

Supporting Information

Revisiting LiCoO_2 Using a State-of-the-Art *In*
***Operando* Technique**

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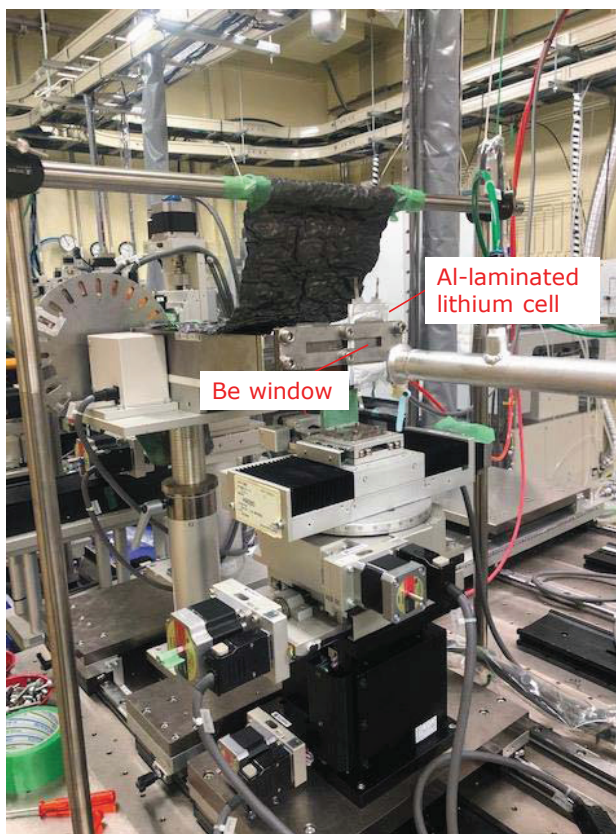


Figure S1: Al-laminated lithium cell covered with the Be window for *in operando* XRD/XAS measurements installed at the Toyota beamline (BL33XU) at SPring-8, Japan. Thickness of the Be window was 0.2 mm. The beam size at the sample position was 3.0 mm (height) \times 0.5 mm (width) for both XRD and XAS measurements.

Table S1: Structural parameters of the pristine OST-LCO sample ($x_0 = 1.1$) determined by Rietveld analysis

Atom	Wyckoff position	Occupancy ^a (g)	x	y	z	B_{iso} (\AA^2)
Li1	$3b$	1.0	0	0	0.5	0.7(1)
Li2	$3a$	0.04	0	0	0	0.1(1)
Co	$3a$	0.96	0	0	0	0.1(1)
O	$6c$	0.98	0	0	0.261(2)	0.2(1)
Space group: $R\bar{3}m$, $a_{\text{h}} = 2.8162(1)$ \AA , and $c_{\text{h}} = 14.0510(1)$ \AA $R_{\text{wp}} = 9.70$ % and $S = 1.01$						

^aWe employed $\delta = 0.04$ by considering the amount of evaporated Li atoms (0.02) during the synthesis.

