Probing Al distribution in $\text{LiCo}_{0.96}\text{Al}_{0.04}\text{O}_2$ materials using ^7Li , ^{27}Al and ^{59}Co

MAS NMR combined with synchrotron X-ray diffraction

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Abstract

We prepared Al-doped LCO (LCA) powders with low Al content (4%) with a controlled Li/(Co+Al) stoichiometry by a solid state reaction using Li_2CO_3 and two types of Co/Al precursors : simply mixed (Co_3O_4 and Al_2O_3) or heat treated (Co_3O_4 and Al_2O_3). These samples were thereby used to propose a reliable protocol aiming to discuss the homogeneity of the Al doping for $\text{LiCo}_{1-y}\text{Al}_y\text{O}_2$ (LCA) prepared with low Al content by evidencing the distribution of Al within the powders, which clearly affect the electrochemical profiles of associated LCA//Li cells. For all samples we initially also characterized by ^7Li MAS NMR the Li/(Co+Al) stoichiometry, to discard the possible effect of Li excess in the samples. Synchrotron XRD combined with ^{27}Al and ^{59}Co MAS NMR provided then a deep understanding of the doping homogeneity at the powder or particle scale. We showed that doping the Co_3O_4 spinel precursor by reacting it with Al_2O_3 may be

avoided, as it most likely leads to an inhomogeneous mixture of Co_3O_4 and $\text{Co}_{3-z}\text{Al}_z\text{O}_4$ as precursor, eventually reflecting in the final $\text{LiCo}_{0.96}\text{Al}_{0.04}\text{O}_2$ powder, which shows a non-homogeneous Al distribution. We believe that such a detailed characterization should be the first step towards a deeper understanding of the real beneficial effect(s) of Al doping on the high voltage performance of LCO.

Introduction

While lithium cobaltite LiCoO_2 (LCO) has been used as positive electrode material in Li-ion batteries for almost 30 years, only 60 % of its theoretical capacity is used in commercial cells. Attempts to reversibly de-intercalate more Li from LCO result in poor cycling performances due to strong degradation of the conventional carbonate-based electrolytes^{1,2}, structural instabilities³⁻⁷ and cobalt dissolution⁸ observed at high voltage ($V > 4.3$ vs. Li^+/Li). The substitution of some Co^{3+} ions with various dopants⁹⁻¹² M (M = Mg, Ti, Zr, Cr...) or more recently co-dopants¹³⁻¹⁵ (M, M') like (Mn, Mg), (Mg, Ti) or (La, Al), has been reported to be an effective strategy to improve the cycle life of LCO at high voltage.

Aluminum ions as dopants were among the first considered, by the means of theoretical calculations from Ceder's group¹⁶, followed by experimental work from Jang *et. al*¹⁷ and other groups¹⁸⁻²⁰. The choice for aluminum was motivated by: i) its low cost and non-toxicity, ii) a similar radius for Al^{3+} compared to Co^{3+} (0.535 Å vs. 0.545 Å) facilitating the substitution of the latter and preserving the initial structure leading to the full solid solution $\text{LiCo}_{1-y}\text{Al}_y\text{O}_2$. Al-doped LCO has been reported to experience: i) less volume changes^{17,18}, ii) a decreased cobalt dissolution¹⁸, and iii) the suppression of spinel disorder onto the surface of the particles as

compared to LCO²¹, even though accelerate capacity fading was also demonstrated^{16,22}. Although Al-doped LCO has been proposed several years ago as positive electrode material, the effect of Al doping on the phase transitions observed for LCO at high voltage and the impact of the Al distribution homogeneity in the material on the cycling performances are still unclear. Here, the challenge is to properly characterize the Al distribution for a low Al content (lower than 5%) which will be one of the requirements to make Al-doped LCO a suitable candidate as positive electrode in Li-ion cells. This would be done using the high angular resolution of synchrotron XRD and solid state ²⁷Al and ⁵⁹Co MAS NMR. In order to address only the problem of the role of the Al distribution, one has to study samples with a proper control of the initial Li/M stoichiometry. Indeed, Levasseur *et al.* previously showed^{23–25} that Li excess during the synthesis of LCO powders leads to the formation of the so-called “overlithiated” Li_{1+t}Co_{1-t}O_{2-t} compounds, whose Li presence in Co sites associated to close-by oxygen vacancies not only changes the electrochemical signature but also significantly increases the capacity losses during the 1st cycle. More recently, we also demonstrated that the phase transitions occurring at high voltage for LCO are also impacted by the initial Li/Co stoichiometry⁷. Thus, a parasitic effect of Li excess in Al-doped LCO with non-controlled Li stoichiometry may have, so far, led to incorrect conclusions. ⁷Li MAS NMR will be used here in order to ensure the Li/M stoichiometry of the studied compounds.

In literature, Al-doped materials are often synthesized through liquid media, featuring co-precipitation routes^{17,18,22,26–28}, usually leading to homogeneous Co³⁺/Al³⁺. For industrial point of view, however, it is interesting to develop further solid state synthesis routes for the preparation of doped LCO, even though achieving a proper Al distribution may be more challenging. Samples studied here were prepared in rather large quantities (~ 200 g) using solid state route with Co₃O₄ and Al₂O₃ as precursors with or without a heat treatment before the addition of lithium carbonate.

Recently, the interdiffusion of Co and Al the interface of LCO and Al₂O₃ pellets using various temperature were studied we the aim to optimize the synthesis of Al₂O₃-coated LCO^{29,30}. Here, we aim to discuss the homogeneity of Al distribution in Li-stoichiometric LiCo_{0.96}Al_{0.04}O₂ phases prepared by solid state from two different precursors compared with a sample prepared via a liquid media. Their electrochemical properties are finally discussed in relation with the Al distribution.

