Supporting Information

Co-sintering Process of LiCoO₂ Cathodes and NASICON-type LATP Solid Electrolytes Studied by X-ray Diffraction and X-ray Absorption Near Edge Structure

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1. XRD data analysis.



Figure S1. Results of Rietveld analysis of the XRD patterns.

Chemical Species	Chemical Formula	Powder Diffraction File card number
Lithium cobalt oxide	LiCoO ₂	01-070-2685
Lithium dititanium tris(phosphate(V))	LiTi ₂ (PO ₄) ₃	01-072-6140
Cobalt oxide	Co ₃ O ₄	01-076-1802
Lithiophosphate	Li ₃ PO ₄	01-087-0039
Cobalt titanium oxide	CoTiO ₃	01-077-1373
Titanium oxide, rutile	TiO ₂	01-070-7347
Lithium cobalt phosphate(V), olivine	LiCoPO ₄	01-089-6192

 Table S1. Powder diffraction files for Rietveld analysis.

2. XAFS data analysis.

The XAFS data were processed using ATHENA program¹ for energy scale calibration, background subtraction, post-edge normalization, and XANES analysis. The photon energy of Co (at 7709 eV) and Ti K-edge (at 4966 eV) XANES spectra was calibrated using the energy threshold E_0 of reference spectra of Co and Ti foils, respectively. In each synchrotron radiation experiment, reference spectra of Co and Ti foils were measured together with the LATP/LCO pellets sintered at various conditions. The energy threshold E_0 was determined as the maximum value of the first derivative of those reference spectra, and XANES spectra of the LCO/LATP pellets measured in the same synchrotron experiment were linearly calibrated against the difference between the obtained E_0 and the tabulated edge energy. The background subtraction and post-edge normalization were performed by AUTOBK algorithm implemented in ATHENA program¹. Linear combination fitting (LCF) was applied to the normalized data for quantitative analysis with the reference compounds (Figures S2 and S3)^{2,3}. The number and type of the reference compounds were assessed by PCA and target transformation (see below).



Figure S2. Results of linear combination fitting of the Co K-edge XANES spectra.



Figure S3. Results of linear combination fitting of the Ti K-edge XANES spectra.

3. LCO/LATP mixture used in the present study.



Figure S4. EDS spectra and mapping of LCO/LATP mixture before sintering.



4. Temperature dependent diffraction peak intensities of LCO and LATP.

Figure S5. Magnified 003 diffraction peak of the $LiCoO_2$ (top) and 113 diffraction peak of the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) (bottom).



5. Thermal stability of pure LCO tested by XANES and XRD.

Figure S6. Normalized Co K-edge XANES spectra of (top) reference samples and (bottom)

LiCoO₂ sintered at various temperature.



Figure S7. X-ray diffraction patterns of LiCoO₂ sintered at various temperature.

6. The effect of grain size.



Figure S8. (a) SEM image of LATP with a larger grain size (10-15 μ m), (b) XRD patterns of LCO/LATP pellets composed of regular LCO (0.5 μ m) and larger LATP (10-15 μ m) sintered at 700°C.

The effect of grain size on the reaction products was also investigated by using LATP with a grain size of 10-15 μ m, larger than the regular LATP with a particle size of 0.7 μ m used throughout the present work (Figure 1b). Figure S8 shows SEM images of the larger LATP and XRD patterns after being sintered with the regular LCO at 700°C. In the case of the regular LATP (0.7 μ m), LATP disappears at 700°C due to the reaction with LCO as shown in Figure 2. However, the diffraction peaks corresponding to LATP are still observed at 700°C in the case of LATP with a larger grain size (10-15 μ m), suggesting that the reaction rate is substantially reduced for the larger grain size probably due to the decrease of contact area between LATP and LCO.

7. The effect of sintering time.



Figure S9. XRD patterns of LCO/LATP pellets sintered at (a) 300°C, (b) 500°C, (c) 700°C, and (d) 900°C for different time periods.



Figure S10. Molar ratio of chemical species in LCO/LATP pellets sintered at (a) 300°C, (b) 500°C, (c) 700°C, and (d) 900°C for different time periods.

Figures S9 and S10 show the XRD patterns and the molar ratio of chemical species in the LCO/LATP pellets sintered at selected temperatures (300, 500, 700, and 900°C) for the different time duration (8, 24 h). This shows that the trends of reaction products in the pellet sintered for 24 h are almost identical to those for 8 h although the molar ratios for 8 h and 24 h are slightly different from each other. Thus, we chose 8 h as a regular sintering time unless otherwise specified.

8. The effect of cooling rate.



Figure S11. XRD patterns of LCO/LATP pellets cooled down with a different cooling rate (black: 5°C/min, red: ~15°C/min) after sintering at (a) 700°C and (b) 900°C.



Figure S12. Molar ratio of chemical species in LCO/LATP pellets cooled down with a different cooling rate (black: 5°C/min, red: ~15°C/min) after sintering at (a) 700°C and (b) 900°C.

Figures S11 and S12 show the XRD patterns and the molar ratio of chemical species in the LCO/LATP pellets cooled down with different cooling rate (5 and \sim 15°C/min) after sintering at 700 and 900 °C for 8h. The samples with different cooling rate show no obvious difference in the XRD patterns and the molar ratio of reaction products.

9. PCA analysis and target transformation.

The concept of PCA is available from the literature⁴⁻⁸ but briefly documented as follow. In the analysis of a series of XANES spectra arising from mixtures of unknow chemical species, PCA enables us to determine the number of components which are used to reproduce the experimental dataset without a priori assumption. In addition, by using a database for reference compounds and corresponding spectra, PCA in combination with "target transformation" helps us to select appropriate reference compounds/spectra that potentially constitute the experimental XANES spectra composed of unknown chemical species. The components proposed by PCA represent main independent features of variation in the experimental dataset. Although these independent features possess no chemical or physical meaning, one can select appropriate reference component is suitable for one of the reference compounds to reproduce the experimental data.

