

Supplementary Information:
**Structure and electronic structure evolution of P2-Na_xCoO₂ phases from XRD
and ²³Na MAS NMR**

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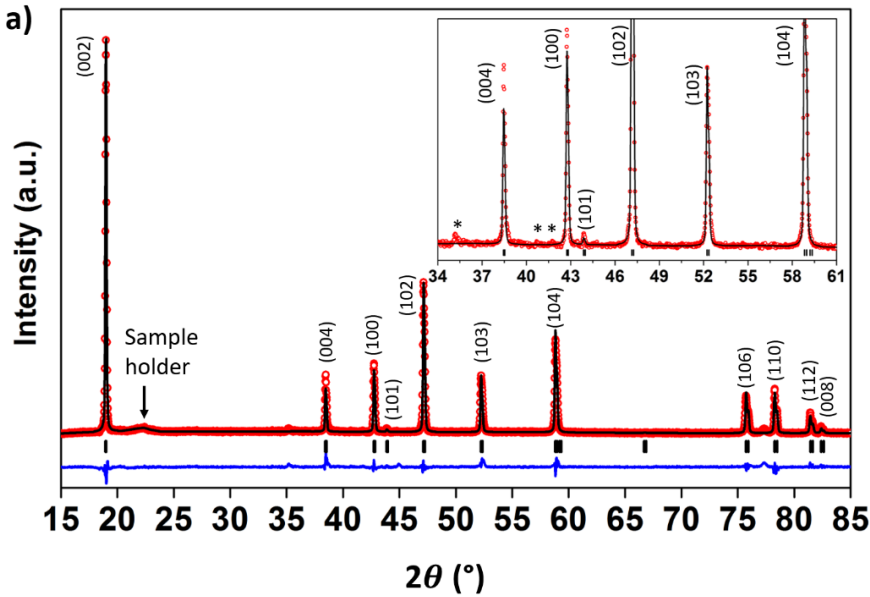
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SI-1: Rietveld refinement of the XRD pattern of the pristine P2- $Na_{0.7}CoO_2$



b)

Space group: $P6_3/mmc$						
$a_{\text{hex.}} = 2.8343(5) \text{ \AA}$			$c_{\text{hex.}} = 10.875(5) \text{ \AA}$			
Atom	Site	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$	Occ.
Co	2a	0	0	0	0.8(1)	1
Na _f	2d	0	0	0.25	1.4(1)	0.19(1)
Na _e	2b	1/3	2/3	0.25	1.4(1)	0.51(3)
O	4f	1/3	2/3	0.0929(2)	0.3(1)	1
				U = 0.065(1)		
				V = -0.049(7)		
				W = 0.024(1)		
				X = 0.001(8)		
				η = 0.39(3)		
Rp = 19.4 %						
Rwp = 15.3 %						

SI-1: Figure a) XRD pattern of the P2- $Na_{0.7}CoO_2$ pristine phase in the $15^\circ - 85^\circ$ range. The $P6_3/mmc$ space group allows indexing the main diffraction peaks. The refined cell parameters are $a_{\text{hex.}} = 2.8343(5) \text{ \AA}$ and $c_{\text{hex.}} = 10.875(5) \text{ \AA}$ and are in good agreement with those reported in the literature¹ for $x_0 \approx 0.7$. Tiny extra peaks are observed as indicated by * and are due to a Na^+ /vacancy order in the interslab space that would have required the use of a supercell to describe the structure, not known. **Table b)** Rietveld refinement result on the P2- $Na_{0.7}CoO_2$ pristine phase with the $P6_3/mmc$ space group.

SI-2: Scanning Electron Microscopy

Scanning electron microscopy images of the pristine phase were taken using a Hitachi S-4500 microscope (**Figure SI-2**). **Figure SI-2a** shows that the particles are agglomerated and formed 200 μm -clusters. SEM (**Figure SI-2b**) images show the hexagonal shape of the structure with particles of 15 μm average diameter and 10 μm thickness. Small imperfections represented by lighter grey particles on the surface are due to an air exposure during the very short transit at air before the gold sputtering. They might correspond to Na_2CO_3 .

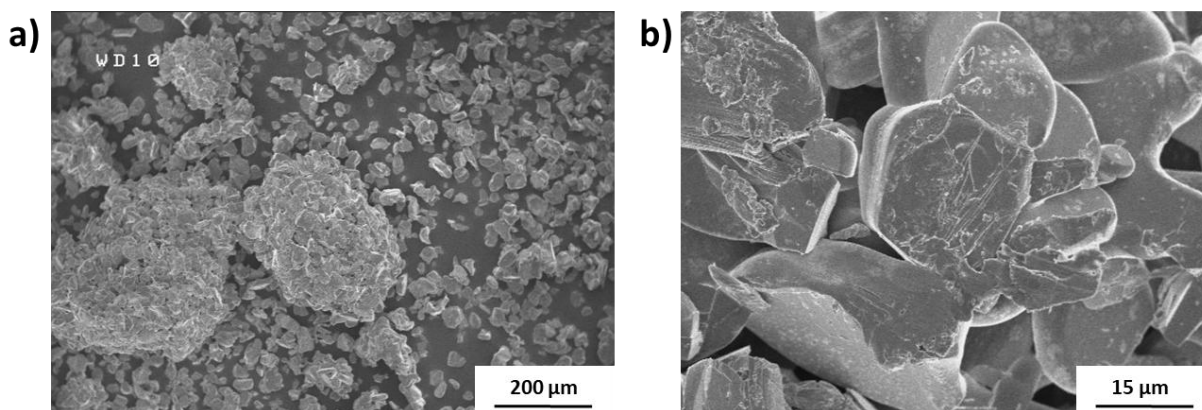


Figure SI-2: SEM images of P2- $\text{Na}_{0.70}\text{CoO}_2$ phase at two different magnifications a) x 150 b) x 1500

