Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

The origin of heavy elemental doping to relieve the lattice thermal vibration of layered materials for high energy density Li ion cathodes

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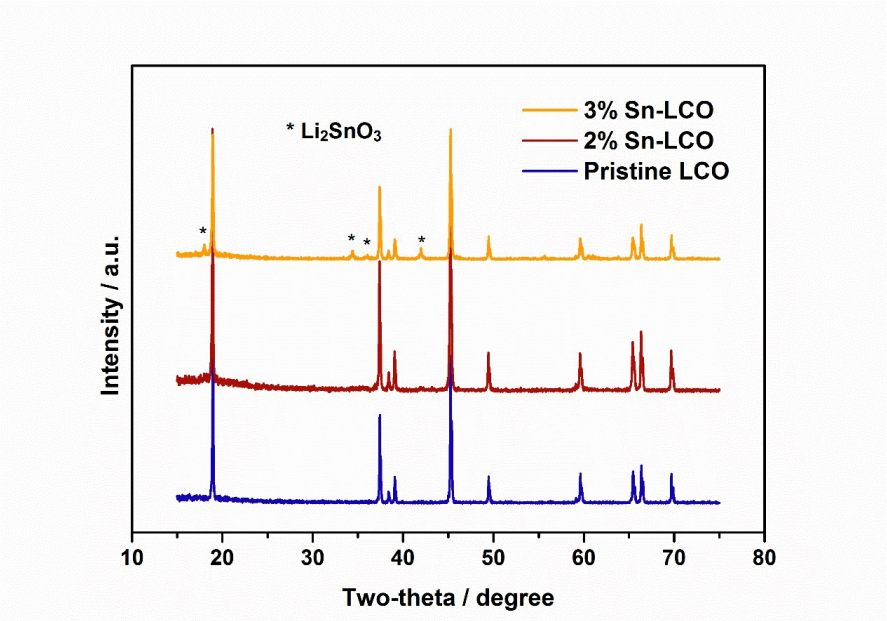

Figure S1. XRD patterns of undoped $LiCoO_2$ (Pristine-LCO), and Sn-doped $LiCoO_2$ at 2% and 3% doping amount.

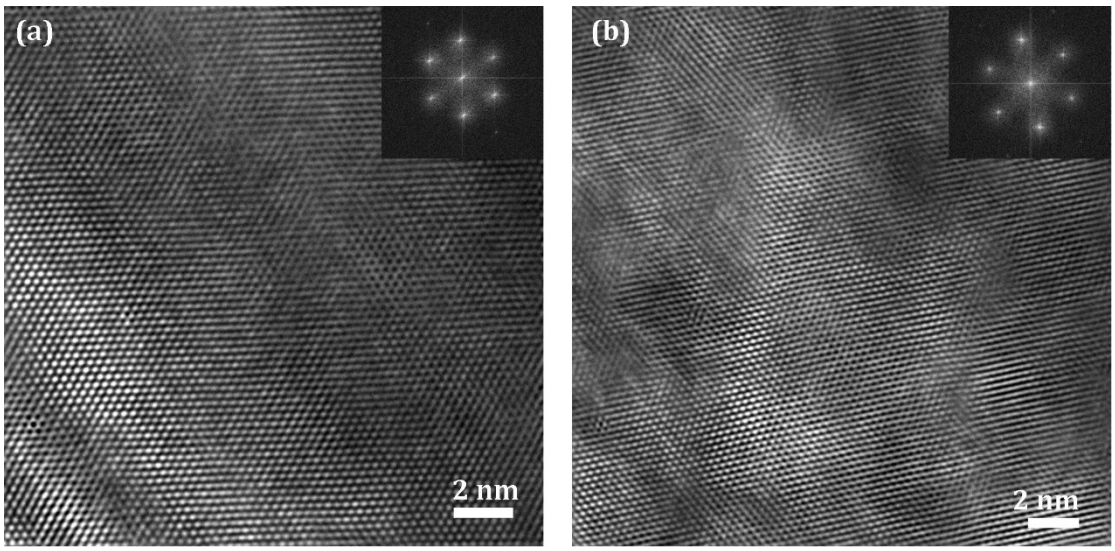

Figure S2. The HRTEM images and the corresponding FFT patterns for (a) LCO and (b) SLCO