Experimental

Sample preparation (A schematic figure summarizing all steps of the synthesis can be found in Supplemental Information-Figure S1):

Precursors: A 2 kg-blend containing Co₃O₄ (Umicore) and Al₂O₃ (Umicore) in a Co/Al ratio of 0.96/0.04 was initially prepared. After homogenizing the mixture for 1 hour at 1000 rpm in a stainless steel container, it was split into two batches. The first batch (now called Precursor 1) was directly used to prepare P1-LCA. Note that a heat treatment of Precursor 1 at moderate temperature (600 °C) did not lead to any reaction between Co₃O₄ and Al₂O₃ (in good agreement with previous studies^{31–33}). In the meantime, a heat treatment at 1000 °C for 10 hours under air flow was applied to the second batch. The fired mixture, now referred to as Precursor 2, was accordingly used to prepare P2-LCA.

LCA samples: Two LiCo_{0.96}Al_{0.04}O₂ (LCA) powders samples called “P1-LCA” and “P2-LCA” were both prepared by solid state synthesis of homogenized mixtures of Li₂CO₃ (Umicore) and a Co- and Al- based oxide precursors (P1 or P2, respectively). The mixtures to form the final LCA samples were prepared in rather large amounts (220 g) in the ratio Li/(Co+Al) = 0.99 and homogenized for 4 hours with Al₂O₃ balls in a plastic container. Both were simultaneously

heat treated in the same furnace for 12 h under air flow at $T = 980\text{ }^{\circ}\text{C}$, followed by a second annealing at $T = 980\text{ }^{\circ}\text{C}$ for 10 h under air. A final post-treatment step using a grinder was mandatory to pulverize the synthesized powder blocks. Additionally, the as-prepared powders were sieved (40 μm mesh).

For comparison purposes, additional reference samples were prepared. Non Al-doped stoichiometric (st-LCO) and overlithiated LiCoO_2 (overl-LCO) were obtained from solid state synthesis of Co_3O_4 and Li_2CO_3 at $T = 980\text{ }^{\circ}\text{C}$ for 10 hours under air flow, with respective Li/Co ratios of 0.99 and 1.05. A 4%-Al doped LCO called “Rf-LCA” was prepared by a citrate co-precipitation route, following the experimental protocol detailed in a previous article from Dahéron *et. al.*²⁸ A solution of Li_2CO_3 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and CoCO_3 in citric acid 0.1 mol/L was heated for 3 hours at $T = 80\text{ }^{\circ}\text{C}$. After ammonia was added to the solution to reach a pH value of 7, the solvent was evaporated using a rotary evaporator. The solid residue was subsequently heat treated 3 times at: i) $T = 200\text{ }^{\circ}\text{C}$ for 10 h under air, ii) $T = 450\text{ }^{\circ}\text{C}$ for 12 h under O_2 and iii) $T = 900\text{ }^{\circ}\text{C}$ for 12 h under O_2 . The residue was systematically grinded and pelletized between each heat treatment, and sieved after the last one (40- μm mesh). To confirm our interpretation of the ^{59}Co MAS NMR spectra a 10% Al doped LCO sample has also been prepared using the same citrate-route.

Samples characterization.

Powder X-ray diffraction (XRD) patterns were collected on a PANalytical X'pert PRO MPD diffractometer in Bragg-Brentano θ - θ geometry equipped with a Fe filter, a spinner and X'Celerator

multi-strip detector. Each measurement was made within an angular range of $2\theta = 10 - 120^\circ$ and lasted for 15 hours, at 0.016° intervals. The Co-K α radiation was generated at 35 kV and 30 mA ($\lambda(K_{\alpha 1}) = 1.789 \text{ \AA}$; $\lambda(K_{\alpha 2}) = 1.793 \text{ \AA}$). Additional high angular resolution synchrotron powder X-ray diffraction (SXRD) experiments were performed on the BL04-MSPD beamline of the ALBA synchrotron (Cerdanyola del Vallès, Spain). All powders were packed in 0.5 mm diameter capillaries. The patterns were recorded in Debye-Scherrer geometry with a wavelength of $\lambda = 0.825 \text{ \AA}$. The typical 2θ angular range was $0 - 70^\circ$ with 0.006° angular step and 3-minute-long accumulation time. Regarding the high crystallinity of the Co₃O₄ and LCO compounds, the angular step of the MYTHEN detector used for this study was not sufficiently low to properly refine the XRD patterns using the Rietveld method. Therefore, only Le Bail refinements were carried out.

⁷Li MAS NMR spectra were recorded on a Bruker 300 Advance spectrometer at 116.66 MHz (7.05 T magnet), with a standard 2.5 mm Bruker MAS probe. A Hahn echo sequence [$t_{\pi/2}-\tau_1-t_{\pi}-\tau_2$] synchronized with one period of rotor rotation was used for a 30 kHz spinning frequency. The 90° pulse duration was equal to $t_{\pi/2} = 2.0 \text{ }\mu\text{s}$ and determined using a LiCl 1 M solution. A recycle time of $D_0 = 40\text{s}$ was used for st-LCO and LCA samples, whereas a shorter $D_0 = 2\text{s}$ was enough for the overl-LCO sample, to avoid T_1 saturation effects.

