Supporting Information

Correlating Structural Changes and Gas Evolution during the Thermal Decomposition of Charged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ Cathode Materials

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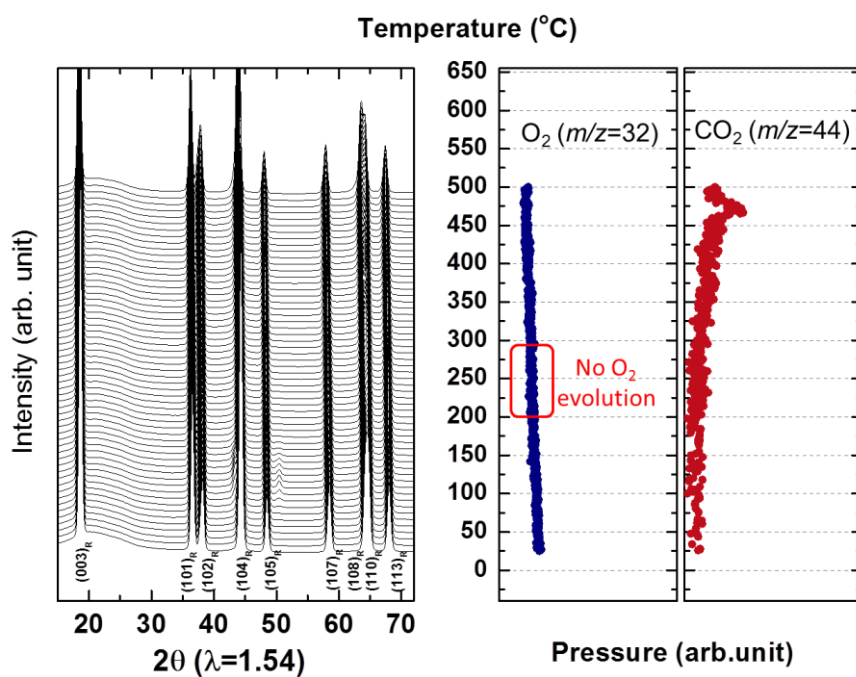
E-mail: knam@bnl.gov (K.N.); kychung@kist.re.kr (K.C.); xyang@bnl.gov (X.Y.)
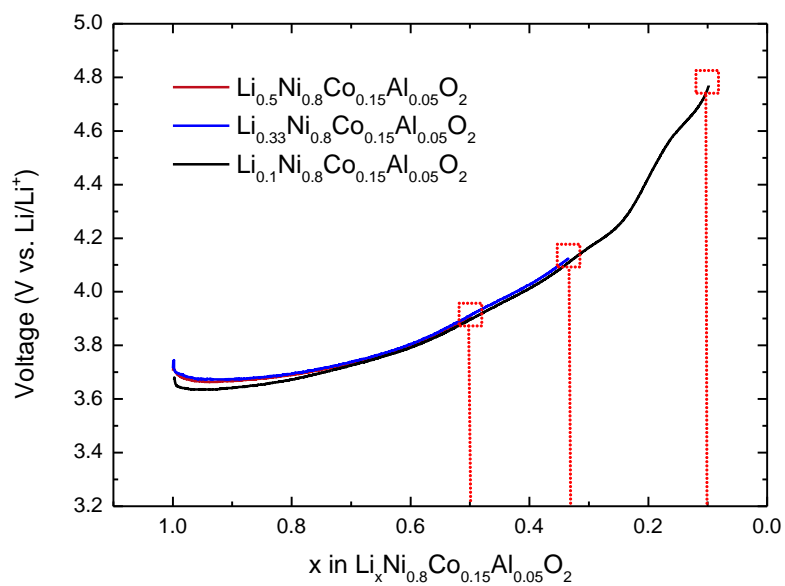
Figure S1. Constant current charge profiles of the $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (x=0.5, 0.33 and 0.1)electrode with a C/18 rate.
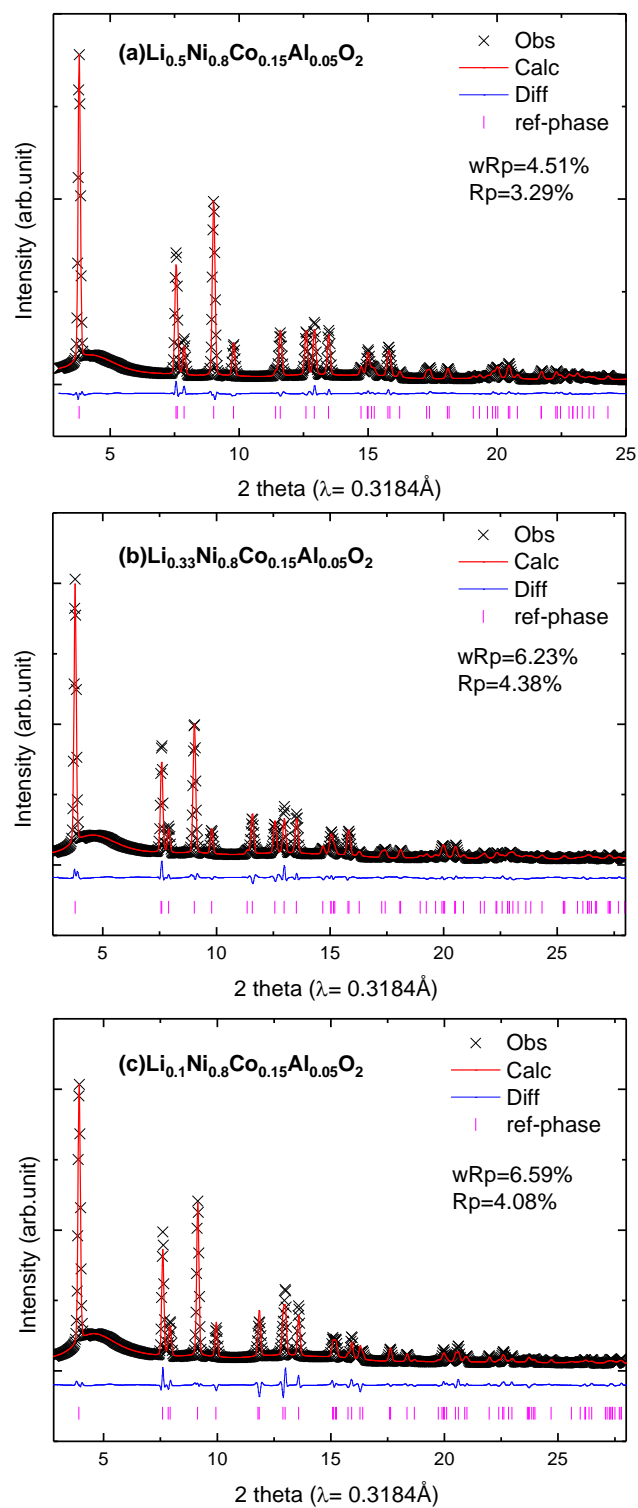
Figure S2. Rietveld refinement of XRD data for $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ with (a) x=0.5, (b) x=0.33, and (c) x=0.1.