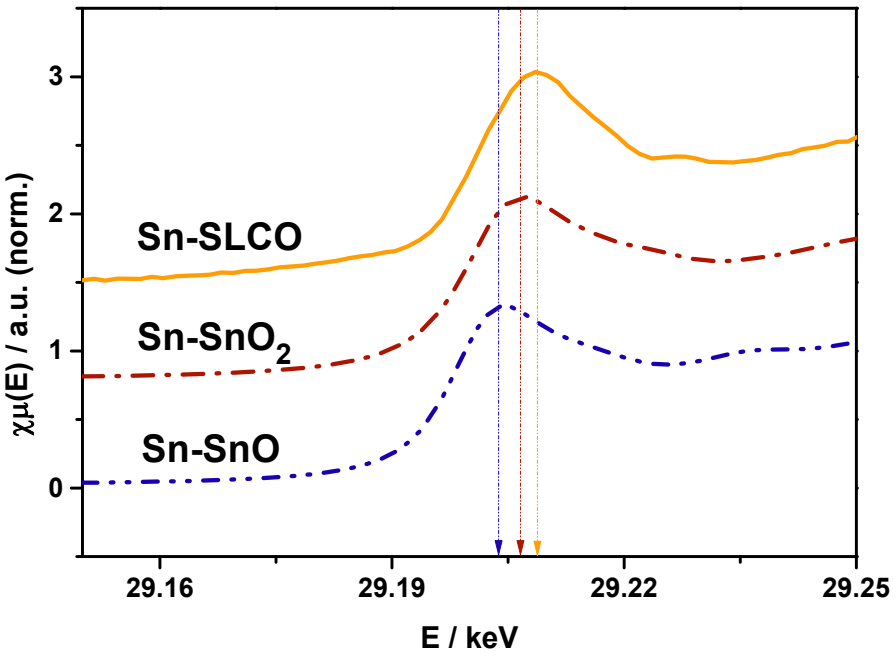

Figure S3 XANES spectra of SLCO and two reference materials, SnO and SnO_2.

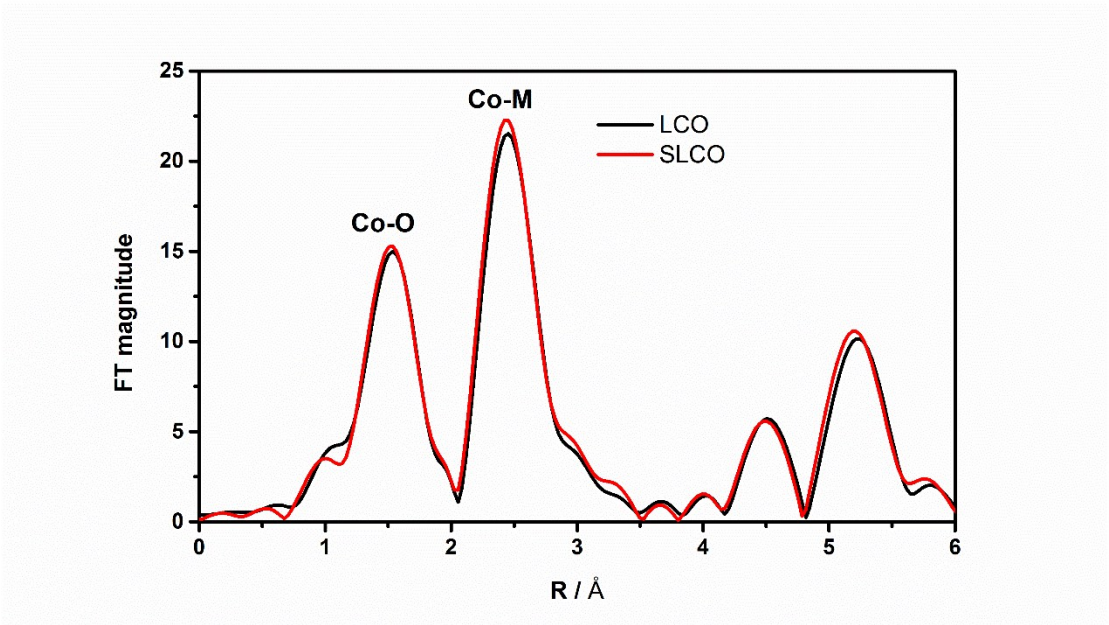

Figure S4. The k^3-weighed Fourier transformed magnitude Co *K*-edge EXAFS spectra of LCO and SLCO

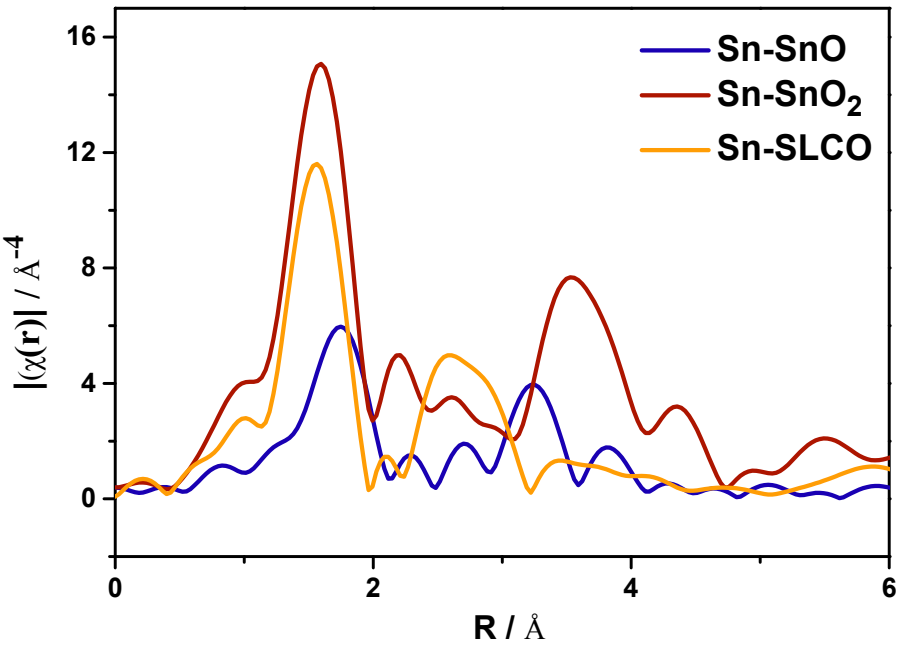

Figure S5 k^3-weighted Fourier transformed magnitude Sn *K*-edge EXAFS spectra of SLCO and also the two reference materials.

