## Supporting information

## New insight into designing the thick-sintered cathode for Li-ion battery; An impact of excess lithium in LiCoO<sub>2</sub> on its electrode performance

Shinichi Takeno<sup>a</sup>, Taiki Suematsu<sup>a</sup>, Ryusei Kunisaki<sup>a</sup>, Gen Hasegawa<sup>b</sup>, Ken Watanabe<sup>\*c</sup>, Kuwata Naoaki<sup>b</sup>, Kazutaka Mitsuishi<sup>b</sup>, Tsuyoshi Ohnishi<sup>b</sup>, Kazunori Takada<sup>b</sup>, Kohichi Suematsu<sup>c</sup> and Kengo Shimanoe<sup>c</sup>,

<sup>a.</sup> Interdisciplinary Graduate School of Engineering Sciences, Department of Interdisciplinary Engineering Science, Kyushu University, Kasuga, Fukuoka,

<sup>b.</sup> National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan.

<sup>c</sup> Department of Advanced Materials Science and Engineering, Faculty of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, 816-8580, Japan



Figure S1 XRD pattern of LiCoO<sub>2</sub> sintered disk after grinding.

<sup>816-8580,</sup> Japan.

Li excess amount (%)	Current (mA)	time (s)
0	$\pm 1.5 \times 10^{-3}$	20
1.0	$\pm$ 1.0 ×10 <sup>-2</sup>	20
2.0	$\pm 2.00$	20
3.0	$\pm 2.00$	20
4.1	$\pm 4.00$	20
5.1	$\pm 0.700$	20
6.2	$\pm 0.400$	20
7.3	$\pm 0.200$	20
8.3	$\pm 0.166$	20
12.8	$\pm 0.100$	20

Table S1 Experimental condition of electronic conductivity measurement

Table S2 Experimental condition of Li-ion conductivity measurement,(a)before charge,(b) after charge.

(a)

Li excess amount (%)	Thickness (µm)	Current (mA)	time (s)
3.0	116	$\pm$ 1.0 $\times 10^{-3}$	60
	200	$\pm$ 2.0 $\times 10^{-3}$	60
	289	$\pm$ 5.0 $\times 10^{-4}$	60
	393	$\pm$ 1.0 ×10 <sup>-3</sup>	60
	484	$\pm$ 5.0 $\times 10^{-4}$	60
4.1	116	$\pm$ 1.0 $\times 10^{-4}$	300
	247	$\pm$ 1.0 $\times 10^{-4}$	900
	391	$\pm$ 5.0 ×10 <sup>-5</sup>	900
5.1	189	$\pm$ 3.0 $\times 10^{-3}$	60
	293	$\pm$ 3.0 $\times 10^{-3}$	60
	390	$\pm$ 3.0 $\times 10^{-3}$	60
7.3	206	$\pm$ 8.0 ×10 <sup>-3</sup>	20
	398	$\pm$ 8.0 ×10 <sup>-3</sup>	20
	573	$\pm 4.0 \times 10^{-3}$	20

(b)

Li excess amount (%)	Thickness (µm)	Current (mA)	time (s)
3.0	184	$\pm 1.0 \times 10^{-2}$	60
	248	$\pm$ 1.0 ×10 <sup>-2</sup>	60
	330	$\pm 1.0 \times 10^{-2}$	60
4.1	141	$\pm$ 5.0 $\times 10^{-3}$	60
	243	$\pm$ 5.0 $\times 10^{-3}$	60
	345	$\pm$ 2.0 $\times 10^{-3}$	60
5.1	159	$\pm$ 1.0 $\times 10^{-2}$	60
	203	$\pm$ 1.0 $\times 10^{-2}$	60
	312	$\pm$ 1.0 $\times 10^{-2}$	60
7.3	142	$\pm$ 1.0 $\times 10^{-2}$	60
	393	$\pm$ 2.0 $\times 10^{-2}$	60
	550	$\pm$ 1.0 $\times 10^{-2}$	60



Figure S2 Schematic diagram of the cell used for charging-discharging test.



Figure S3 Schematic diagram of the cell used for measuring Li-ion conductivity.



Figure S4 SEM image of  $LiCoO_2$  powder after ball-milling (a,b)Stoichiometry,(c,d)Li12.8% excess.



Figure S5 Correlations between current and voltage of electronic conductivity measurements of (a)stoichiometry, (b)1.0%, (c)2.0%,(d) 3.0%, (e)4.1%, (f)5.1%, (g)6.2%, (h)7.3%, (i)8.3%, and (j)12.8% Li-excess LiCoO<sub>2</sub>.



Figure S6 (a)STEM image of grain boundary of Li7.3% excess. (b-d)EELS spectra of grain boundary of Li7% excess. EELS spectra of (e)LiCoO<sub>2</sub>, (f)Li<sub>2</sub>CO<sub>3</sub>.



Figure S7 Correlation between cycle number and discharge capacities of charge/discharge tests at 0.1C using LCO sintered disks with a thickness of approximately  $130\mu m$ .



Figure S8 Correlations between current and voltage of Li-ion conductivity measurements of LiCoO<sub>2</sub> in the composition of 3.0% Li-excess with thickness of (a) 116  $\mu$ m, (b) 200  $\mu$ m, (c) 289  $\mu$ m, (d) 393  $\mu$ m, (e) 484  $\mu$ m, 4.1% Li-excess with thickness of (f) 116  $\mu$ m, (g) 247  $\mu$ m, (h) 391  $\mu$ m, 5.1% Li-excess with thickness of (i) 189  $\mu$ m, (j) 293  $\mu$ m, (k) 390  $\mu$ m, 7.3% Li-excess with thickness of (l) 206  $\mu$ m, (m) 398  $\mu$ m and (n) 573  $\mu$ m.



Figure S9 Correlations between current and voltage of Li-ion conductivity measurements of LiCoO<sub>2</sub> after CCCV 4.2V charge in the composition of 3.0% Li-excess with thickness of(a) 184  $\mu$ m, (b) 248  $\mu$ m, (c) 330  $\mu$ m, 4.1% Li-excess with thickness of (d) 141  $\mu$ m, (e) 243  $\mu$ m, (f) 345  $\mu$ m, 5.1% Li-excess with thickness of (g) 159  $\mu$ m, (h) 203  $\mu$ m, (i) 312  $\mu$ m, 7.3% Li-excess with thickness of (j) 142  $\mu$ m, (k) 393  $\mu$ m and (l) 550  $\mu$ m.