Supporting Information

Superionic Conduction in Co-Vacant P2-Na$_x$CoO$_2$ Created by Hydrogen Reductive Elimination

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Sample preparation:
P2-Na₅CoO₂ has been synthesized according to the following procedure[1]. CH₃COONa and (CH₃COO)₂Co·4H₂O (Na : Co = 1.6 : 2.0) are dissolved in distilled water and evaporated. The dried powder is calcined at 750 °C for 5 h in the air, and is pressed into the form of disk. The disk is calcined at 790 °C for 3 h in the air, and crushed into powder. Thus the P2-Na₅CoO₂ powder has been obtained. The powder is pressed into a disk with the diameter of 20 mm and the thickness of 1 mm. The disk is sintered at 900 °C for 24 h in the air. The composition obtained by inductively coupled plasma-mass spectroscopy (ICP-MS) is consistent with that by the Rietveld refinement of SXPD data before any chemical treatments.

Electrochemical analyses:
Measurements of AC and DC conductivities employ specimens in the form of circular disk with the diameter of 20 mm and the thickness of 1 mm. One of specimens is treated by hydrogen at 290 °C for 30 min. The measurement under ambient conditions (28% RH and 25 °C) is done right after the hydrogen treatment. Each measurement at 30, 40, 50 and 60% RH is performed after maintaining their respective humidities at 25 °C for 1 h. The specimen sandwiched between two Au-coated Cu electrodes is placed in the thermo-humidistat (ESPEC SH-221) to control the relative humidity. Using the specimen, impedance spectroscopy measurements are carried out by the quasi-four-terminal method to estimate the AC conductivity. The frequency varies from 1 Hz to 10 MHz by the frequency response analyzer (Solartron 1260). The AC conductivity σ is given by the following equation: \( \sigma = d/(R\cdot A) \), where \( d \) is the measured thickness of a specimen, \( R \) is the real part of impedance, and \( A \) is the effective cross section of a specimen. Here \( R \) is obtained by fitting a semicircle observed at higher frequency in the Nyquist plot (Figure S6). The DC conductivity is measured by the two-terminal method using the digital multimeter (Fluke 115). The EMF are measured by the water vapor concentration cell. The cell employs either the hydrogen-treated (at 300 °C for 30 min) Na₅CoO₂ disk, a proton-exchange membrane (Nafion NRE-212), or a hydroxide-exchange membrane (Tokuyama A201) as the electrolyte, which is sandwiched between a pair of Pt-loaded carbon sheets. One and the other sides of the cell are exposed to humid and dry O₂/N₂ (50/50 cm³ min⁻¹) gas at 30 °C, respectively.

In situ SXPD experiments and analyses:
SXPD experiments were performed at the RIKEN Materials Science Beamline BL44B2[2] of SPring-8. The data were acquired using the Debye-Scherrer camera equipped with an
image plate as the X-ray detector. The wavelength of incident X-rays ($\lambda = 0.5002(1)$ Å) is calibrated using a standard powder sample CeO$_2$ by NIST. The temperature and humidity control cell made of glass capillaries (Figure S1) is employed for in situ SXPD experiments. The X-ray beam was collimated by a double slit (0.5 $\times$ 1.0 mm$^2$). In situ SXPD data have been analyzed by the Rietveld method with the program SPC$^3$ developed for SPring-8 powder diffraction data. The charge density analysis has been conducted by MEM with the program ENIGMA$^4$. Electrostatic potentials and electric fields are visualized based on MEM charge densities.$^5$

The lattice parameter of CoO at $t = 22$ min, when its mass ratio reaches the maximum, is refined by the Rietveld method to be 4.26076(3) Å with a cubic structure ($Fm$-3$m$). The lattice parameters of Co(OH)$_2$ at $t = 644$ min, when its mass ratio reaches the maximum, are refined by the Rietveld method to be $a = 3.18395(3)$ Å and $c = 4.65364(8)$ Å with a trigonal structure ($P$-3$m$1).

**Raman spectroscopy:**
Raman spectroscopy measurements employ Na$_x$CoO$_2$ disks before and after the hydrogen treatment at 300 °C for 30 min, and after its treatment followed by the humidification with 50%RH and 25 °C for 5 h. Raman The disks are in the form of circular disk with the diameter of 20 mm and the thickness of 1 mm. Raman spectra are measured by the spectrometer (HORIBA Jobin Yvon Inc., iHR320), which is equipped with the charge-coupled device (CCD) detector (HORIBA Jobin Yvon Inc., Synapse). The excitation source is a diode-pumped solid-state laser with the wavelength of 532 nm. The laser power and size at the sample position are estimated to be approximately 0.55 mW and 5 $\mu$m in diameter, respectively. All the measurements have been conducted under argon gas.