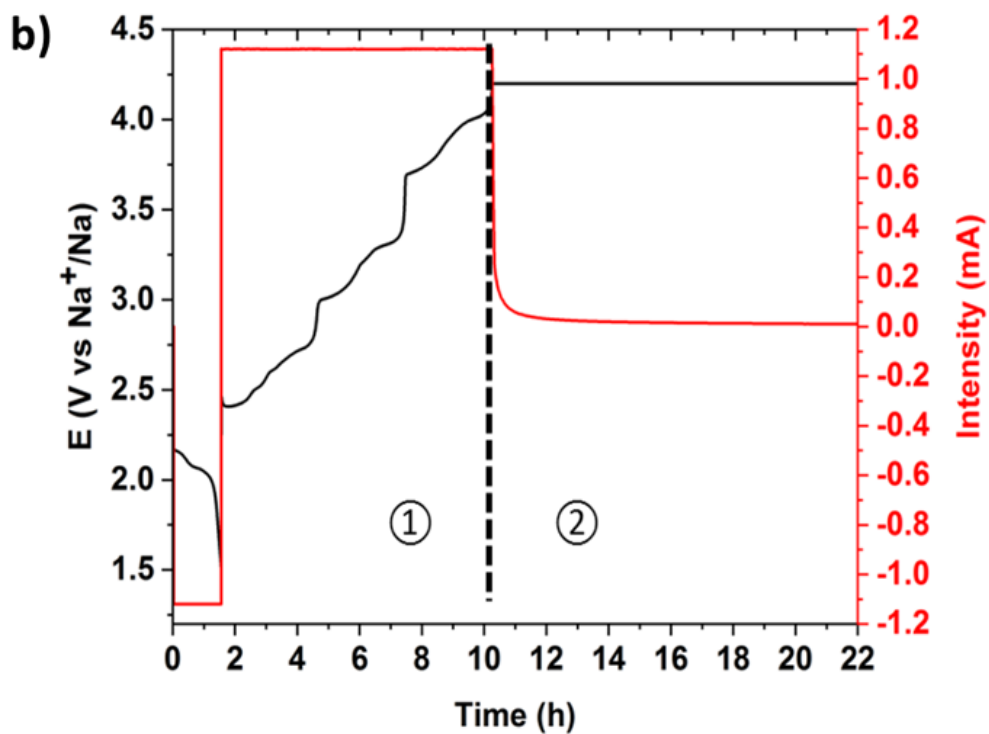
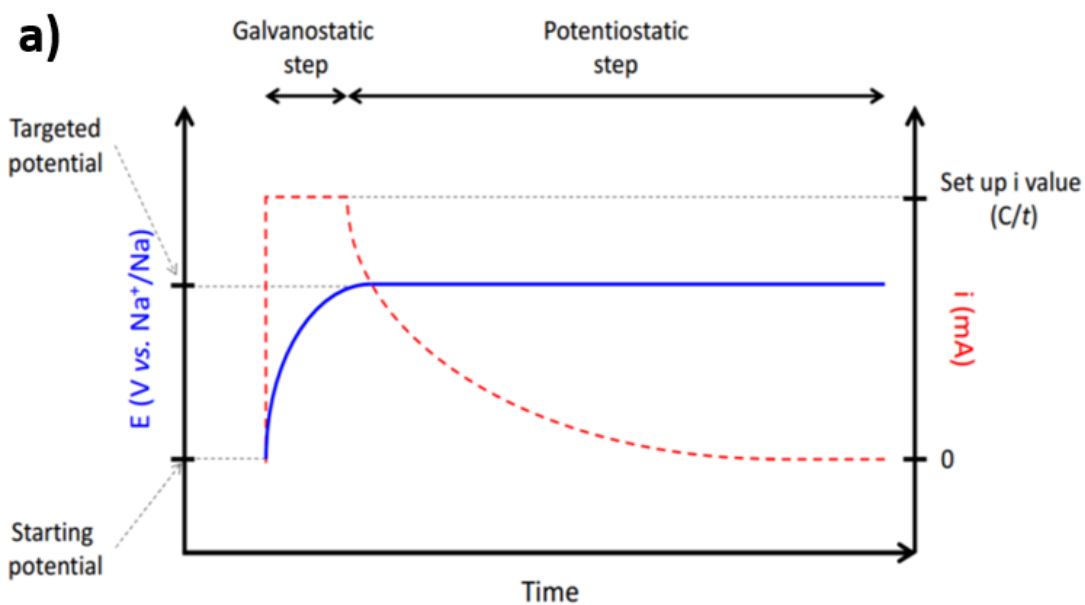


Figure SI-3: a) Principle of the electrochemical preparation of the P2- Na_xCoO_2 phases for *ex-situ* characterizations. First, a galvanostatic step was performed at $C/20$ to the targeted voltage. Then, a potentiostatic step was used until the current reaches negligible value. b) Example of electrochemical curves (voltage and current as a function of time) obtained for the preparation of the P2- Na_xCoO_2 phase at 4.2 V vs Na^+/Na .