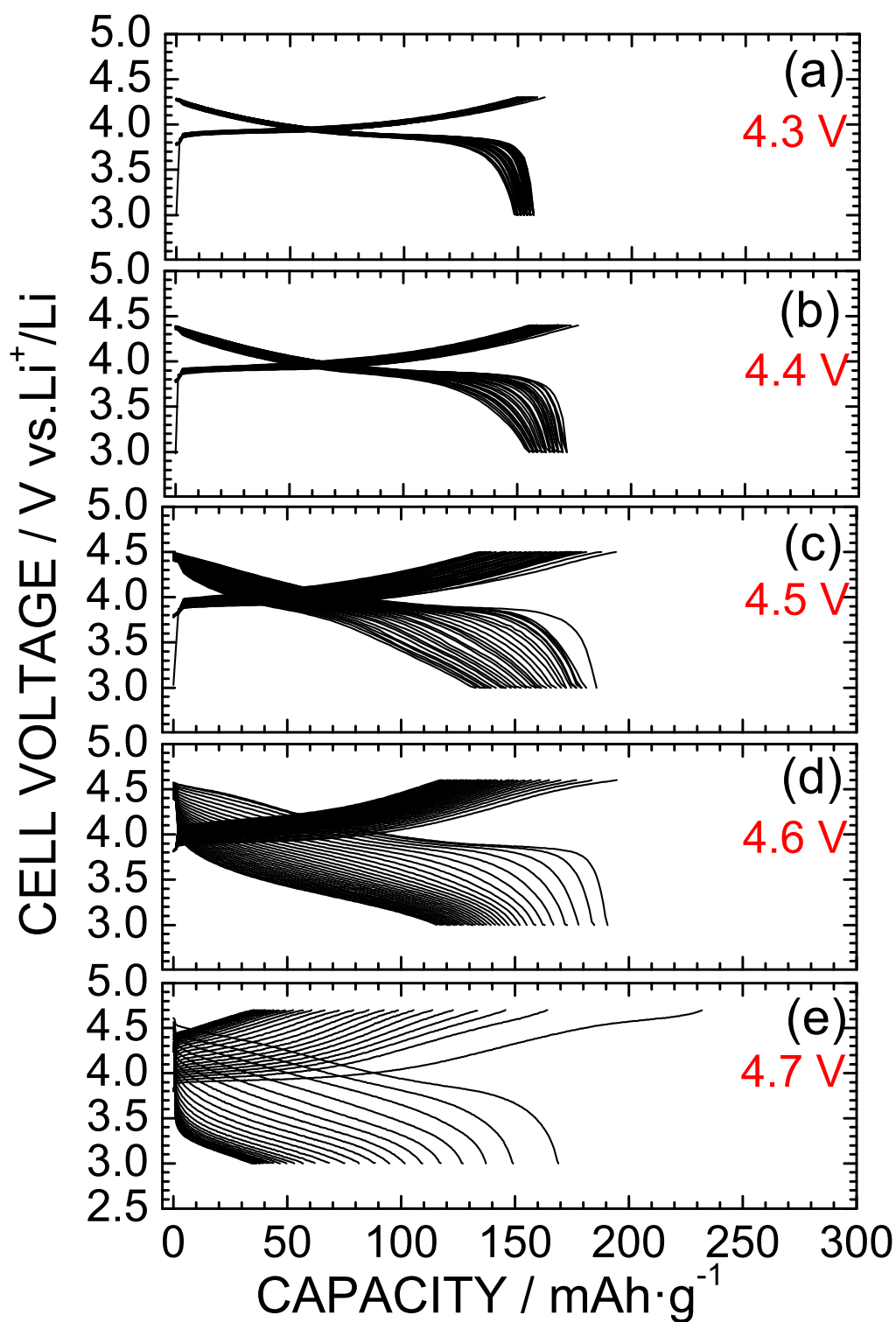


Figure S2: Charge and discharge curves of the Li/OST-LCO ($x_0 = 1.1$) cells operated with $V_{\text{cut-off}} =$ (a) 4.3 V, (b) 4.4 V, (c) 4.5 V, (d) 4.6 V, and (e) 4.7 V. The applied current was 0.3 mA ($\simeq 0.15 \text{ mA} \cdot \text{cm}^{-2}$) and the environmental temperature was 25 °C.

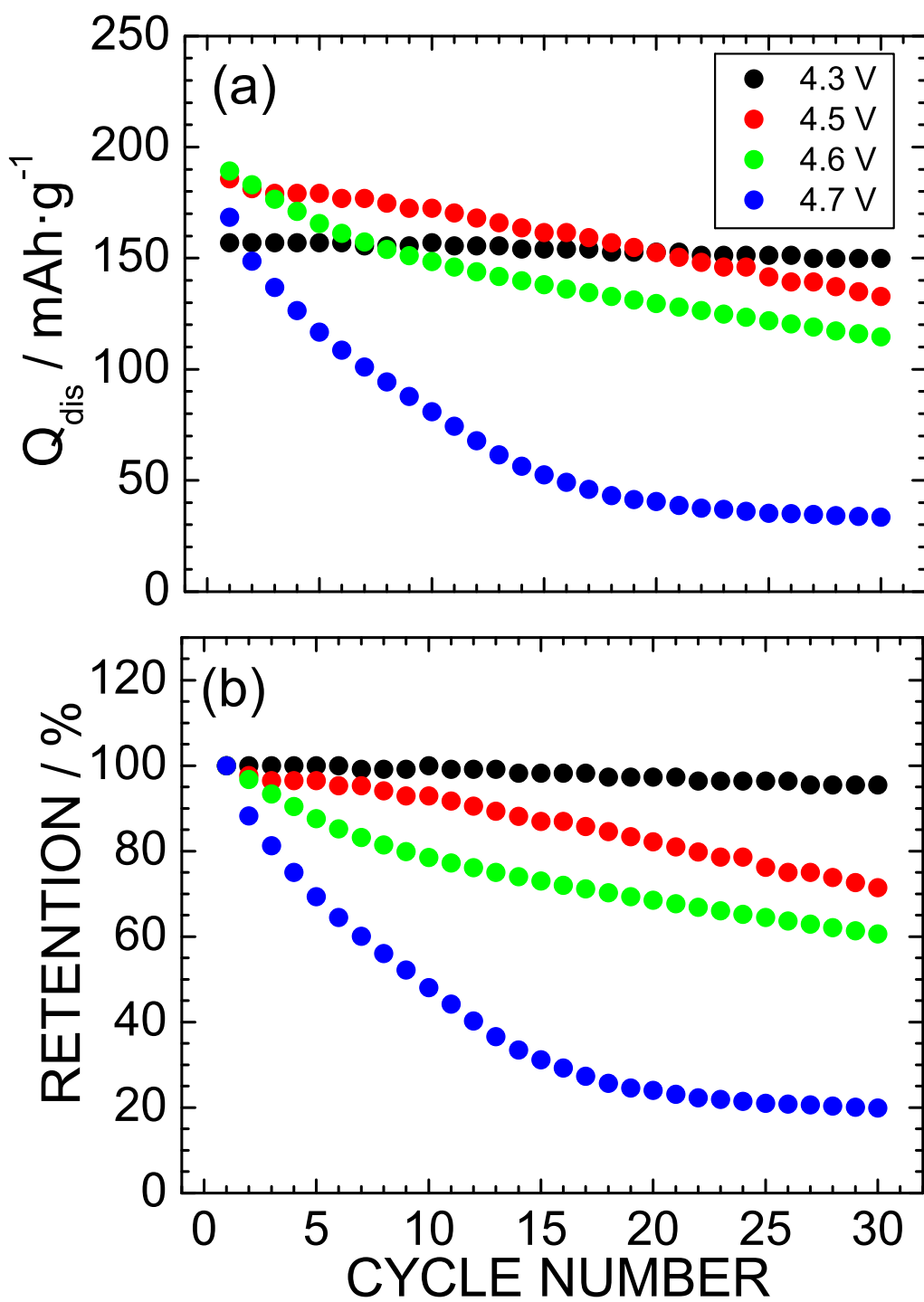


Figure S3: (a) Q_{dis} and (b) capacity retention as a function of the number of cycles operated with $V_{\text{cut-off}} = 4.3, 4.5, 4.6,$ and 4.7 V.

