

Supporting Information

Understanding the role of Al doping of LiCoO₂ on the mechanisms upon cycling up to high voltages ($\geq 4.6\text{V}$ vs. Li⁺/Li)

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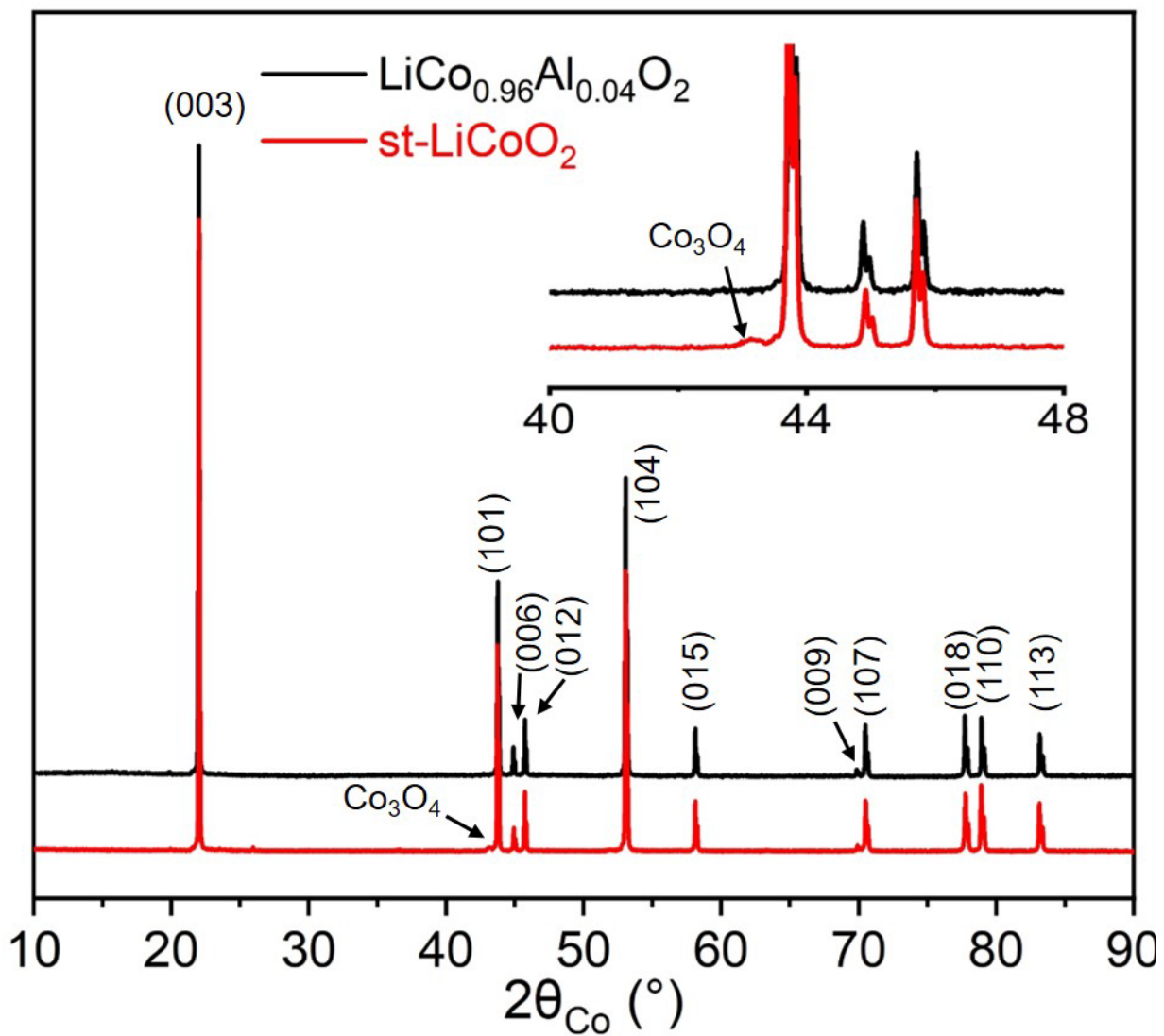
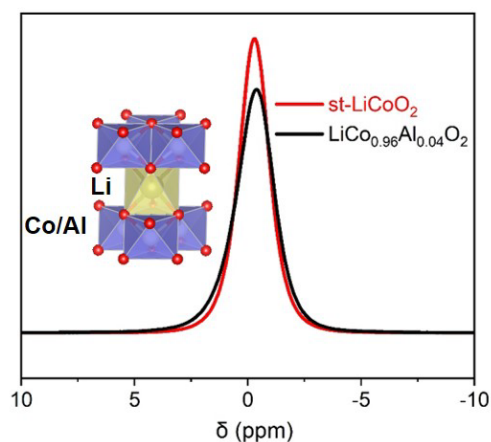
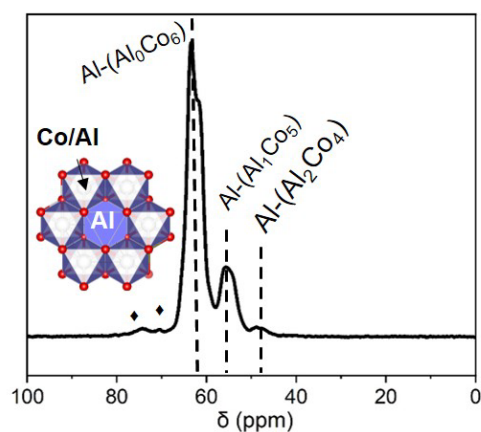


Figure S1: X-ray diffraction patterns of $\text{LiCo}_{0.96}\text{Al}_{0.04}\text{O}_2$ compared to st-LiCoO_2 , including a zoom in a selected 2θ regions.