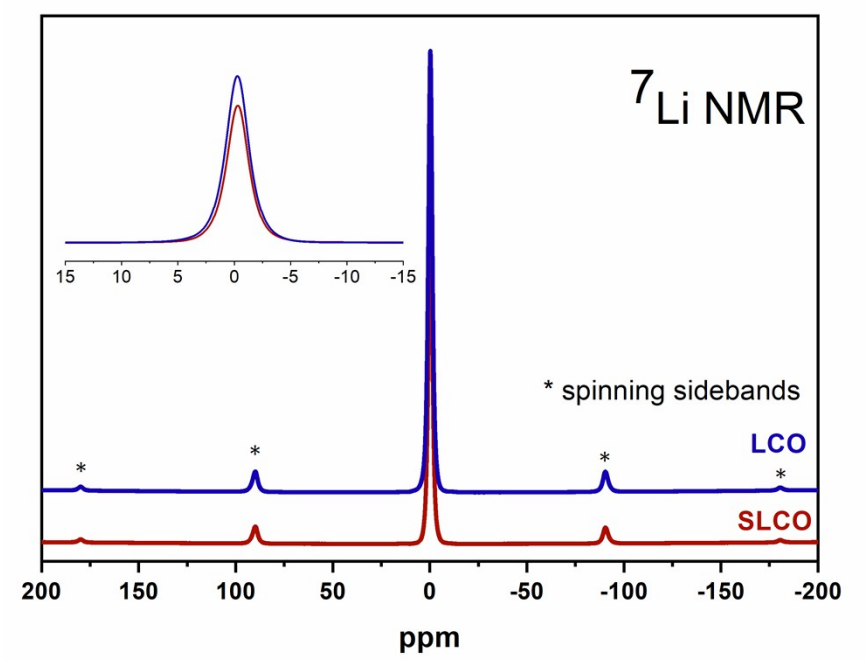

Figure S6 ^{7}Li NMR for the doped and undoped sample.