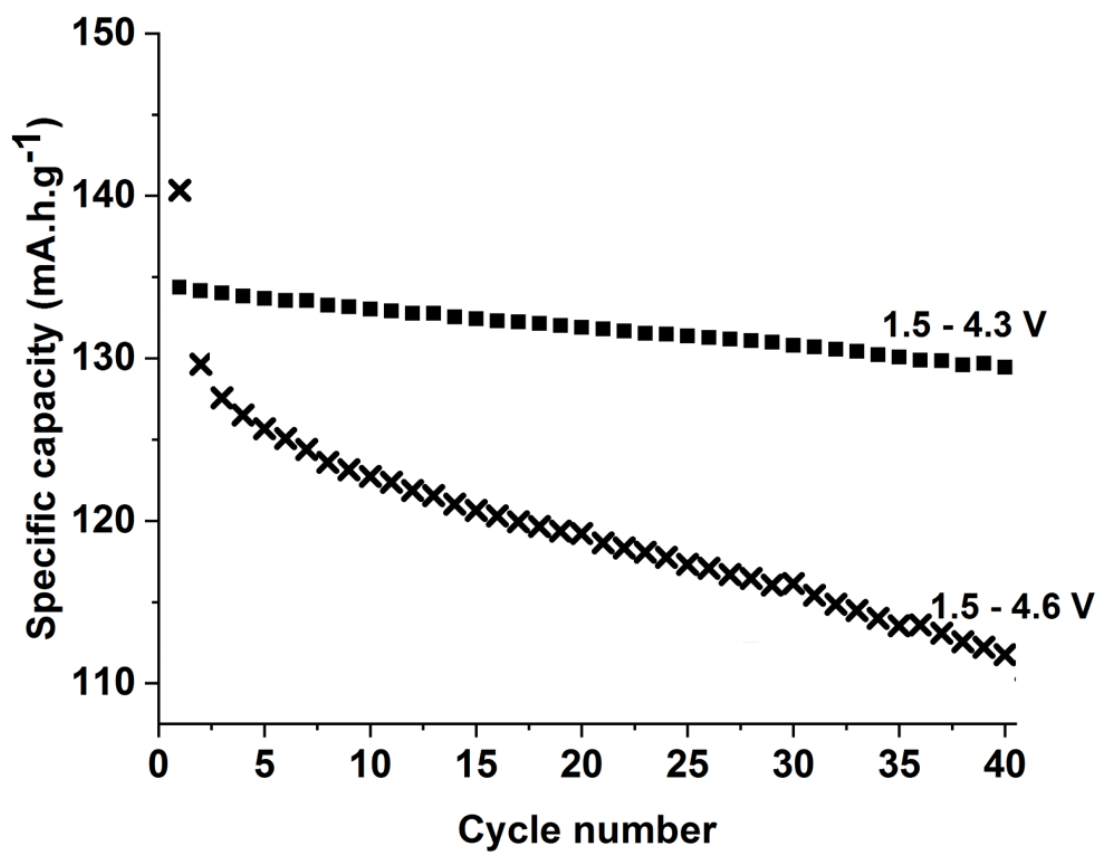
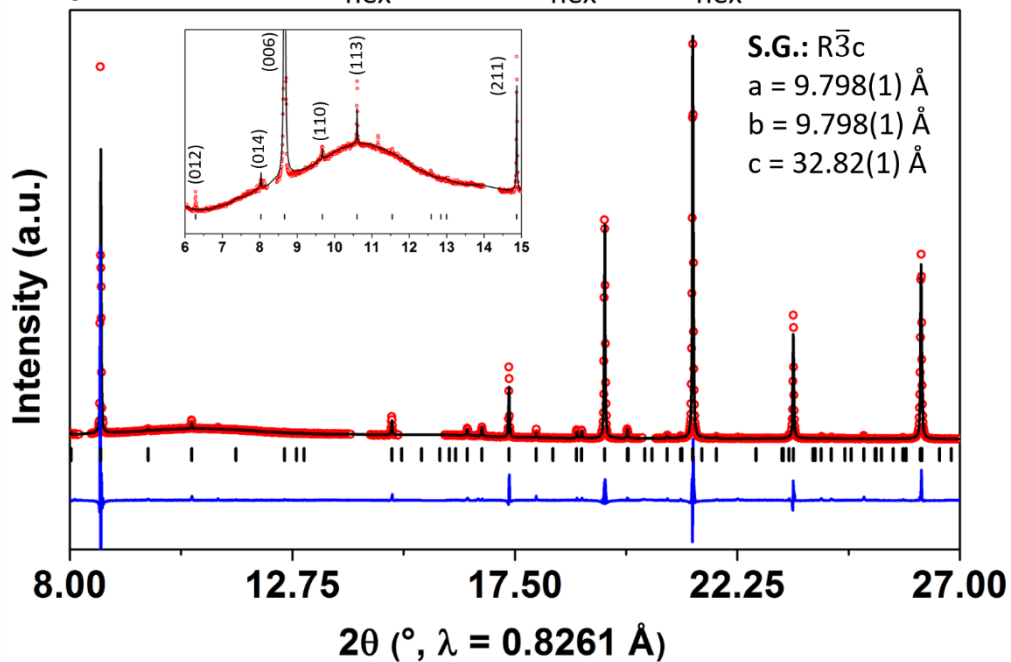


Figure SI-4: Evolution of the specific capacity in the 1.5 – 4.3 V range and in the 1.5 – 4.6 V range at C/20 of the P2-Na_xCoO₂ system after 40 cycles

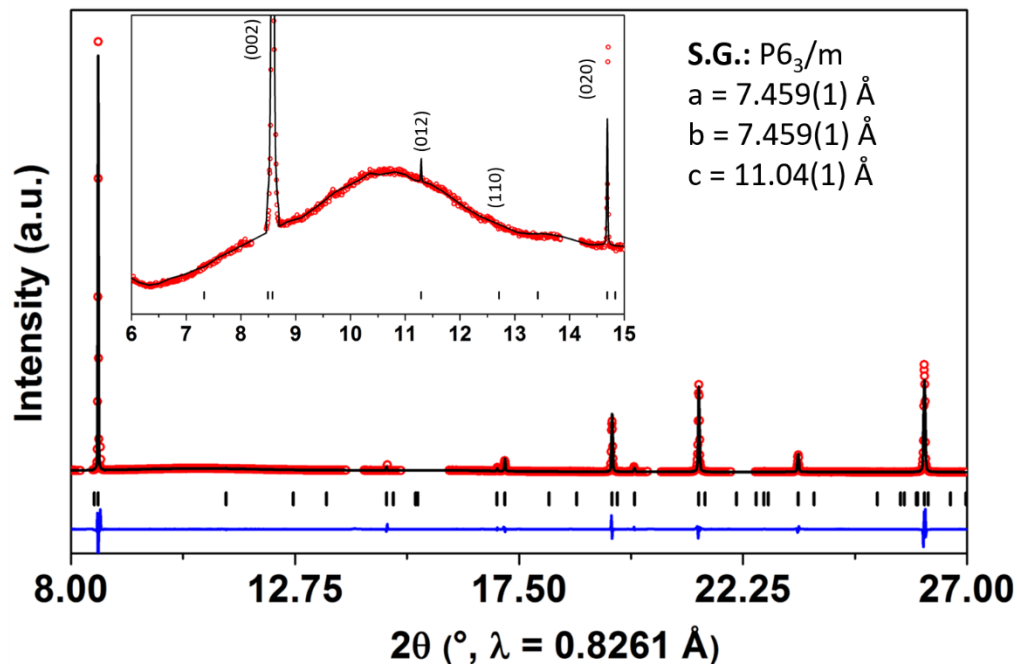
a) $\text{Na}_{2/3}\text{CoO}_2$

Supercell: $2\sqrt{3} a_{\text{hex}} \times 2\sqrt{3} a_{\text{hex}} \times 3 c_{\text{hex}}$



b) $\text{Na}_{4/7}\text{CoO}_2$

Supercell: $\sqrt{7} a_{\text{hex}} \times \sqrt{7} a_{\text{hex}} \times c_{\text{hex}}$



c) $\text{Na}_{1/2}\text{CoO}_2$

Supercell: $\sqrt{3} a_{\text{hex}} \times 2 a_{\text{hex}} \times c_{\text{hex}}$

