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Electronic Supplementary Information for

Correlation between structure and mixed ionic–electronic conduction mechanism for $(La_{1-x}Sr_x)CoO_{3-\delta}$ using synchrotron X-ray analysis and first principle calculations

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Table S1 First principle calculation conditions for estimating band structure

Parameters	Fig.12 (a)	Fig.12 (b)	Fig.12 (c)	Fig.12 (d)	Fig.12 (e)	Fig.12 (f)
Lattice parameters of *a* and *b*-axis (Å)	5.44110	5.44511	5.42491	5.44110	5.44511	5.42491
Lattice parameter of *c*-axis (Å)	13.08837	13.18596	13.22622	13.08837	13.18596	13.22622
x of oxygen site	0.4496	0.4598	0.4742	0.4496	0.4496	0.4496

Table S2 First principle calculation conditions for estimating activation energies of oxygen diffusion

Parameters	○	●	△	▲
Lattice parameters of *a* and *b*-axis (Å)	5.44110 (*x* = 0.00), 5.44511 (*x* = 0.25), 5.42491 (*x* = 0.50)	5.44511 (*x* = 0.0, 0.25, 0.50)	5.44110 (*x* = 0.00), 5.44511 (*x* = 0.25), 5.42491 (*x* = 0.50)	5.44110 (x = 0.0, 0.25, 0.50)
Lattice parameter of *c*-axis (Å)	13.08837 (*x* =0.00), 13.18596 (*x* =0.25), 13.22622 (*x* =0.50)	13.18596 (*x* = 0.0, 0.25, 0.50)	13.08837 (*x* =0.00), 13.18596 (*x* =0.25), 13.22622 (*x* =0.50)	13.08837 (x = 0.0, 0.25, 0.50)
x(O) of oxygen site	0.4496 (*x* =0.00), 0.4598 (*x* =0.25), 0.4496 (*x* =0.50)	0.4496 (*x* =0.00), 0.4598 (*x* =0.25), 0.4496 (*x* =0.50)	0.4496 (x = 0.0, 0.25, 0.50)	0.4496 (x = 0.0, 0.25, 0.50)
La_1, La_2, La_3 site	La_1, La_2, La_3 site : La	La_1, La_2, La_3 site : La	La_1, La_2, La_3 site : La	La_1, La_2, La_3 site : La, (*x* = 0.00) La_1, La_2, La_3 site : Sr, La, La (*x* = 0.167) La_1, La_2, La_3 site : Sr, Sr, La (*x* = 0..333) La_1, La_2, La_3 site : Sr (*x* = 0.50)

Note: *x*(O) : the oxide ion site fractional coordinate.

Table S3 Positional parameters for $(La_{1-x}Sr_x)CoO_{3-\delta}$ in Rietveld refinements

Space group $R\bar{3}c$ setting 1 (No. 167) $\alpha = \beta = 90°$, $\gamma = 120°$			
Atoms	Sites	Site occupancy	Atomic coordinates
La, Sr	6*a*	1	0, 0, ¼
Co	6*b*	1	0, 0, 0
O	18*e*	*g*(O) ~ 1	*x* ~ 0.5, 0, ¼

Note: g(O) : the oxide ion site occupancy calculated from Co valence estimated by potentiometric-titration.

Table S4 Structural parameters and reliability factors of $(La_{1-x}Sr_x)CoO_{3-\delta}$ between $x = 0.00$ and 0.50 from Rietveld refinements