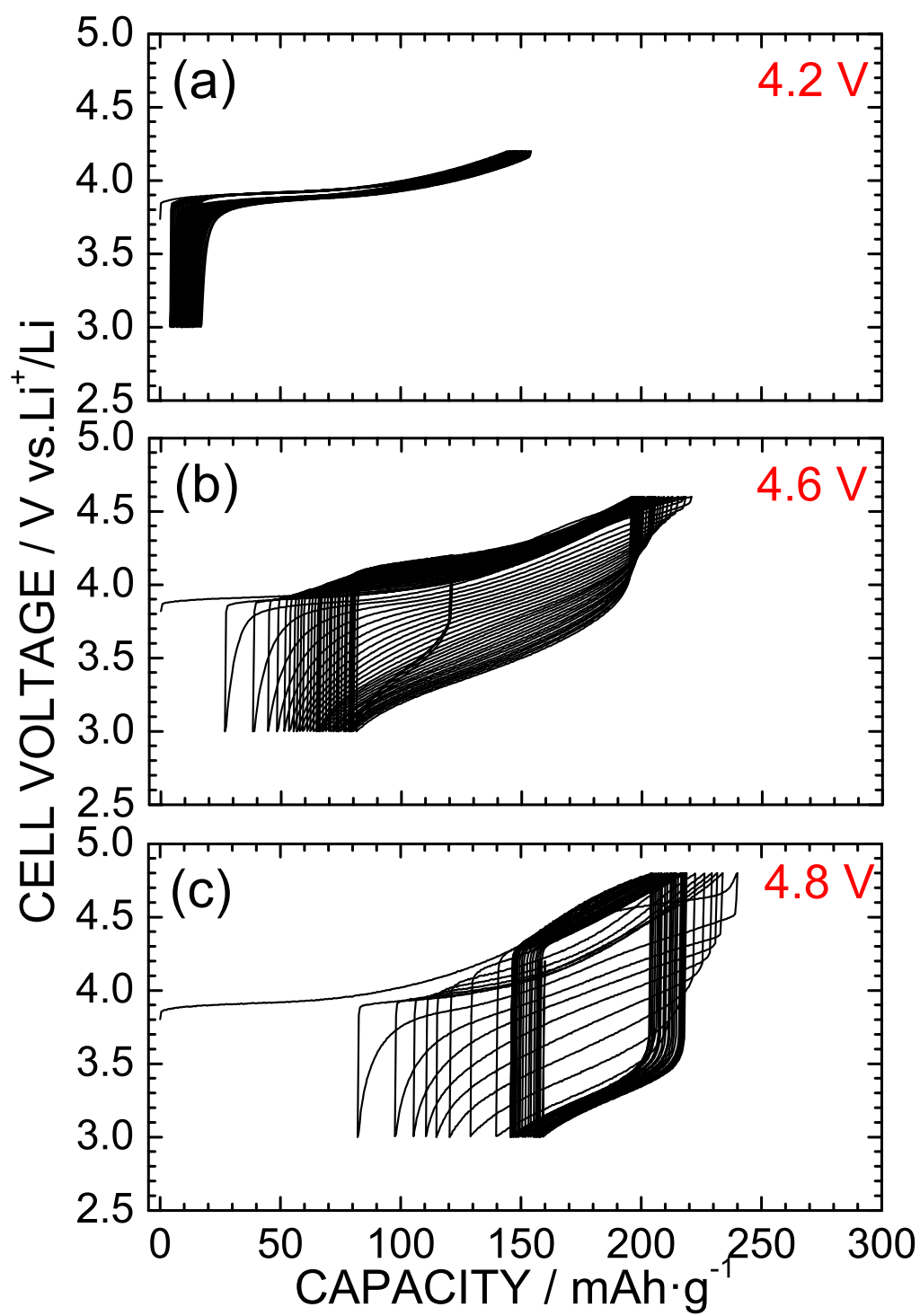


Figure S4: Charge-discharge curves by a single stroke with $V_{\text{cut-off}} =$ (a) 4.2, 4.6, and 4.8 V.

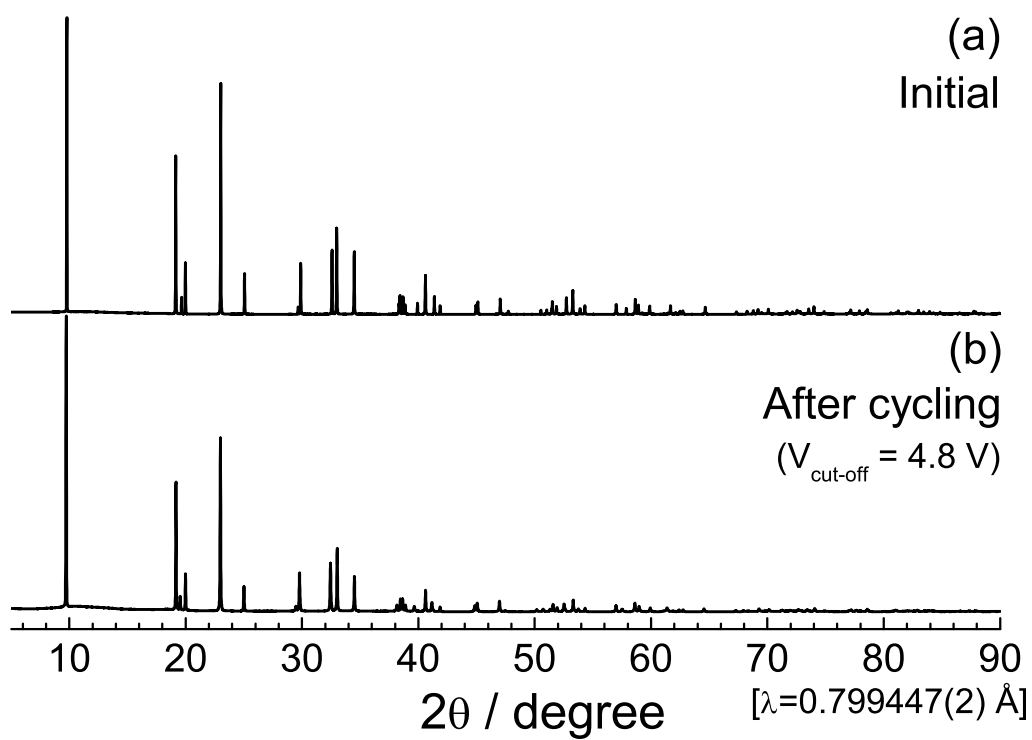


Figure S5: XRD patterns of the OST-LCO sample ($x_0 = 1.1$) at the (a) initial and (b) after cycling. The lithium cell was operated at a current of 0.3 mA with $V_{\text{cut-off}} = 4.8$ V.