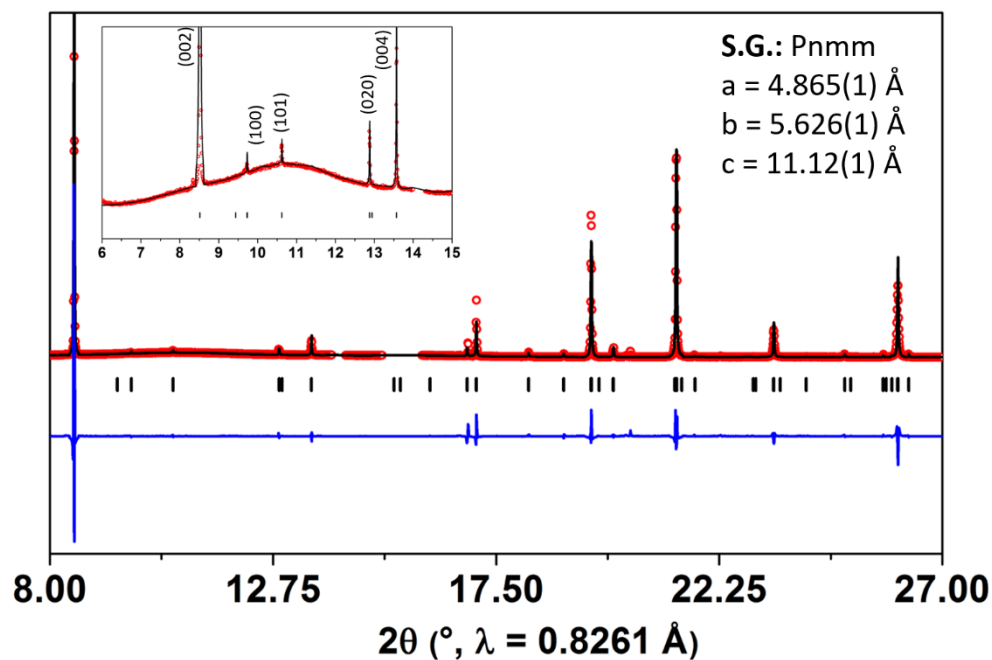
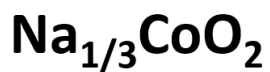


Figure SI-5: Le Bail refinement results on P2- Na_xCoO_2 peculiar phases for a) $x = 2/3$ b) $x = 4/7$ and c) $x = 1/2$. Observed (red points), calculated (black line), difference between calculated and observed (blue line) Synchrotron XRD patterns. The black ticks represent the Bragg positions. The insets are zooms in the $6-15^\circ$ range to highlight the presence of superstructure peaks.



Supercell: $\sqrt{3} a_{\text{hex}} \times \sqrt{3} a_{\text{hex}} \times 3 c_{\text{hex}}$