a) ^7Li MAS NMR



b) ^{27}Al MAS NMR



c) ^{59}Co MAS NMR

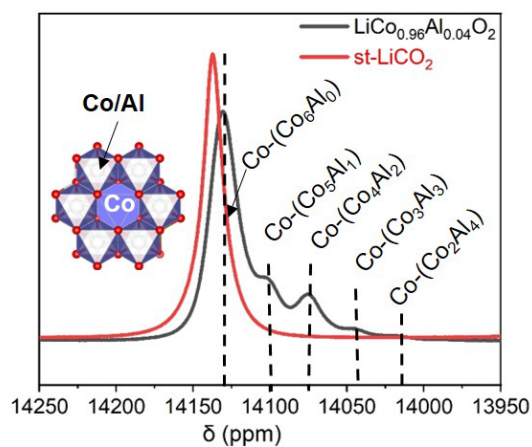


Figure S2: a) ^7Li , b) ^{27}Al and c) ^{59}Co MAS NMR of the $\text{LiCo}_{0.96}\text{Al}_{0.04}\text{O}_2$ compared to st-LiCoO_2 (♦:small signals located around 70 ppm are assigned to the satellite ($\pm 1/2$; $\pm 3/2$) and ($\pm 3/2$; $\pm 5/2$) transitions expected for the main ^{27}Al signal).

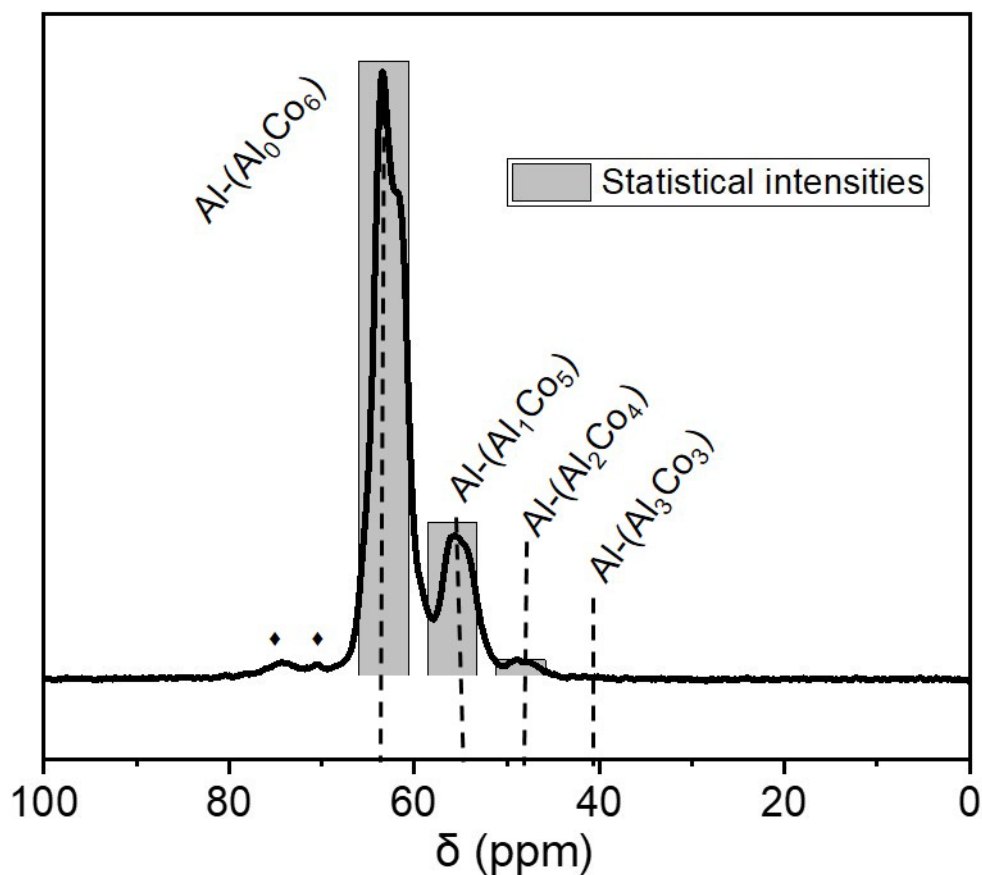


Figure S3: ^{27}Al MAS NMR spectra recorded at 130.33 MHz using a 30 kHz spinning frequency of the $\text{LiCo}_{0.96}\text{Al}_{0.04}\text{O}_2$ sample (\blacklozenge : Satellite transitions). The probability $P(y, 6-n)$ for a composition with $y = 0.04$ and $(6-n)$ cobalt atoms ($0 \leq n \leq 6$) 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 grey rectangles.

For such a low Al-doping amount, negligible signal intensity is expected for $\text{Al}-(\text{Al}_3\text{Co}_3)$ environments and for Al-richer ones ($n > 3$).

