metallic in LiCoO₂(D) in Chapter 3.1 and the conductivity and rate capability properties discussed in Chapters 3.2 and 3.3.

3.5. Cycle life in pouch cells with a graphite negative electrode

The investigation described above elucidates the effect of Li/Co synthesis ratio and doping on the electrochemical behaviour and rate capability of LiCoO₂. Here, the cycle life of the samples is investigated using LiCoO₂/graphite pouch cells. The charge and discharge curves of the pouch cells are presented in Fig. 6 and relative capacity decrease of these cells are presented in Fig. 7. The cycle aging was done in two different cell voltage ranges (likewise the rate capability measurements in the half-cells); the lower was

from 3.0 V to 4.2 V and the larger from 3.0 V to 4.4 V. The specific capacity of the cells in Fig. 6 is given relative to the active mass of the LiCoO_2 electrode. The higher capacities seen in Fig. 7, at every 51st measurement point result from one 0.1 C cycle done after every 50 cycles with 0.5 C, and they provide information about the capacity retention at smaller C-rates. Because of the smaller C-rate, the voltage losses in the cell are smaller and thus larger discharge capacity is achieved, which can be taken to represent the electrochemically available capacity remaining in the cells. As expected from the rate capability testing in half-cells, the capacity retention for the $\text{LiCoO}_2(\text{D})$ cells is clearly the best in both the voltage ranges. However, in the smaller voltage range, the capacity retention of the $\text{LiCoO}_2(\text{S})$ cells is clearly better than that of the $\text{LiCoO}_2(\text{R})$ cells. This is surprising, because based on the half-cell tests (Fig. 4), $\text{LiCoO}_2(\text{S})$ can be expected to have similar cycle life properties to $\text{LiCoO}_2(\text{R})$. A clear explanation for this is not observed, but it should be taken into consideration that different electrolytes are used in the half-cells (1 M LiPF_6 in 1:1 EC:DMC) and in the pouch cells (1 M LiPF_6 in 25:70:5 EC:DEC:PC with 1 mol% VC and 1 mol% PS), which could affect the material cyclability. In the larger voltage range, $\text{LiCoO}_2(\text{S})$ and $\text{LiCoO}_2(\text{R})$ behave differently in the full-cell tests. Up to approximately 30 cycles, $\text{LiCoO}_2(\text{S})$ has a slower capacity decrease rate compared to $\text{LiCoO}_2(\text{R})$. However, after this the $\text{LiCoO}_2(\text{S})$ capacity decrease rate increases and the capacity quickly drops below the capacity of $\text{LiCoO}_2(\text{R})$. The capacity retention of the cells cycled in the higher voltage range are presented enlarged in the supplementary data, Fig. S7.

Fig. 6. Charge-discharge curves of the $\text{LiCoO}_2/\text{graphite}$ full cells at 0.5 C, a) $\text{LiCoO}_2(\text{S})$ in the voltage range of 3.0–4.2 V, b) $\text{LiCoO}_2(\text{S})$ in 3.0–4.4 V, c) $\text{LiCoO}_2(\text{R})$ in 3.0–4.2 V, d) $\text{LiCoO}_2(\text{R})$ in 3.0–4.4 V, e) $\text{LiCoO}_2(\text{D})$ in 3.0–4.2 V and f) $\text{LiCoO}_2(\text{D})$ in 3.0–4.4 V.

Fig. 7. Relative capacity drop of the LiCoO₂/graphite full cells cycled with C-rate of 0.5 C.

Generally, the cell is considered to have reached the end of its cycle life when the capacity decreases to 80 % of the initial capacity. [54] Based on Fig. 7, in the lower voltage range, LiCoO₂(D) has a capacity retention of 89% and LiCoO₂(S) that of 85% after 1000 cycles. The capacity of LiCoO₂(R) decreases below 80 % already after 500 cycles. In the larger voltage range, LiCoO₂(D) has the cycle life of 240 cycles, and both LiCoO₂(S) and LiCoO₂(R) approximately 50 cycles. The differences in the cycle lives in different voltage ranges are expected. However, the difference observed here indicates the importance of the selection of the voltage range. Discussion of the aging mechanism of the LiCoO₂ materials is out of the scope of this study. These investigations are in progress, and the results will be discussed in a following publication.

3.6. EIS

To investigate the changes in internal resistances induced by the cycling, the full-cell impedance spectra were measured after every 50th cycle. The impedance data of the LiCoO₂/graphite full cells is presented in Fig. 8. The Nyquist plots of the LiCoO₂/graphite full cells presented in the figure consist of two semicircles and a straight or slightly curved line. The smaller one of the semicircles is observed at high frequencies

and is usually attributed to the solid electrolyte interphase (SEI) on the graphite electrode. The larger semicircle at mid-frequencies corresponds to the charge-transfer resistances at the electrodes. The line at low frequencies originates from solid-phase diffusion.

Fig. 8. The evolution of the Nyquist diagrams of the LiCoO₂/graphite full cells at SoC of 50 % cycled in the voltage range of a) 3.0–4.2 V, and b) 3.0–4.4 V.

The high-frequency intersection with Z(real)-axis is at approximately 0.2 Ω for all the cells, and does not depend on the amount of cycles. This is the value of the cell resistance of the full cells, which results mostly from ionic conduction in the separator-electrolyte phase of the cells and the electric conduction in the electrodes and current collectors. As the value is similar for all the cells, their fabrication can be concluded to be reproducible.