**MD simulations:**
Using the model based on the superionic-conductor (fourth) phase (Table S4) identified by in situ SXPD and Raman spectroscopy as the initial structure model, MD simulations have been performed with the New-RYUDO program$^6$. The isothermal-isobaric (NPT) ensemble is applied at a pressure of 0.1 MPa, in which the temperature is controlled by scaling the velocity of atoms in a system. The time step is 0.2 fs. The stabilization of an initial model takes 500,000 steps under the temperature of 27 °C. For MD simulations using the stabilized model, 1,000,000 steps have been performed at the elevated temperature of 400 °C to facilitate the diffusion. The structure model is composed of 154 Na, 240 Co, 512 O (CoO$_2$), 156 H, and 52 O (H$_3$O$^+$) atoms.

Four types of force field are used in the present simulations: The Born-Mayer-
Huggins (BMH) potential is given by

\[ S_{ij}(r_{ij}) = \frac{Z_i^2 \alpha^2}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6}, \]  

(1)

where \( r_{ij} \) is the distance between \( i \)-th and \( j \)-th atoms, \( Z_i \) is the atomic charge of the \( i \)-th atom, \( e \) \((=4.803\times10^{-10} \text{ esu})\) is the elementary electric charge, and \( f_0 \) \((=6.9490\times10^{-11} \text{ N})\) is the constant for unit adaptations between the terms. \( a_i \) and \( b_i \) are the repulsion term parameters related to the atomic size and the potential-curve stiffness, respectively. \( c_i \) is the parameter of the molecular force term. The Morse potential is given by

\[ T_{ij}(r_{ij}) = D_{ij}\{\exp[-2\beta_{ij}(r_{ij} - r_{ij}^0)] - 2\exp[-\beta_{ij}(r_{ij} - r_{ij}^0)]\}, \]  

(2)

where \( D_{ij}, \beta_{ij}, \) and \( r_{ij}^0 \) are the bond energy, potential-curve stiffness, and bond length between \( i \)-th and \( j \)-th atoms, respectively. The KKY2 potential is given by

\[ V_{ij}(r_{ij}) = D_{1ij}\exp(-\beta_{1ij}r_{ij}) + D_{2ij}\exp(-\beta_{2ij}r_{ij}) + D_{3ij}\exp[-\beta_{3ij}(r_{ij} - r_{ij}^*)^2], \]  

(3)

where \( D_{1ij}, D_{2ij}, D_{3ij}, \beta_{1ij}, \beta_{2ij}, \beta_{3ij}; \) and \( r_{ij}^* \) are the bond energy; potential-curve stiffness; and bond length. The three-body potential is given by

\[ U_{ijk}(r_{ij}, r_{ik}, \theta_{jik}) = -f_k\{\cos[2(\theta_{jik} - \theta_0)] - 1\}\sqrt{k_j k_k}, \]  

(4.1)

\[ k_j = \frac{1}{\exp[g_r(r_{ij} - r_m)+1]}, \]  

(4.2)

where \( \theta_{jik} \) is the bond angle between \( r_{ij} \) and \( r_{ik} \). \( f_k, \theta_0, g_r, \) and \( r_m \) are the parameters to reproduce the angular portion of the covalent bond in a \( \text{H}_2\text{O} \) molecule\(^7\).