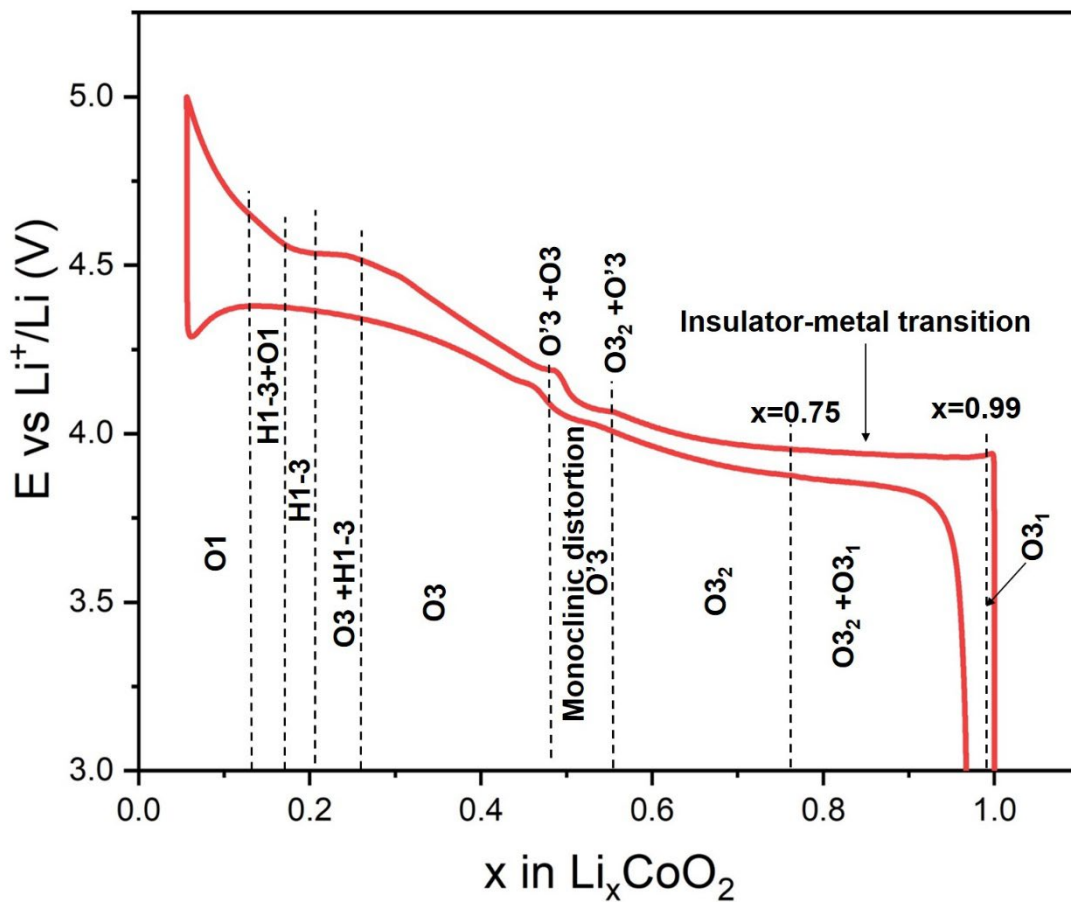


Figure S4: The first charge–discharge curve of st-LiCoO₂ indicating the different phases reported in literature.

_ slurry composition: 90:05:05

_ electrode density $\sim 3.0\text{g/cm}^3$

_ electrode loading weight $\sim 12\text{mg/cm}^2$

_ schedule:

Charge				Discharge				Num	Num
C Rate	E-Curr	Rest	V	Rate	E-Curr	Rest	V	#	total
	(min)				(min)				
0.10	-	30	4.5	0.10	-	30	3.0	1	1
0.25	0.05C	10	4.5	0.20	-	10	3.0	1	2
0.25	0.05C	10	4.5	0.50	-	10	3.0	1	3
0.25	0.05C	10	4.5	1.00	-	10	3.0	1	4
0.25	0.05C	10	4.5	2.00	-	10	3.0	1	5
0.25	0.05C	10	4.5	3.00	-	10	3.0	1	6
0.25	0.1C	10	4.6	0.10	-	10	3.0	1	7
0.25	0.1C	10	4.6	1.00	-	10	3.0	1	8
0.50	0.1C	10	4.6	1.00	-	10	3.0	22	9-30
0.25	0.1C	10	4.6	0.10	-	10	3.0	1	31
0.25	0.1C	10	4.6	1.00	-	10	3.0	1	32

1C= 160 mA/g

Table S1: Cycling conditions used to investigate the electrochemical properties of st-LiCoO₂ and LiCo_{0.96}Al_{0.04}O₂ versus Li plotted in Figure 2.