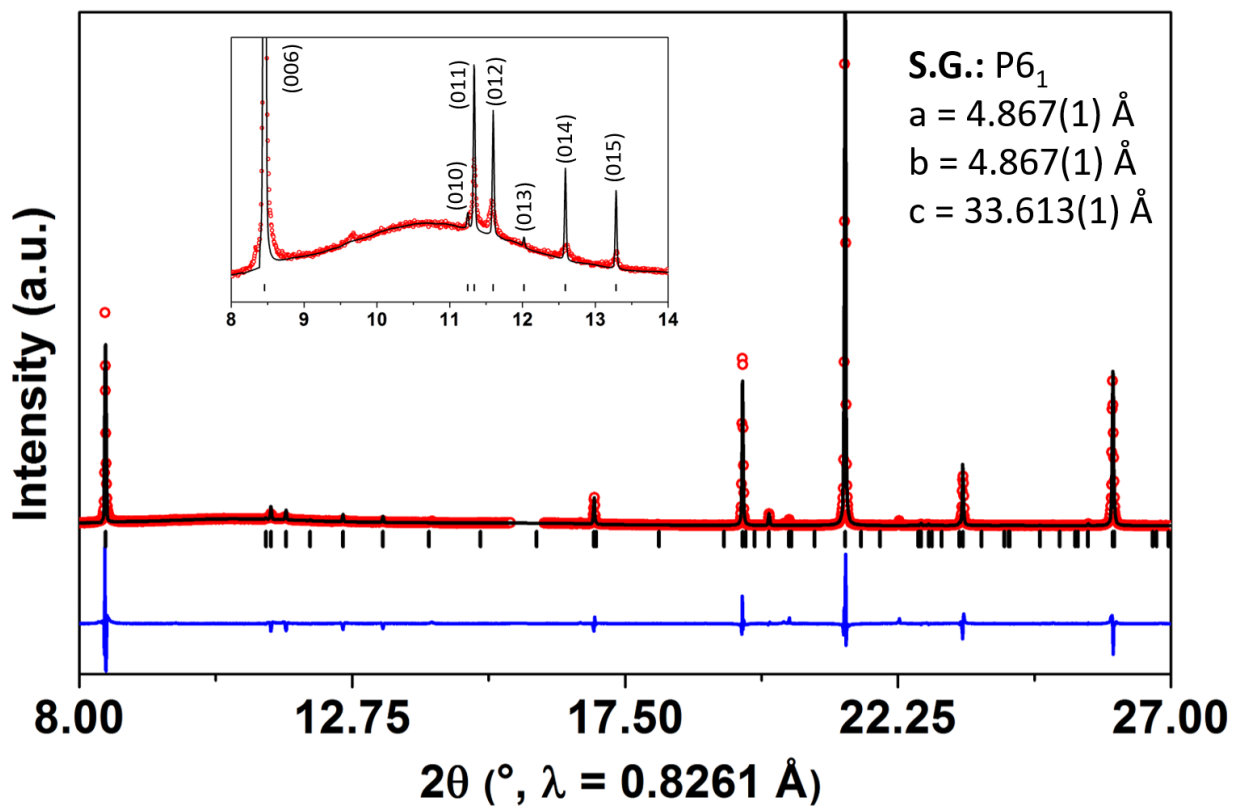


Figure SI-6: Observed (red points), calculated with the Le Bail refinement method (black line), difference between calculated and observed (blue line) XRD patterns of P2- $\text{Na}_{1/3}\text{CoO}_2$. The black ticks represent the Bragg positions. The inset represents a zoom in the 8-14 $^\circ$ range.

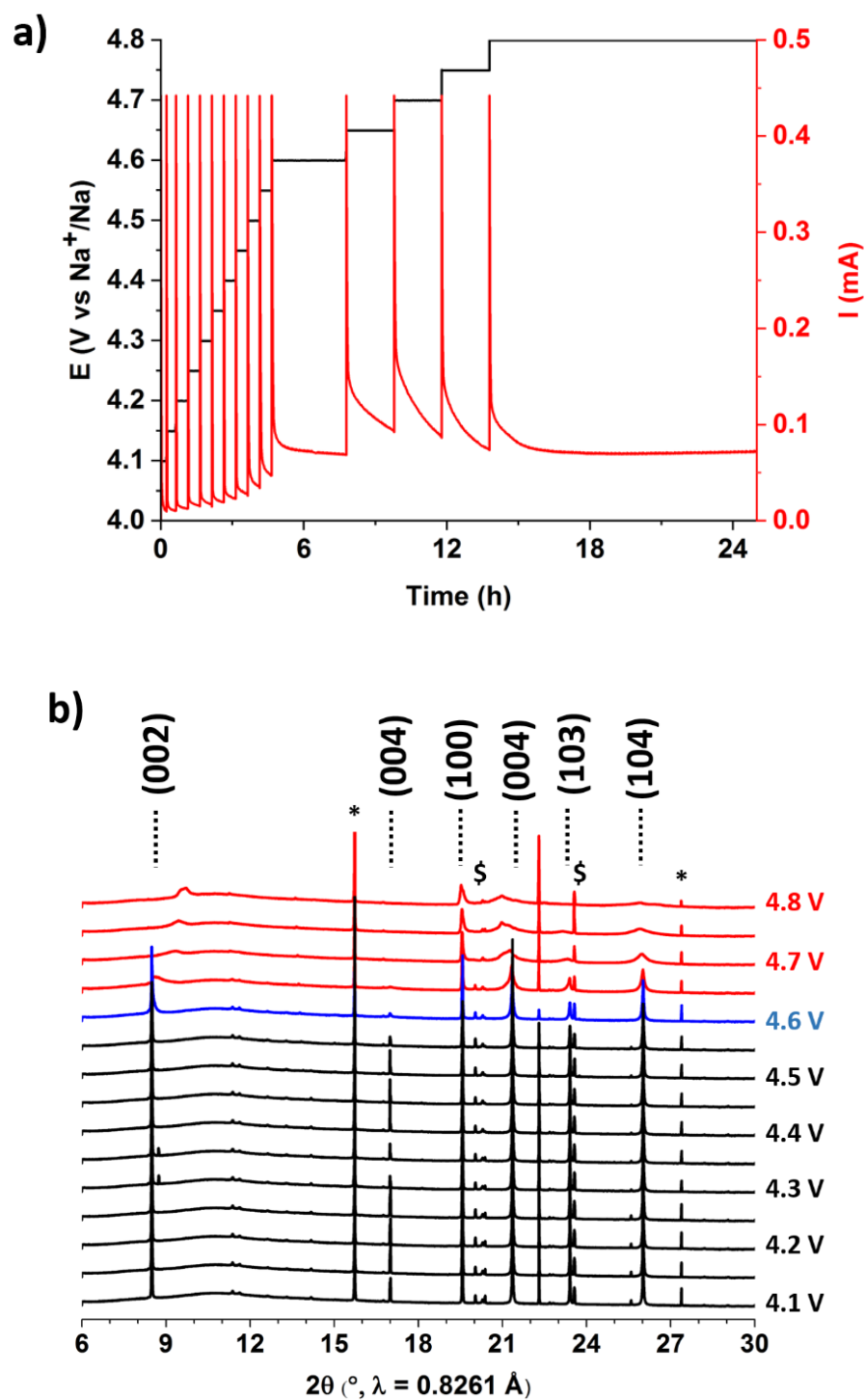


Figure SI-7: a) Voltage (in black) and current (in red) evolution during the potentiostatic measurements on $\text{P2-Na}_x\text{CoO}_2$ as a function of time. b) SXRCD patterns of stabilized $\text{P2-Na}_x\text{CoO}_2$ phases by potentiostatic steps at different voltages from 4.1 V to 4.8 V for $6 < 2\theta < 30^\circ$