The BMH and Morse potential functions in Equation 1 and 2 are used for the fourth P2-Na\(_2\)CoO\(_2\) phase, whereas the KKY2 and three-body potential functions in Equations 3 and 4 are employed to reproduce H\(_3\)O\(^+\) in the fourth P2-Na\(_2\)CoO\(_2\) phase\(^8\). The O-H bond generation and dissociation is treated based on the KKY2 potential. All parameters are listed in Table S5-8. The H trajectory in Figure 5c is drawn by 39 atoms. The O (H\(_3\)O\(^+\)) and Na trajectory in Figure 5d are depicted by 13 and 38 atoms, respectively.
References:
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Figure S1. Photographs of temperature and humidity control under hydrogen gas flow using a glass capillary cell, which is installed on the Debye-Scherrer camera at RIKEN Materials Science beamline BL44B2, SPring-8.
Figure S2. In situ SXPD patterns under various reductive conditions using the capillary cell. The primary peaks of the second Na$_x$CoO$_2$ phase and CoO are highest and lowest, respectively, when the first Na$_x$CoO$_2$ phase is treated at 260 °C for 12 min, which is the optimal condition. Note that no chemical reaction occurs at 250 °C.
Figure S3. Part of SXPD data during chemical reactions in Na$_x$CoO$_2$. The hydrogen gas flows into the capillary cell heated up to 260 °C from $t = 0$ to 12 min. During the flow, data are taken every 3 minutes. The hydrogen treatment is followed by the exposure to the air with 30%RH and 27 °C, the duration of which is about 10 h. In the meantime, data measurements are conducted every 18 min. Notice that the 002 reflection of P2-Na$_x$CoO$_2$ shifts to higher 2θ by the hydrogen treatment and then appears to return gradually after the humidification.
Figure S4. Results of the Rietveld analysis of the SXPD data at (a) $t < 0$, (b) $t = 22$, (c) $t = 374$, and (d) $t = 644$ min, which are refined with one, three, five, and four phases as indicated by green bars (calculated reflection positons), respectively. Black dots, red curves, and blue curves stand for observed data, calculated patterns, and the residual between them, respectively. Enlarged fitting results at higher $2\theta$ are insetted in each figure with the reliability factors based on Bragg intensities $R_I$ and weighted patterns $R_{wp}$.
**Figure S5.** Results of the Rietveld analysis of the SXPD data at (a) \( t < 0 \), (b) \( t = 22 \), (c) \( t = 374 \), and (d) \( t = 644 \) min, which are refined with one, three, five, and four phases as indicated by green bars (calculated reflection positions), respectively. Black dots, red curves, and blue curves stand for observed data, calculated patterns, and the residual between them, respectively. The figures on the right of phase are the reliability factors based on Bragg intensity \( R_I \) for each phase.
Figure S6. Bode plots with impedance spectroscopy on the hydrogen-treated (at 290 °C for 30 min) and untreated Na₅CoO₂ disks. Each plot is measured at 25 °C and 50% RH. Before each measurement, the disk is exposed under each measurement condition for 1 h.
Figure S7. Nyquist plots with impedance spectroscopy on the Na$_x$CoO$_2$ disk that is treated by hydrogen at 290 °C for 30 min before a series of measurements. Each plot is measured at 25 °C with increasing relative humidity: (a) 28% RH, (b) 30% RH, (c) 40% RH, (d) 50% RH, and (e) 60% RH. Before each measurement, the disk is exposed under each measurement condition for 1 h. Semicircle components observed in the range of high frequency are fitted by the least-square method (red curves) to obtain ionic conductivity.
Figure S8. Charge densities in the Na layer obtained by the MEM analysis of in situ SXPD data at $t < 0$, $t = 22$, and $t = 644$ min, which correspond to the (a) first, (b) second, and (d) fourth phases of P2-Na$_x$CoO$_2$. The site numbers 1, 2, and 3 for Na are indicated in each density. Contour lines are drawn from 0.0 to 4.0 e Å$^{-3}$ at intervals of 0.4 e Å$^{-3}$. For simplicity, the lower range of densities from 0.0 to 1.0 e Å$^{-3}$ is colored with gradations and the view range of densities is the same with that in Figure 5b, 5c, and 5d. Notice that the sites 1 and 3 in the fourth phase appear to be disordered as opposed to the site 2 and all the sites in the first and second phases.
Figure S9. Time evolution of the electron charge at the Na sites (a) 1, (b) 2, and (c) 3 for each Na$_x$CoO$_2$ phase, which are obtained by calculating the number of electron within the Na ionic radius in MEM charge densities. The total amounts of electron charge at the sites 1, 2, and 3 are plotted in (d) as a function of time. Blue arrows for the site 1 and 3 indicate gains in electron charge during chemical reactions.
Figure S10. Electric fields (red arrows) projected onto electrostatic potentials in the Na layer for the (a) first and (b) fourth Na$_x$CoO$_2$ phases. Contour lines in potentials are drawn from -14.4 to 23.0 eV at interval of 2.9 eV.
Table S1. Atomic sites, fractional coordinates x, y and z, occupancies g, and isotropic displacement parameters B of the first phase for P2-Na$_x$CoO$_2$, which have been obtained by the Rietveld analysis of the SXPD data at t < 0 min. The space group is P6$_3$/mmc (No. 194). Lattice parameters a and c, the composition, and the oxidation number calculated based on the composition are listed in Table 1. Notice that a small amount of electron is found at Na3 as a result of careful refinement.