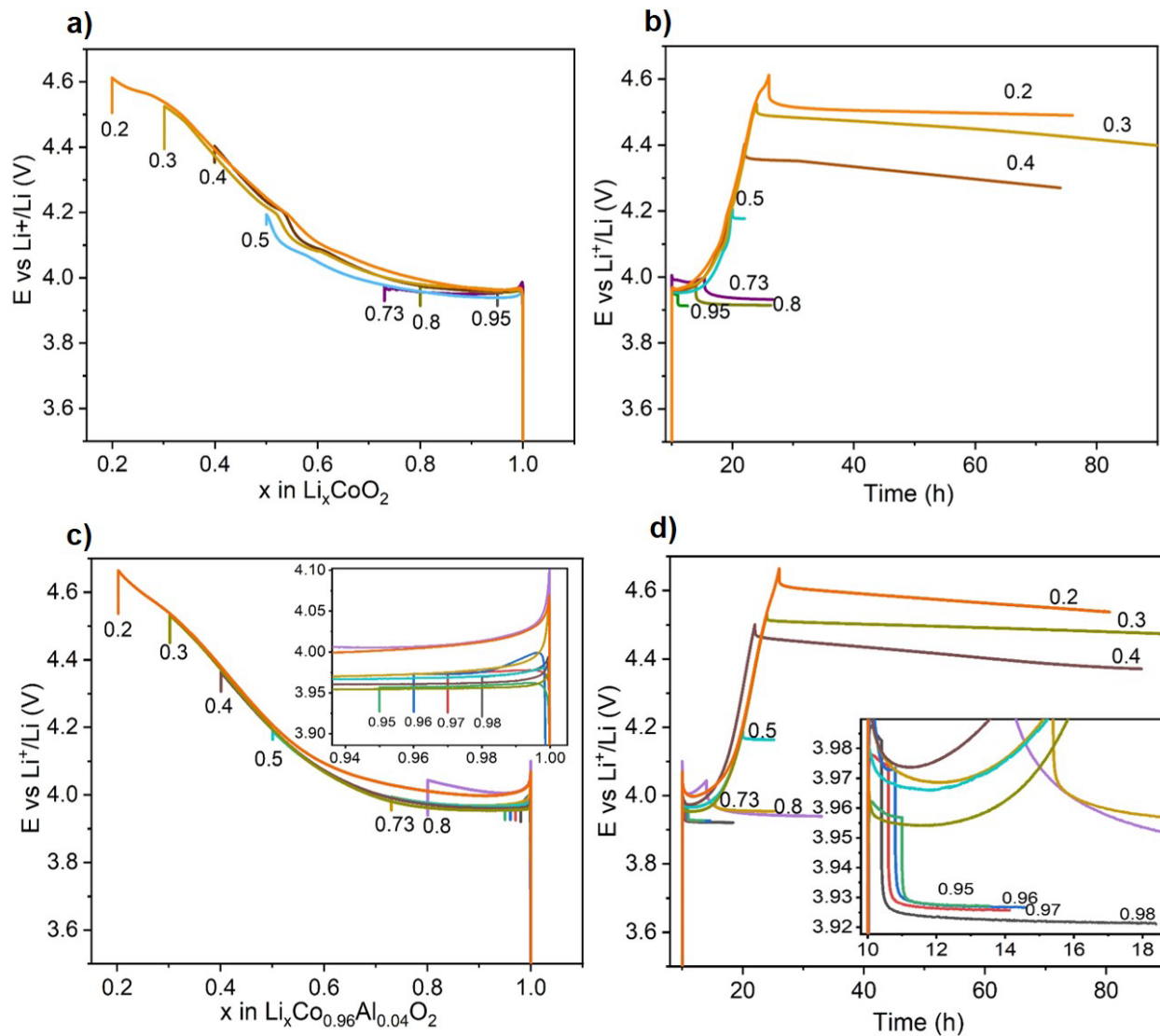


Figure S5: Galvanostatic charge curves of the Li/ Li_xMO_2 cells (C/20 rate) used to prepare the various Li_xCoO_2 plotted versus Li content (x) (a) and versus time (b) and to prepare the various $\text{Li}_x\text{Co}_{0.96}\text{Al}_{0.04}\text{O}_2$ phases plotted versus x (c) and time (d).

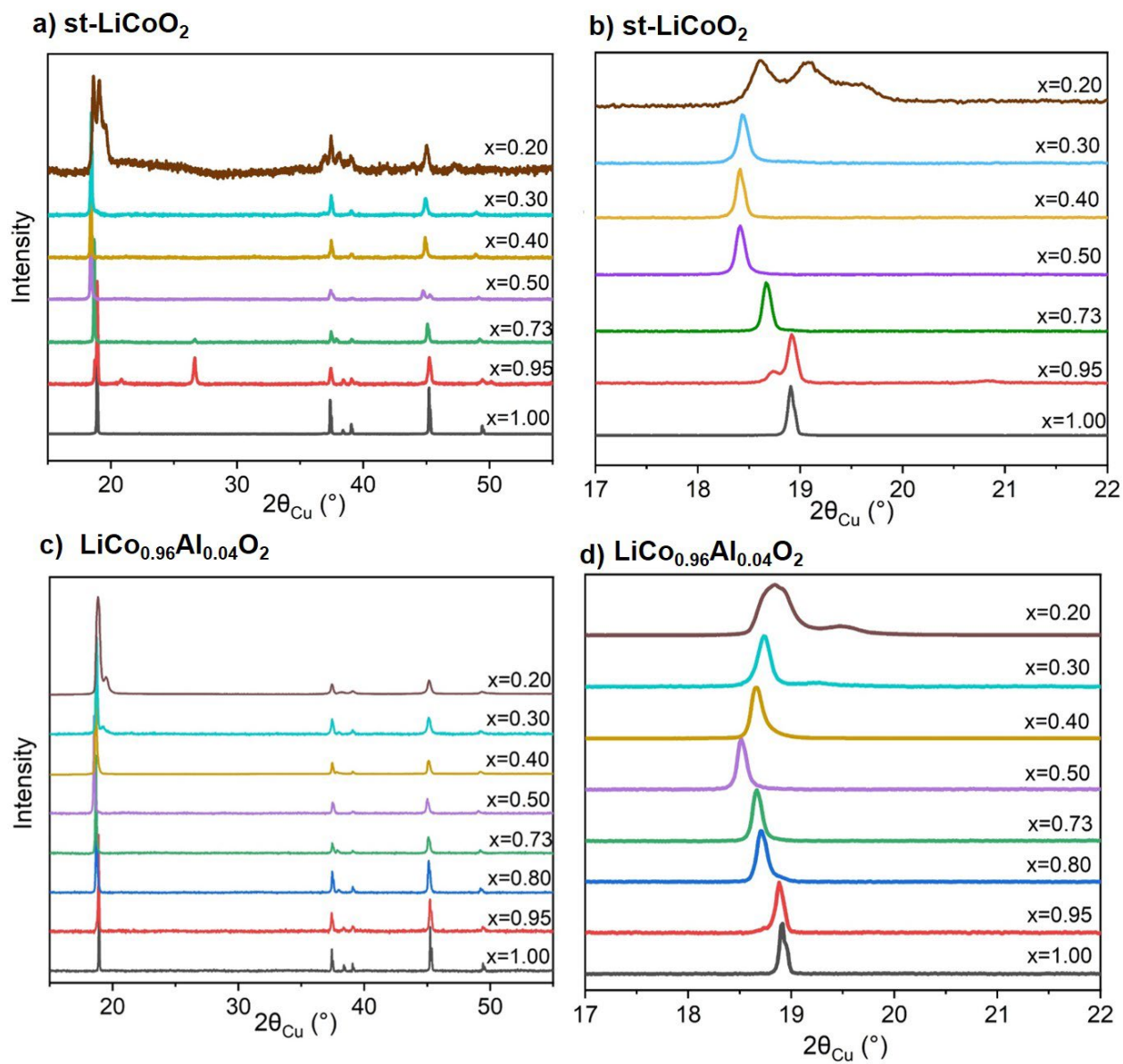


Figure S6: a) X-ray diffraction patterns of the electrochemically deintercalated Li_xCoO_2 materials with b) Zoom in the $17\text{-}22^\circ$ 2θ region. a) X-ray diffraction patterns of the electrochemically deintercalated $\text{Li}_x\text{Co}_{0.96}\text{Al}_{0.04}\text{O}_2$ materials with b) Zoom in the $17\text{-}22^\circ$ 2θ region.