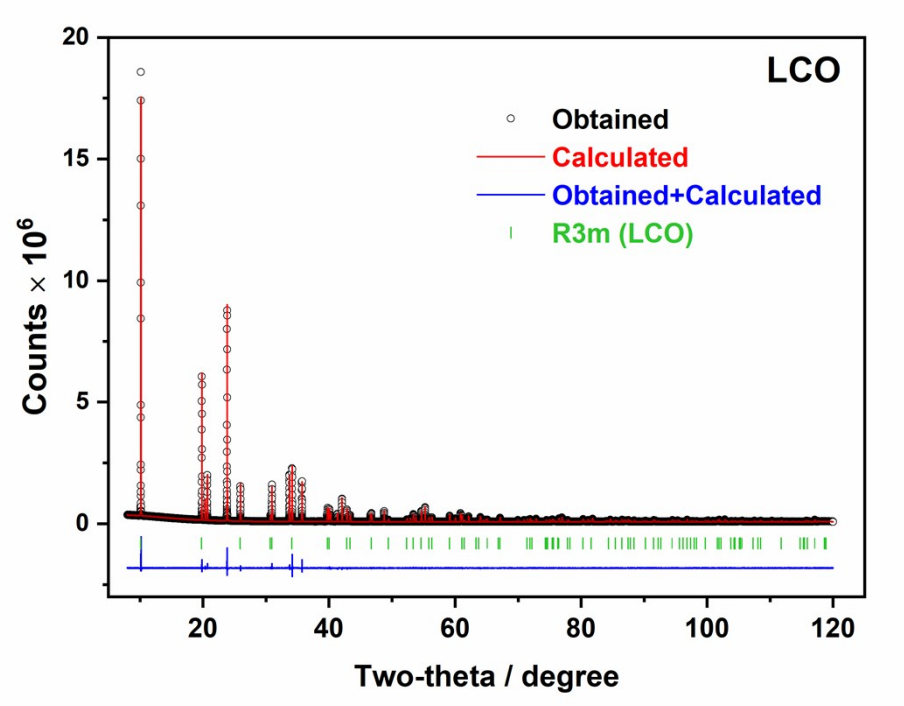

Figure S7. Rietveld refinement on synchrotron XRD pattern of LCO

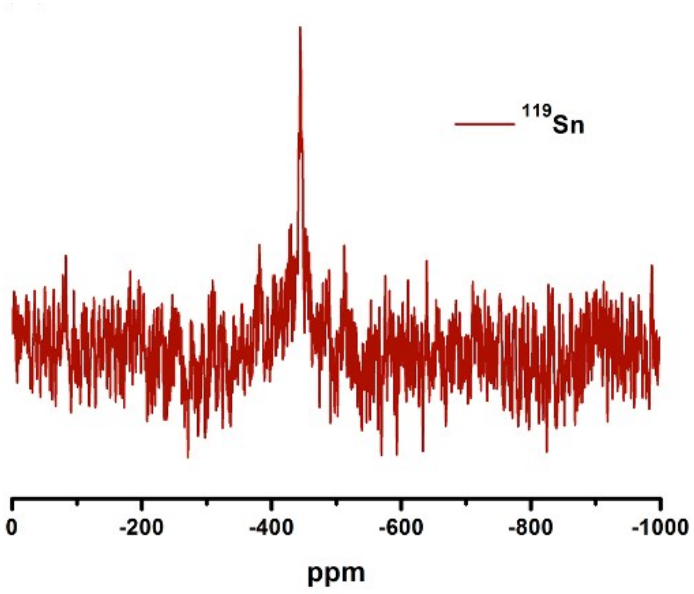

Figure S8. ^{119}Sn MAS NMR spectrum of Sn in SLCO.

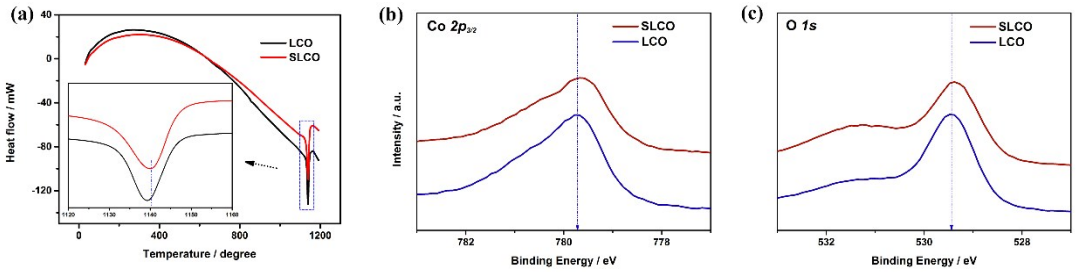

Figure S9. **DSC profiles and fine XPS spectra for LCO and SLCO.** (a) DSC profiles for LCO and SLCO samples. (b) Co $2p_{3/2}$ and O *1s* (c) region of the XPS spectra of LCO and SLCO.

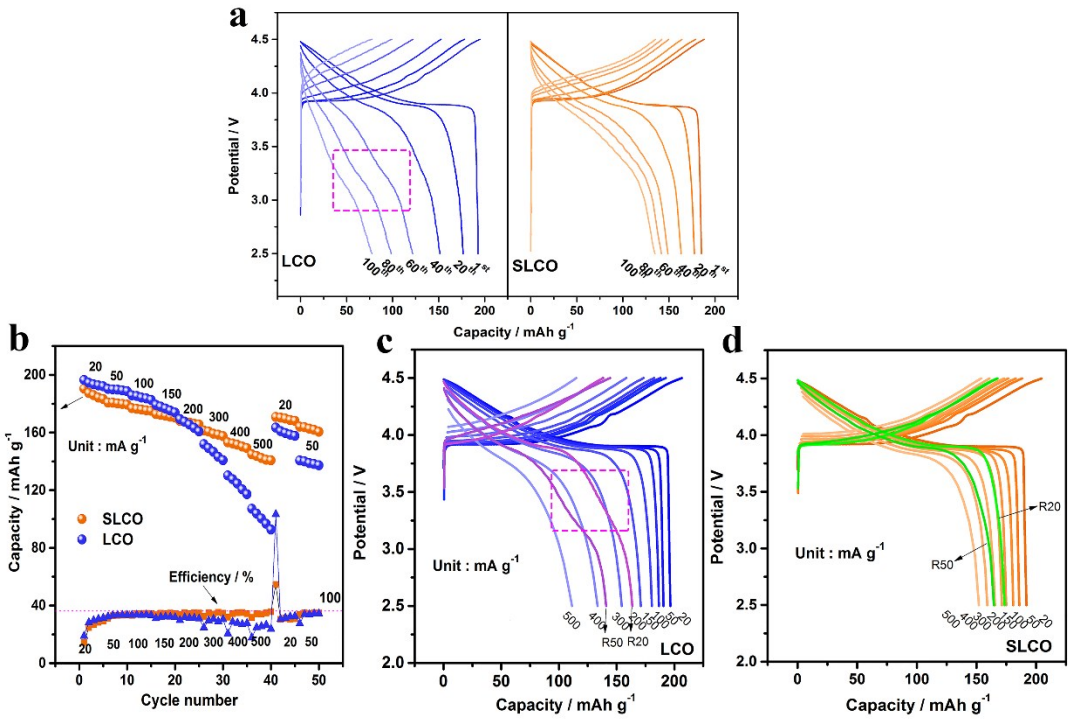

Figure S10. Electrochemical charge/discharge details for LCO and SLCO. (a) Charge/discharge profiles at different cycles when LCO and SLCO were cycled in the potential range of 2.5-4.5 V. (b) Rate capabilities and Coulombic efficiency of the two samples. Charge/discharge profiles at various current densities of LCO (c) and SLCO (d).