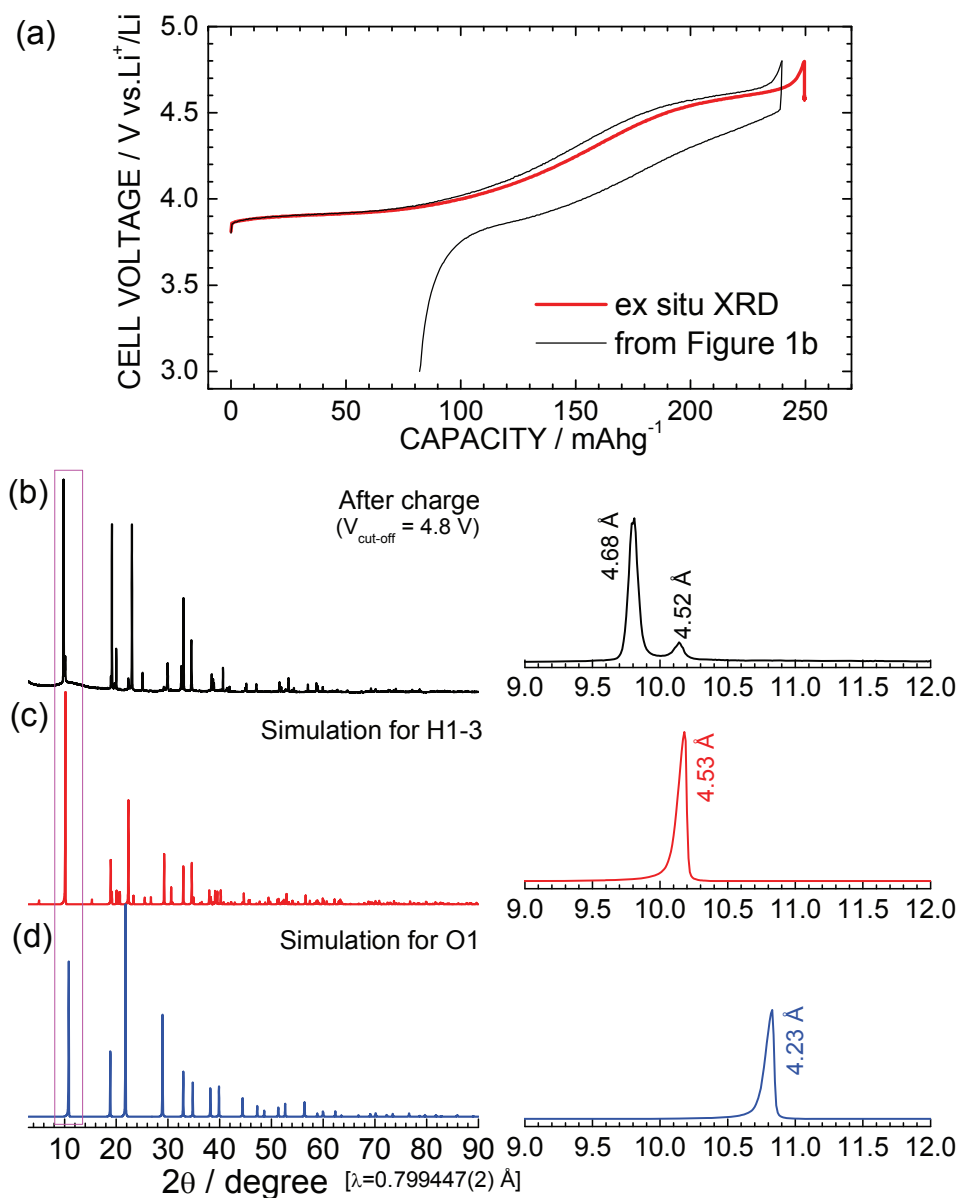


Figure S6: (a) Charge curve of the OST-LCO sample ($x_0 = 1.1$) for an *ex situ* XRD measurement. (b) *Ex situ* XRD pattern of the OST-LCO sample in (a) and simulated XRD patterns for the (c) H1-3 and (d) O1 phases. The magnified XRD patterns in the 2θ range between 9 and 12° are shown in the right side.