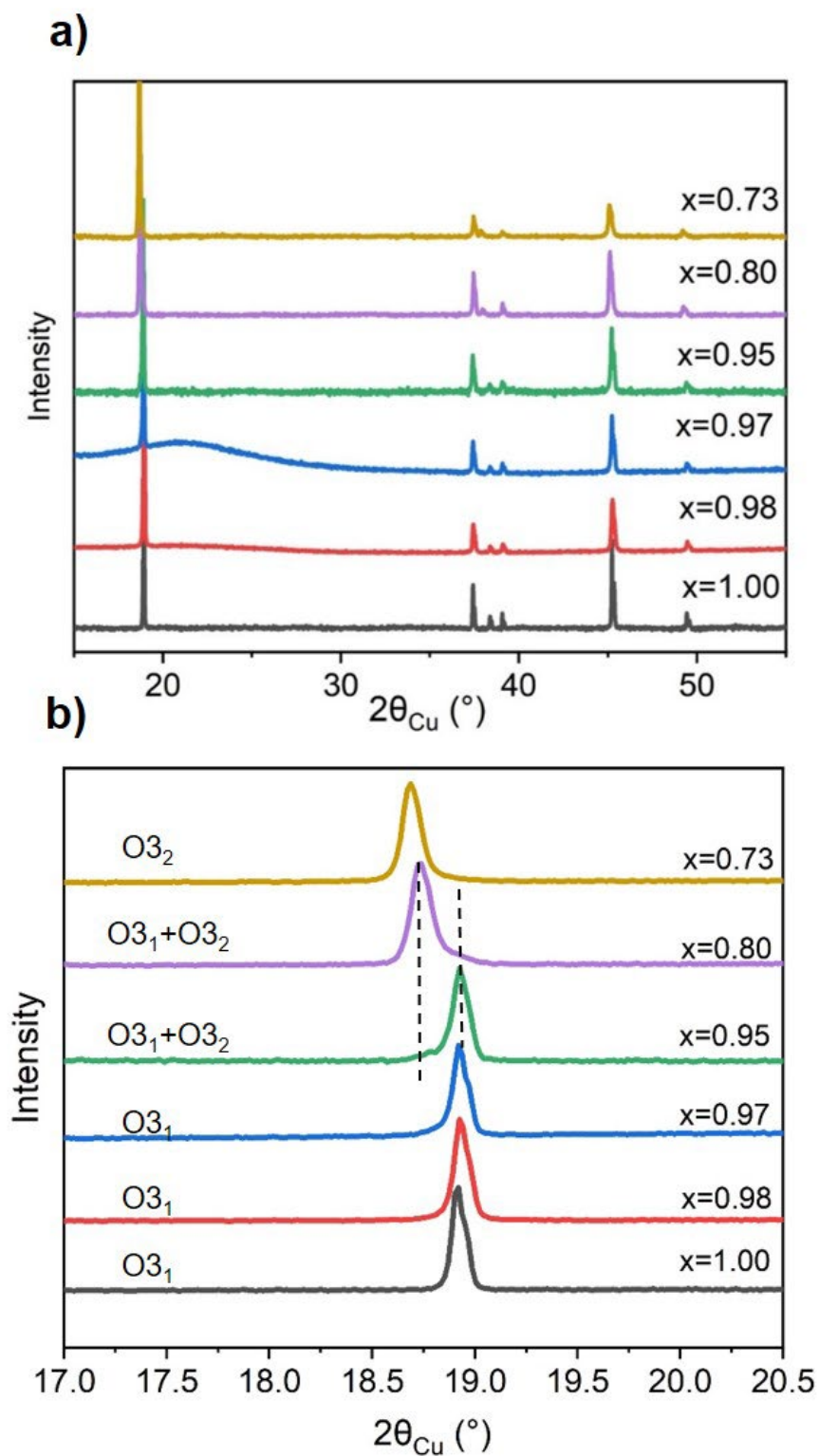


Figure S7. a) X-ray diffraction patterns of the electrochemically deintercalated $\text{Li}_x\text{Co}_{0.96}\text{Al}_{0.04}\text{O}_2$ materials prepared with targeted Li compositions by controlling the Li content, in the low potential region $V < 4\text{V}$ vs Li^+/Li with b) the detail in the (003) line