Figure S3. TR-XRD patterns and mass spectroscopy results for the pristine (uncharged) $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ after washing with DMC solvent.
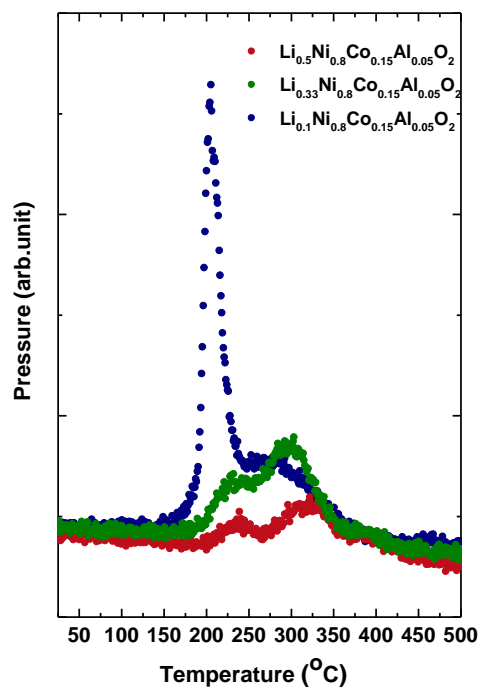
Figure S4. Mass spectroscopy (MS) results for O_2 release from $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (x=0.5, 0.33 and 0.1) during heating to 500^oC.