Single pulse ²⁷Al MAS NMR spectra were recorded on a Bruker 500 MHz spectrometer at 130.33 MHz (11.7 T magnet) using a standard Bruker 2.5 mm MAS probe with a 30 kHz typical spinning frequency. The spectral width was set to 0.5 MHz and the recycle time to $D_0 = 5 \text{ s}$, long enough to avoid T_1 saturation effects. As ²⁷Al is a strong quadrupolar nucleus with $I = 5/2$, a short pulse length of $1.1 \text{ }\mu\text{s}$ corresponding to a $\pi/12$ pulse determined using an aqueous 1 M Al(NO₃)₃ solution was employed. In these conditions, all of the $-1/2 \rightarrow +1/2$ central transitions are equally excited regardless of the magnitude of the nuclear quadrupole coupling constants and one can

extract quantitative data. The external reference was a 1 M $\text{Al}(\text{NO}_3)_3$ aqueous solution. For the samples containing only 4% of Al, overnight experiments (10240 scans) were carried out to ensure a good signal/noise ratio. No baseline subtraction was done in the figures presented here.

^{59}Co MAS NMR spectra were recorded on a Bruker 500 MHz spectrometer at 120.35 MHz (11.7 T magnet) using a standard Bruker 2.5 mm MAS probe with a 30 kHz typical spinning frequency. The spectral width was set to 0.5 MHz and the recycle time to $D_0 = 1$ s. Single $\pi/16$ pulse and rotor-synchronized Hahn echo sequences were used. A comparison of the spectra for one sample is given in **Figure S2**. Even if not quantitative, only spectra recorded with a Hahn echo sequence $[t_{\pi/2}-\tau_1-t_{\pi}-\tau_2]$ with $t_{\pi/2} = 2.5 \mu\text{s}$ are presented here. This sequence facilitates the phasing of all the signals and ensures the observation of possible very wide signals which are lost during the receiver dead time. The external reference was a 1M $\text{K}_3\text{Co}(\text{CN})_6$ aqueous solution.

Electrochemical tests were performed in coin cells, using pure lithium as counter-electrode and 1 M LiPF_6 in EC:DEC:DMC as electrolyte. LCA:C:PVDF electrodes (90:5:5 %_{wt}) were prepared from a slurry using N-methyl-pyrrolidone (NMP) as solvent casted onto a 30 μm -thick-aluminum foil. After evaporating the NMP for 2 hours at $T = 80^\circ\text{C}$, $\Phi 15$ mm electrodes were cut in the obtained film with typical active material loading of 10 mg/cm^2 . The electrodes were then dried overnight under vacuum at $T = 120^\circ\text{C}$ and stored in an argon-filled glovebox, whose cell assembling was carried out.

Scanning electron micrographs were taken using a Hitachi Model S-4500 microscope after metallizing the powders with gold.

Inductively Coupled Plasma (ICP) measurements were carried out on Agilent ICP-720ES equipment after sample dissolution in concentrated HCl solution under heating.

Results and discussion

A. Precursors characterization

The major difference between the two LCA samples prepared by solid state chemistry lies in the used Co/Al-based precursor: homogenized mixture of Co_3O_4 and Al_2O_3 (Precursor 1) or same mixture heat treated at 1000°C heat (Precursor 2). Therefore, a special attention to the Co/Al-based precursor is then given in the following to establish the relevance of the heat treatment of Co_3O_4 and Al_2O_3 with $\text{Co/Al} = 0.96/0.04$ prior to the addition of lithium carbonate, using SEM, SXRD, and ^{27}Al MAS NMR.

SEM micrographs of Precursors are given in **Figure 1**. A population of < 10 nm-sized particles corresponding to Al_2O_3 can be clearly distinguished on top of Co_3O_4 particles whose average size is several hundreds of nanometers for Precursor 1 (Fig. 1a). On the other hand, only one type of bigger particles (μm -size) is observed for Precursor 2 (Fig. 1b). This suggests that the reaction between Al_2O_3 and Co_3O_4 has occurred at 1000°C , jointly with crystalline growth usually observed at high temperatures.

SXRD patterns for Precursors 1 and 2 are plotted in **Figure 2**. A reference pattern from Co_3O_4 is also provided for better comparison. Recording of XRD patterns using synchrotron radiation was motivated by the expected noticeable gain in detection limit that may reveal information regarding impurities or alumina itself. No matter the Al content z , the evolution of the a_{cub} cell parameter for $\text{Co}_{3-z}\text{Al}_z\text{O}_4$ is expected to be negligible due to comparable ionic radiuses of Co^{3+} ($0.545 \text{ \AA}$) and Al^{3+} ($0.535 \text{ \AA}$). Values of $8.084 \text{ \AA}$ for Co_3O_4 , $8.086 \text{ \AA}$ for Co_2AlO_4 and $8.104 \text{ \AA}$ for CoAl_2O_4 are typically reported for a_{cub} .³². Thus, within the angular resolution limits of the

SXRD experiment, not surprisingly the diffraction peaks for Co_3O_4 , Precursor 1 and Precursor 2 are found at identical 2θ positions. All peaks can be indexed in the $Fd3m$ space group with a cell parameter a_{cub} equal to 8.084(2) Å. In particular, no signal ascribed to the presence of crystalline alumina could be detected for either Precursor 1 or Precursor 2 in **Figure 2**, even though alumina is clearly seen in **Figure 1** for the former. The Al_2O_3 particles present in P1 thus, must be really disordered with very small particles size (< 10 nm). After such heat treatment used to form Precursor 2, the formation of mix- $\text{Co}_{3-z}\text{Al}_z\text{O}_4$ phase is expected^{31,32}. The diffraction peaks of Precursor 1 are found to be slightly broader than those of Precursor 2 ($T = 1000$ °C). No additional information regarding the Al distribution itself within the precursors could be gathered from SXRD.

