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The interplay between thermodynamics and kinetics in the solid-state synthesis of layered oxides

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SUPPLEMENTARY INFORMATION

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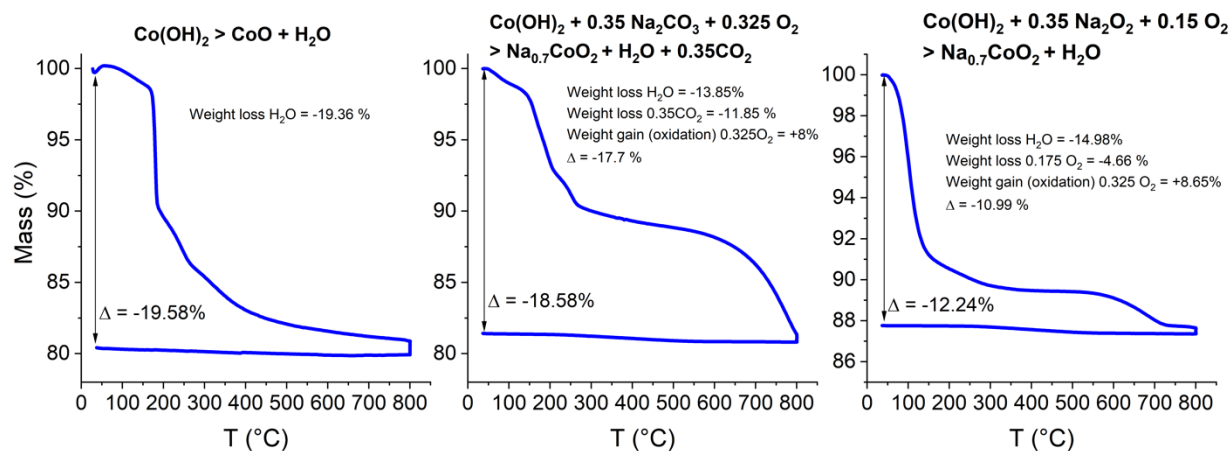


Figure S1: Thermogravimetric analysis (TGA) curves for Co(OH)_2 , a mixture of $\text{Co(OH)}_2 + 0.35 \text{Na}_2\text{CO}_3$ (middle) and a mixture of $\text{Co(OH)}_2 + \text{Na}_2\text{O}_2$ (right). All samples are heated in air in alumina crucibles at 5 °C/min. It can be seen that the Co hydroxide dehydrates below 200 °C. When mixed with Na precursors, the curve has a two-step behavior; a first low temperature step corresponding to dehydration, and a second one at higher temperature corresponding to solid-state reactions.

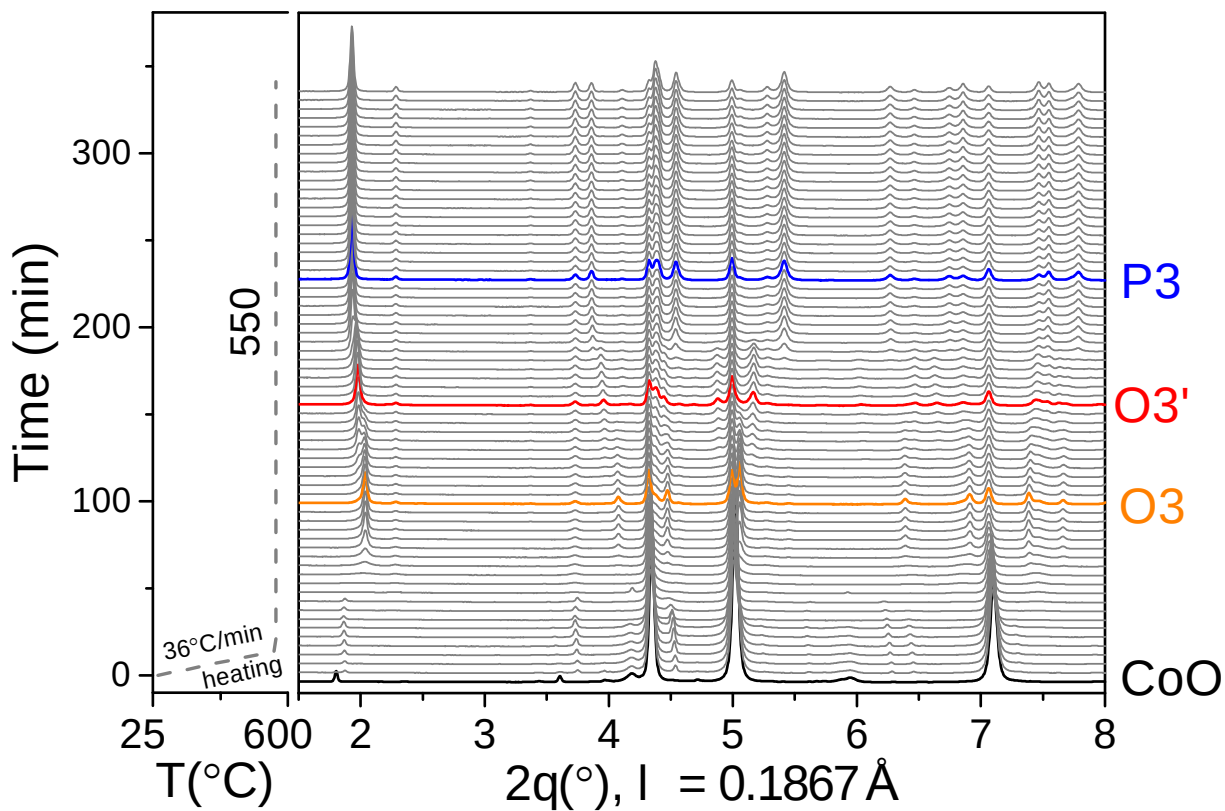


Figure S2: Synchrotron XRD (28-ID-2, NSLS-II, BNL) upon synthesis of CoO + 0.35 Na₂O₂ at 550 °C, with fast heating (36 °C/min). The first scan is shown in black representing the crystalline phase of precursor (CoO), and other colored curves represent the scans at which one layered phase is well formed (orange: O3; red: O3'; blue: P3). One scan is recorded every ~3 minutes.