Compound	Phase	a (Å)	c (Å)
LiCo_{0.96}Al_{0.04}O₂	O3 ₁	2.814 (1)	14.062 (1)
Li_{0.98}Co_{0.96}Al_{0.04}O₂	O3 ₁	2.813 (1)	14.063 (2)
Li_{0.97}Co_{0.96}Al_{0.04}O₂	O3 ₁	2.813 (1)	14.063 (4)
Li_{0.95}Co_{0.96}Al_{0.04}O₂	O3 ₁	2.813 (1)	14.064 (2)
	O3 ₂	2.809 (1)	14.171 (2)
Li_{0.80}Co_{0.96}Al_{0.04}O₂	O3 ₁	2.796 (1)	14.086 (2)
	O3 ₂	2.810 (1)	14.211 (2)
Li_{0.73}Co_{0.96}Al_{0.04}O₂	O3 ₂	2.809 (1)	14.239 (6)
Li_{0.50}Co_{0.96}Al_{0.04}O₂	O3	2.807 (1)	14.355 (7)
Li_{0.40}Co_{0.96}Al_{0.04}O₂	O3	2.812 (1)	14.247 (4)
Li_{0.30}Co_{0.96}Al_{0.04}O₂	O3	2.817 (1)	14.214 (4)
	H1-3	2.807 (1)	27.740 (2)
Li_{0.20}Co_{0.96}Al_{0.04}O₂	O3	2.835 (1)	13.90 (1)
	H1-3	2.784 (1)	27.34 (1)

Table S2. Cell parameters of Li_xCo_{0.96}Al_{0.04}O₂ samples obtained from the LeBail refinement of the XRD patterns using the R-3m space group.

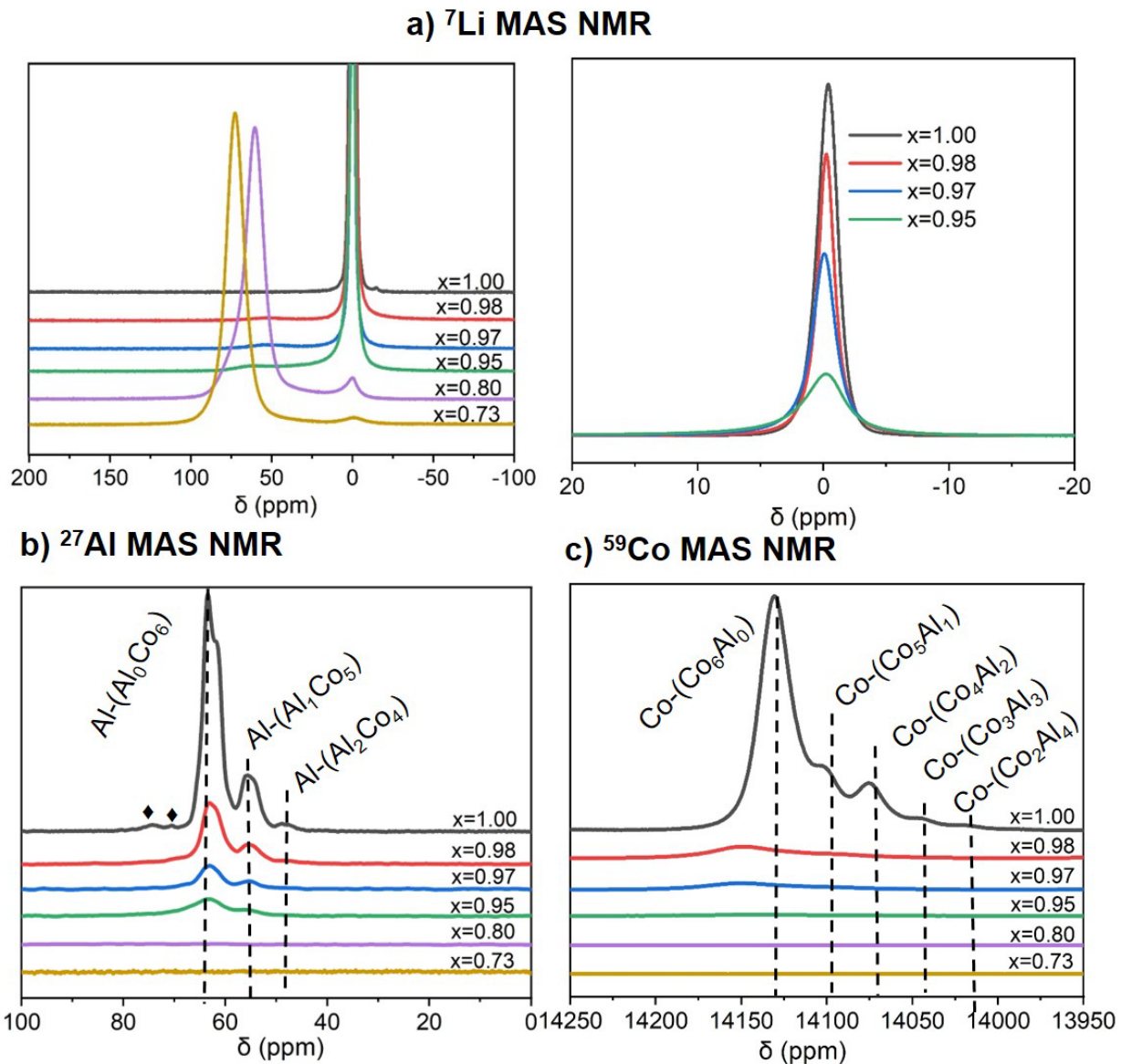


Figure S8. Ex-situ a) ^7Li , b) ^{27}Al and c) ^{59}Co MAS NMR of the deintercalated $\text{Li}_x\text{Co}_{0.96}\text{Al}_{0.04}\text{O}_2$ by controlling the Li content, in the low voltage region (◆: satellite transitions)