Figure 3 shows the ^{27}Al MAS NMR spectra recorded for the different precursors used for the LCA materials synthesis. The Al_2O_3 precursor exhibits a spectrum typical of the γ -form of Al_2O_3 with two broad signals localized around 65 and 9 ppm, assigned respectively to Al in tetrahedral and octahedral environments^{34–36}. The strong asymmetrical broadening of the signals toward lower shifts originates from distributions of quadrupolar couplings typically observed in disordered compounds. The Co_3O_4 mixed with Al_2O_3 (Precursor 1) still logically exhibits the same ^{27}Al MAS NMR signature as γ - Al_2O_3 , therefore un-reacted. On the contrary, as no signal is observed in the same recording conditions after a heat treatment of these precursors at 1000 °C for 10h (Precursor 2), we conclude that Al_2O_3 did react with Co_3O_4 in good agreement with the SEM observations and with the literature (a minimum temperature of 800 °C was reported^{31–33} for the reaction of Co_3O_4 and γ - Al_2O_3 to form $\text{Co}_{3-z}\text{Al}_z\text{O}_4$). The absence of signal for Al in doped Co_3O_4 is most likely due to strong hyperfine coupling with paramagnetic cobalt species either leading to very fast relaxation times or to such a broadening that they cannot be resolved in our conditions.

Similar effect was also reported for CoAl_2O_4 and for other paramagnetic materials^{37,38}. Therefore, no further information about the distribution of Al within Precursor 2 could be gathered here. Nonetheless, at this point, SEM, SXRD and ^{27}Al MAS NMR helped proving the different chemical natures of Precursor 1 or 2, the latter containing an Al-doped spinel phase as opposed to the former.

B. $\text{LiCo}_{0.96}\text{Al}_{0.04}\text{O}_2$ characterization

General characterizations

As aluminum is found in different environments for Precursor 1 or 2, (i. e. included in Co_3O_4 matrix or not), two final associated LCA materials were prepared after addition of Li_2CO_3 . The goal of this study was to investigate the homogeneity of the aluminum distribution within the LCA phases and evaluate its influence on the electrochemical behavior, without any interference due to the presence of Li excess. Therefore, we strictly prepared the samples using $\text{Li}/(\text{Co}+\text{Al}) = 0.99$ in the precursors mixture in order to get real stoichiometric samples LCA with $\text{Li}/(\text{Co}+\text{Al}) = 1.00$ with possibly remaining spinel and Al_2O_3 .

Table I gives the final $\text{Al}/(\text{Co}+\text{Al})$ and $\text{Li}/(\text{Co}+\text{Al})$ ratios measured with ICP for P1- and P2-LCA. Both samples exhibit $\text{Al}/(\text{Co}+\text{Al})$ values close to the expected 4 % one ($\text{Al}/(\text{Co}+\text{Al}) = 0.038$ for P1-LCA and $\text{Al}/(\text{Co}+\text{Al}) = 0.040$ for P2-LCA). Accurate control of the final $\text{Li}/(\text{Co}+\text{Al})$ was achieved, as revealed by the measured values always found slightly below 1.00 ($\text{Li}/(\text{Co}+\text{Al}) = 0.995$ for P1-LCA, and $\text{Li}/(\text{Co}+\text{Al}) = 0.992$ for P2-LCA). Laboratory XRD and ^7Li MAS NMR were respectively used to check the possible presence of unreacted Co_3O_4 (expected if $\text{Li}/(\text{Al}+\text{Co}) < 1$) and the stoichiometry of the LCA samples, as extra signals are expected if $\text{Li}/(\text{Al}+\text{Co}) > 1$. In **Figure 4.a**, all XRD patterns show the peaks associated to layered crystallized

(O3) structure indexed in the $R\bar{3}m$ space group, similarly to the un-doped LiCoO_2 we used as reference here (st-LCO). Two additional weak peaks are observed at $2\theta^\circ = 36.5^\circ$ and $2\theta = 43.1^\circ$ in all XRD patterns, indexed as the (220) and (311) in the $Fd\bar{3}m$ space group showing the presence of some remaining cobalt-based oxide precursors, as expected from the use of the $\text{Li}/(\text{Co}+\text{Al}) = 0.99$ ratio in the precursors mixture. For the O3 LCA phases, a small overall peak broadening can be observed with the addition of aluminum in the samples. A slightly larger c_{hex} parameter is obtained from refinement of the XRD patterns for the 4 % Al-doped samples (14.063(7) Å for P1-LCA and 14.065(8) Å for P2-LCA) compared to their undoped analogue st-LCO (14.047(1) Å). Such change (0.13%) is clearly highlighted in **Figure 4.b** by the shift observed for the (003) peak. The evolution of the a_{hex} parameter is expected to follow the reverse trend, even though with much less variation. The change trend of the cell parameters are here in good agreement with the observations already reported in the literature for LCA with larger aluminum content^{17,18,26,39}. **Figure 5** shows the recorded ^7Li MAS NMR spectra for P1- and P2-LCA. Both are plotted and compared to that of undoped LiCoO_2 materials prepared without and with an excess of lithium carbonate designed as st-LCO (stoichiometric, $\text{Li}/\text{Co} = 1.00$) and overl-LCO (overlithiated, $\text{Li}/\text{Co}=1.05$), respectively. As already reported, ^7Li MAS NMR is the key technique to probe the Li/Co stoichiometry in those materials^{23,24}; in st-LCO, Li is present in a single diamagnetic environment as all cobalt ions are in low spin state (LS-Co^{3+}), leading to a single signal located at -0.4 ppm. On the other hand, several signals are observed for overl-LCO. Indeed, intermediate spin state paramagnetic (IS-Co^{3+}) cobalt ions are formed due to the presence of Li in the Co site associated with an O vacancy²⁴. Due to the Fermi contact interaction, adjacent Li can exhibit negative or positive shifted signals (out of the narrow chemical shifts range of ^7Li), depending on its environment. The spectrum of overl-LCO does exhibit, therefore, in addition to the main signal at -0.4 ppm, a large number of more shifted signals (Figure 5). Since the ^7Li MAS

