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Supporting Information

Correlation of Lithium Ion Distribution and X-ray Absorption Near-Edge Structure in O3- and O2-Lithium Cobalt Oxides from First-Principle Calculation

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Table S1. Crystallographic parameters and XANES simulating conditions

O3-$LiCoO_2$	Space group:	*R*-3*m*
	Unitcell formula:	$Li_3Co_3O_6$
	Size of supercell:	3 × 3 × 1
k -point grid[b]:	SCF (grand state)	12 × 12 × 12
	SCF & XANES (exicied state)	8 × 8 × 4

Lattice parameter:	*a*	*b*	*c*
	2.816	=*a*	14.054

	functional coodination of atomic position		
	x	*y*	*z*
Li1	0	0	0
Co1	0	0	1/2
O1	0	0	0.2395

O2-$LiCoO_2$	Space group:	$P6_3/mc$
	Unitcell formula:	$Li_2Co_2O_4$
	Size of supercell:	3 × 3 × 1
k -point grid[b]:	SCF (grand state)	12 × 12 × 12
	SCF & XANES (exicied state)	8 × 8 × 8

Lattice parameter:	*a*	*b*	*c*
	2.8025	=*a*	9.5358

	functional coodination of atomic position		
	x	*y*	*z*
Li1	1/3	2/3	0.2412
Co1	2/3	1/3	0
O1	0	0	0.1082
O2	2/3	1/3	0.3917

O1-$Li_{0.5}CoO_2$	Space group:	*P*2/*m*
	Unitcell formula:	$LiCo_2O_4$
	Size of supercell:	2 × 3 × 3
k -point grid[b]:	SCF (grand state)	12 × 12 × 12
	SCF & XANES (exicied state)	4 × 4 × 4

Lattice parameter:	*a*	*b*	*c*
	4.8653	2.8093	5.0633
	β = 108.685		

	functional coodination of atomic position		
	x	*y*	*z*
Li1	0	0	0
Co1	0	0	1/2
Co2	0	1/2	1/2
O1	0.2337	0	0.7066
O2	0.7355	1/2	0.7058

$T^{\#}2$-$Li_{0.5}CoO_2$	Space group:	*P*2
	Unitcell formula:	$Li_2Co_4O_8$
	Size of supercell:	3 × 2 × 1
k -point grid[b]:	SCF (grand state)	12 × 12 × 12
	SCF & XANES (exicied state)	4 × 4 × 4

Lattice parameter:	*a*	*b*	*c*
	2.8547	9.7901	4.8648

	functional coodination of atomic position		
	x	*y*	*z*
Li1	0	1/2	0.7314
Li2	0	0	0
Co1	0.8519	0.7500	0.3661
Co2	0.359	0.7500	0.8654
O1	0.6496	0.1512	0.1978
O2	0.3502	0.6508	0.5337
O3	0.1421	0.1525	0.7031
O4	0.8578	0.6531	0.0285

O1-CoO_2	Space group:	*P*-3*m*1
	Unitcell formula:	CoO_2
	Size of supercell:	3 × 3 × 3
k -point grid[b]:	SCF (grand state)	12 × 12 × 12
	SCF & XANES (exicied state)	8 × 8 × 4

Lattice parameter:	*a*	*b*	*c*
	2.8222	=*a*	4.2929

	functional coodination of atomic position		
	x	*y*	*z*
Co1	0	0	0
O1	1/3	2/3	0.2341

O2-CoO_2	Space group:	$P6_3/mc$
	Unitcell formula:	Co_2O_4
	Size of supercell:	3 × 3 × 1
k -point grid[b]:	SCF (grand state)	12 × 12 × 12
	SCF & XANES (exicied state)	8 × 8 × 8

Lattice parameter:	*a*	*b*	*c*
	2.8264[a]	=*a*	8.7259[a]

	functional coodination of atomic position		
	x	*y*	*z*
Co1	2/3	1/3	0
O1	0	0	0.1058
O2	2/3	1/3	0.3942

[a] Optimized using WIEN2k.

[b] GS and ES denote the ground and exctited states, respectively.