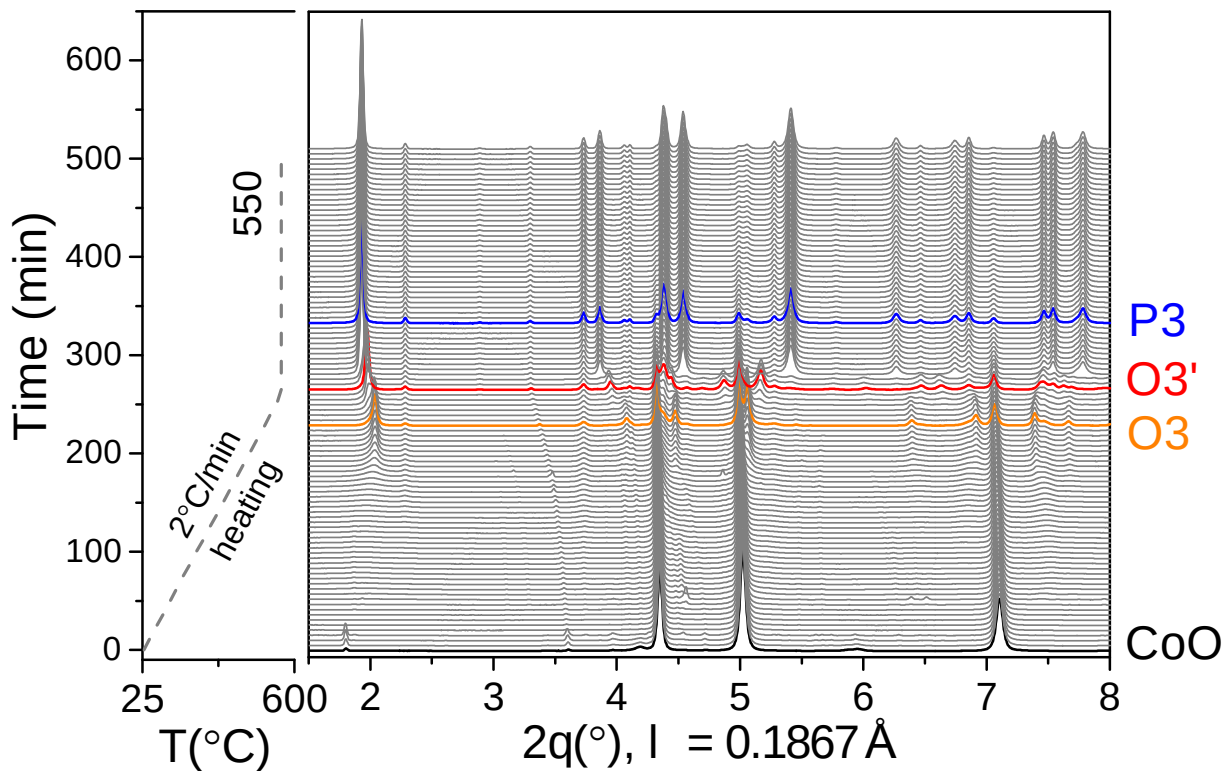


Figure S3: Synchrotron XRD (28-ID-2, NSLS-II, BNL) upon synthesis of $\text{CoO} + 0.35 \text{Na}_2\text{O}_2$ at 550°C , with slow heating ($0.5^\circ\text{C}/\text{min}$). The first scan is shown in black representing the crystalline phase of precursor (CoO), and other colored curves represent the scans at which one layered phase is well formed (orange: O3; red: O3'; blue: P3). One scan is recorded every 5 minutes.

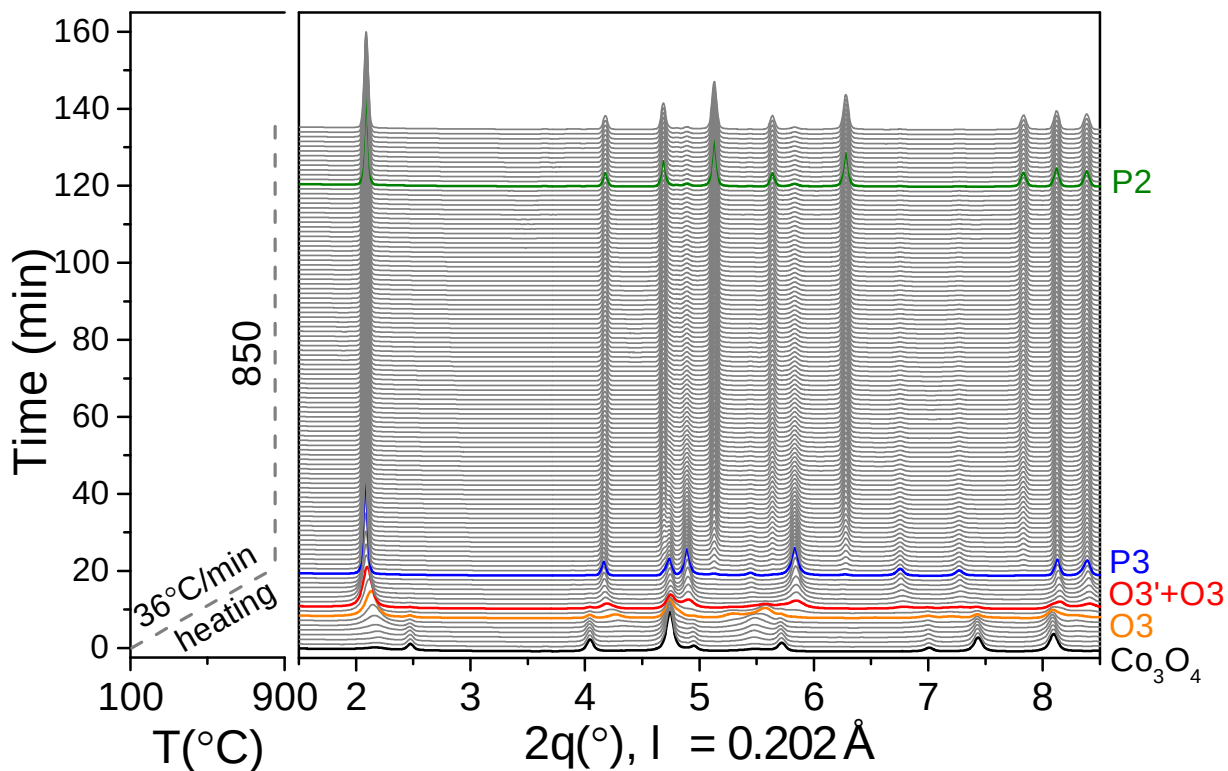


Figure S4: Synchrotron XRD (F2, CHESS) upon synthesis of $1/3\text{ Co}_3\text{O}_4 + 0.35\text{ Na}_2\text{O}_2$ at $850\text{ }^\circ\text{C}$, with fast heating ($36\text{ }^\circ\text{C/min}$). The first scan is shown in black representing the crystalline phase of precursor (Co_3O_4), and other colored curves represent the scans at which one layered phase is well formed (orange: O3; red: O3' and O3 co-exist; blue: P3; green: P2). One scan is recorded every 75 s. The initial formation of O3 appears to be even faster when using Co_3O_4 with respect to CoO .

