Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


Supplementary information for

# Multiscale Investigation Elucidating the Structural Complexities and Electrochemical Properties of Layered-Layered Composite Cathode Materials Synthesized at Low Temperatures

Songyoot Kaewmala [a], Narinthorn Wiriya [b], Patcharapohn Chantrasuwan [b], Visittapong Yordsri [c], Wanwisa Limphirat [d], Shoaib Muhammad [e], Won-Sub Yoon [e], Jeffrey Nash[f], Sutham Srilomsak [a, b], Pimpa Limthongkul [c,*], and Nonglak Meethong [a, b, *]

[a] Institute of Nanomaterials Research and Innovation for Energy (IN-RIE), Research Network of NANOTEC- KKU (RNN), Khon Kaen University, Khon Kaen, 40002, Thailand

[b]Materials Science and Nanotechnology Program, Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen, 40002, Thailand

[c] National Metal and Materials Technology Center, National Science and Technology Development Agency, Pathumthani, 12120, Thailand

[d] Synchrotron Light Research Institute, 111 University Avenue, Suranaree, Muang, Nakhon Ratchasima, 30000, Thailand

[e] Department of Energy Science, Sungkyunkwan University, Suwon, 16419, Republic of Korea

[f] The Graduate School, Udon Thani Rajabhat University, Udon Thani, 41000, Thailand

*Corresponding authors: nonmee@kku.ac.th (NM) and pimpal@mtec.or.th (PL)