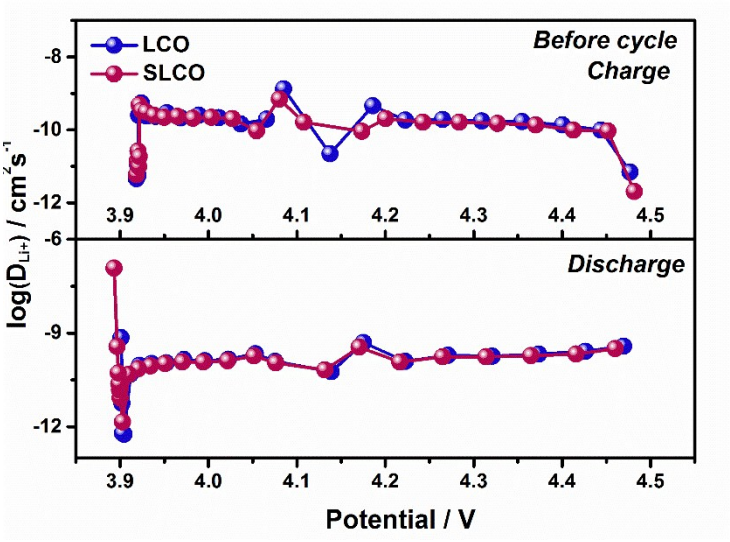

Figure S11. Lithium diffusion coefficients as calculated from GITT curves for the charge and discharge process in the first cycle.

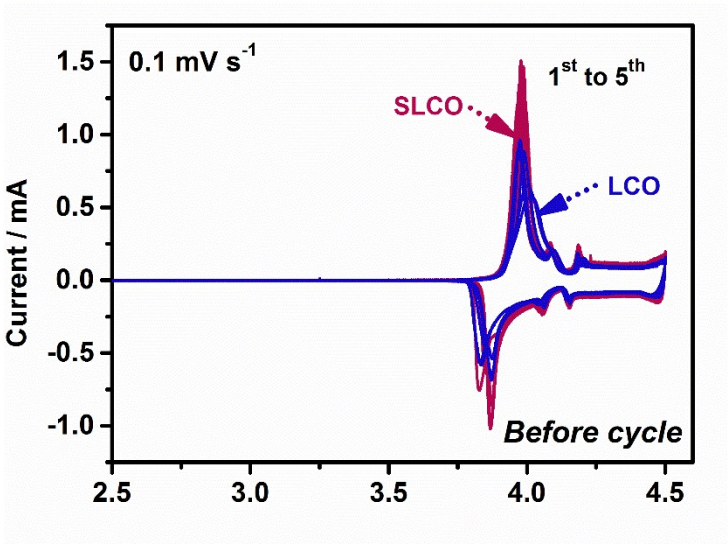

Figure S12. CV curves obtained after cell assembly.