According to the literature [55,56], the large semicircle obtained at mid-frequencies originates from the charge-transfer resistances at the positive and negative electrodes. Both electrodes generate their own semicircles but as the electrode processes often occur at the same frequencies, the semicircles overlap forming one larger one. [55] As can be seen in Fig. 8, the sizes of both the high-frequency and the mid-frequency semicircles increase as a function of cycle number. Especially the size of the mid-frequency semicircle increases, which indicates that the charge-transfer resistance of the electrodes increases with cycle number. The increase of the high frequency semicircle is mainly attributed to side reactions occurring with the electrolyte, such as the thickening of the SEI at the graphite electrode. However, especially at large cycle numbers, also the structural changes in the positive electrode material have been reported to affect the charge-transfer resistance. [57,58] For example, a hexagonal-to-spinel transition during cycling has been shown to take place on the surface of LiCoO_2 materials as reported by Yazami *et al.* [57] As only one semicircle representing both the negative and positive electrode is observed in Fig. 8, it is difficult to identify in which electrode the changes are occurring. However, as the same negative electrode material (graphite) is used in all the full cells, most of the differences in the large semicircles can be presumed to be caused by the differences in the LiCoO_2 materials. This is verified by the EIS results of the three-electrode cell setup presented in the supplementary data, Fig. S8.

Fig. 8 also shows that among the LiCoO_2 /graphite full cells, the charge-transfer resistance of the $\text{LiCoO}_2(\text{R})$ full cell is the largest after cell formation. One possible explanation for this could be the slightly poorer crystallinity of the sample, as already discussed in context of the CV measurements (see section 3.2). With

the formation cycle, the slight disordering could increase, and therefore increase the charge-transfer resistance compared to the other LiCoO_2 materials.

The charge-transfer resistance of the $\text{LiCoO}_2(\text{D})$ full cell shows the slowest increase as a function of cycle number with both the voltage ranges. In the smaller voltage range (3.0–4.2 V), the charge-transfer resistance of the $\text{LiCoO}_2(\text{R})$ full cell increases faster than the corresponding resistances of the other two full cells. In contrast, in the larger voltage range (3.0–4.4 V), $\text{LiCoO}_2(\text{S})$ and $\text{LiCoO}_2(\text{R})$ have similar charge-transfer resistances after formation and 50 cycles, but after 100 cycles, that of $\text{LiCoO}_2(\text{S})$ is clearly larger. These results concur with the cycle life results so that cells with shortest cycle lives have the largest charge-transfer resistances. Therefore, it can be concluded that the large increase in charge-transfer resistance causes the cell capacity to diminish more and thus results in shorter cycle life. As the charge-transfer resistance of the doped LiCoO_2 material increases the slowest, it appears that the heteroatom doping stabilizes the lithium cobalt oxide structure, slowing the material degradation such as cobalt dissolution and the hexagonal-to-spinel transition. This is in line with the results by Liu *et al.* [9] It is also plausible that the slightly smaller crystallite size of $\text{LiCoO}_2(\text{D})$ reduces the strain within the particles upon cycling and thus decreases the particle degradation such as cracking.

4. Conclusion

In this work, the effects of Li and Mg-Ti doping replacing some of the stoichiometric Co in LiCoO_2 synthesis on the performance and cycle life are investigated and compared. The materials have been prepared from the same commercial precursor to provide comparable data of the two modification methods. Regardless of the material, the particles are oval shaped and have an average diameter of 16 μm . However, the doped LiCoO_2 has slightly smaller crystallite size that is most likely caused by the doping. The Mg-Ti doped

material also has superior rate capability properties compared to the over-lithiated and the stoichiometric materials, which is attributed to the decreased Co valence caused by Ti doping that increases the material conductivity. In addition, the smaller crystallite size of $\text{LiCoO}_2(\text{D})$ further enhances the better rate capability properties. This is supported by the larger Li diffusion coefficient value measured for doped LiCoO_2 .

In addition to the enhanced rate capability properties, the doped LiCoO_2 also shows the longest cycle life of the three LiCoO_2 materials. This is observed even at a wide voltage range from 3.0 V to 4.4 V. However, not only the doping, but also the Li/Co ratio affects the cycle life of LiCoO_2 . The stoichiometric LiCoO_2 provides notably longer cycle life in the voltage range of 3.0–4.2 V but the over-lithiated ages slower in the range of 3.0–4.4 V after 80 % of the initial capacity has been reached. The differences in the cycle life properties are shown to converge with the charge-transfer impedances of the LiCoO_2 materials.

Acknowledgements

This work made use of the Aalto University Nanomicroscopy Center (Aalto-NMC) and RaMI premises. The authors wish to thank Dr. Hua Jiang for performing the EELS measurements and Mr. Olli Sorsa for performing the Raman measurements. The authors also thank Dr. Juho Välikangas and Mr. Tuomo Vähätiitto from University of Oulu for optimizing and preparing the pouch cells. Financial support from Academy of Finland, Strategic Research Council (the CloseLoop project), Business Finland (the B4B project) and Freeport Cobalt is also greatly acknowledged.

Supplementary data

Supplementary data related to this manuscript is included.

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