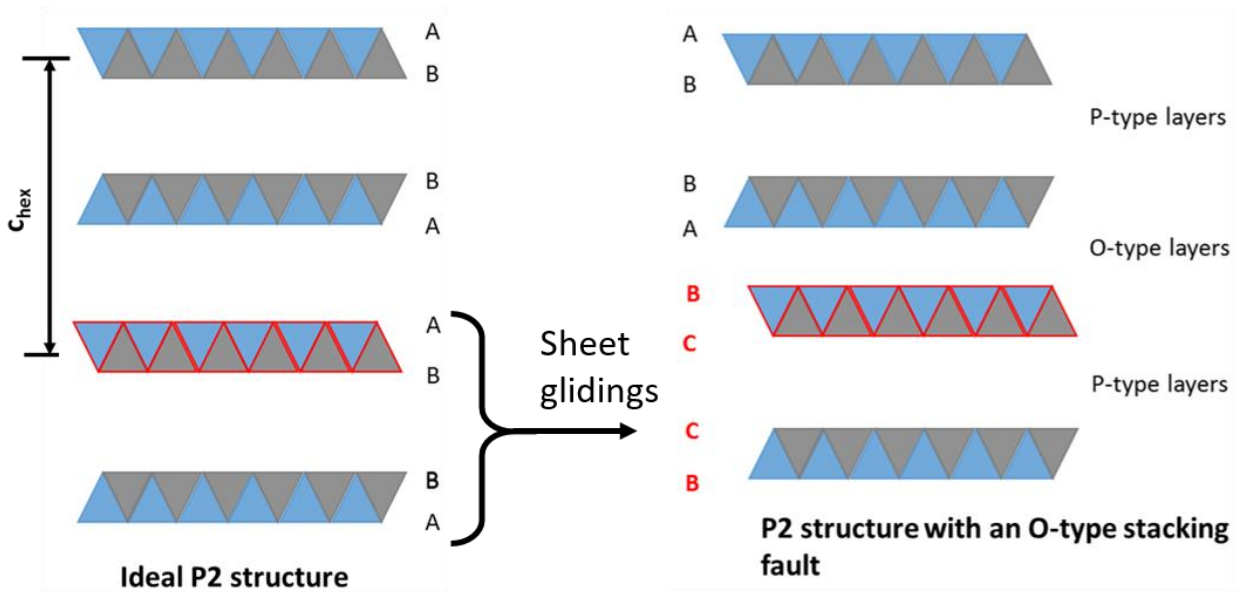
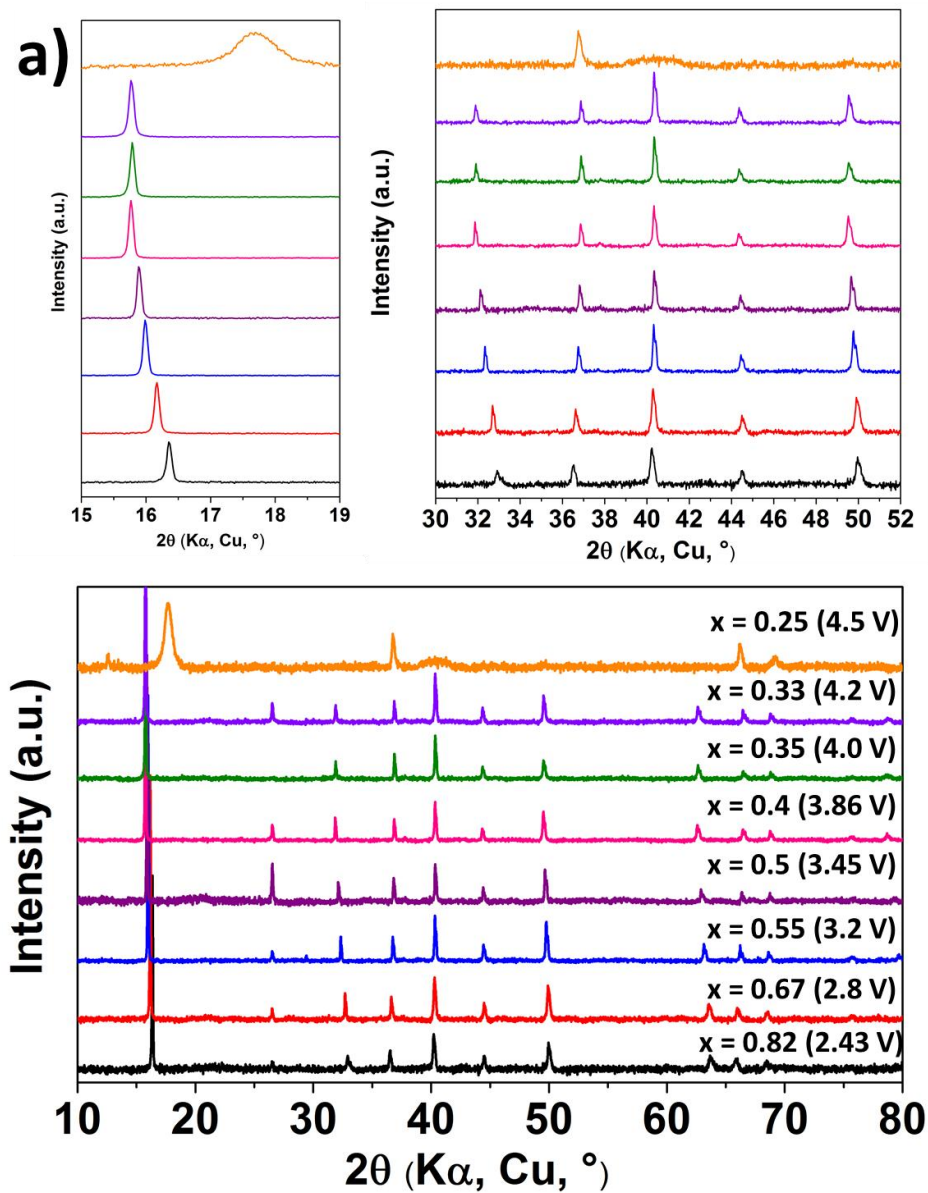


Figure SI-8: Representation of the CoO₂ stacking in an ideal P2 structure and in a P2 structure with an O-type stacking fault after sheets glidings.