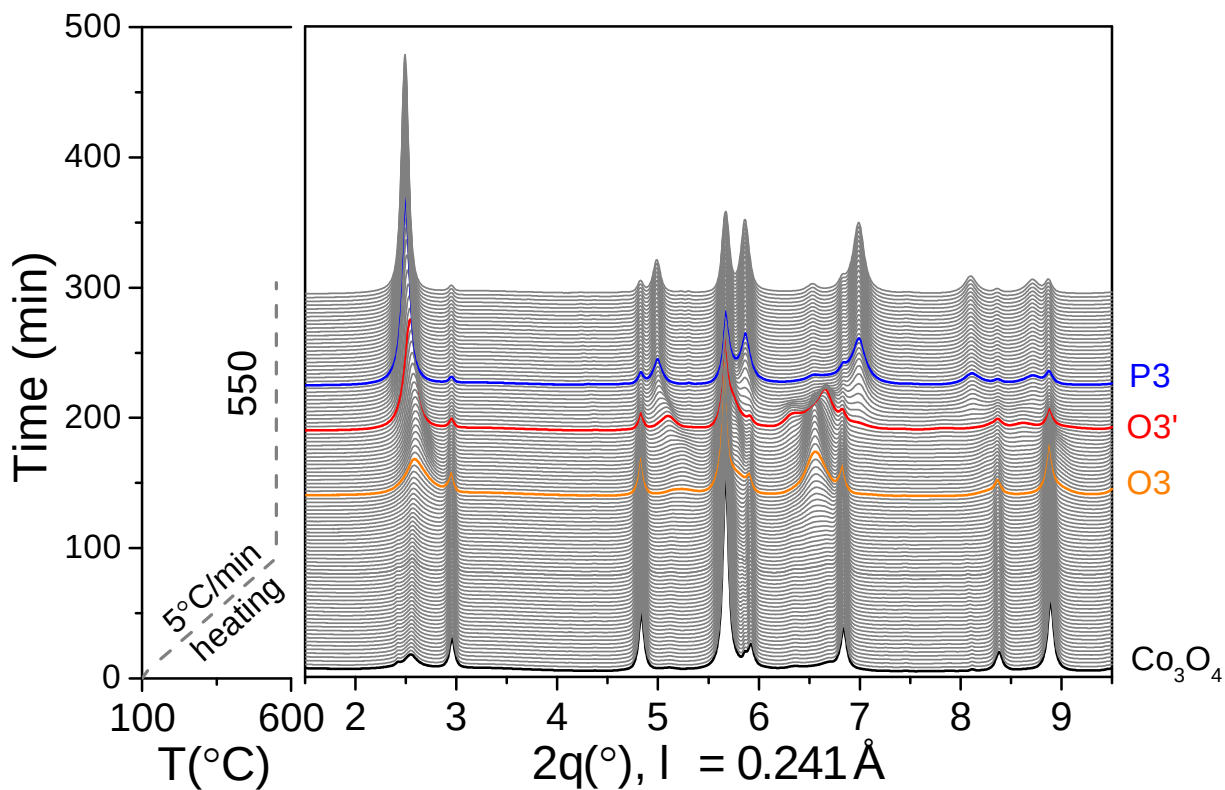


Figure S5: Synchrotron XRD (17-BM-B, APS, ANL) upon synthesis of $1/3 \text{ Co}_3\text{O}_4 + 0.35 \text{ Na}_2\text{O}_2$ at 550 °C, intermediate heating (5 °C/min). The first scan is shown in black representing the crystalline phase of precursor (Co_3O_4), and other colored curves represent the scans at which one layered phase is well formed (orange: O3; red: O3'; blue: P3). One scan is recorded every 1 minute. The initial formation of O3 appears to be even faster when using Co_3O_4 with respect to CoO.

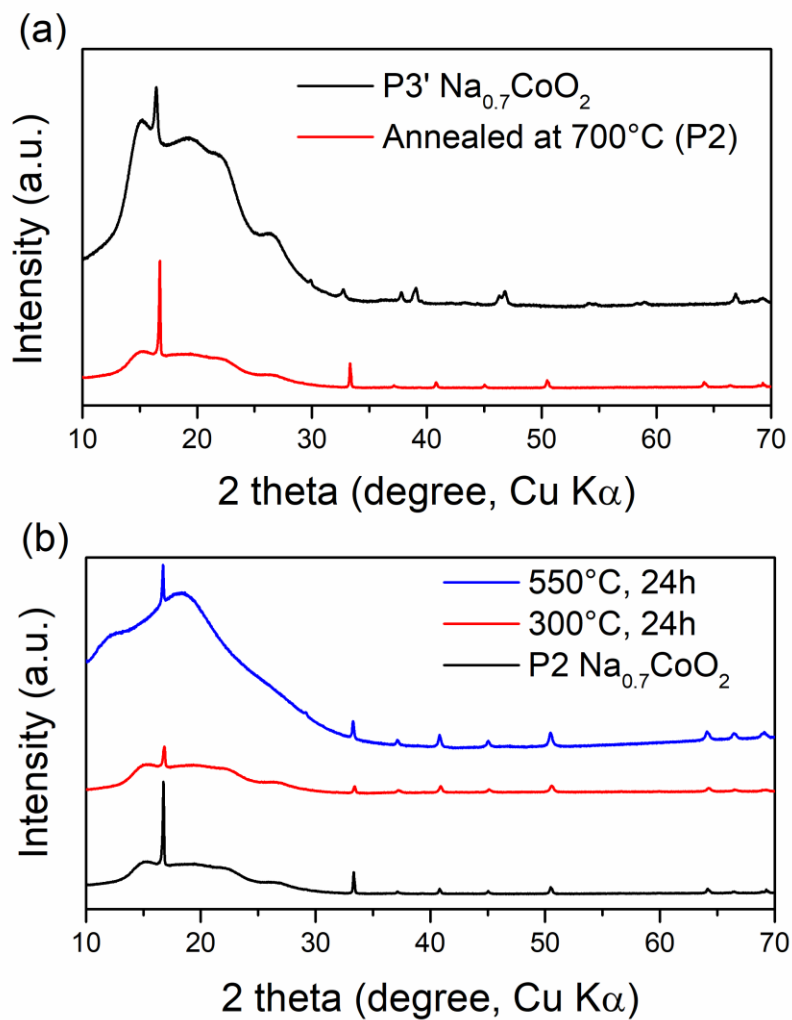


Figure S6: P3 Na_{0.7}CoO₂ transforming into P2 at 700 °C (a). On the other hand, P2 Na_{0.7}CoO₂ does not transform back to P3 when held at 300 or 550 °C for 24 hours (b).

Supplementary notes 1:

Although the actual nucleation mechanism of a P2 phase within a P3 framework is unknown, we suggest a simple model to estimate the energetics of the energy barriers involved in the process. We consider an ideal $O3 \rightarrow P3 \rightarrow P2$ transformation path in Na_xCoO_2 . We use the solid-state nudged elastic band method on the potential energy surface described by DFT with the SCAN functional. Figure S7 shows the activation barrier required for all Co layer to slide from P3 Co sites to P2 Co sites. For simplicity, we only show results calculated using one unit cell of Na_xCoO_2 with $x = 1$. We verified that the Na content does not significantly affect the phase transition mechanism by computing the same energy barrier in a sodium-depleted structure ($x = 0$, Figure S7). From the SSNEB calculation, we find that the Co migration barrier in a P3-P2 transition is high due to the existence of high-energy intermediate states with Co in a tetrahedral site, corresponding to the change in anionic framework (O stacking) requiring the collective breaking of Co-O bonds. The SSNEB results clearly demonstrates that the migration of Co atoms to form P2 from P3 (or O3) would be more difficult than layer gliding to form P3 from O3.

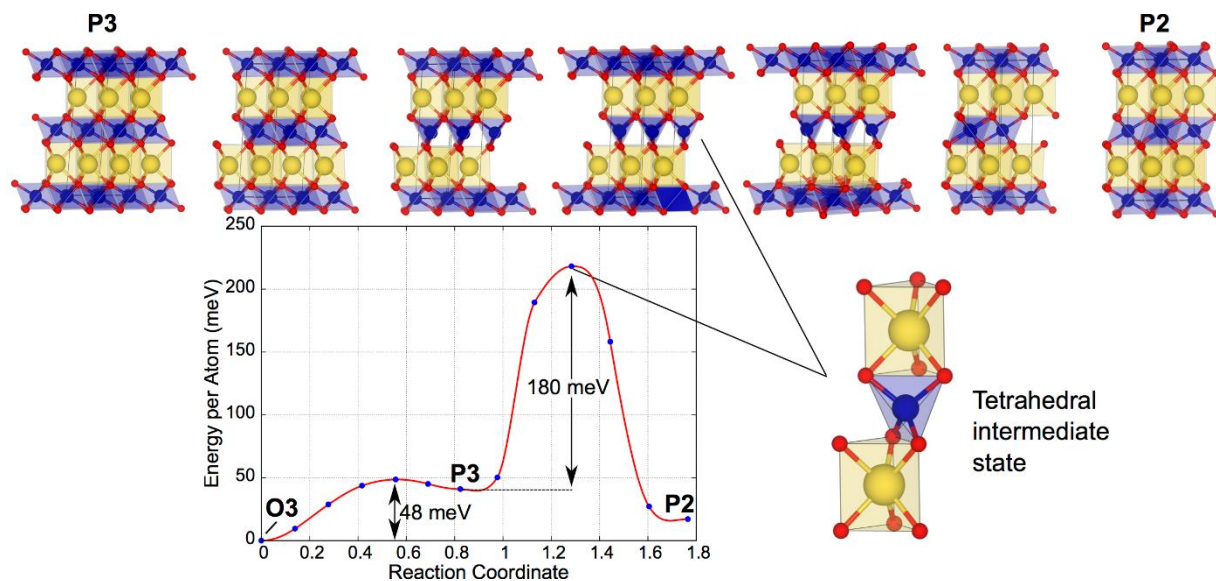


Figure S7: Transition from the P3 to the P2 layered structure. An intermediate state with Co in tetrahedral coordination is identified as the transition bottleneck. The curve shows the energy barrier calculated with SSNEB. All structures are ideally fully sodiated.