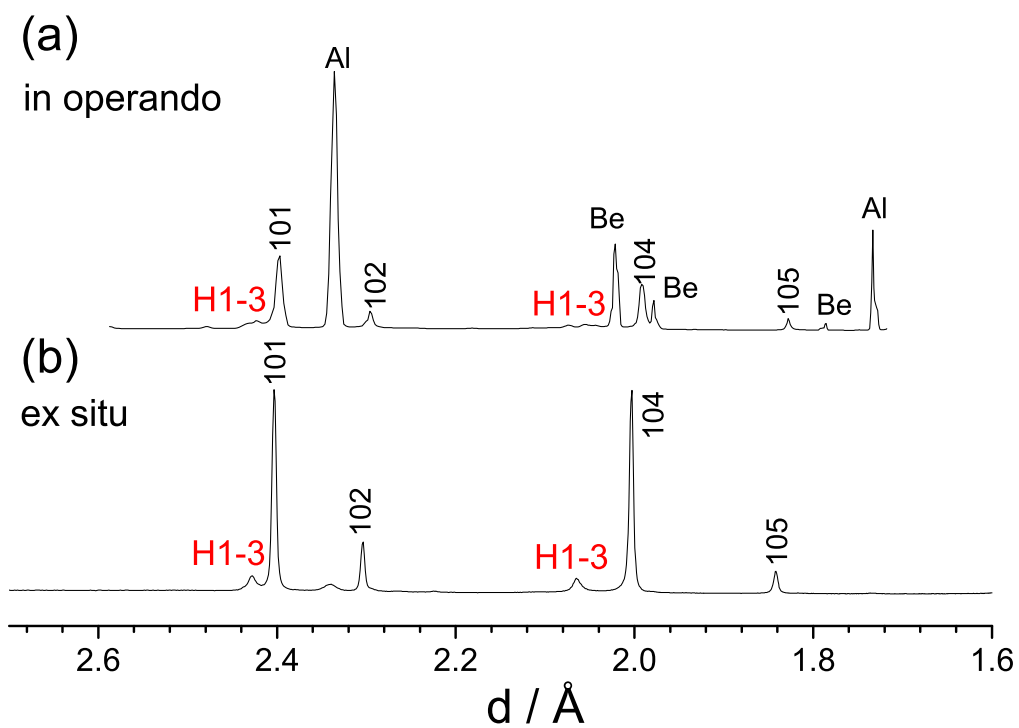


Figure S7: (a) *In operando* and (b) *ex situ* XRD patterns at the fully charged state up to 4.8 V, where the diffraction angles were given by d values.

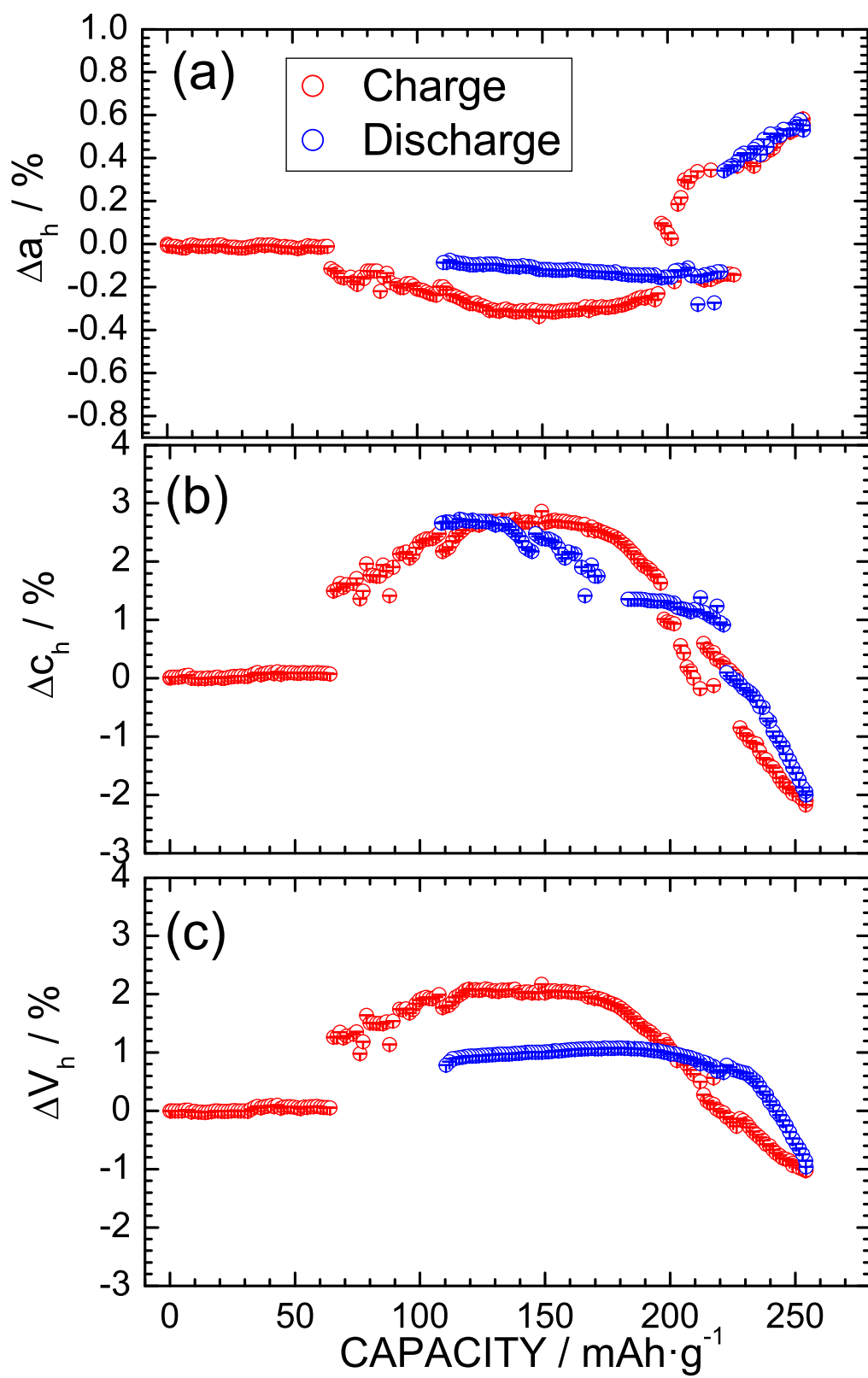


Figure S8: Changes in (a) Δa_h , (b) Δc_h , and (c) ΔV_h determined by the *in operando* XRD measurements.