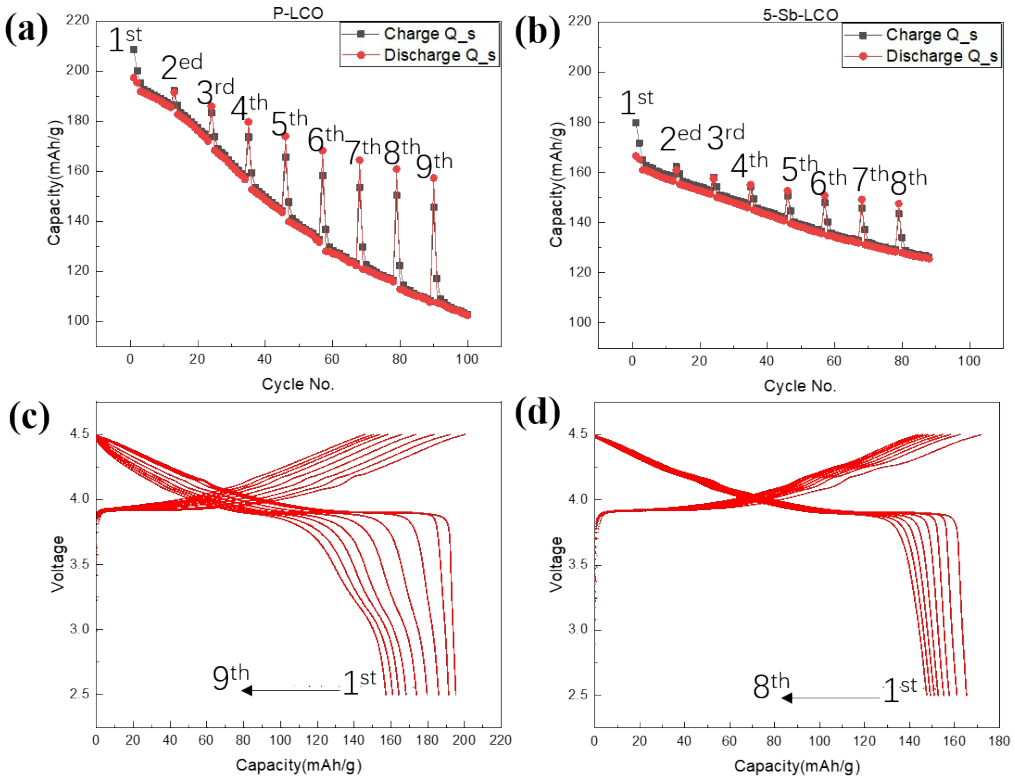

Figure S13. Electrochemical properties of pristine LCO and 5% Sb-doped LCO (Sb-LCO). The cycling performance was evaluated using 10 cycles under the current of 200 mA g^{-1} followed by 1 cycle under 20 mA g^{-1} of (a) LCO and (b) Sb-LCO; the detailed charge/discharge profiles of selected cycles for (c) LCO and (d) Sb-LCO.

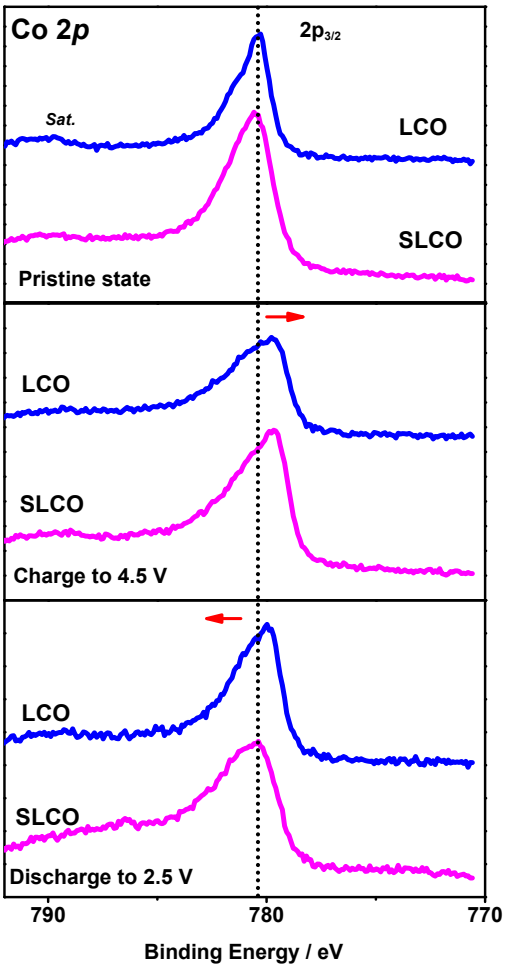

Figure S14. XPS spectra in the Co 2*p* region collected for the pristine electrodes, the electrodes charged to 4.5 V, and discharged to 2.5 V.

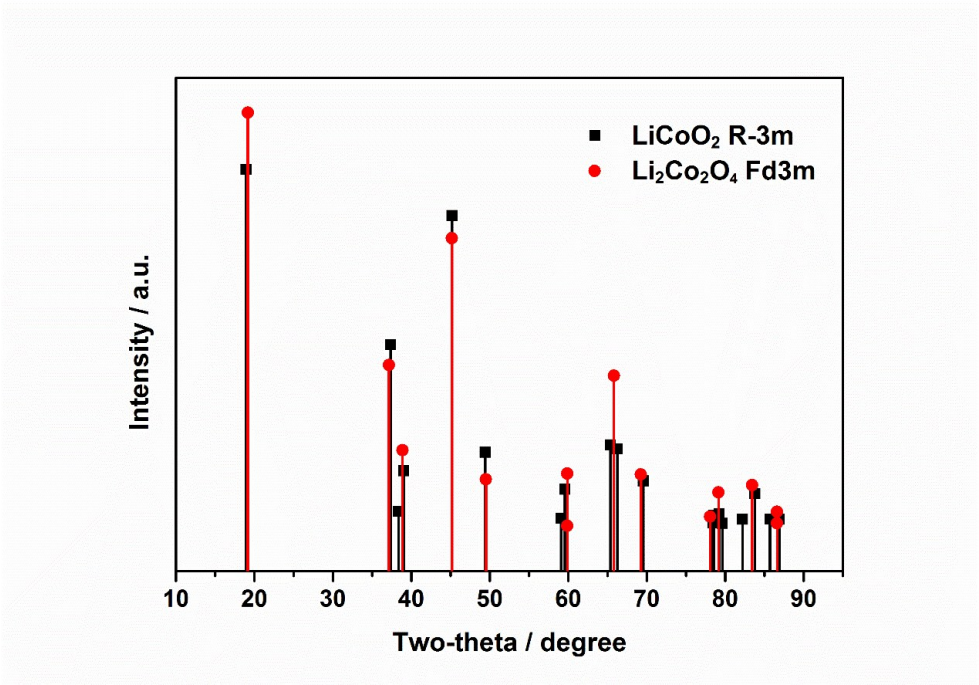

Figure S15. Calculated diffraction patterns of hexagonal $LiCoO_2$ (R-3m) and spinel $Li_2Co_2O_4$ (Fd3m)