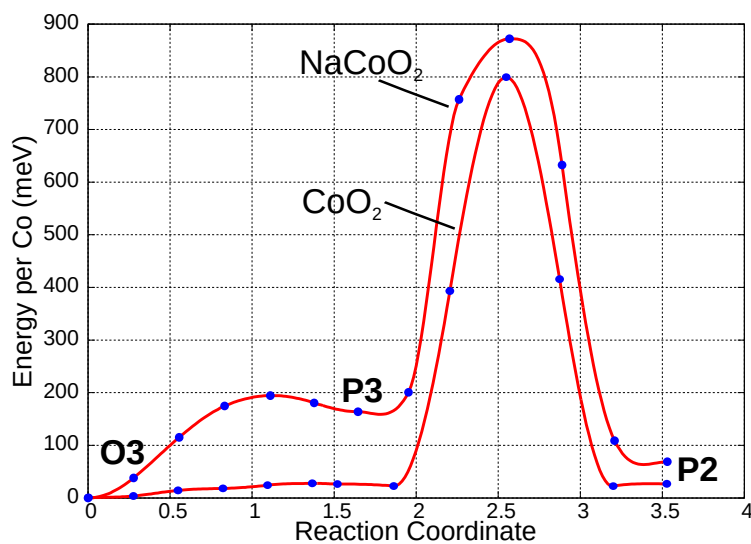


Figure S8: Activation barriers (in meV/Co or meV/f.u.) for the O3 → P3 → P2 transformation calculated with SSNEB in the fully sodiated (NaCoO_2) and fully desodiated (CoO_2) case.

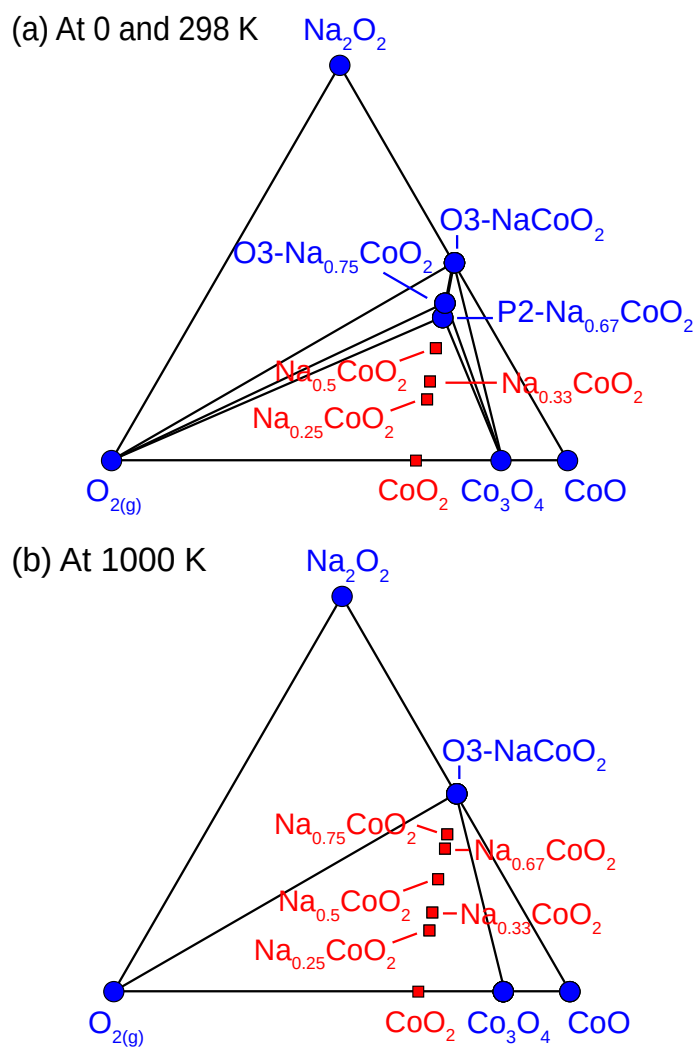


Figure S9: Ternary Na-Co-O phase diagrams for the region enclosed by Na_2O_2 , CoO and $\text{O}_{2(g)}$ at 0 and 298 K (a) and at 1000 K (b). Blue dots and red squares represent stable and unstable compounds, respectively. Note that these phase diagrams are only representative of the relevant phases present in the considered chemical space, but their actual stability during synthesis in air should be evaluated in a grand canonical ensemble as is done in the main text.

Supplementary notes 2:

We investigate the relative stability of O3, P2 and P3 Na_xCoO_2 ($0 \leq x \leq 1$) phases in their lowest-energy Na/vacancy configuration using density functional theory (DFT) calculations. Note that the crystallographically-distinct O3/O3' and P3/P3' phases are not distinguished computationally due to the relaxation of symmetry constraints. Finite-temperature ternary Na-Co-O phase diagrams for the region enclosed by Na_2O_2 , CoO and $\text{O}_{2(\text{g})}$ are reported in Figure S9. Formation energies with respect to CoO, Co_3O_4 , Na_2O_2 and $\text{O}_{2(\text{g})}$, energies above the convex hull and potential decomposition phases of all the materials considered here are listed in the Supplementary Tables S1 (at 298 K).

Table S1: Formation energies with respect to cobalt oxides, Na_2O_2 and $\text{O}_{2(\text{g})}$, energies above the convex hull and potential decomposition phases of all compounds considered in the phase diagrams presented at 298 K:

Composition	Formation energy (eV / atom)	Energy above the hull (meV / atom)	Decomposition phases
$\text{O}_{2(\text{g})}$	0.000	0.0	--
Na_2O_2	-1.191	0.0	--
CoO	-1.035	0.0	--
Co_3O_4	-1.374	0.0	--
O3- NaCoO_2	-1.797	0.0	--
P2- NaCoO_2	-1.780	16.5	O3- NaCoO_2

P3-NaCoO ₂	-1.757	40.3	O3-NaCoO ₂
O3-Na _{0.75} CoO ₂	-1.718	0.0	--
P2-Na _{0.75} CoO ₂	-1.716	1.5	O3-Na _{0.75} CoO ₂
P3-Na _{0.75} CoO ₂	-1.716	1.1	O3-Na _{0.75} CoO ₂
O3-Na _{0.66} CoO ₂	-1.678	4.2	P2-Na _{0.66} CoO ₂
P2-Na _{0.66} CoO ₂	-1.683	0.0	--
P3-Na _{0.66} CoO ₂	-1.682	1.0	P2-Na _{0.66} CoO ₂
O3- Na _{0.5} CoO ₂	-1.596	7.17	P3-Na _{0.5} CoO ₂
P2-Na _{0.5} CoO ₂	-1.596	7.18	P3-Na _{0.5} CoO ₂
P3-Na _{0.5} CoO ₂	-1.603	0.0	--
O3-Na _{0.33} CoO ₂	-1.476	26.51	P3-Na _{0.5} CoO ₂ , Co ₃ O ₄ , O ₂ (g)
P2-Na _{0.33} CoO ₂	-1.481	21.79	P3-Na _{0.5} CoO ₂ , Co ₃ O ₄ , O ₂ (g)
P3-Na _{0.33} CoO ₂	-1.474	28.37	P3-Na _{0.5} CoO ₂ , Co ₃ O ₄ , O ₂ (g)
O3-Na _{0.25} CoO ₂	-1.386	63.77	P3-Na _{0.5} CoO ₂ , Co ₃ O ₄ , O ₂ (g)
P2-Na _{0.25} CoO ₂	-1.383	67.41	P3-Na _{0.5} CoO ₂ , Co ₃ O ₄ , O ₂ (g)
P3-Na _{0.25} CoO ₂	-1.381	69.33	P3-Na _{0.5} CoO ₂ , Co ₃ O ₄ , O ₂ (g)
O1-CoO ₂	-1.088	192.72	Co ₃ O ₄ , O ₂ (g)