SI-9: Ex-situ capillary laboratory XRD patterns of the Na_xCoO_2 phases studied by ^{23}Na MAS

NMR



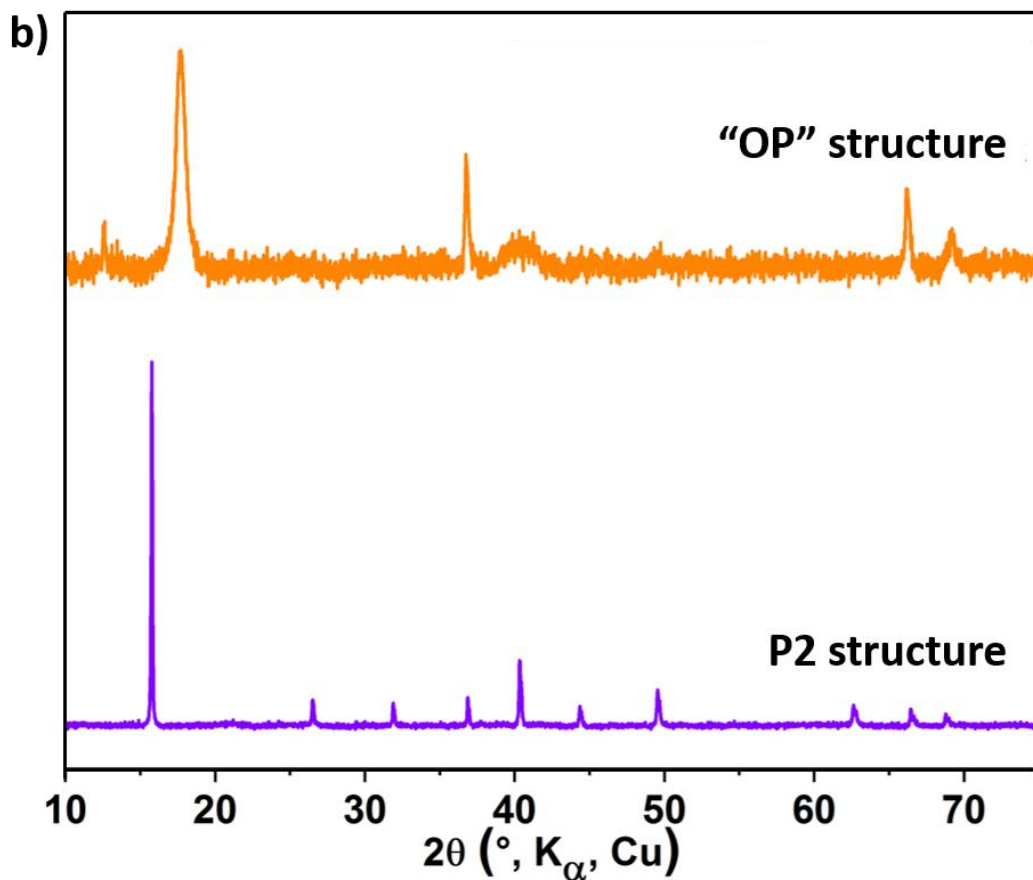
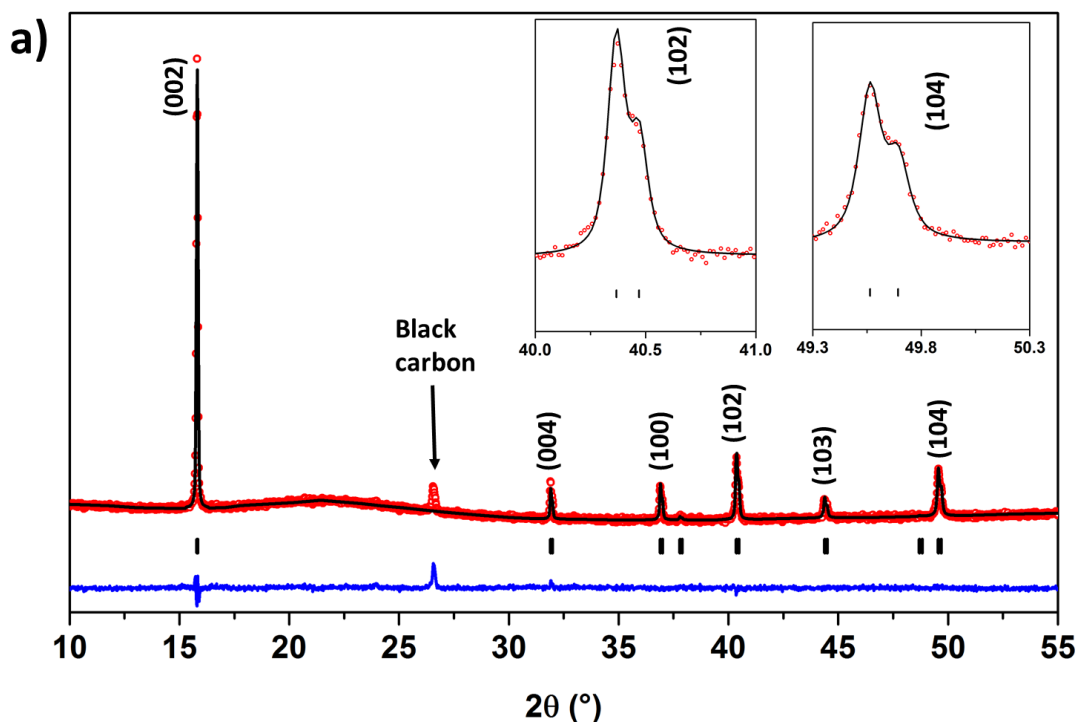


Figure SI-9: a) XRD patterns of the deintercalated P2- Na_xCoO_2 phases. The inserts correspond to zooms from 15° to 19° and from 30° to 52° . Figure SI-9a confirms that the P2 structure is maintained for x values up to $1/3$, therefore, all the concerning XRD patterns can be refined in the $P6_3/mmc$ space group. b) XRD patterns of a phase before sheets glidings in purple ($\text{Na}_{0.33}\text{CoO}_2$) and the phase after ($\text{Na}_{0.25}\text{CoO}_2$) sheets glidings in orange.



b)

Space group : $P6_3/mmc$						
$a_{\text{hex.}} = 2.810(1) \text{ \AA}$				$c_{\text{hex.}} = 11.21(1) \text{ \AA}$		
Atom	Site	x	y	z	B (\AA^2)	Occ.
Co	2a	0	0	0	0.5	1
Na _f	2d	0	0	0.25	1.2	0.16(1)
Na _e	2b	2/3	1/3	0.25	1.2	0.24(1)
O	4f	1/3	2/3	0.083(1)	0.5	1
					U = 0.14(1)	
					V = -0.05(1)	
					W = 0.009(1)	
					X = 0.008(1)	
					$\eta = 0.46(1)$	
Rp = 12.2 %						
Rwp = 16.2 %						

