## **Supplementary Information**

# An experimental and first-principle investigation of the Ca-substitution effect on P3-type layered Na<sub>x</sub>CoO<sub>2</sub>

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Space gro	up á	a [Å]	b [Å]	c [Å]	α [°]	β[°]	γ <b>[°]</b>
C2/m	4.90	201(62)	2.82413(34)	5.70590(106)	90.0	106.1891(113)	90.0
Atom	Site	g	x		У	z	U <sub>iso.</sub> [Ų]
Na	8j	0.1822	0.78910(	(355) 0.07	7661(710)	0.50258(116)	0.02570
Ca	8j	0.0100	0.78910(	(355) 0.07	7661(710)	0.50258(116)	0.02570
Со	2a	1.0	0.0		0.0	0.0	0.00240
0	<b>4</b> i	1.0	0.39722(	(176)	0.0	0.16917(38)	0.00656



**Fig. S1** Characterization results of as-prepared NCO and NCCO. Powder XRD patterns (a), structural refinement of NCCO (b), and SEM-EDX mapping of the Na<sub>0.5</sub>Ca<sub>0.05</sub>CoO<sub>2</sub> (c).



Fig. S2 Charge-discharge profiles of 1<sup>st</sup> to 3<sup>rd</sup> cycle of NCO (a) and NCCO (b)



**Fig. S3** Cycling performances of NCO operated at narrow voltage range(green). The P'3-O3' phase transition at high voltage causes the severe capacity decay of NCO. Though the utilized capacity is reduced, the capacity retention of the NCO is still lower than NCCO. It suggests that the Ca-substitution prevents the irreversible side reaction during the P'3-O3' phase transition.



Fig. S4 XRD patterns of the charged NCO and NCCO at 4.5 V.



**Fig. S5** Migration paths of Na ions in (a) P3-Na<sub>0.333</sub>CoO<sub>2</sub> and (b), (c) P3-Na<sub>0.278</sub>Ca<sub>0.056</sub>CoO<sub>2</sub>. Yellow prisms and a light blue prism represent the Na sites and a Ca site, respectively. The light green spheres represent the Na ions at the bottlenecks. Note that the monoclinic lattices are used here. The crystal structures were visualized by using VESTA.<sup>1</sup>



**Fig. S6** O-O bond length of the Na layer in the P3 and P2 structures. P3 and P2 structures are shown as the monoclinic (C2/m) and the hexagonal ( $P6_3/mmc$ ), respectively.

	Average O-O bond length of the Na layer / Å			
	Na <sub>0.33</sub> CoO <sub>2</sub>	Na <sub>0.28</sub> Ca <sub>0.056</sub> CoO <sub>2</sub>		
P3	3.580	3.597		
P2	3.629	3.529		

### Methods

#### Material synthesis and characterization

 $Na_xCoO_2$  (NCO) and Ca-doped  $Na_xCoO_2$  (NCCO) were synthesized by a solid-state method. NaOH,  $Ca(OH)_2$  and  $Co(OH)_2$  were mixed in an agate mortar in an Ar-filled glove box. 15 wt.% of excess NaOH was used to compensate Na species evaporation during calcination. The mixed sample was pelletized and heated at 500 °C under oxygen flow for 36 hours.

The X-ray diffraction (XRD) experiments were performed using an X-ray diffractometer (Bruker D8 Advance) with Co K $\alpha$  radiation.

Elemental analyses of the NCO and NCCO were performed using an ICP-AES (Horiba Jobin Yvon ULTIMA 2000).

#### **Electrochemical Test**

NCO and NCCO electrodes were prepared by mixing 80 wt% of the active material, 10 wt% of acetylene black and 10 wt% of polyvinylidene fluoride in NMP. The obtained electrode slurry was coated on aluminum foil and dried in a vacuum at 80 °C.

The electrochemical tests were performed using two electrode cells (TJ-ACC; Tomcell Japan) with the prepared electrode as a working electrode, sodium metal as a counter electrode and 1 mol  $L^{-1}$  NaPF<sub>6</sub> in EC:DEC (1:1 in volume) 97 wt% + FEC 3 wt% as an electrolyte. Galvanostatic measurements were carried out using BTS2004H, Nagano JAPAN.

#### **Computational Methods**

Density functional theory (DFT) calculations were performed with the projector augmented wave (PAW) approach,<sup>2,3</sup> which is implemented in the Vienna Ab initio Simulation Package (VASP).<sup>4,5</sup> The optB86b-vdW functional was used to account for the Van der Waals interaction between  $CoO_2$  layers.<sup>6,7,8</sup> Hubbard U correction was not applied, since +U correction can lead to incorrect results for  $Na_xCOO_2$ .<sup>9</sup> The cutoff energy was set to 520 eV. A gamma-centered k-point for which the density is more than 500 / (number of atoms) was adopted.

Structure generation and analysis were performed with the Pymatgen package.<sup>10</sup> For O1 structures, a 3x3x2 supercell was generated from a CoO<sub>2</sub> (ICSD No. 88722) unit cell. For P3 structures, a 3x3x1 supercell was generated from a Na<sub>0.672</sub>CoO<sub>2</sub> (ICSD No. 59606) unit cell. For O3 structures, an NaCoO<sub>2</sub> (ICSD No. 6152) cell was manually transformed to a triclinic primitive cell, and then a 6x3x1 supercell was generated from the triclinic cell. The compositions of the supercells were represented as Na<sub>x</sub>Co<sub>18</sub>O<sub>36</sub> and Na<sub>x</sub>CaCo<sub>18</sub>O<sub>36</sub>, as mentioned in the main text. In the Na<sub>x</sub>Ca<sub>y</sub>CoO<sub>2</sub> structure, there are various possible Na-(Ca)-vacancy orderings. All possible orderings within the supercells were chosen. The most stable configurations at each composition were selected from the DFT calculations.

The formation energies of non-substituted  $Na_xCoO_2$  were calculated by using Equation 1. O3-type  $NaCoO_2$  and O1  $CoO_2$  were used as references.

$$E_f(Na_x CoO_2) = E(Na_x CoO_2) - x E(NaCoO_2) - (1 - x) E(CoO_2)$$
(1)

Here, E is the calculated energy.

The formation energies of Ca-substituted  $Na_xCoO_2$  were calculated by using Equation 2. O3- $Na_{0.89}Ca_{0.056}CoO_2$  and O1-Ca<sub>0.056</sub>CoO<sub>2</sub> were used as references.

$$E_{f}(Na_{0.89x}, Ca_{0.056}CoO_{2}) = E(Na_{0.89x}, Ca_{0.056}CoO_{2}) - x'E(Na_{0.89}Ca_{0.056}CoO_{2}) - (1 - x')E(Ca_{0.056}CoO_{2})$$
(2)

The migration barriers for Na ions in P3-Na<sub>x</sub>Ca<sub>y</sub>CoO<sub>2</sub> were calculated by the Climbing Image Nudged Elastic Band (CI-NEB) method, which is implemented in VASP Transition State Theory (VTST) tools<sup>12,13</sup> as an extension of VASP code. In the NEB calculations, a 3x6x1 supercell was used for the P3-type structure so that the hopping Na ions achieved a sufficient distance between their periodic images. The force is converged within 0.02 eV Å<sup>-1</sup>.

## References

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