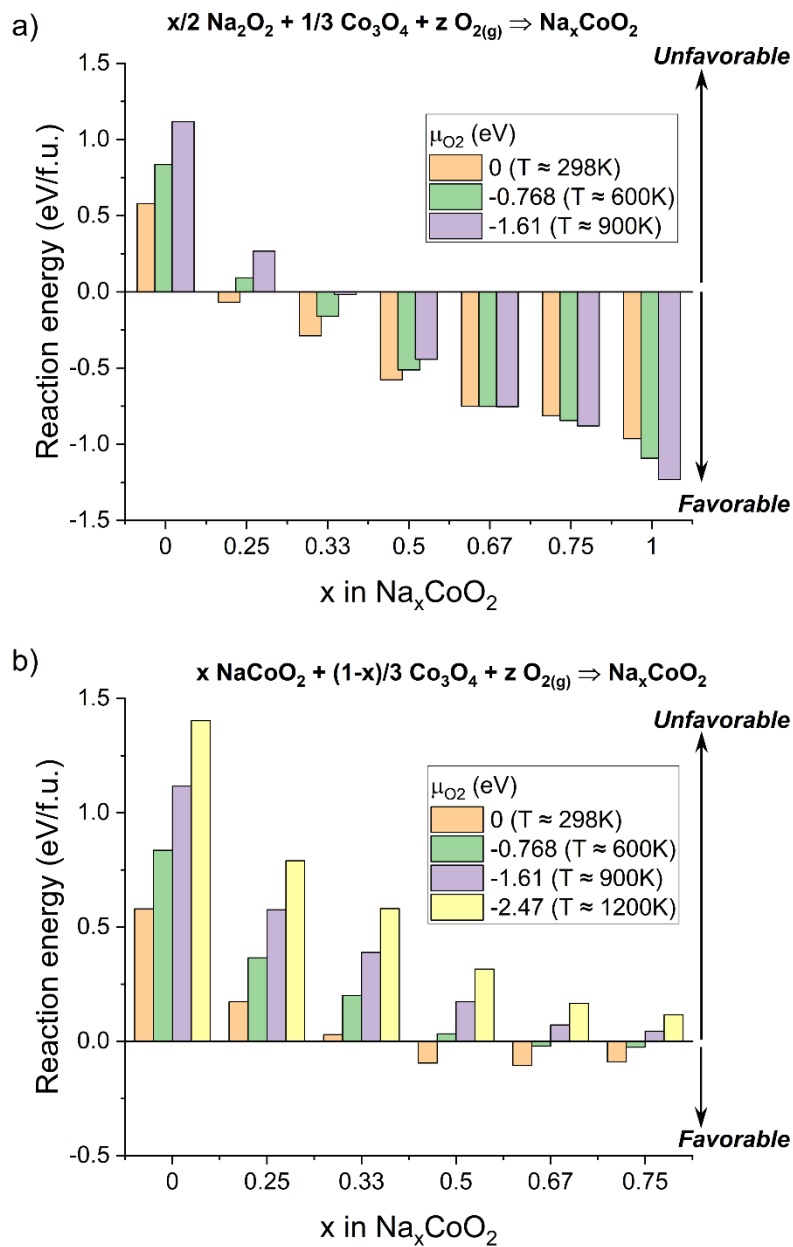
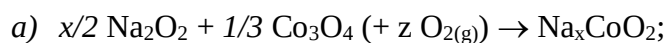
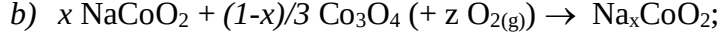


Figure S10: Reaction energies corresponding to the formation of Na_xCoO_2 phases from a Co_3O_4 precursor are calculated for different values of μ_{O_2} , using a procedure similar to that employed in the main text. In this case, the two reactions considered are:





The reaction energies corresponding to the formation of the lowest energy Na_xCoO_2 ($0 \leq x \leq 1$) polytypes (see Table S1) according to reactions (1) and (2) are plotted against x in Figures S10a and S10b. Similarly to the case when CoO is used as precursor (see Figure 5 in the main text), O3 NaCoO_2 formation from Na_2O_2 and Co_3O_4 has the most negative reaction energy of all layered Na_xCoO_2 compounds and therefore the strongest driving force at all μ_{O_2} considered (see Figure S10a). We note that the reaction energy to form $\text{Na}_{0.67}\text{CoO}_2$ from Na_2O_2 and Co_3O_4 does not depend on μ_{O_2} as, at $x = 2/3$, reaction (1) is balanced without the need for $\text{O}_{2(\text{g})}$ participation.

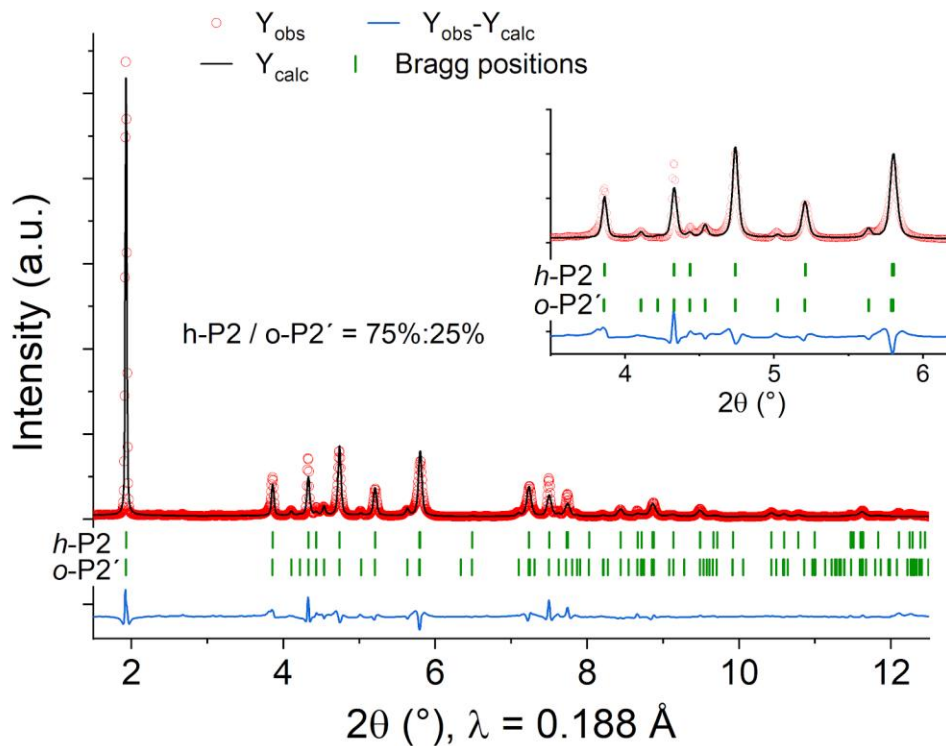


Figure S11: Rietveld refinement of the XRD pattern corresponding to the end of the *in situ* synthesis experiment of $\text{Mn}_2\text{O}_3 + \text{Na}_2\text{O}_2$, after cooling. We find that the RT phase is a mixture of orthorhombic o-P2' and hexagonal h-P2 in a ratio of 25%:75%, as expected from the fact that we do not control the cooling, i.e. neither slow cooling nor quenching. The results confirm the importance of cooling in the Mn system.