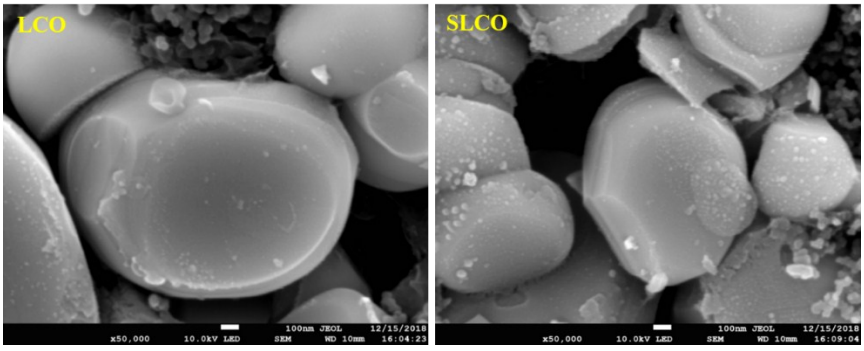

Figure S16. SEM images of LCO and SLCO after 50 cycles at 200 mA g^{-1}.

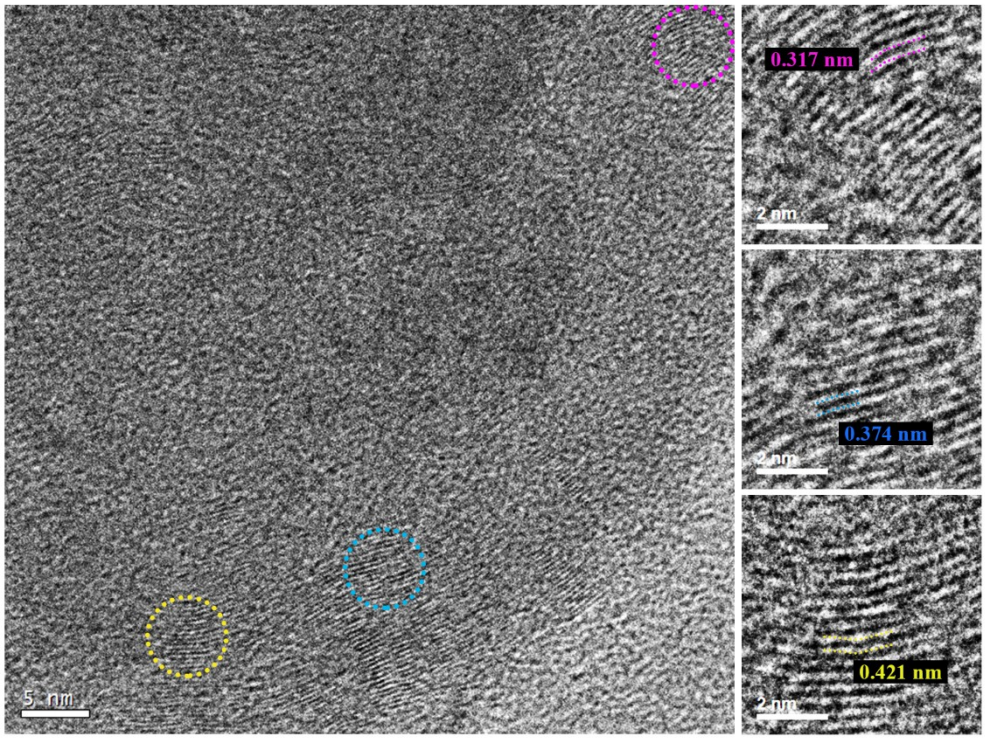

Figure S17 The HRTEM of LCO after 100 cycles at 200 mA g^{-1} and the enlarged parts to show the lattice fringes

Table S1: The elemental composition and structural information obtained from ICP, EXAFS and structural refinement.

	ICP results*			Bond length fitted from EXAFS data			
	Li (RSD[$])	Co (RSD)	Sn (RSD)	**Bond$_{(shell)}$**	R (Å)	σ^2 (Å^2)	r-factor
LCO	0.9822 (0.28%)	1.0038 (0.87%)		**Co-O**	1.916	0.00234	0.0067
				Co-M	2.825	0.00246	
SLCO	0.9837 (0.27%)	0.9902 (0.73%)	0.0136 (1.28%)	**Co-O**	1.909	0.00205	0.0060
				Co-M	2.822	0.00218	

Selected crystallographic parameters of LCO and SLCO

Atom	**Site**	***x***	***y***	***z***	**occupancy**	**B_{iso} (Å^2)**
LCO (space group: *R*-3*m*, No. 166): *a*=*b*=2.8162(2) Å, *c*=14.0529(5) Å, *V*=96.52(1) Å^3, R_{wp}=5.1 %,R_p=3.68 %						
Li^+	3*b*	0	0	1/2	1	**0.73(8)**
Co^{3+}	3*a*	0	0	0	1	**0.26(2)**
O^{2-}	6*c*	0	0	0.2612(2)	0.99(1)	**0.36(3)**
SLCO (space group: *R*-3*m*, No. 166): *a*=*b*=2.8153(1) Å, *c*=14.0605(2) Å, *V*=96.51(1) Å^3, R_{wp}=4.37 %,R_p=3.27 %						
Li^+	3*b*	0	0	1/2	1	**0.52(9)**
Co^{3+}	3*a*	0	0	0	0.959(3)	**0.09(2)**
Sn^{4+}	3*a*	0	0	0	0.038(3)	**0.09(2)**
O^{2-}	6*c*	0	0	0.2612(2)	0.99(1)	**0.06(2)**

*All samples were analyzed three times and averaged.