In the present study, PCA was performed to assess the number of components that constitute the experimental dataset. The PCA results of Co and Ti K-edge XANES dataset show that, in both cases, the four components are sufficient to reproduce the experimental dataset with a residue of less than 0.005%. Therefore, LCFs were performed with four reference compounds/spectra (Tables S2 and S4).

The four reference compounds used for each LCF were then selected by target transformation. In target transformation, LCF was applied to a XANES spectrum of a given reference compound using "the four components" proposed by PCA, and the suitability of the given compound as one of the reference compounds that constitute the experimental dataset was judged by comparing the mean square error. The possible reference compounds tested by target transformation and the resulting mean square error are listed in Tables S3 and S5. The compounds to reproduce the series of XANES spectra. For the Co K-edge, LCO, Co₃O₄, LiCoPO₄, and CoTiO₃ were selected as reference compounds. For the Ti K-edge, LATP, rutile TiO₂, CoTiO₃, and amorphous TiO₂ were selected as reference compounds.

Components	Eigenvalues	Variance	Cumulative variance
1	13.22671	0.944765	0.944765
2	0.745323	0.053237	0.998003
3	0.026473	0.001891	0.999893
4	0.000819	0.000059	0.999952
5	0.000374	0.000027	0.999979
6	0.000167	0.000012	0.999991
7	0.000108	0.000008	0.999998
8	0.000009	0.000001	0.999999
9	0.000006	0	0.999999
10	0.000004	0	1
11	0.000002	0	1
12	0.000001	0	1
13	0.000001	0	1
14	0	0	1

Table S2. Results of PCA for Co K-edge XANES spectra.

Target materials	Mean square error
LCO	4.11689E-5
Co_3O_4	3.34936E-4
CoTiO ₃	9.07454E-4
LiCoPO ₄	4.1102E-4
CoO	0.00419
Co(OH) ₂	0.0016
Co(NO ₃) ₂ 6H ₂ O	0.00927
Co ₂ P	0.01831
Co metal	0.01437
CoCO ₃	0.00716
CoCl ₂	0.00864
CoO(OH)	0.00202
Co ₃ (PO ₄) ₂ 8H ₂ O	0.00534

 Table S3. Possible reference compounds for LCF of Co K-edge XANES spectra together with mean square error of target transformation.

Components	Eigenvalues	Variance	Cumulative variance
1	13.95546	0.996819	0.996819
2	0.040105	0.002865	0.999684
3	0.003562	0.000254	0.999939
4	0.000565	0.00004	0.999979
5	0.000168	0.000012	0.999991
6	0.000089	0.000006	0.999997
7	0.000018	0.000001	0.999999
8	0.00001	0.000001	0.999999
9	0.000003	0	1
10	0.000002	0	1
11	0.000002	0	1
12	0.000001	0	1
13	0.000001	0	1
14	0	0	1

 Table S4. Results of PCA for Ti K-edge XANES spectra.

Target materials	Mean square error
LATP	8.4675E-6
Rutile TiO ₂	1.66967E-4
CoTiO ₃	7.46717E-4
Amorphous TiO ₂	0.00105
Anatase TiO ₂	0.00116
$Li_4Ti_5O_{12}$	0.00123
Li ₂ TiO ₃	0.00671
Ti ₂ O ₃	0.05307
Ti metal	0.05634

Table S5. Possible reference compounds for LCF of Ti K-edge XANES spectra together withmean square error of target transformation results for LCF.

10. Thermal analysis.



Figure S13. (a) TG curves and (b) DTA signals of pure LCO, LATP and LCO/LATP mixture.

Figure S13 shows the results of TG-DTA measurements. TG curves show that the weight loss of pure LCO and LATP in the heating from room temperature to 900°C is 0.8% and 2.51%, respectively. Since these substances are thermally stable, the weight loss should be due to the evaporation of surface-adsorbed chemical species such as water. ^{9, 10} The LCO/LATP mixture shows a weight loss of 5.21%, which is larger than those of pure LCO and LATP. Since the weight ratio of this LCO/LATP mixture is 0.74:1.00, the expected weight loss due to the evaporation of adsorbed species from LCO and LATP is 0.34% and 1.44%, respectively. Thus, the difference, 3.43% is attributable to chemical reactions such as the oxygen release accompanying with the reduction of Co³⁺ to Co²⁺. When all the Co³⁺ in the starting material LCO is completely reduced to Co²⁺ species, the weight loss due to the accompanying oxygen release is estimated to 3.48% which is in good agreement with the experimental value, 3.43%. The cooling process from 900°C to room temperature shows no weight change in TG curves, suggesting that no reactions occur during the cooling process. No obvious endothermic or exothermic signal is observed in DTA, indicating persistent physical processes or chemical reactions occur in such a wide temperature range.

11. Combination of Rietveld analysis and LCF.



Figure S14. Molar ratio determined by Rietveld analysis of the XRD patterns and LCF of the XANES spectra.

12. Total amount of Co and Ti cations in the LCO/LATP pellets sintered at various temperatures.



Figure S15. The total molar amount of Co- and Ti-containing species in the pellets with respect to the sintering temperature.

Figure S15 shows the total amount of Co and Ti cations in the LCO/LATP pellets sintered at various temperature. It confirms that the total amount of Co and Ti cations in the pellets are not much changed. Thus, volatilization of Co and Ti cations seems to be rather minor.

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