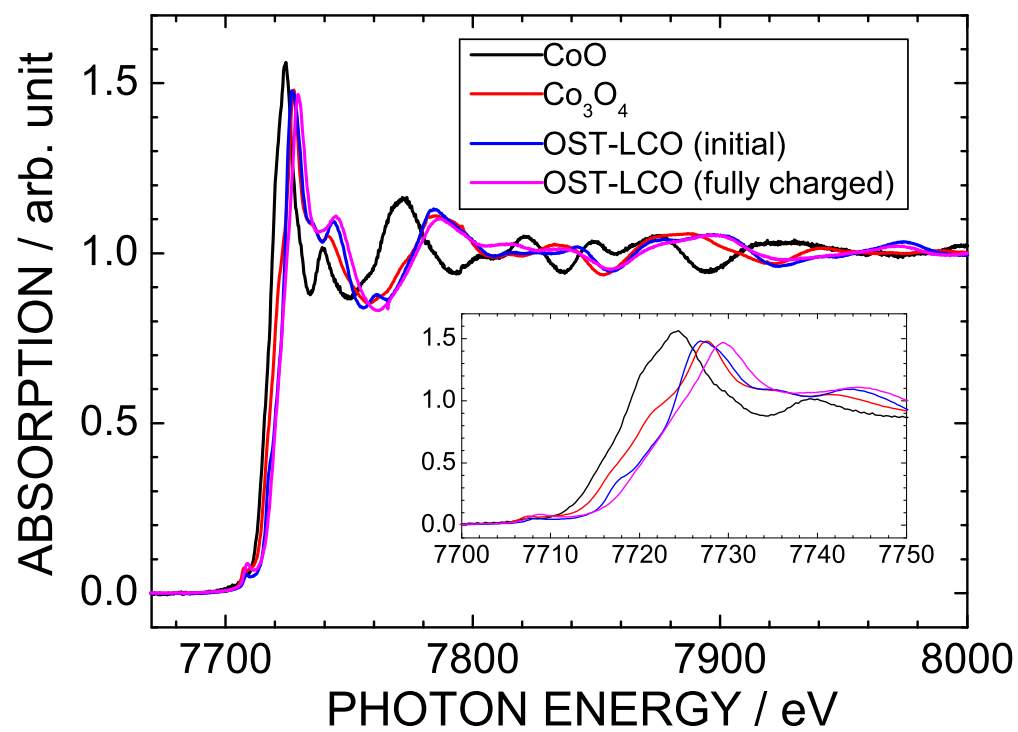


Figure S9: XANES spectra of CoO and Co₃O₄ together with those of OST-LCO ($x_0 = 1.1$) at the initial fully charged states.

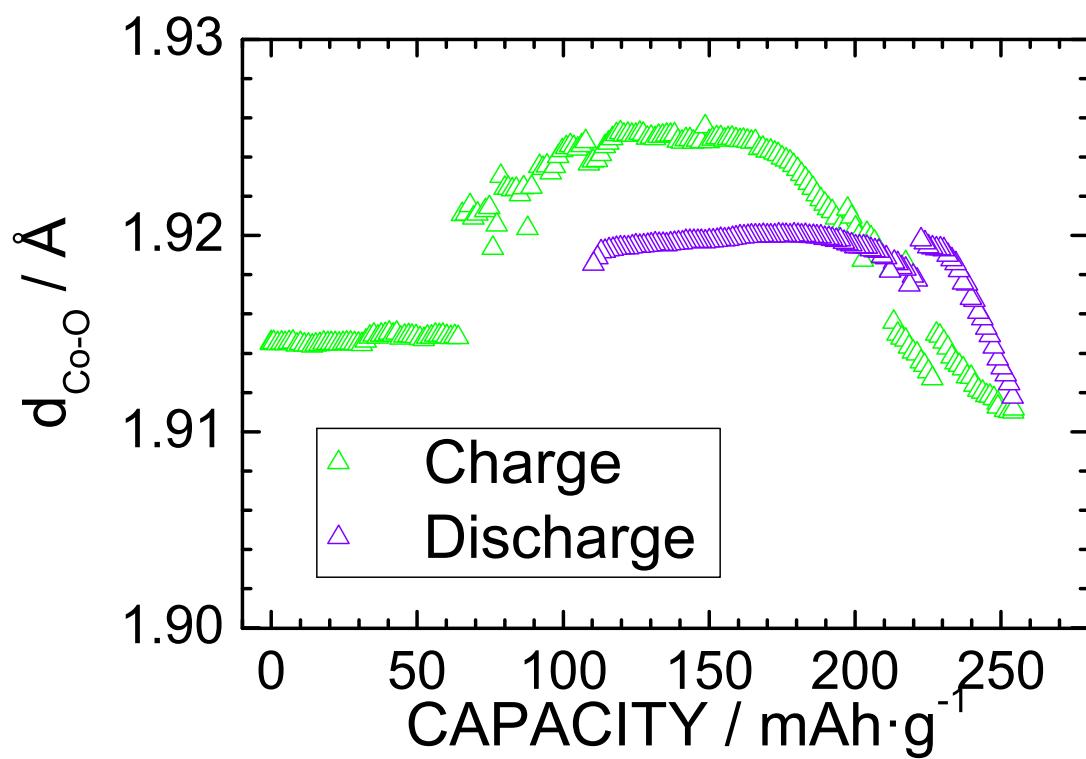


Figure S10: Enlarged $d_{\text{Co-O}}$ obtained by the *in operando* XRD measurements.