NMR spectra of the two 4% Al-doped LCA samples do not exhibit those extra signals, this confirms that these materials are really Li-stoichiometric and do not contain any paramagnetic species. These results are therefore in good agreement with the previous $\text{Li}/(\text{Co}+\text{Al})$ ratios measured by ICP. Moreover, long T_1 relaxation times, typical for diamagnetic materials, were determined ($T_1 \sim 5$ s). Note that the ^7Li MAS signal of the two LCA samples is slightly broader than the one of st-LCO due to a distribution of Li environments versus Co/Al in the materials (Figure S3).

Homogeneity of Al-doping within P1- and P2-LCA

To further investigate the homogeneity of Al distribution within P1- and P2-LCA (which could not be debated from laboratory XRD or ^7Li MAS NMR), SXRD patterns and ^{27}Al and ^{59}Co MAS NMR spectra were collected.

Figure 6.a gives a general view of the SXRD patterns for P1- and P2-LCA and first leads to the similar conclusions as laboratory XRD, i.e. pure layered phases crystallizing in the $R-3m$ space group were obtained, with small traces of spinel precursor impurity. Diffraction peaks for Al-doped samples are also found broader and at different 2Θ positions than those of undoped st-LCO, as shown by the shifts of the (018) and (110) diffraction peaks (**Figure 6.c** and **6.d**). This confirms the substitution of Co^{3+} with Al^{3+} in LCA samples which leads to a decrease of the a_{hex} parameter and an increase of the c_{hex} one. Those two diffraction lines have been chosen here to reflect the evolution of the a_{hex} and c_{hex} parameters. The evolution of the c_{hex} parameter is predominating in the shift of the (018) peak. Note that **Figure 6.c** and **6.d** were normalized to the overall peak area. An alternative plot of the data after normalization to the peak maxima is also provided in **Figure S4**. Moreover, strong additional peak asymmetries can clearly be observed for

P1- and P2-LCA, while it does not exist for st-LCO. This asymmetry is found for any of the diffraction peaks collected within our 2θ range, as shown by **Figure 6.b**; it varies with the (hkl) values of the diffraction lines. As shown by Gaudin et al.²⁶ for the $\text{Li}(\text{Co}_{1-x}\text{Al}_x)\text{O}_2$ solid solution, the c_{hex} increases of 1% in the overall composition range ($0 \leq x \leq 1$) whereas the a_{hex} parameter decreases of 0.5%. As shown in **Figure 6.b**, the asymmetry of the (10l) lines is observed towards smaller 2θ angles for LCA samples, since the variation of c_{hex} is predominating. On the other hand, as the (110) line is only affected by the a_{hex} parameter, the asymmetry is observed toward higher angles (Fig. 6.d). This asymmetry is further evidence of the presence of a distribution of Al concentration in the particles of the two LCA samples. Nevertheless, P2-LCA shows slightly more asymmetry than P1-LCA, suggesting that an even less homogeneous distribution of Al is achieved for P2-LCA. In **Figure 6.d**, the (110) peak for P2-LCA does also exhibit a shoulder centered at the (110) peak position of the undoped st-LCO, implying that domains without Al within P2-LCA do exist (their contribution better seen for this diffraction line). In **Figure 7**, the shape of the (110) and (018) diffraction lines of P1-LCA and P2-LCA is compared to the one of Rf-LCA sample prepared by precipitation route, known to yield a more homogenous doping^{26,27} as expected, Rf-LCA does exhibit symmetrical lines due to a homogeneous Al/Co cation mixing. Therefore, these SXRD results first suggest that i) in our solid state synthesis conditions, heterogeneous Al distribution was observed and ii) the final Al distribution is dependent on the Co- and Al-based oxide precursor type (with or without a 1000°C heat treatment).

²⁷Al MAS NMR was additionally used to locally probe the different Al environments distribution in the LCA materials at a local scale. Complete spectrum included spinning sidebands manifold can be found in **Figure S4**. A zoom on the central transitions is shown in **Figure 8**. As shown in Figure 8.a, the P2-LCA compound clearly exhibits seven signals. They can be assigned

to the different Al environments versus second Co neighbors in the transition metal (TM) layer, as already reported by Gaudin et al²⁶. The signal located around ~ 62 ppm is assigned to Al surrounded only by LS-Co³⁺ ions as second neighbors denoted as Al-(Al₀Co₆). Note that this signal exhibits a clear second order quadrupolar lineshape could be fitted (see **Figure S6**) leading to $\delta_{\text{iso}} = 64.7$ ppm, $\nu_Q = 386$ kHz and $\eta = 0.15$ as parameters. A value close to zero was indeed expected for the Al-(Al₀Co₆) local environment as it is expected to exhibit an axial symmetry if one considers only this first cationic coordination sphere. The set of other signals located equally spaced by 7-8 ppm, located at ~ 55, ~ 48, ~ 40, ~ 33, ~ 26, ~ 18 ppm are assigned to Al surrounded by n Al³⁺ and (6-n) Co³⁺ as second neighbors with n varying respectively from 0 to 6, denoted Al-(Al_nCo_{6-n}). Those signals do not exhibit a clear second order lineshape anymore due to a distribution of possible local configurations for each Al-(Al_nCo_{6-n}) ($0 \leq n \leq 6$) environment. Small signals located around 69 and 73 ppm are assigned to the satellite transitions expected for the main signal arising from Al-(Al₀Co₆) environments. Satellites transitions of the other signals are probably overlapping their neighboring signal on the left, preventing a highly precise quantitative analysis. Nevertheless, we computed the probability $P(y, 6-n)$ for a composition with $y = 0.04$ and (6-n) cobalt atoms ($0 \leq n \leq 6$) as second neighbors using a binomial law:

$$P(y, 6-n) = C_6^{6-n} y^n (1-y)^{6-n}$$

The resulting theoretical intensity distribution is schematically depicted by the yellow rectangles in **Figure 8.b**. For such a low Al-doping amount, negligible signal intensity is expected for Al-(Al₃Co₃) environments and for Al-richer ones ($n > 3$). Therefore, the two LCA prepared by solid-state route do not exactly follow this trend, confirming inhomogeneity in the Al-distribution within the samples suspected from SXRD. We also compared these materials to the 4% Al-doped LiCoO₂ material obtained from a citrate precursor route (Rf-LCA). Signals assigned to Al-rich environments are less intense for the latter than those of P1- and P2-LCA, and closely follows the

intensity distribution theoretically expected. Therefore, this result confirms the high homogeneity of Al distribution for LCA prepared by the citrate route while infirming it for P1- and P2-LCA. Nevertheless, the departure from the ideal Al distribution is larger for P2-LCA than for P1-LCA in good agreement with the SXRD results.

^{59}Co MAS NMR was reciprocally used to characterize the Co local environments in the materials. This is the first report of ^{59}Co MAS NMR study of Al-doped LiCoO_2 samples. The complete spectrum of P2-LCA included spinning sidebands manifold can be found in **Figure S5**. **Figure 9** shows the spectra recorded for P1- and P2-LCA compared with those of undoped stoichiometric LiCoO_2 (st-LCO) and 4% doped via the citrate route (Rf-LCA). The MAS spectra are observed to break into spinning side bands and the resolution is good enough to evidence different signals. For st-LCO, a single resonance is observed at 14132 ppm in agreement with Siegel *et al.*⁴⁰ and is assigned to the single octahedral LS- Co^{3+} site in the material. In the Al-doped samples, a set of other as broad signals are observed located at 14105, 14077, 14047, and 14021 ppm, that we propose to respectively assigned to Co with various 2nd ($\text{Al}_n\text{Co}_{6-n}$) neighbor environments as given in **Figure 9**. To confirm our signal assignment a 10% Al-doped sample prepared by the citrate route was also studied by ^{59}Co and is presented in Figure S7 and S8. Despite broader signals observed for ^{59}Co MAS NMR, compared to ^{27}Al MAS NMR, distinct signals can be resolved. It appears that the most homogeneous samples exhibit weaker signal broadening (also seen in Figure S9). Indeed, the ^{59}Co NMR chemical shift range is very large and the shift position is very sensitive to the local environments (distances, angles). For example, a signal was observed at 14115 ppm in O3- LiCoO_2 by Siegel *et al.*⁴⁰ and at 14722 ppm in O3- NaCoO_2 ⁴¹. An inhomogeneous Al-doping in LiCoO_2 thus generates a larger distribution of distances and angles around Co, leading to a broadening of the lines.

SXRD, ^{27}Al and ^{59}Co MAS NMR all lead to the same conclusions. Our solid state synthesis route, even performed at relatively high temperature (980°C) with either Al_2O_3 just mixed with Co_3O_4 or pre-heated at 1000°C as precursors, do not allow to prepare materials as homogeneous as the one prepared by the citrate route. A small gradient in composition is remaining in the P1- and P2-LCA samples. Nevertheless, the Al-doping of LCO was effective, since no signal of remaining Al_2O_3 is observed by ^{27}Al MAS NMR. While we initially thought that a pre-heat treatment of the Al and Co precursor might help to get homogeneous LCA samples, the opposite effect is actually observed: P2-LCA sample shows even more inhomogeneity of Al distribution than P1-LCA. These differences may arise from several causes. The formation of an inhomogeneous mixture of Co_3O_4 and $\text{Co}_{3-z}\text{Al}_z\text{O}_4$ for Precursor 2 most likely leads to further heterogeneous Al distribution in the final P2-LCA phase. A preferential reaction between Li_2CO_3 and $\gamma\text{-Al}_2\text{O}_3$ may also be more favorable for the final Al distribution within P1-LCA. The particle size may also have played a role, as homogenization processes may be harder in the bigger particles of Precursor 2 as opposed to Precursor 1 during the formation of the associated LCA. Even though no clear conclusions on the precursors can be drawn, differences of Al distribution were still evidenced in both resulting LCA prepared from solid state synthesis thanks to the remarkable resolutions of SXRD and ^{27}Al MAS NMR.