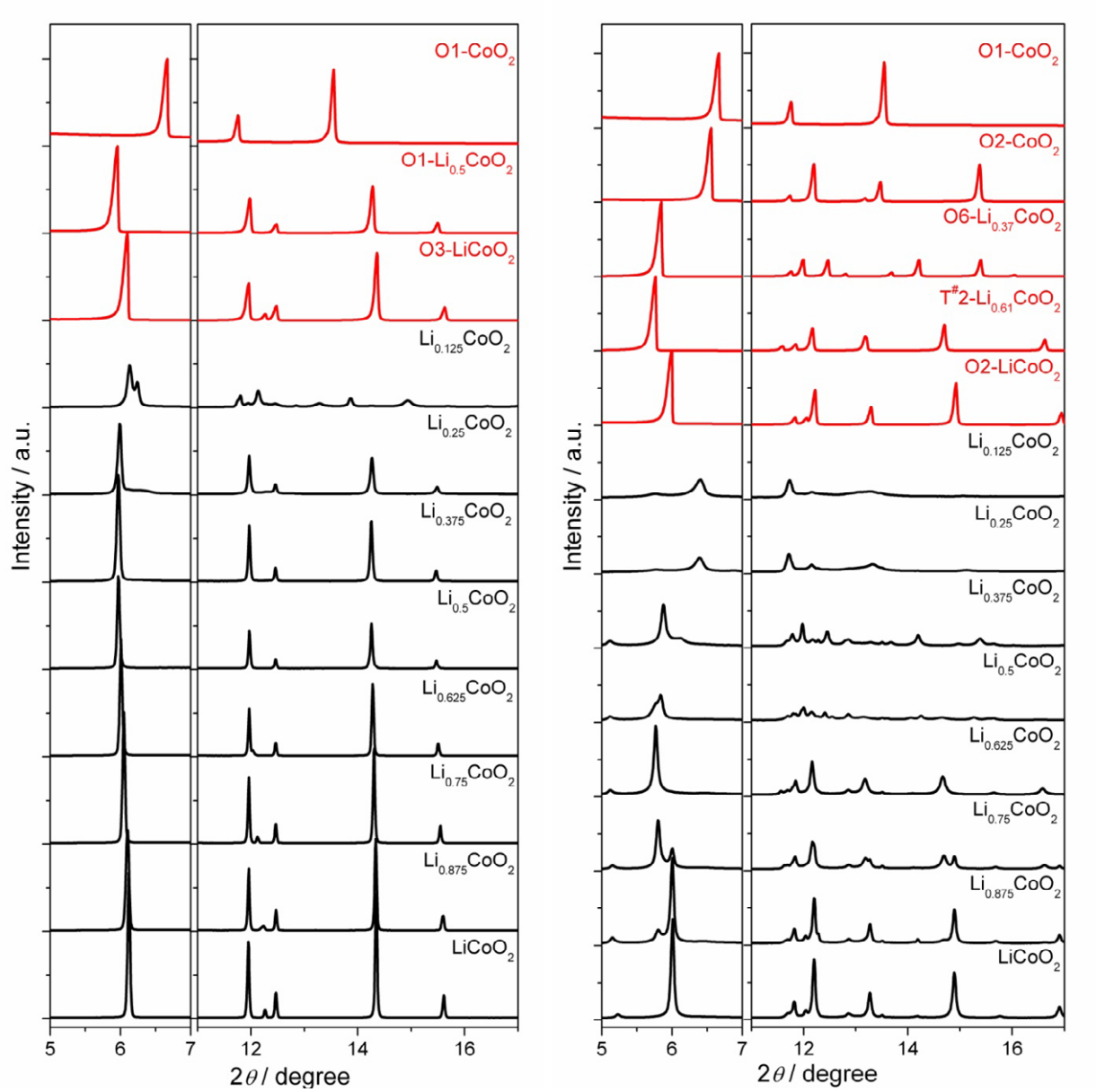

Figure S2. Synchrotron X-ray diffraction patterns of electrochemical lithium-ion de-intercalated samples of O3-$LiCoO_2$ and O2-$LiCoO_2$ drawn by black lines. The simulated patterns are also displayed by red lines.