| Atom | Site | x   | y   | z    | g     | B (Å$^2$) |
|------|------|-----|-----|------|-------|-----------|
| Na1  | 2b   | 0   | 0   | 1/4  | 0.218(3) | 1.9(1)$^{[a]}$ |
| Na2  | 2d   | 2/3 | 1/3 | 1/4  | 0.421(4) | 1.9(1)$^{[a]}$ |
| Na3  | 2c   | 1/3 | 2/3 | 1/4  | 0.049(4) | 1.9(1)$^{[a]}$ |
| Co   | 2a   | 0   | 0   | 0    | 1$^{[b]}$  | 0.334(8)  |
| O    | 4f   | 1/3 | 2/3 | 0.0849(1) | 1$^{[b]}$ | 0.53(3)   |

[a] The B parameters for Na1, 2, and 3 are maintained with an identical value while refined.
[b] The g parameters for Co and O are fixed at 1 in the final step since these values during the refinement process do not deviate from 1 within the error.
Table S2. Atomic sites, fractional coordinates $x$, $y$ and $z$, occupancies $g$, and isotropic displacement parameters $B$ of the second phase for P2-Na$_x$CoO$_2$, which have been obtained by the Rietveld analysis of the SXPD data at $t = 22$ min. The space group is $P6_3/mmc$ (No. 194). Lattice parameters $a$ and $c$, the composition, and the oxidation number calculated based on the composition are listed in Table 1. Notice that a larger amount of electron than that of the first phase is found at Na2 and Na3 as a result of careful refinement.

| Atom | Site | $x$  | $y$  | $z$  | $g$    | $B$ (Å$^2$) |
|------|------|------|------|------|--------|-------------|
| Na1  | 2$b$ | 0    | 0    | 1/4  | 0.053(3)| 0.65(5)$^a$|
| Na2  | 2$d$ | 2/3  | 1/3  | 1/4  | 0.806(3)| 0.65(5)$^a$|
| Na3  | 2$c$ | 1/3  | 2/3  | 1/4  | 0.177(3)| 0.65(5)$^a$|
| Co   | 2$a$ | 0    | 0    | 0    | 0.875(3)| 0.37(1)    |
| O    | 4$f$ | 1/3  | 2/3  | 0.0892(1)| 1$^b$ | 0.64(3)    |

$^a$ The $B$ parameters for Na1, 2, and 3 are maintained with an identical value while refined.

$^b$ The $g$ parameter for O is fixed at 1 in the final step since the value during the refinement process does not deviate from 1 within the error.
Table S3. Atomic sites, fractional coordinates \(x\), \(y\) and \(z\), occupancies \(g\), and isotropic displacement parameters \(B\) of the third phase for \(\text{P2-}\text{Na}_x\text{CoO}_2\), which have been obtained by the Rietveld analysis of the SXPD data at \(t = 374\) min. The space group is \(P6_3/mmc\) (No. 194). Lattice parameters \(a\) and \(c\), the composition, and the oxidation number calculated based on the composition are listed in Table 1. Notice that part of \(\text{Na}1\) is presumed to be exchanged for \(\text{H}_2\text{O}\) based on Raman spectroscopy and MEM charge densities.

| Atom  | Site | \(x\) | \(y\) | \(z\) | \(g\)     | \(B\) (Å\(^2\)) |
|-------|------|-------|-------|-------|----------|-----------------|
| \(\text{Na}/\text{H}_2\text{O} 1\) | 2b   | 0     | 0     | 1/4   | 0.152(3) | 1.00(7)[a]      |
| \(\text{Na}_2\)         | 2d   | 2/3   | 1/3   | 1/4   | 0.595(3) | 1.00(7)[a]      |
| \(\text{Na}_3\)         | 2c   | 1/3   | 2/3   | 1/4   | 0.090(4) | 1.00(7)[a]      |
| \(\text{Co}\)           | 2a   | 0     | 0     | 0     | 0.931(4) | 0.61(1)         |
| \(\text{O}\)            | 4f   | 1/3   | 2/3   | 0.0877(2) | 1[b] | 0.89(5)       |

[a] The \(B\) parameters for \(\text{Na}1\), 2, and 3 are maintained with an identical value while refined.