Electrochemical properties

In the case of LCA powders, it seems reasonable to expect differences in the electrochemical profiles depending on the homogeneity of the Al distribution within the samples. **Figure 10.a** shows the 1st cycle between 3.0 and 5.0 V at C/20, for coin cells with either st-LCO, P1-LCA, P2-LCA and Rf-LCA as positive electrodes. Discharge capacities and coulombic

efficiency upon cycling are provided in **Figure S11**. Typical features characteristic of stoichiometric LiCoO_2 (st-LCO) are clearly seen: i) the voltage jump corresponding to the $\text{O}3 \leftrightarrow \text{O}'3$ monoclinic transition resulting from the formation of a Li-vacancy ordering at $x = 0.5$, (**Figure 10.b** and **Figure 10.c**): ii) the formation of the H1-3 phase around $x \approx 0.17$, also revealed by a clear change of slope. The homogeneously Al-doped material Rf-LCA shows none of the above, as revealed by the overall slopping profile of the electrochemical curve. In particular, the $\text{O}3 \leftrightarrow \text{O}'3$ monoclinic transition does not occur (**Figure 10.c**). Note that in the case of LCO, even a very little excess of Li found in the Co layers hinders the Li-vacancy ordering at $x = 0.5$ ^{23,24}. The occurrence of this transition is thus extremely sensible to the local perturbations within LCO-type materials. Since we controlled the initial $\text{Li}/(\text{Co}+\text{Al})$ ratios in this study, only the presence of homogeneously distributed Al^{3+} in substitution of some Co^{3+} can explain the absence of the $\text{O}3 \leftrightarrow \text{O}'3$ monoclinic transition. As a matter of fact, this could then be considered a first indirect tool to probe the dopants repartition within the doped LCO, when an accurate control of the $\text{Li}/(\text{Co}+\text{Al}) = 1.00$ is achieved. For both P1 and P2-LCA, this $\text{O}3 \leftrightarrow \text{O}'3$ monoclinic transition occurs – as clearly evidenced by the small change of slope in the near $x = 0.5$ region (**Figure 10.b**) and in the derivative dx/dV curve (**Figure 10.c**). One can assume the coexistence of un-doped and Al doped domains due to the inhomogeneous distribution of Al ions to explain this behavior. This supports the previous conclusions obtained from SXRD and MAS NMR, i.e. that non homogeneous Al-doping was achieved by our solid state synthesis of LCA. It is though impossible to discriminate between P1- and P2-LCA respective performances after one cycle. Note that the polarization at high voltage, in discharge, is substantial for st-LCO compared to any other LCA. However, aluminum content itself cannot strictly explain this improvement: other parameters such as the difference in particle size observed in **Figure S10** may also play a role. Nonetheless, this

polarization makes it hard to discuss the existence, or not, of the H1-3 phase itself for LCA samples, especially for Rf-LCA. Weak changes of slope can still be observed in the high voltage region for all LCA, mainly evidenced during the discharge. Additionally, all Al-doped LCO show higher irreversible capacity vs undoped LiCoO_2 , following previous conclusions¹⁸.

Conclusion

In this paper, we prepared Al-doped LCO (LCA) powders with low Al content (4%) with a controlled $\text{Li}/(\text{Co}+\text{Al})$ stoichiometry by a solid state reaction using Li_2CO_3 and two type of Co/Al precursors : mixed Co_3O_4 and Al_2O_3 or heat treated mixture. We established a reliable protocol to characterize the Al distribution within these LCA powders at different scales through the combined use of synchrotron XRD and $^{27}\text{Al} / ^{59}\text{Co}$ MAS NMR. Our samples were compared to a phase prepared by a precipitation technique used as a reference sample. For all samples we initially also characterized by ^7Li MAS NMR the $\text{Li}/(\text{Co}+\text{Al})$ stoichiometry, to discard the possible effect of Li excess in the samples. We showed that doping the Co_3O_4 spinel precursor by reacting it with Al_2O_3 may be avoided, as it most likely leads to an inhomogeneous mixture of Co_3O_4 and $\text{Co}_{3-z}\text{Al}_z\text{O}_4$ as precursor, eventually reflecting in the final $\text{LiCo}_{0.96}\text{Al}_{0.04}\text{O}_2$ powder, which shows a non-homogeneous Al distribution. The comparison of the electrochemical performance of both LCA powders with a reference LCA sample prepared from co-precipitation route confirmed the inhomogeneity of Al doping, as typical features (such as the $\text{O}3 \leftrightarrow \text{O}'3$ transition) obtained for undoped LCO were still distinguished for the former. Nonetheless, higher irreversible capacity was achieved at the outcome of the 1st cycle for all LCA as compared to undoped LCO, confirming previous findings from Myung *et. al*¹⁸. As we carefully controlled the $\text{Li}/(\text{Co}+\text{Al})$ stoichiometries of all LCA powders through ^7Li MAS NMR, the possible contribution of Li excess to the increase of capacity losses during the first cycle is discarded.

Although both samples investigated in this section showed poor homogeneity of Al doping, this is still a first encouraging step towards the preparation of homogenous Al-doped LCO materials by solid state route for high energy density LCA. Further studies will aim to improve the homogeneity of the samples using different temperature treatments and times and/or other precursors.

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Associated Contents/Supporting Information paragraph

The Supporting Information is available free of charge on the ACS Publications website

Figure S1: Summarizing scheme of syntheses for P1- and P2-LCA. **Figure S2:** ^{59}Co MAS NMR spectra $\text{LiCo}_{0.96}\text{Al}_{0.04}\text{O}_2$ (ref-LCA) comparing Hahn Echo versus Single pulse sequences. **Figure S3:** Zoom on the ^7Li MAS NMR spectra. **Figure S4:** Zoom on the (0 1 8) and (1 1 0) SXRD peaks normalized to the (1 1 0) peak maximum, as opposed to Figure 7.b and 7.c in which the data was normalized to the peak areas. **Figure S5:** Typical entire spectra recorded for a) ^{27}Al and b) ^{59}Co MAS NMR for the P2-LCA sample. **Figure S6:** Typical fit of a ^{27}Al MAS NMR spectrum. **Figure**

S7: ^{59}Co MAS NMR spectra of 4% and 10% Al-doped LiCoO_2 samples prepared by the citrate route. **Figure S8:** ^7Li , ^{27}Al and ^{59}Co MAS NMR spectra of $\text{LiCo}_{0.90}\text{Al}_{0.10}\text{O}_2$ sample prepared by the citrate route. **Figure S9:** ^{59}Co MAS NMR spectra recorded at 120.35 MHz using a 30 kHz spinning frequency of the P1-LCA and P2-LCA samples compared with the ones recorded for undoped st-LCO and a 4% Al doped LCA samples prepared by a citrate route used as references. **Figure S10:** SEM micrographs of the powders of **a)** P1-LCA, **b)** P2-LCA and **c)** Rf-LCA. **Figure S11:** Discharge capacities and coulombic efficiency upon cycling of P1-LCA and P2-LCA at C/20 as positive electrode in Li//LCA cells, as compared to those of the undoped LCO (st-LCO).

