Supporting Information:

Nano-scale Observation of the Electronic and Local Structures of $LiCoO_2$ Thin Film Electrode by Depth-Resolved X-ray Absorption Spectroscopy

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S1. Depth resolution of DR-XAS

We estimated the depth resolution of DR-XAS as shown in Figure S1. For this measurement, we used the $LiCoO_2$ thin film (thickness was *ca*. 50 nm) deposited on Ni substrate. Note that the sample setting for PILATUS is reverse in this experiment as shown in Fig. S1(a). As a result, large channel

numbers correspond to low exit angle (only surface information) and the small channel numbers correspond to high exit angle (include bulk information), respectively. The X-ray absorption of both Co *K*-edge detected around 7708 eV and Ni *K*-edge detected around 8338 eV were observed. The difference in the channel number in which X-ray absorption was observed for each edge can give the information on depth resolution. Figure S1(b) shows the plots of X-ray absorption intensity at each edge as a function of the channel number of the PILATUS. The X-ray absorption was not observed at the large number channels. With decreasing the channel number, the X-ray absorption intensity at Co *K*-edge increased from #185. This channel where X-ray absorption intensity appeared gives the surface information of the $LiCoO_2$ film. The Ni *K*-edge absorption appeared from the smaller number channel (#170). It is expected that the $LiCoO_2$ film exists between the channels where Co *K*-edge absorption intensity appeared and where Ni *K*-edge absorption intensity appeared. From the results, the number of the channel difference was 15. Taking into account the thickness of $LiCoO_2$ film (*ca*. 50 nm), the depth resolution is calculated to be 3.3 nm / channel.

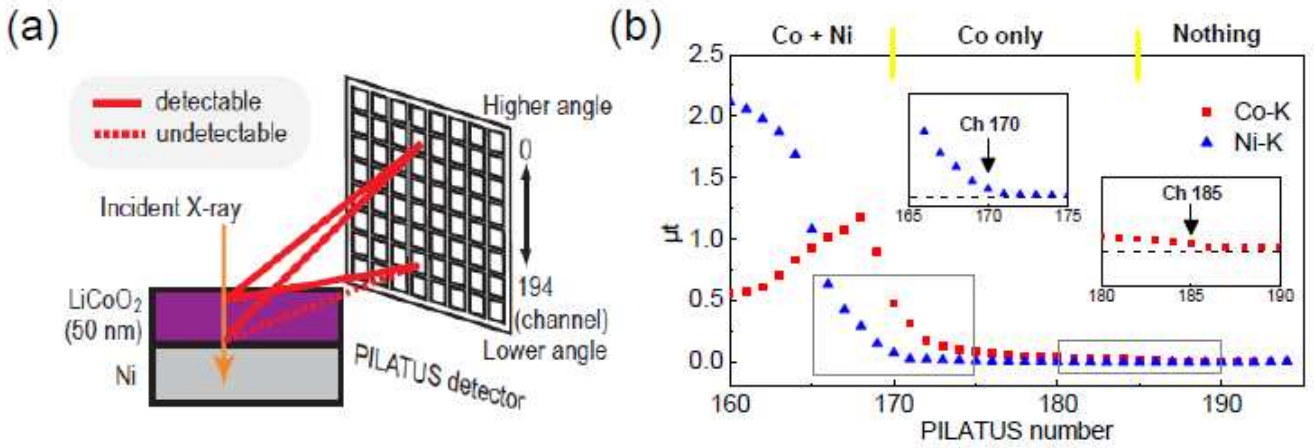


Figure S1. (a) Schematic illustration for the estimation of depth resolution in DR-XAS. The $LiCoO_2$ / Ni substrate was used. (b) The plots of X-ray absorption intensity at both Co-*K* and Ni-*K* edges as a function of the channel number of the PILATUS.

S2. The EXAFS analytical methods and determined structural parameters

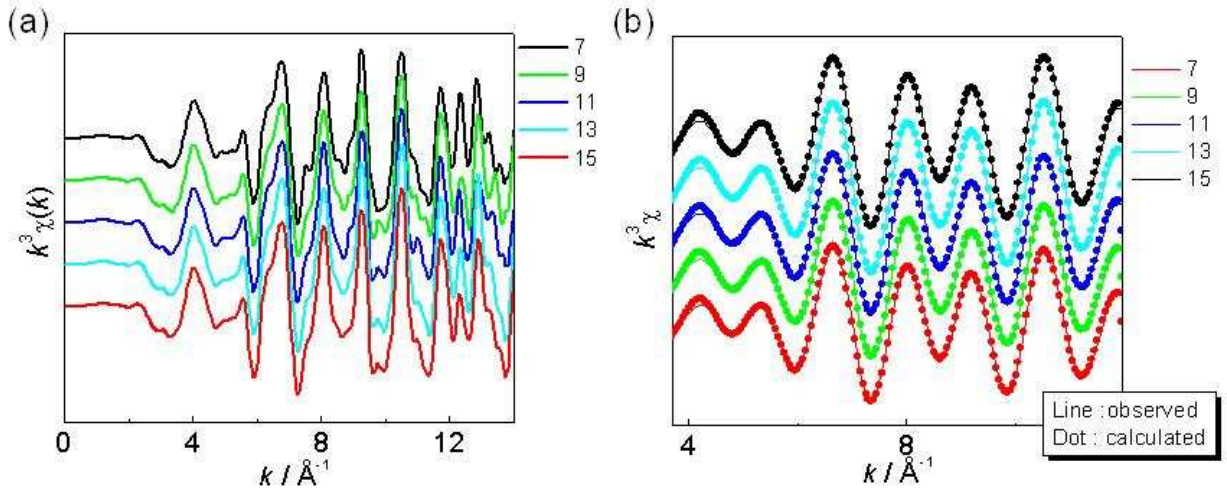
Fourier transformations (FTs) were performed using k^3 weighting and the structural parameters were determined by curve-fitting procedures using Rigaku REX2000 data analysis software.[1] The effective backscattering amplitude *f* and the total central atom phase shift $\phi(k)$ were calculated using the multiple-scattering theoretical calculation program, FEFF8.20.[2] In the curve fitting procedure, we fixed the coordination numbers (CN) of Co ions as 6. The $\chi(k)$ function was fitted according to the equation:

$$\chi(k) = \sum \frac{N|f(k,\pi)|\, exp(-2\sigma_i^2 k^2) exp(-2R_i/\lambda_i)\, sin[2kR_i + \phi(k)]}{kR^2}$$

where *N* is the number of neighboring atoms, *R* is the atomic distance to the neighboring atom, σ is the Debye-Waller (DW) factor, and λ is the mean free path. The fitting procedure was repeated until the *residue* become suitable value as much as possible.

$$Residue = \sum \{k^3\chi_{obs}(k) - k^3\chi_{al}(k)\}^2 / \sum \{k^3\chi_{obs}(k)\}^2$$

Here, we explain the fitting procedure of EXAFS obtained at 3.2 V (before charge) as a typical example. Figure S2(a) shows the k^3-weighted EXAFS raw spectra of Co-K edge at each channel of PILATUS around the interface. Figure S2(b) shows the curve fitting of the EXAFS oscillations examined under fixing the CN as 6. Determined structural parameters: atomic distance (*R*) and DW factor (σ) of $LiCoO_2$ thin film, is summarized in Fig. S2(c). Figure S3(a) shows the results obtained at 4.2 V (after charging) and Fig. S3(c) shows the result obtained at 4.4 V (after overcharge), respectively.



(c)

	Co-O			Co-Co			Residue
channel	CN	R/Å	σ/Å	CN	R/Å	σ/Å	(%)
7	6	1.906	0.069	6	2.817	0.058	0.383
8	6	1.907	0.069	6	2.818	0.056	0.423
9	6	1.905	0.068	6	2.818	0.055	0.487
10	6	1.906	0.065	6	2.816	0.053	0.35
11	6	1.904	0.063	6	2.817	0.05	0.347
12	6	1.904	0.063	6	2.818	0.049	0.425
13	6	1.907	0.064	6	2.818	0.05	0.25
14	6	1.905	0.063	6	2.817	0.051	0.483
15	6	1.905	0.062	6	2.818	0.051	0.436
16	6	1.906	0.064	6	2.818	0.05	0.439

Figure S2. The fitting procedure of EXAFS obtained at 3.2 V (before charge). (a) The k^3-weighted EXAFS raw spectra of Co-K edge at each channel of PILATUS around the interface. (b) The curve fitting of the EXAFS oscillations. (c) Determined structural parameters: coordination number (CN), atomic distance (R) and Debye-Waller factor (σ) of $LiCoO_2$ thin film.

(a)

	Co-O			Co-Co			Residue
channel	CN	R/Å	σ/Å	CN	R/Å	σ/Å	(%)
7	6	1.896	0.084	6	2.821	0.067	1.941
8	6	1.9	0.081	6	2.82	0.064	2.76
9	6	1.898	0.08	6	2.822	0.061	1.083
10	6	1.898	0.078	6	2.82	0.059	2.321
11	6	1.898	0.073	6	2.818	0.059	0.965
12	6	1.899	0.072	6	2.817	0.058	1.029
13	6	1.898	0.069	6	2.816	0.062	1.322
14	6	1.9	0.067	6	2.817	0.061	1.284
15	6	1.898	0.065	6	2.818	0.059	1.632
16	6	1.901	0.066	6	2.818	0.06	1.2

(b)

	Co-O			Co-Co			Residue
channel	CN	R/Å	σ/Å	CN	R/Å	σ/Å	(%)
7	6	1.898	0.087	6	2.842	0.077	2.896
8	6	1.899	0.092	6	2.837	0.078	3.393
9	6	1.895	0.082	6	2.833	0.075	3.629
10	6	1.897	0.079	6	2.84	0.071	1.392
11	6	1.893	0.083	6	2.839	0.076	1.823
12	6	1.891	0.082	6	2.836	0.074	1.471
13	6	1.891	0.08	6	2.838	0.072	1.242
14	6	1.891	0.08	6	2.837	0.075	1.264
15	6	1.89	0.076	6	2.836	0.072	1.599
16	6	1.891	0.077	6	2.838	0.075	1.518

Figure S3. Determined structural parameters obtained (a) at 4.2 V (after charge) and (b) at 4.4 V (after overcharge), respectively.

References

(1) Rehr, J. J.; Albers, R. C. Theoretical approaches to x-ray absorption fine structure. *Rev. Mod. Phys.***2000**, *72*, 621- 654.

(2) Ankudinov, A. L.; Ravel, B.; Rehr, J. J.; Conradson, S. D. Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure. *Phys. Rev. B*. **1998**, *58*, 7565-7576.