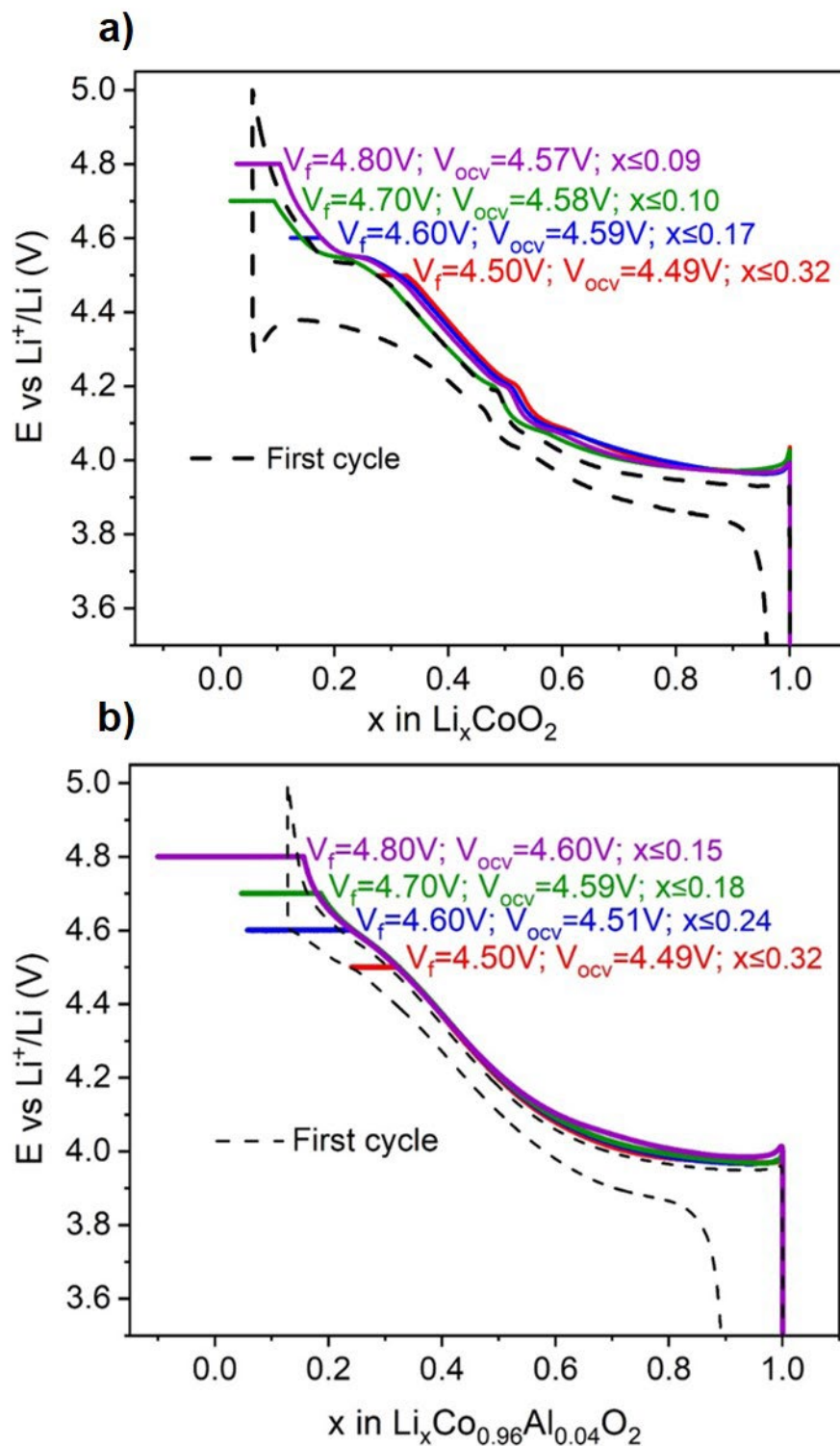


Figure S9: Galvanostatic charge of Li//LiMO₂ cells stopped at different voltages, followed by a floating compared to a first cycle curve for a) st-LiCoO₂ and b) LiCo_{0.96}Al_{0.04}O₂ ($V_f=V_{floating}$ and V_{ocv} corresponds to the voltage measured before disassembling the cell)

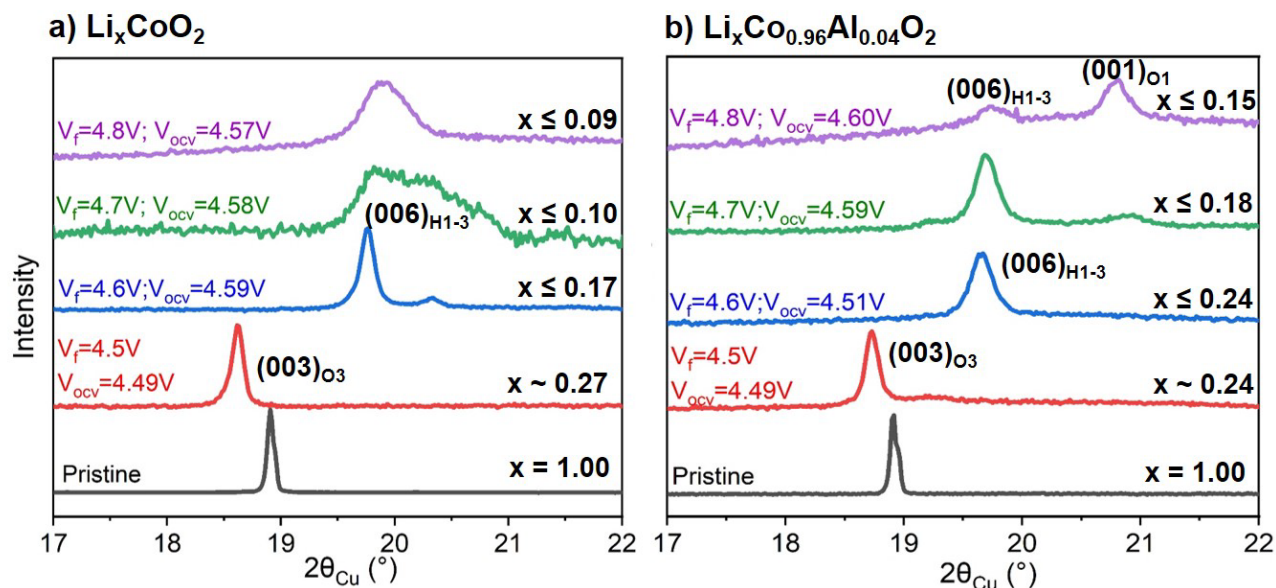


Figure S10: Detail in the $(00l)$ line from XRD for a) Li_xCoO_2 and b) $\text{Li}_x\text{Co}_{0.96}\text{Al}_{0.04}\text{O}_2$ ($V_f=V_{\text{floating}}$ and V_{ocv} corresponds to the voltage measured before disassembling the cell)