SI-10: Figure a) XRD pattern of the $P2\text{-Na}_{0.40}\text{CoO}_2$ pristine phase in the $10^\circ - 55^\circ$ range. The $P6_3/mmc$ space group allows indexing the main diffraction peaks. The refined cell parameters are $a_{\text{hex.}} = 2.810(1) \text{ \AA}$ and $c_{\text{hex.}} = 11.21(1) \text{ \AA}$. **Table b)** Rietveld refinement results on the $P2\text{-Na}_{0.40}\text{CoO}_2$ pristine phase with the $P6_3/mmc$ space group.

x	Na_e	Na_f
0.70 (pristine)	0.51(1)	0.19(1)
0.67	0.44(1)	0.23(1)
0.55	0.34(1)	0.23(1)
0.50	0.27(1)	0.23(1)
0.40	0.24(1)	0.16(1)
0.35	0.31(1)	0.04(1)
0.33	0.31(1)	0.02(1)

Table SI-11: Repartition of the Na^+ ions in the interslab spaces between the two prismatic sites labelled Na_e and Na_f following the description given in Figure 1.

x	δ_{iso} (ppm)	C_Q (MHz)	η
0.82	298(1)	4.20(1)	0.083(1)
0.70 (pristine)	351(1)	4.08(1)	0.18(1)
0.67	395(1)	3.86(1)	0.22(1)
0.55	386(1)	3.32(1)	0.24(1)
0.50	361(1)	3.10(1)	0.51(1)
0.40	292(1)	2.80(1)	0.47(1)
0.35	286(1)	2.38(1)	0.36(1)
0.33	280(1)	2.36(1)	0.5(1)

Table SI-12: NMR parameters of the $\text{P2-Na}_x\text{CoO}_2$ samples. The different spectra shown on figure 8 have been fitted using a second order quadrupolar model. C_Q corresponds to the nuclear quadrupole coupling constant and η indicates the asymmetry of the quadrupolar interaction.

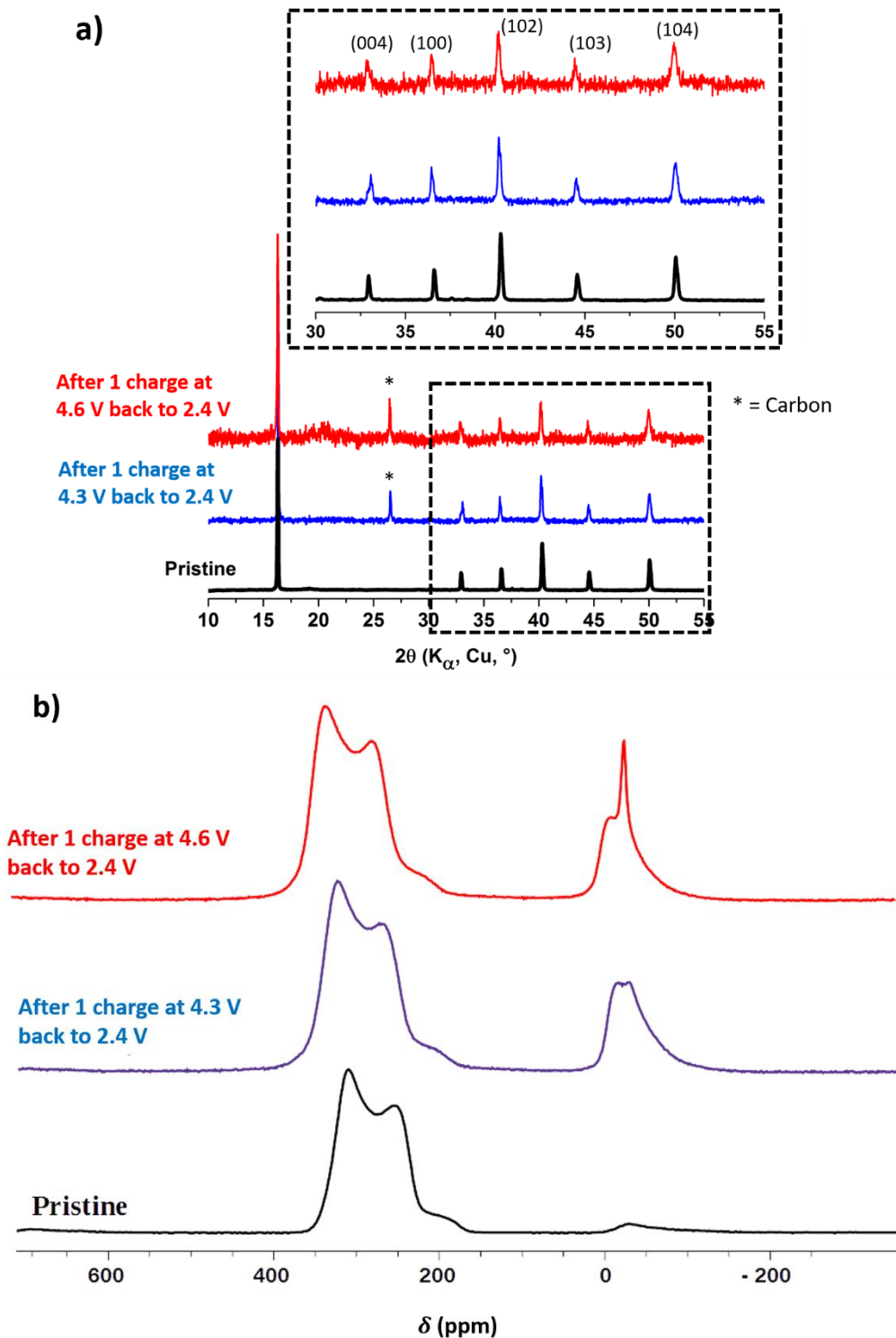


Figure SI-13: a) XRD patterns and b) ^{23}Na MAS NMR spectra of the pristine P2-phase and two P2- Na_xCoO_2 phases recovered at 2.4 V after a charge at 4.3 and 4.6 V (vs Na^+/Na) using a 7.05 T magnetic field. The spinning frequency of the rotors was 30 kHz and the NMR sequence was a single pulse.