[b] The \(g\) parameter for \(\text{O}\) is fixed at 1 in the final step since the value during the refinement process does not deviate from 1 within the error.
Table S4. Atomic sites, fractional coordinates $x$, $y$ and $z$, occupancies $g$, and isotropic displacement parameters $B$ of the fourth phase for P2-$\text{Na}_x\text{CoO}_2$, which have been obtained by the Rietveld analysis of the SXPD data at $t = 644$ min. The space group is $P6_3/mmc$ (No. 194). Lattice parameters $a$ and $c$, the composition, and the oxidation number calculated based on the composition are listed in Table 1. Notice that part of Na1 and Na3 are presumed to be exchanged for $\text{H}_3\text{O}$ based on Raman spectroscopy and MEM charge densities, and the Na1 and Na3 sites adopt the disordered site $6h$ as observed in MEM charge densities.

| Atom   | Site | $x$   | $y$   | $z$   | $g$    | $B$ (Å²) |
|--------|------|-------|-------|-------|--------|----------|
| Na/H₃O 1 | 6h  | 0.950(8) | 0.050(8) | 1/4 | 0.084(2) | 1.4(2)^[a] |
| Na2     | 2d  | 2/3   | 1/3   | 1/4  | 0.428(5) | 1.4(2)^[a] |
| Na/H₃O 3 | 6h  | 0.39(4) | 0.61(4) | 1/4 | 0.037(2) | 1.4(2)^[a] |
| Co      | 2a  | 0     | 0     | 0    | 0.927(5) | 0.52(2) |
| O       | 4f  | 1/3   | 2/3   | 0.0832(2) | 1^[b] | 0.66(6) |

^[a] The $B$ parameters for Na1, 2, and 3 are maintained with an identical value while refined.

^[b] The $g$ parameter for O is fixed at 1 in the final step since the value during the refinement process does not deviate from 1 within the error.
### Table S5. BMH potential parameters for the fourth Na\textsubscript{x}CoO\textsubscript{2} phase.

| i         | Z\textsubscript{i} | a\textsubscript{i} (Å) | b\textsubscript{i} (Å) | c\textsubscript{i} (kJ\textsuperscript{1/2} mol\textsuperscript{-1/2} Å\textsuperscript{3}) |
|-----------|---------------------|-------------------------|-------------------------|---------------------------------------------------------------------------------|
| O (CoO\textsubscript{2}) | -1.21               | 1.886                   | 0.180                   | 84.91                                                                            |
| Co        | 1.84                | 0.915                   | 0.100                   | 0.00                                                                             |
| Na        | 1.00                | 1.218                   | 0.120                   | 25.41                                                                            |
| H         | 0.46                | 0.035                   | 0.058                   | 0.00                                                                             |
| O (H\textsubscript{2}O) | -0.92               | 1.728                   | 0.124                   | 48.86                                                                            |

### Table S6. Morse potential parameters for the fourth Na\textsubscript{x}CoO\textsubscript{2} phase.

| i−j       | D\textsubscript{ij} (kJ mol\textsuperscript{-1}) | β\textsubscript{ij} (Å\textsuperscript{-1}) | r\textsubscript{ij} (Å) |
|-----------|-----------------------------------------------|---------------------------------|----------------|
| Na–O (CoO\textsubscript{2}) | 125.5                                         | 3.60                             | 2.45            |
| Co–O (CoO\textsubscript{2}) | 104.6                                         | 2.55                             | 1.93            |

### Table S7. KKY2 potential parameters for the fourth Na\textsubscript{x}CoO\textsubscript{2} phase.

| i−j       | D\textsubscript{1ij} (kJ mol\textsuperscript{-1}) | β\textsubscript{1ij} (Å\textsuperscript{-1}) | D\textsubscript{2ij} (kJ mol\textsuperscript{-1}) | β\textsubscript{2ij} (Å\textsuperscript{-1}) | D\textsubscript{3ij} (kJ mol\textsuperscript{-1}) | β\textsubscript{3ij} (Å\textsuperscript{-1}) | r\textsuperscript{ij} (Å) |
|-----------|-----------------------------------------------|---------------------------------|---------------------------------|----------------|---------------------------------|----------------|----------------|
| H–O (H\textsubscript{2}O) | 13711                                        | 7.4                             | -523                            | 3.13           | 8.3                             | 12.8            | 1.283          |
| H–O (CoO\textsubscript{2}) | 13711                                        | 7.4                             | -523                            | 3.13           | 8.3                             | 12.8            | 1.283          |

### Table S8. Three-body potential parameters for the fourth Na\textsubscript{x}CoO\textsubscript{2} phase.

| j−i−k     | f\textsubscript{ik} (kJ) | θ\textsubscript{ij} (°) | r\textsubscript{im} (Å) | g\textsubscript{r} (Å\textsuperscript{-1}) |
|-----------|-------------------------|------------------------|------------------------|---------------------------------|
| H–O–H (H\textsubscript{2}O) | 1.15×10\textsuperscript{-22} | 99.5                   | 1.43                    | 9.2                             |