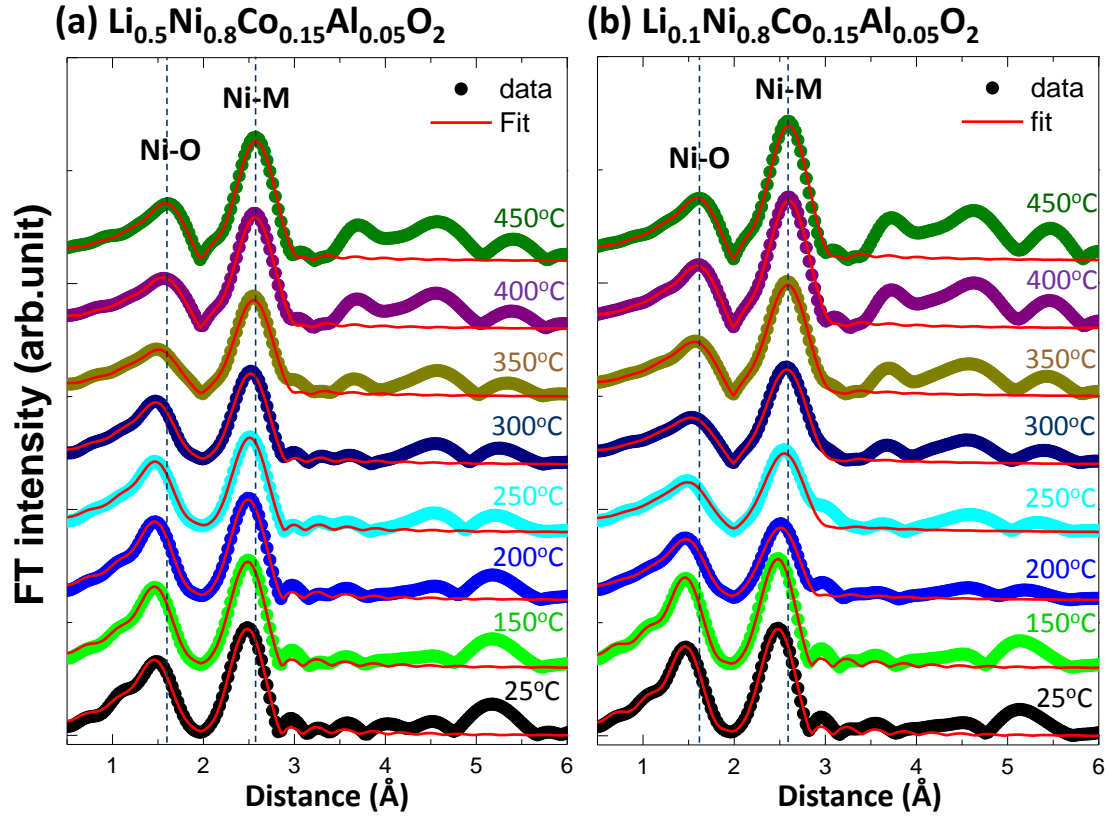
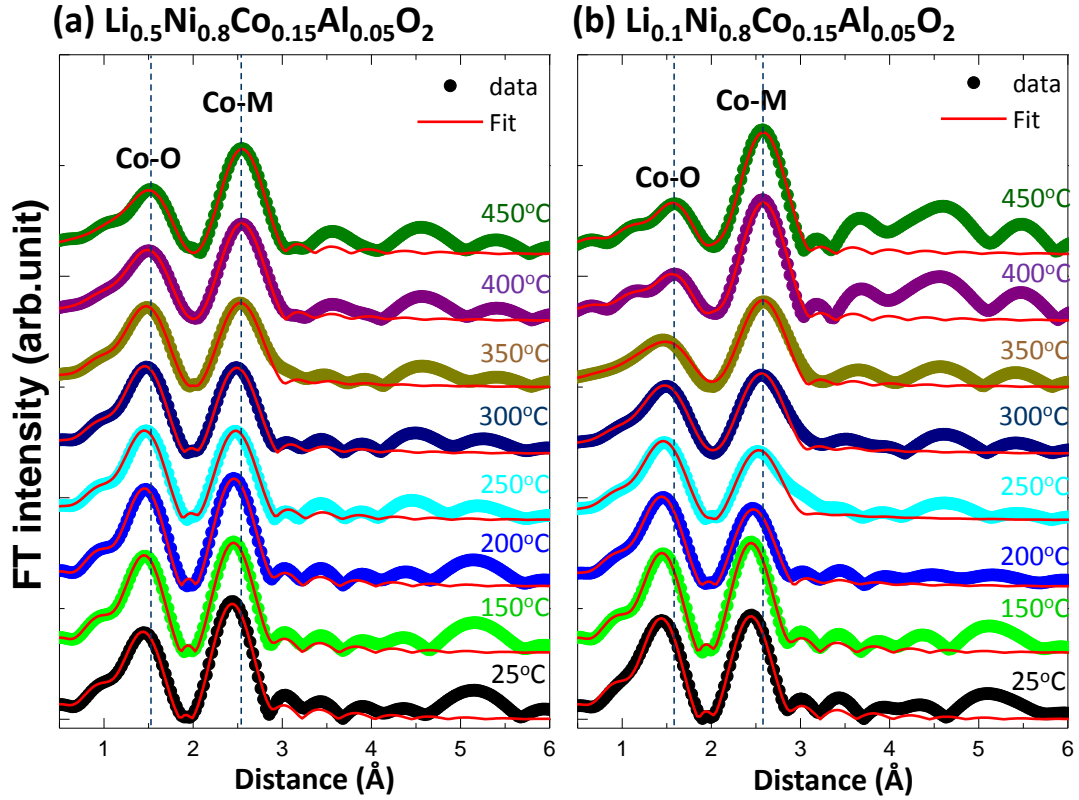**Figure S5.** Experimental (solid circle) and fitted (red line) Fourier-transformed EXAFS spectra at Ni K-edge for the (a) $Li_{0.5}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ and (b) $Li_{0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ with heating temperatures.