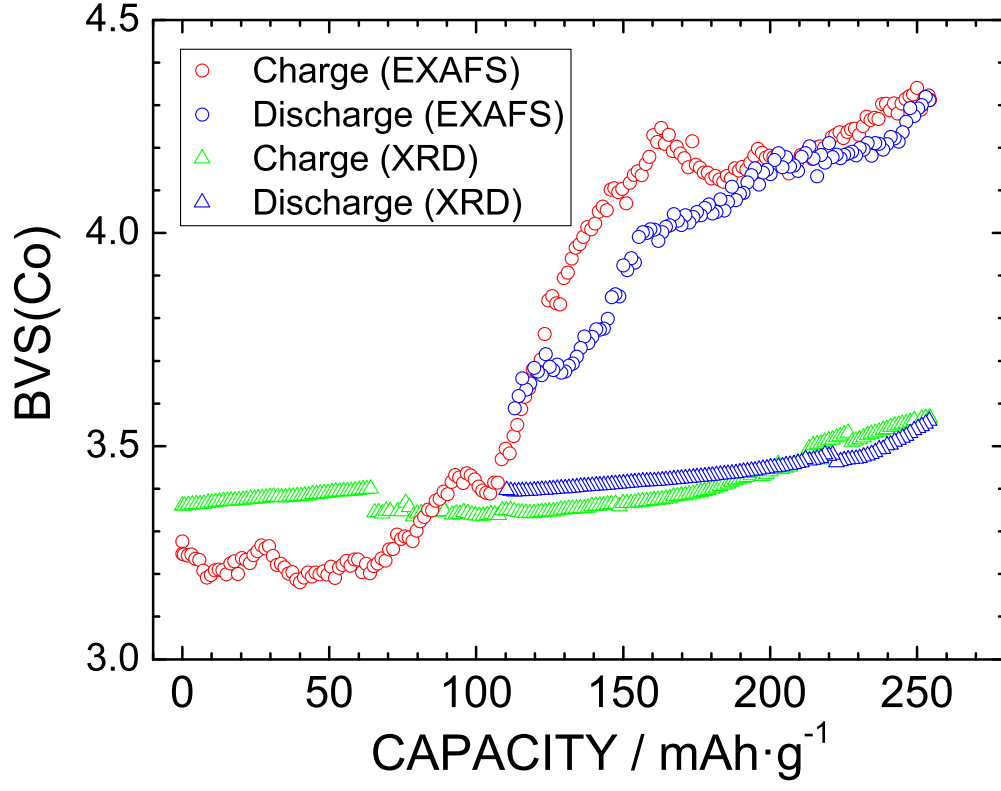


Figure S11: BVS(Co) obtained by the XRD and EXAFS studies.

The BVS(Co) value was calculated by following equation:

$$\text{BVS}(\text{Co}) = \sum_i^6 \exp \frac{(r_0 - r_i)}{0.37}, \quad (1)$$

where $r_i = d_{\text{Co-O}}$. Furthermore, we employed variable r_0 with Q , i.e., $r_0 = 1.70$ for Co^{3+} and $r_0 = 1.72$ for Co^{4+} , to reflect the amount of Co^{3+} (or Co^{4+}) ions in OST-LCO.

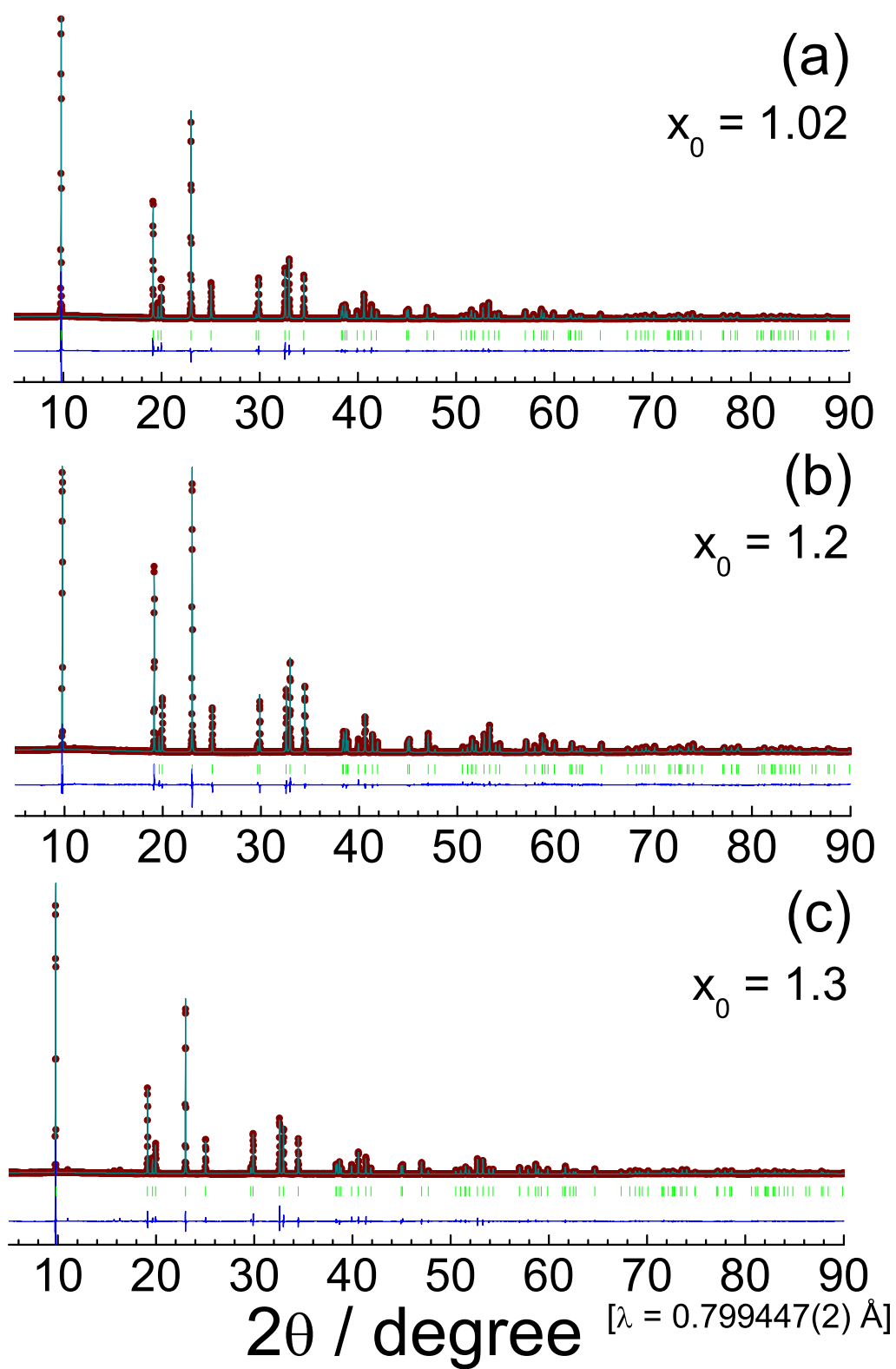


Figure S12: Rietveld results of the OST- (or ST-) LCO samples prepared with (a) $x_0 = 1.02$, (b) $x_0 = 1.2$, and (c) $x_0 = 1.3$.