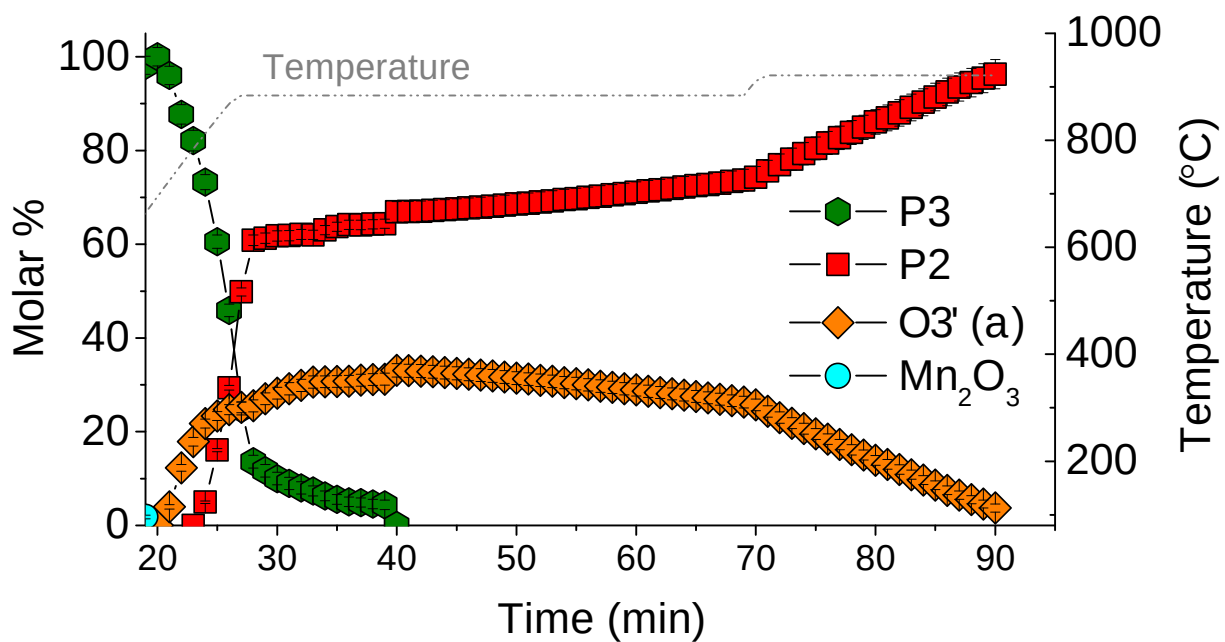


Figure S12: Evolution of the molar % of the observed crystalline phases vs. time of the reaction between $1/2\text{Mn}_2\text{O}_3 + 1/3\text{Na}_2\text{O}_2$ in the 20 – 90 min time interval.

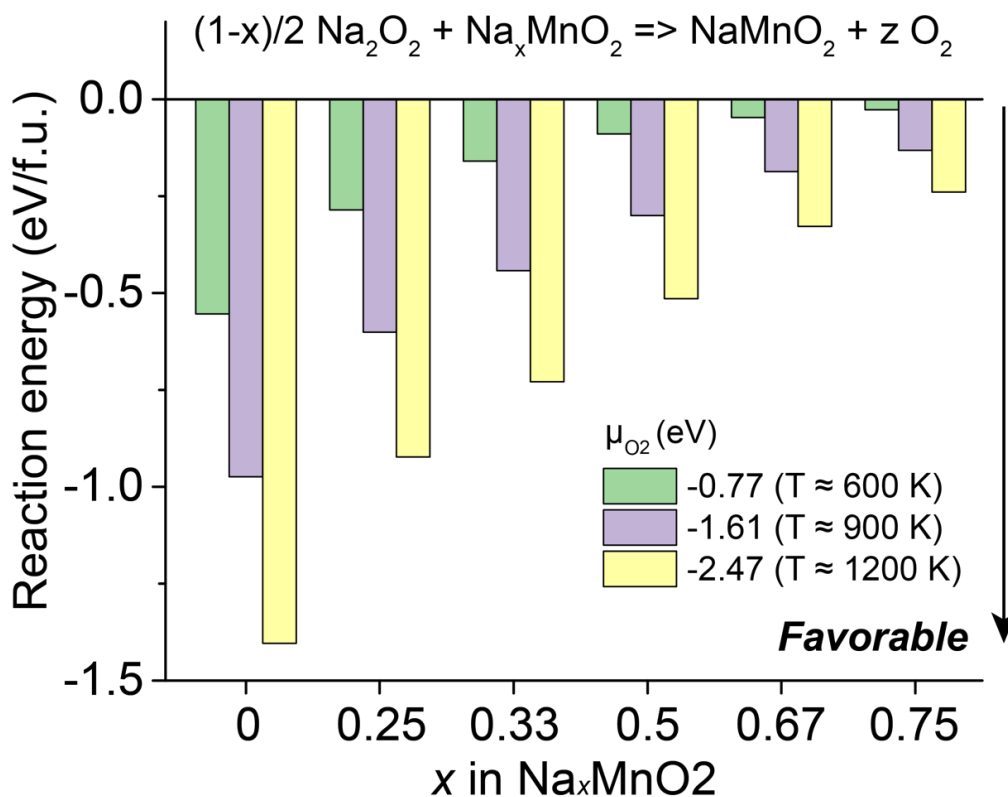
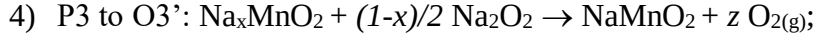
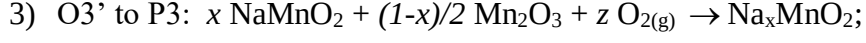


Figure S13: Reaction energies between P3- Na_xMnO_2 and Na_2O_2 , according to the reaction: $(1-x)/2 \text{ Na}_2\text{O}_2 + \text{Na}_x\text{MnO}_2 \rightarrow \text{NaMnO}_2 + z \text{ O}_{2(\text{g})}$.

Supplementary notes 3:

After P3 crystallizes, the Mn and Co systems start to differ. First, as obtained from Rietveld refinement, the P3 Na_xMnO_2 compound contains significantly less sodium (0.42) than the Co counterpart (0.61) (Figure S14), which means that there should be a large amount of leftover sodium in the mixture. Second, P3 $\text{Na}_{0.61}\text{CoO}_2$ transforms into P2 $\text{Na}_{0.67}\text{CoO}_2$ at elevated temperature (Figure 2), while P3 $\text{Na}_{0.42}\text{MnO}_2$ transforms into a mixture of P2 and O3' phases, and only afterwards the P2 phase grows by consuming O3' (Figure S12). Interestingly, P3 $\text{Na}_{0.42}\text{MnO}_2$ is originally formed from the O3' phase, but it partially reverts back to O3' at higher temperature.

The direction of the O3' to P3 transformation is largely controlled by μ_{O_2} , thus we have calculated reaction (3) in Figure 6c and (4) in Figure S13:



The former requires a high μ_{O_2} , consistent with the fact that the O3' to P3 transformation is observed at relatively low temperature. However, when the temperature further increases, μ_{O_2} becomes smaller and the inverse transformation, reaction (4), becomes more favorable as indicated by the reaction energies in Figure S13.