The EXAFS signal, $\chi(k)$, for the Ni K-edge was weighted by k^2 to emphasize the high-energy oscillations and then Fourier-transformed in k-ranges of 3.5 ~ 13.5 Å^{-1} using a Hanning window function ($\Delta k = 1.0$ Å^{-1}) to obtain the magnitude plots of the EXAFS spectra in a R-space (Å). The filtered FTs of the EXAFS spectra in a R range of 1.0 ~ 2.9 Å covering the first Ni-O and second Ni-M shells were fitted using theoretical single scattering paths generated with the FEFF 6.0 *ab-initio* simulation code based on a rock-salt model structure. The amplitude reduction factor (S_0^2) was determined to be 0.75 from the preliminary fitting of the spectrum at 25°C (i.e., as charged samples) and then fixed during the final fitting unless noted otherwise. The same inner shell potential shift (ΔE) was shared for the Ni-O and Ni-M shells (M=Co and Ni) while separate fitting parameters of the bond distance (R) and Debye-Waller factor (i.e., mean square disorder, σ^2) were used for each shell. The coordination number for the first Ni-O shell was fixed to 6 (i.e., octahedral coordination) while those of the second Ni-M shell were refined during fitting. Therefore total number of parameters varied during the fit was 6 which is far less than the number of independent parameters of around 12 which is given by the relation $N_{idp} \approx (2\Delta k\Delta R)/\pi$ where ΔR is the fitting range in R space and Δk is the data range in k space. The fitted ΔE values for all of the Ni K-edge EXAFS spectra were between -5.0 and