Table S2: Structural parameters of OST- (or ST-)LCO samples prepared with $x_0 = 1.02$, 1.2, and 1.3

x_0	Atom	Wyckoff position	Occupancy ^a (g)	x	y	z	B_{iso} (\AA^2)
1.02	Li1	$3b$	1.0	0	0	0.5	1.2(1)
	Co	$3a$	1.0	0	0	0	1.0(1)
	O	$6c$	1.0	0	0	0.260(2)	0.9(1)
Space group: $R\bar{3}m$, $a_h = 2.8149(1)$ Å, and $c_h = 14.0532(1)$ Å $R_{\text{wp}} = 11.11$ % and $S = 1.05$							
1.2	Li1	$3b$	1.0	0	0	0.5	0.8(2)
	Li2	$3a$	0.08	0	0	0	0.1(2)
	Co	$3a$	0.92	0	0	0	0.1(2)
	O	$6c$	0.96	0	0	0.262(2)	0.2(2)
Space group: $R\bar{3}m$, $a_h = 2.8162(1)$ Å, and $c_h = 14.0493(1)$ Å $R_{\text{wp}} = 8.77$ % and $S = 0.93$							
1.3	Li1	$3b$	1.0	0	0	0.5	1.4(2)
	Li2	$3a$	0.12	0	0	0	0.1(2)
	Co	$3a$	0.88	0	0	0	0.1(2)
	O	$6c$	0.94	0	0	0.260(2)	0.4(2)
Space group: $R\bar{3}m$, $a_h = 2.8161(1)$ Å, and $c_h = 14.0522(1)$ Å $R_{\text{wp}} = 13.14$ % and $S = 1.21$							

^aWe employed $\delta = 0$ for $x_0 = 1.02$, $\delta = 0.08$ for $x_0 = 1.2$, and $\delta = 0.12$ for $x_0 = 1.3$, by considering the amount of evaporated Li atoms (0.02) during the synthesis.

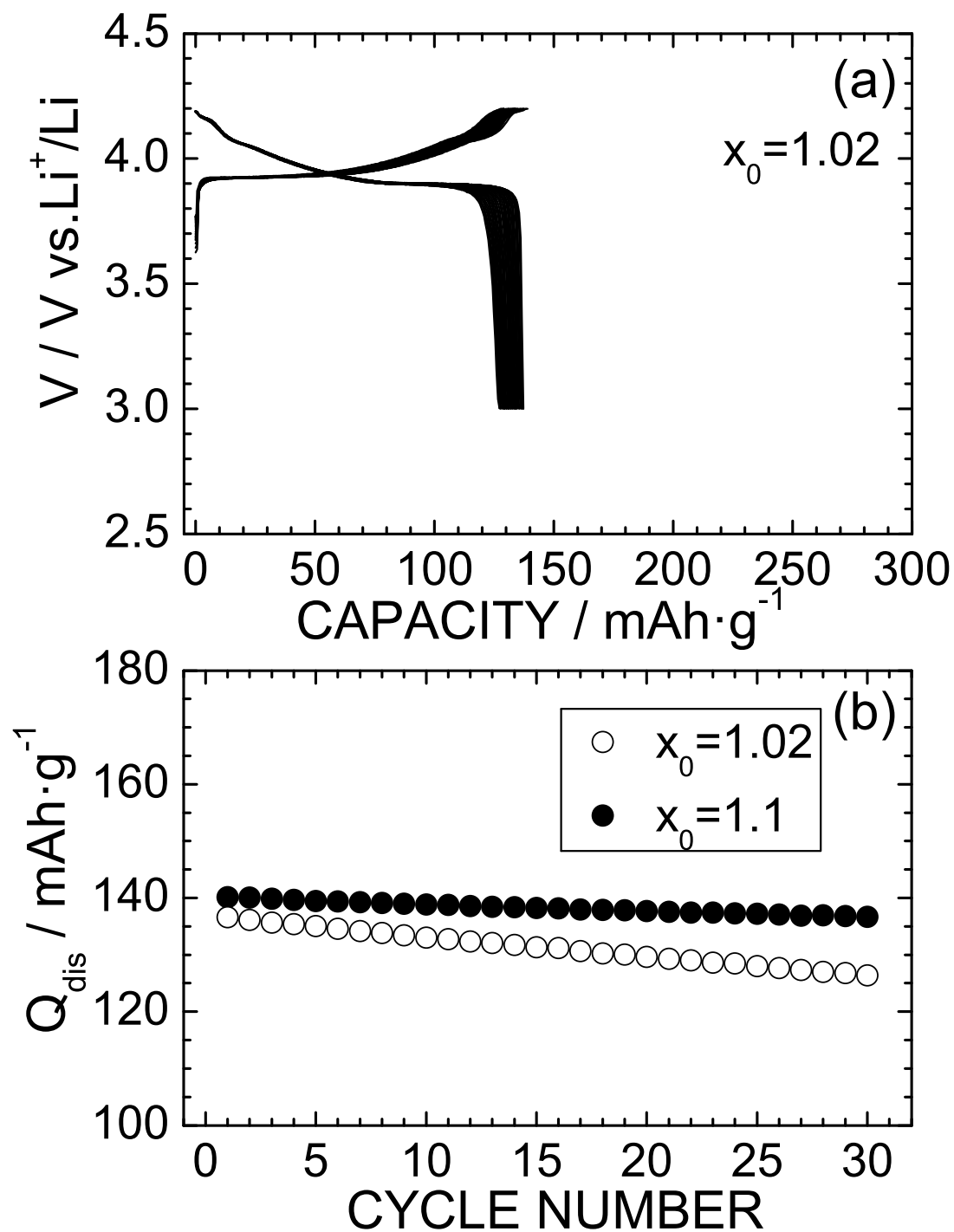


Figure S13: (a) Charge-discharge curves of the ST-LCO sample ($x_0 = 1.02$) and (b) comparison of cyclability between ST- and OST-LCO ($x_0 = 1.1$) samples.