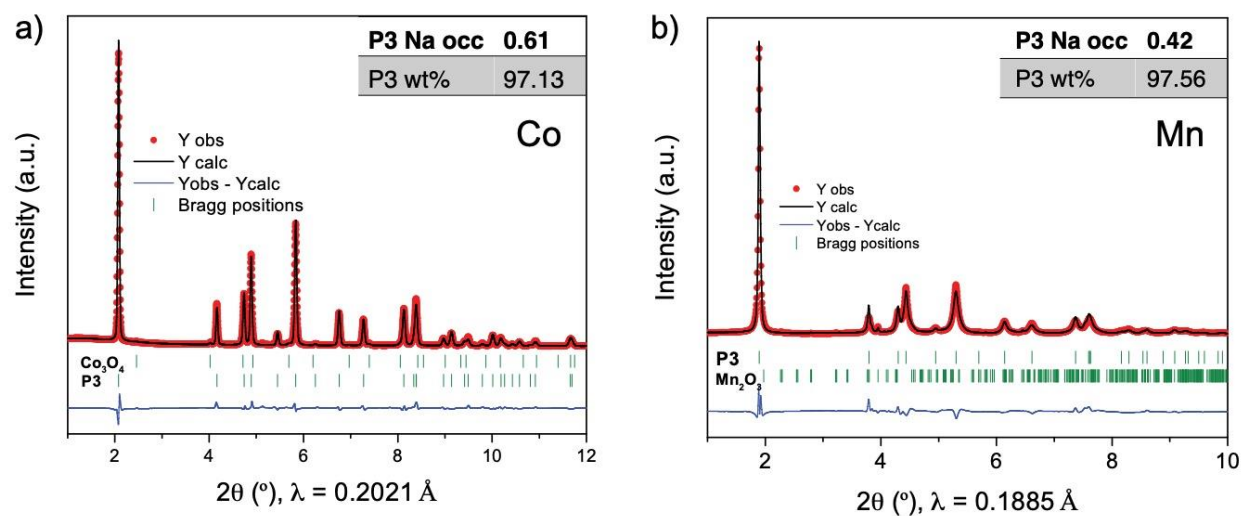


Figure S14: Rietveld refinement profiles of a) $\text{P3 Na}_{0.61}\text{CoO}_2$ and b) $\text{P3 Na}_{0.42}\text{MnO}_2$. The XRD scans were taken from the *in situ* data shown in Figure 2 and 6, respectively.

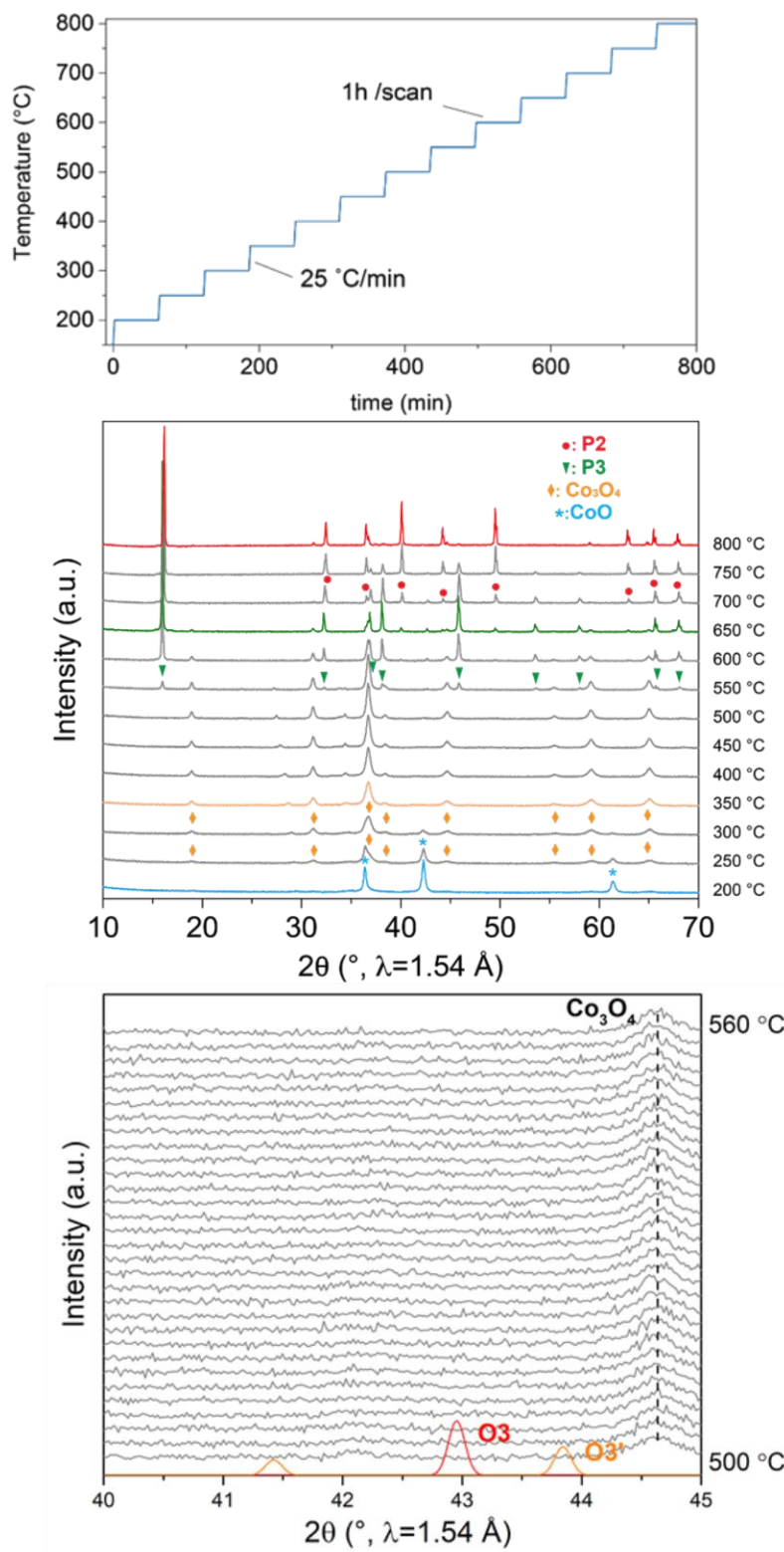


Figure S15: top) temperature profile used for the *in situ* synthesis of CoO + 0.35 Na₂CO₃. The precursors mixture was ball milled and measured in our in-house Bruker diffractometer. The *in*

situ measurement starts from 200 °C with a ramping rate of 25 °C/min, and 1h-long XRD scans are taken every 50 °C. Middle) *In situ* XRD data. CoO is first fully oxidized to Co₃O₄, then the P3 phase forms, and P3 transforms into P2 in the end. Bottom) to verify there is no O3 formation, the *in situ* experiment is repeated by taking 1-min scan every 2 °C from 500 to 560 °C in the angular region where the most intense O3 peak should appear.