Sites	Parameters	$x = 0$	$x = 0.05$	$x = 0.10$	$x = 0.15$	$x = 0.20$	$x = 0.25$	$x = 0.30$	$x = 0.35$	$x = 0.40$	$x = 0.45$	$x = 0.50$
La, Sr (6*a*)	U_{11}, U_{22} (Å^2)	0.00386(9)	0.00387(10)	0.00489(9)	0.00431(8)	0.00445(8)	0.00449(9)	0.00448(9)	0.00464(10)	0.00459(10)	0.00449(9)	0.00454(9)
	U_{33} (Å^2)	0.00436(8)	0.00434(9)	0.00455(8)	0.00445(9)	0.00439(9)	0.00431(9)	0.00431(9)	0.00458(10)	0.00460(9)	0.00469(9)	0.00455(8)
	U_{12} (Å^2)	0.0025(2)	0.0025(2)	0.0026(2)	0.0028(2)	0.0027(2)	0.0027(2)	0.0028(2)	0.0028(2)	0.0029(2)	0.0029(2)	0.0028(2)
	U_{13} U_{23} (Å^2)	0.0000(2)	0.0000(3)	0.0001(2)	0.0000(2)	-0.00001(2)	-0.0001(2)	-0.0002(2)	0.0000(3)	-0.0002(3)	-0.0003(2)	-0.0003(2)
Co (6*b*)	U_{11}, U_{22} (Å^2)	0.00253(9)	0.0026(10)	0.00323(9)	0.00292(10)	0.00314(9)	0.00302(10)	0.00304(10)	0.00298(9)	0.00300(10)	0.00303(10)	0.00301(9)
	U_{33} (Å^2)	0.00317(9)	0.00323(10)	0.00360(9)	0.00325(10)	0.00303(8)	0.00302(10)	0.00299(10)	0.00287(9)	0.00290(10)	0.00292(10)	0.00291(8)
	U_{12} (Å^2)	0.00123(9)	0.00131(10)	0.00145(8)	0.00159(10)	0.00151(9)	0.00159(10)	0.00154(10)	0.00153(9)	0.00170(10)	0.00159(10)	0.00154(9)
	U_{13} U_{23} (Å^2)	-0.0010(4)	-0.0012(5)	-0.0012(5)	-0.0005(6)	-0.0007(5)	-0.0005(5)	-0.0007(5)	-0.0005(4)	-0.0002(5)	-0.0004(5)	-0.0003(4)
O (18*e*)	*g*(O)	1.00	1.00	1.00	1.00	0.998	0.995	0.991	0.988	0.984	0.980	0.977
	3-δ	3.00	3.00	3.00	3.00	2.994	2.985	2.973	2.964	2.952	2.940	2.931
	x(O)	0.4496(4)	0.4516(4)	0.4534(4)	0.4552(4)	0.4574(4)	0.4598(4)	0.4624(4)	0.4651(3)	0.4683(3)	0.4715(3)	0.4742(3)
	U_{11}, U_{22} (Å^2)	0.0058(3)	0.0062(4)	0.0071(3)	0.0073(4)	0.0069(3)	0.0063(3)	0.0061(2)	0.0066(3)	0.0066(4)	0.0066(3)	0.0064(4)
	U_{33} (Å^2)	0.0064(3)	0.0078(3)	0.0080(3)	0.0079(4)	0.0077(3)	0.0074(3)	0.0068(3)	0.0072(3)	0.0072(4)	0.0072(3)	0.0075(4)
	U_{12} (Å^2)	0.0022(10)	0.0022(10)	0.0026(10)	0.0017(10)	0.0019(10)	0.0012(10)	0.0012(9)	0.0018(10)	0.0017(10)	0.0019(10)	0.0019(10)
	U_{13} U_{23} (Å^2)	-0.0059(8)	-0.0056(8)	-0.0055(8)	-0.0058(8)	-0.0057(8)	-0.0064(8)	-0.0064(8)	-0.0062(7)	-0.0056(8)	-0.0057(8)	-0.0049(7)
	Lattice parameters	$x = 0$	$x = 0.05$	$x = 0.10$	$x = 0.15$	$x = 0.20$	$x = 0.25$	$x = 0.30$	$x = 0.35$	$x = 0.40$	$x = 0.45$	$x = 0.50$
	a, b-axis (Å)	5.44110(4)	5.44657(4)	5.44795(4)	5.44850(4)	5.44731(3)	5.44511(4)	5.44208(4)	5.43550(5)	5.43576(5)	5.43173(4)	5.42491(2)
	c-axis (Å)	13.08837(7)	13.11980(8)	13.14057(7)	13.15758(6)	13.17271(6)	13.18596(6)	13.19695(6)	13.19934(8)	13.21706(8)	13.22491(7)	13.22622(7)
	r_{Co-O} (Å)	1.9318(3)	1.9331(3)	1.9331(3)	1.9328(3)	1.9318(3)	1.9303(3)	1.9285(3)	1.9256(3)	1.9248(3)	1.9228(3)	1.9201(3)
	Co-O-Co (°)	164.040(7)	164.671(7)	165.286(7)	165.355(7)	166.785(7)	167.543(7)	168.050(7)	168.487(7)	170.689(7)	171.006(7)	171.636(7)
	R_{wp} (%)	5.353	4.386	4.326	3.920	3.709	3.763	3.684	4.175	4.038	3.552	3.961
	S	1.4192	1.1751	1.0646	0.9883	1.0014	0.9855	1.0335	1.1297	1.1474	1.0617	1.2010
	R_B (%)	0.929	1.050	1.389	1.432	1.209	1.356	1.356	1.281	1.268	1.345	1.507

Note: U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, and U_{23}: the atomic anisotropic displacement parameter R_{wp} : the reliability weighted pattern factors, *S* : the goodness of fit factors (= R_{wp}/R_e, R_e: the reliability expected factor), R_B : the reliability Bragg factor.

Table S5 Reliability factor and full width at half maximum of $(|F_{MEM}|-|F_{obs}|)/\sigma_{obs}$ of Maximum Entropy Method analysis

Parameters	x = 0.00	x = 0.05	x = 0.10	x = 0.15	x = 0.20	x = 0.25	x = 0.30	x = 0.35	x = 0.40	x =0.45	x = 0.50
R_w (%)	1.2475	1.2139	1.0458	1.3795	1.4092	1.4400	1.3513	1.4799	1.4039	1.3599	1.4070
FWHM of $(\|F_{MEM}\|-\|F_{obs}\|)/\sigma_{obs}$	0.646549	0.550178	0.660847	0.394815	0.625231	0.714376	0.502304	0.660986	0.632016	0.646843	0.778402

Note: R_w : reliability structure factor of MEM analysis, FWHM : full width at half maximum, $|F_{MEM}|$: structure factor calculated by MEM analysis, $|F_{obs}|$: observed structure factors, σ_{obs} : estimated standard deviations of observed structure factor.