[$] Relative standard derivation.

Table S2. Results from different initial structures in refinement

Atom	Site	*x*	*y*	*z*	occupancy
Structure I: initial structure					
Li^{+}	3*b*	0	0	1/2	0.96
Sn^{4+}	3*b*	0	0	1/2	0.04
Co^{3+}	3*a*	0	0	0	1
O^{2-}	6*c*	0	0	0.2612	1
Structure I: refined structure					
Li^{+}	3*b*	0	0	1/2	1
Sn^{4+}	3*b*	0	0	1/2	0
Co^{3+}	3*a*	0	0	0	1
O^{2-}	6*c*	0	0	0.2612	1
Structure II: initial structure					
Li^{+}	3*b*	0	0	1/2	0.98
Sn^{4+}	3*b*	0	0	1/2	0.02
Co^{3+}	3*a*	0	0	0	0.98
Sn^{4+}	3*a*	0	0	0	0.02
O^{2-}	6*c*	0	0	0.2612	1
Structure II: refined structure					
Li^{+}	3*b*	0	0	1/2	1
Sn^{4+}	3*b*	0	0	1/2	0
Co^{3+}	3*a*	0	0	0	0.96
Sn^{4+}	3*a*	0	0	0	0.04
O^{2-}	6*c*	0	0	0.2612	1
Structure III: initial structure					
Li^{+}	3*b*	0	0	1/2	1
Co^{3+}	3*a*	0	0	0	0.96
Sn^{4+}	3*a*	0	0	0	0.04
O^{2-}	6*c*	0	0	0.2612	1
Structure III: refined structure					
Li^{+}	3*b*	0	0	1/2	1
Co^{3+}	3*a*	0	0	0	0.96
Sn^{4+}	3*a*	0	0	0	0.04
O^{2-}	6*c*	0	0	0.2612	1

Table S3. Electrolyte resistance (R_s), surface film resistance (R_{sf}) and charge transfer resistance (R_{ct}) for LCO and SLCO electrodes.

Material	State	R_s (Ω)	R_{sf} (Ω)	R_{ct} (Ω)
LCO	Pristine electrode	3.54	146.30	—
	after 50 cycles	2.73	16.68	2355.80
SLCO	Pristine electrode	3.55	146.29	—
	after 50 cycles	2.18	13.81	430.41

Table S4. Electrochemical performance of high-voltage $LiCoO_2$ modified by single elemental doping from previous literature

Compound	Discharge capacity (mAh g^{-1})	Voltage range (V)	Current density	Capacity (cycle number) (mAh g^{-1})	Reference
$LiMn_{0.05}Co_{0.95}O_2$	180	3.5-4.5	0.2 C	158 (50)	1
$LiFe_{0.05}Co_{0.95}O_2$	160	3.5-4.5	0.2 C	130 (50)	1
$LiCu_{0.05}Co_{0.95}O_2$	165	3.5-4.5	0.2 C	130 (50)	1
$LiZn_{0.05}Co_{0.95}O_2$	170	3.5-4.5	0.2 C	110 (50)	1
$LiBi_{0.05}Co_{0.95}O_2$	165	3.5-4.5	0.2 C	60 (50)	2
$LiZr_{0.05}Co_{0.95}O_2$	164	3.5-4.5	0.2 C	135 (50)	2
$LiCr_{0.05}Co_{0.95}O_2$	164	3.5-4.5	0.2 C	90 (50)	2
$LiSn_{0.05}Co_{0.95}O_2$	160	3.5-4.5	0.2 C	140 (50)	2
1 mol% Ni-doped $LiCoO_2$	160	3.0-4.5	1 C	120 (100)	3
$LiTi_{0.05}Co_{0.95}O_2$	165	3.5-4.5	0.2 C	143 (50)	4
$LiCo_{0.8}Ba_{0.2}O_2$	170	3.0-4.5	0.1 $mA.cm^{-2}$	160 (25)	5
$LiCo_{0.995}Ga_{0.005}O_2$	150	2.6-4.5	0.1 C	100 (30)	6
$LiCo_{0.99}Si_{0.01}O_2$	175	2.8-4.5	0.4 mA cm^{-2}	150 (50)	7
$LiCo_{0.985}Sn_{0.015}O_2$	**182**	**2.5-4.5**	**50 mA g^{-1} (~0.3 C)**	**150 (100)**	**This work**

Reference.

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