0.0 which were acceptable. During the phase transition from ordered rock salt (i.e., layered structure) to disordered rock-salt (i.e., NaCl type rock salt structure) structure, S_0^2 values needed to be adjusted from 0.75 to 0.98 since the fixed value of 0.75 resulted in the significant increase of the EXAFS reliability R-factor (i.e., absolute misfit between the data and fitting) for the spectra with high temperatures. Therefore, adjusted S_0^2 value of 0.98 was used for the following Ni K-edge spectra;

- $Li_{0.5}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ spectra $\geq 350^o C$
- $Li_{0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ spectra $\geq 250^o C$.

Figure S6. Fourier transformed experimental (solid circle) and fitted (red line) EXAFS data at Co K-edge for the (a) $Li_{0.5}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ and (b) $Li_{0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ with heating temperatures.

The EXAFS signal, $\chi(k)$, for the Co K-edge was weighted by k^2 to emphasize the high-energy oscillations and then Fourier-transformed in k-ranges of 3.4 ~ 11.0 Å^{-1} using a Hanning window function ($\Delta k = 1.0$ Å^{-1}) to obtain the magnitude plots of the EXAFS spectra in a R-space (Å). For the Co K-edge spectra, k range was limited to 11.0 Å^{-1} due to the existence of Ni which appears at around 12 Å^{-1} in the EXAFS signal, $\chi(k)$. The filtered FTs of the EXAFS spectra in a R range of 1.0 ~ 2.9 Å covering the first Co-O and second Co-M shells were fitted using theoretical single scattering paths generated with the FEFF 6.0 *ab-initio* simulation code based on a rock-salt model structure. The amplitude reduction factor (S_0^2) was determined to be 0.84 from the preliminary fitting of the spectrum at 25°C (i.e., as charged samples) and then fixed during the final fitting unless noted otherwise. The similar fitting scheme used for the Ni K-edge fitting was applied to the Co K-edge data for the inner shell potential shift (ΔE), bond distance (R), Debye-Waller factor (i.e., mean square disorder, σ^2), the coordination number. Total number of fitting parameters varied during the fit was 6 which is less than the number of independent parameters of around 9. The fitted ΔE values for all of the Co K-edge EXAFS spectra were in the range of ±2.5 which is acceptable. The S_0^2 values were also adjusted from 0.84 to 0.95 in case of the Co K-edge spectra over 350°C for the highly charged

$Li_{0.1}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ sample while the $S_0{}^2$ values for the spectra of the less charged $Li_{0.5}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ samples were kept with the original value of 0.84.
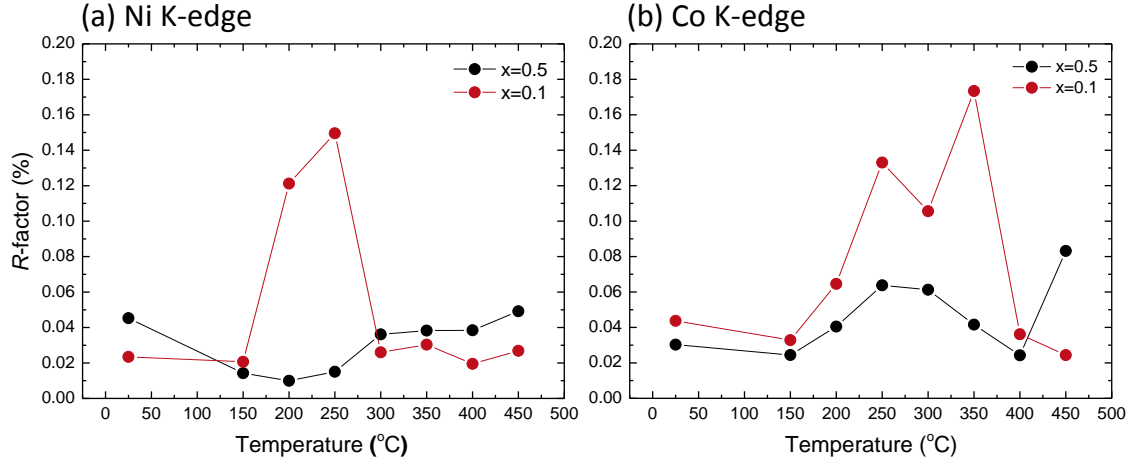
Figure S7. The EXAFS reliability R-factors for the fitting of Ni and Co K-edge EXAFS spectra of the charged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ with x=0.5 and 0.1.

The EXAFS reliability R-factor was estimated based on the following equation;

$$R = \sum_{i=1}^{N_{pts}} \frac{\left[Im\left(\chi_{dat}(R_i) - \chi_{th}(R_i)\right)\right]^2 + \left[Re\left(\chi_{dat}(R_i) - \chi_{th}(R_i)\right)\right]^2}{\left[Im\left(\chi_{dat}(R_i)\right)\right]^2 + \left[Re\left(\chi_{dat}(R_i)\right)\right]^2}$$

The EXAFS R-factors were less than 0.2% in all cases showing a good quality of the fitting based on the rock-salt model structure. However, compared with, the R-factors for the Co K-edge fitting (Fig. S7(b)) were relatively higher than those for the Ni K-edge fitting results (Fig. S7(a)) regardless of the states of charge. This may suggest that the formation of a different local structure (e.g., Co_3O_4 spinel) around Co, which is not a layered or rock-salt structure (only a rock-salt model was considered in the fitting). Alternative fittings of the Co and Ni K-edge EXAFS spectra for those which showed large misfit based on the rock-salt structure will be tested using different model structures such as spinel- Co_3O_4 and $LiCo_2O_4$ structures with some modifications (e.g., site occupancy and site mixing) in the future work.