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Figure 1. SEM micrographs of the powders of **a)** Precursor 1 ($\text{Co}_3\text{O}_4 + \text{Al}_2\text{O}_3$) and **b)** Precursor 2 ($\text{Co}_3\text{O}_4 + \text{Al}_2\text{O}_3$, heat treated at 1000°C for 10h under air).

Figure 2. a) Synchrotron X-ray diffraction (SXRD) patterns obtained for a non-doped Co₃O₄ (black), as compared to the mixtures of Co₃O₄ + Al₂O₃ (Precursor 1, in blue) or heat treated at T = 1000 °C (Precursor 2, in red). All patterns were collected for $\lambda = 0.826 \text{ \AA}$, but are converted here to $\lambda(\text{CoK}\alpha) = 1.790 \text{ \AA}$ for better comparison with all XRD patterns showed throughout the article. Miller indexes are specified for the most intense peaks. A zoom focusing on (2 2 0), (2 2 2) and (4 2 0) peaks is provided in **b)**.

Figure 3. ^{27}Al MAS NMR spectra recorded at 130.33 MHz using a 30kHz spinning frequency for Precursor 1, ($\text{Co}_3\text{O}_4 + \text{Al}_2\text{O}_3$) in blue) and Precursor 2 ($\text{Co}_3\text{O}_4 + \text{Al}_2\text{O}_3$, heat treated at $T = 1000\text{ }^\circ\text{C}$) (in red), as compared to the spectra of pure γ -alumina (in black).

Sample	Li/(Co+Al)	Al/(Co+Al)
P1-LCA	0.995 (2)	0.038 (2)
P2-LCA	0.992 (2)	0.040 (2)

Table I: Measured ICP ratios for the two final LCA powders.

Figure 4. **a)** X-ray diffraction (XRD) data recorded for P1- and P2-LCA as compared to undoped LCO (st-LCO). These patterns were collected using a laboratory diffractometer equipped with a cobalt source ($\lambda(\text{Co}_{K\alpha 1}) = 1.789 \text{ \AA}$, $\lambda(\text{Co}_{K\alpha 2}) = 1.793 \text{ \AA}$). Miller indexes are specified for all the peaks visible for $2\Theta < 90^\circ$. A zoom on the (003) diffraction peak is given in **b)**, while (018) and (110) peaks are presented in **c)** and **d)** Representation of the O3 structure of the LCA phases.

Figure 5. ^7Li MAS NMR spectra recorded at 116.66 MHz using a 30kHz spinning frequency of the P1-LCA and P2-LCA samples compared with the ones of undoped LCO samples prepared in the stoichiometric conditions (Li/Co = 1.00, st-LCO) or with an excess of Li-carbonate (Li/Co = 1.05, overl-LCO) used as references.

Figure 6. a) Synchrotron X-ray diffraction (SXRD) patterns obtained for P1- and P2-LCA, as compared to undoped LiCoO_2 (st-LCO). All patterns were collected for $\lambda = 0.826 \text{ \AA}$, but are converted here to $\lambda(\text{Co}_{\text{K}\alpha 1}) = 1.790 \text{ \AA}$ for better comparison with all XRD patterns showed throughout the article. Zooms on several lines is shown in b) and a larger zoom in (0 1 8) and (1 1 0) peaks is provided in c) and d).

Figure 7. Zoom on the a) (0 1 8) and b) (1 1 0) SXRD peaks for P1- and P2-LCA normalized to the peak areas, as compared to the reference sample prepared from co-precipitation (Rf-LCA).

Figure 8. a) ^{27}Al MAS NMR spectra recorded at 130.33 MHz using a 30 kHz spinning frequency of the P1-LCA and P2-LCA samples compared with the one recorded for a 4% Al doped LCA samples prepared by a citrate route used as reference and **b)** comparison with the theoretical intensity distribution of the different Al environments versus Co, expected for a 4% Al-doped sample.

Figure 9. ⁵⁹Co MAS NMR spectra recorded at 120.35 MHz using a 30 kHz spinning frequency of the P1-LCA and P2-LCA samples compared with the ones recorded for undoped st-LCO and a 4% Al doped LCA samples prepared by a citrate route used as references.

Figure 10. **a)** 1st cycle for P1-LCA (in black) and P2-LCA (in red) at C/20 as positive electrode in Li//LCA cells, as compared to those of the reference LCA prepared from a co-precipitation route (Rf-LCA) and undoped LCO (st-LCO). A zoom corresponding to the O3 $\leftrightarrow$ O'3 transition is given in **b)**. Associated dx/dV curves for 4.00 – 4.25 V window are plotted in **c)**.

T.O.C

Synopsis:

Synchrotron XRD and ⁷Li, ²⁷Al and ⁵⁹Co MAS NMR were used to probe, at different scales, the Li stoichiometry and Al homogeneity in 4% Al doped LiCoO₂ samples used as positive electrode for Li-ion batteries, prepared with various synthesis routes.