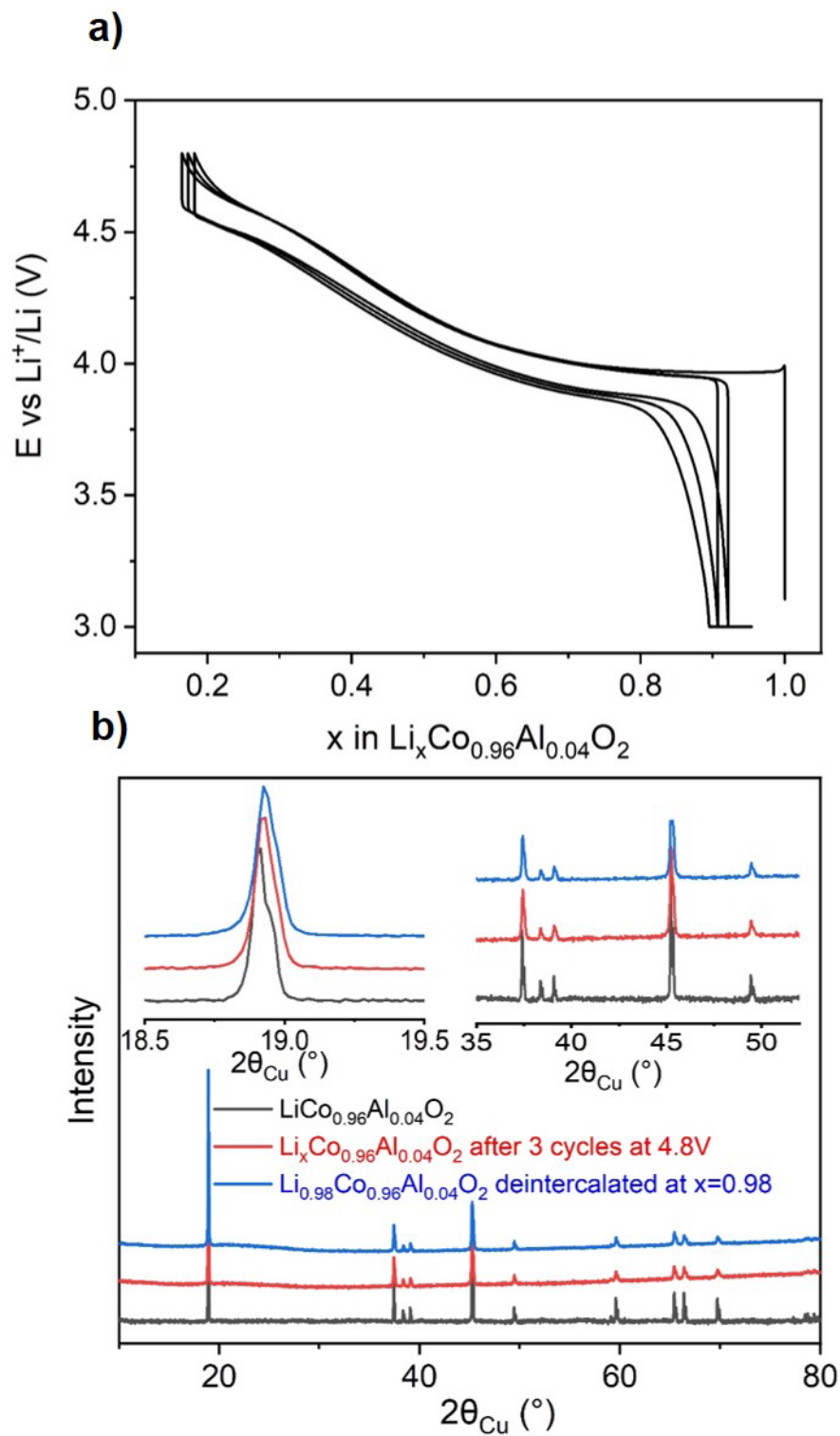


Figure S11. a) Three first cycles of galvanostatic charge / discharge (3V-4.8V) of Li // $\text{Li}_x\text{Co}_{0.96}\text{Al}_{0.04}\text{O}_2$ cell at C/20. b) X-ray diffraction pattern of $\text{Li}_x\text{Co}_{0.96}\text{Al}_{0.04}\text{O}_2$ cycled compared to the pristine and the deintercalated $\text{Li}_{0.98}\text{Co}_{0.96}\text{Al}_{0.04}\text{O}_2$

Compound	Space-group	Phase	a (Å)	c (Å)
LiCo_{0.96}Al_{0.04}O₂	R-3m	O3 ₁	2.814 (1)	14.062 (1)
Li_{0.98}Co_{0.96}Al_{0.04}O₂	R-3m	O3 ₁	2.813 (1)	14.063 (2)
Li_xCo_{0.96}Al_{0.04}O₂ after 3 cycles at 4.8V	R-3m	O3 ₁	2.813 (1)	14.064 (3)

Table S3. Refined unit cell parameters for Li_xCo_{0.96}Al_{0.04}O₂ cycled 3 times between (3V-4.8V) and recovered after a floating at 3V compared to the pristine and the deintercalated