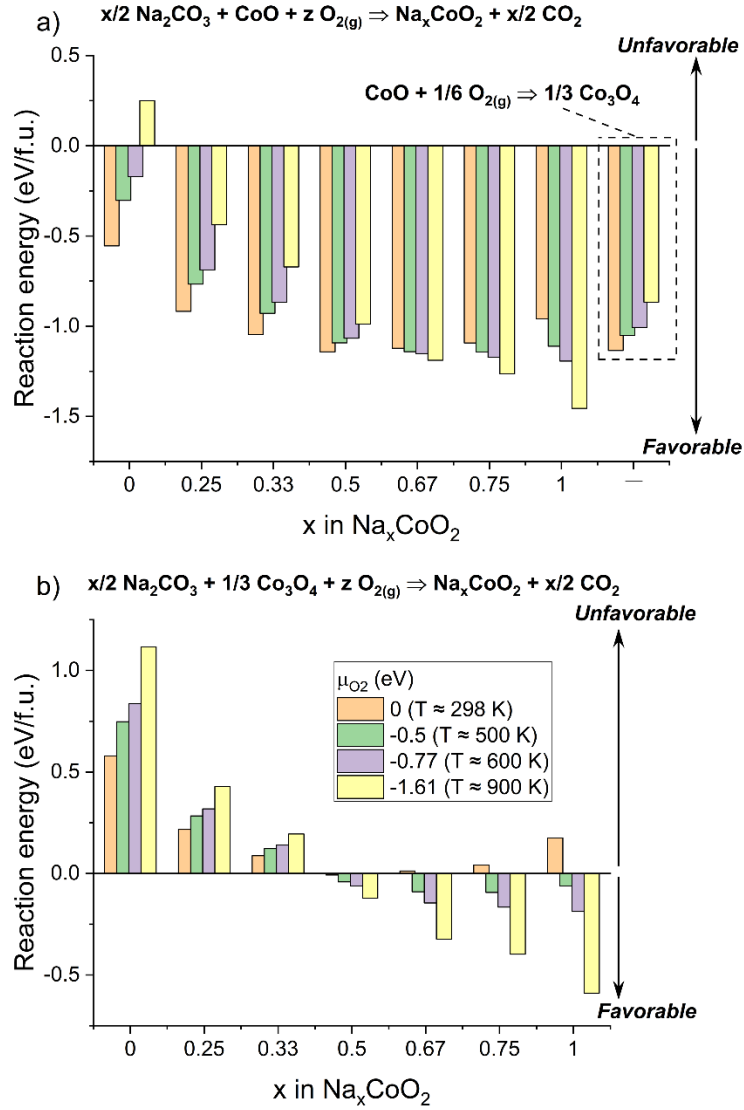
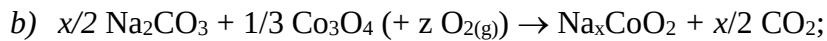
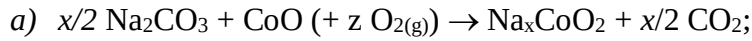


Figure S16: Reaction energies corresponding to the formation of Na_xCoO_2 phases from CoO (top) and Co_3O_4 (bottom) in presence of Na_2CO_3 calculated for different values of μ_{O_2} , using a procedure similar to that employed in the main text. In this case, the two reactions considered are:



In a), reaction $\text{CoO} + 1/6 \text{ O}_2 \rightarrow 1/3 \text{ Co}_3\text{O}_4$ is also shown, having reaction energy comparable to (or more negative than, at low temperature) the one for the formation of layered oxides. In b), one

can see that at intermediate T (500 K), formation of low-Na layered phases is favored over the formation of O3-NaCoO₂. O3 would ultimately form when increasing the T further, but no sodium is available in our mixture.

Supplementary notes 4 – Role of Entropy

To determine the influence of vibrational entropy in this system, we calculated the phonon frequencies of the P2, P3, and O3 phases at the Na_{0.67}CoO₂ composition in DFT using *phonopy* (Togo, Atsushi, and Isao Tanaka. "First principles phonon calculations in materials science." Scripta Materialia 108 (2015): 1-5). We show below in Figure S17a the change in free-energies of O3 and P3, referenced against P2, due to vibrations. The Zero-Point Energy (ZPE) is also included in the graph, shown as the offset between the curves at 0 Kelvin. We find that the entropic phonon contribution to the free energy difference is very small, $\Delta G_{vib} \ll 1$ meV/atom. The total free energies, $G = H - TS$, are therefore dominated by the H term (shown in Figure 1a). We show the total free energies in Figure S17b.

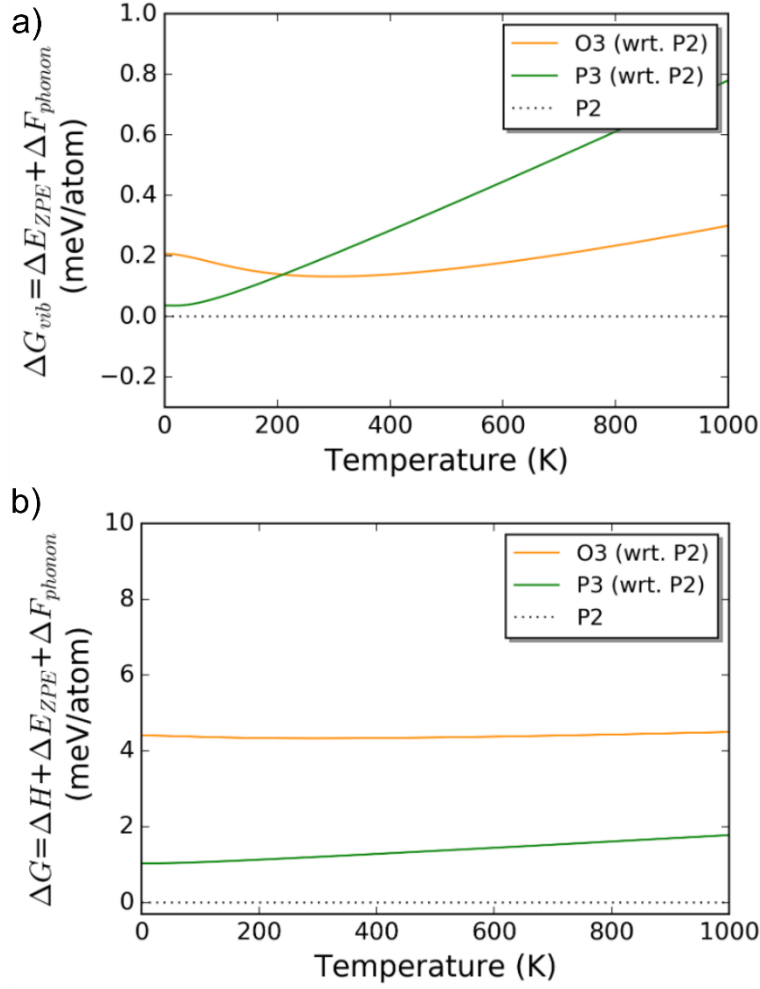


Figure S17: a) Calculated vibrational entropy contribution (phonon) to the free-energies of O3 and P3 structures at $\text{Na}_{0.67}\text{CoO}_2$ composition, referenced against P2 phase. b) Calculated total free energies of the O3 and P3 phases with respect to (wrt.) the P2 phase of $\text{Na}_{0.67}\text{CoO}_2$, including the 0 K DFT enthalpy, zero-point energy (ZPE) correction and phonon free energy.

We find that S_{vib} is ordered $S_{\text{P2}} > S_{\text{O3}} > S_{\text{P3}}$. Despite the small quantitative differences, DFT is generally robust on calculating *relative* entropies, suggesting that our conclusion on the entropic ordering of $S_{\text{P2}} > S_{\text{O3}} > S_{\text{P3}}$ is trustworthy.

Regarding configurational entropy, one can evaluate the relative Na configurational entropy between P2/P3 phases and O3-like phases using basic counting principles (as discussed previously in Lei, Yuechuan, et al. "Synthesis and stoichiometry of different layered sodium cobalt oxides." *Chemistry of Materials* 26.18 (2014): 5288-5296). In P3 and P2, there are two sodium sites per formula unit. In P3 these are equivalent whereas in P2 a small energy difference exists between them. In O-phases there is only one Na site per formula unit. Hence one expects the high-temperature configurational entropy to behave as $S_{P2} \sim S_{P3} > S_{O3}$. Similar arguments have been made in the literature [Carlier et al., *Chem. Mat.* 2003, 15 (13), 2651-2660; Lei et al., *Chem. Mat.* 2014, 26, 5288–5296]. Therefore, at partial desodiation configurational entropy should also further stabilize P2/P3 over O3.