## Supplementary information

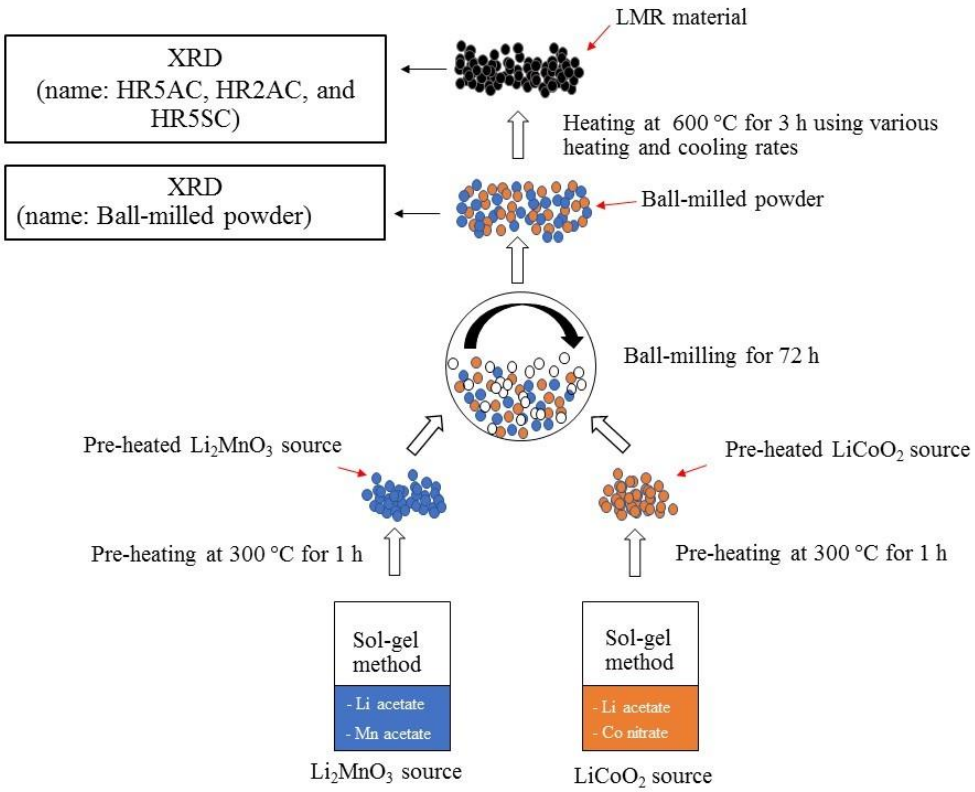


**Figure S1.** Schematic diagram of the preparation procedures of the layered-layered composite materials.

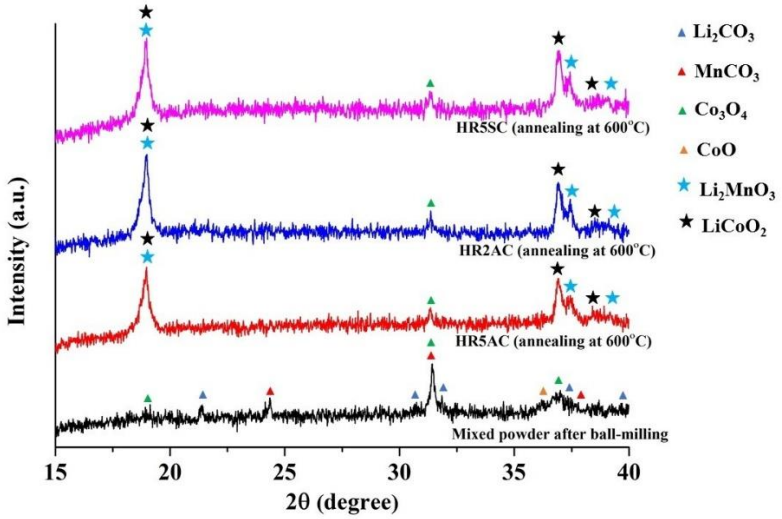


**Figure S2.** XRD patterns of the HR5AC, HR2AC, and HR5SC samples.

As presented in Fig. S2, the final XRD patterns of the HR5AC, HR2AC, and HR5SC samples prepared using various firing schedules could be indexed to both of the $Li_2MnO_3$ (C2/m) and $LiCoO_2$ ($R\bar{3}m$) phases with quite broad XRD peaks. Moreover, a $Co_3O_4$ phase was also observed and their broad XRD patterns indicate that the samples exhibited low crystallinity. This results from a low annealing temperature (600 ℃). Figure 1 presents HRTEM results of the HR5AC, HR2AC and HR5SC samples. The results revealed that both the $Li_2MnO_3$-like domain with a C2/m space group and the $LiCoO_2$-like domain with an $R\bar{3}m$ space group were clearly observed coexisting within the same particles. The results indicate that the HR5AC, HR2AC, and HR5SC samples formed a LMR-type material with low crystallinity.

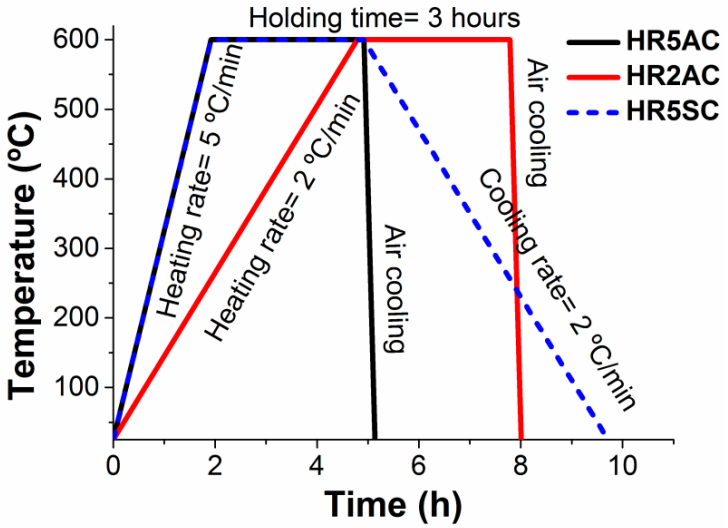


**Figure S3.** Firing schedule of each heat treatment condition.

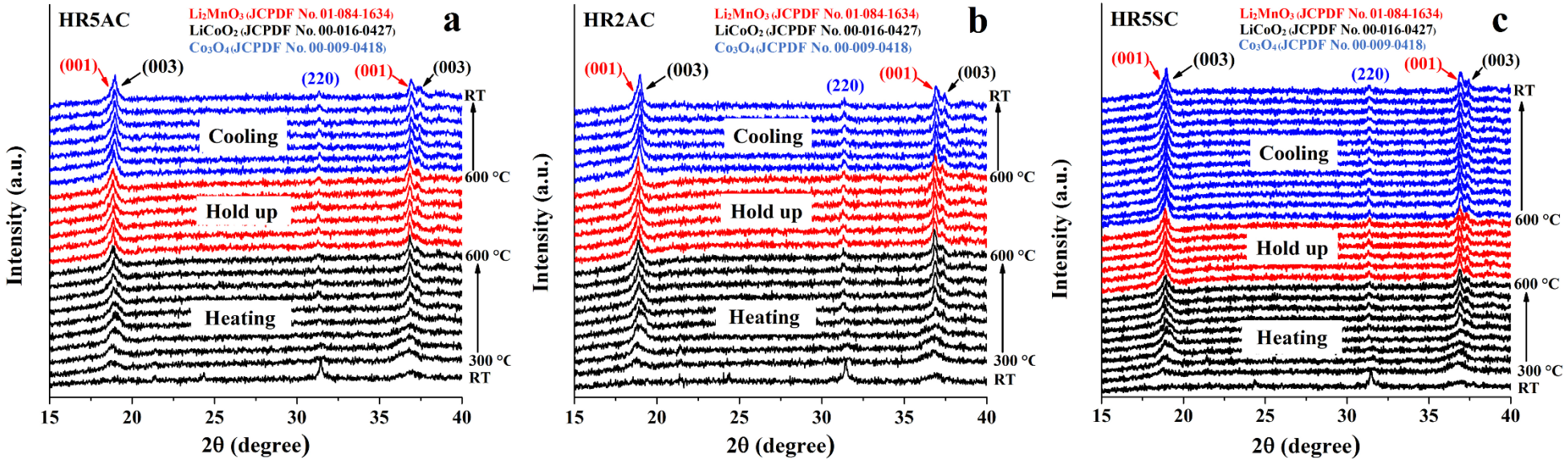


**Figure S4.** XRD patterns of the HR5AC (a), HR2AC (b), and HR5SC (c) samples measured during heating processes with various heating and cooling rates.

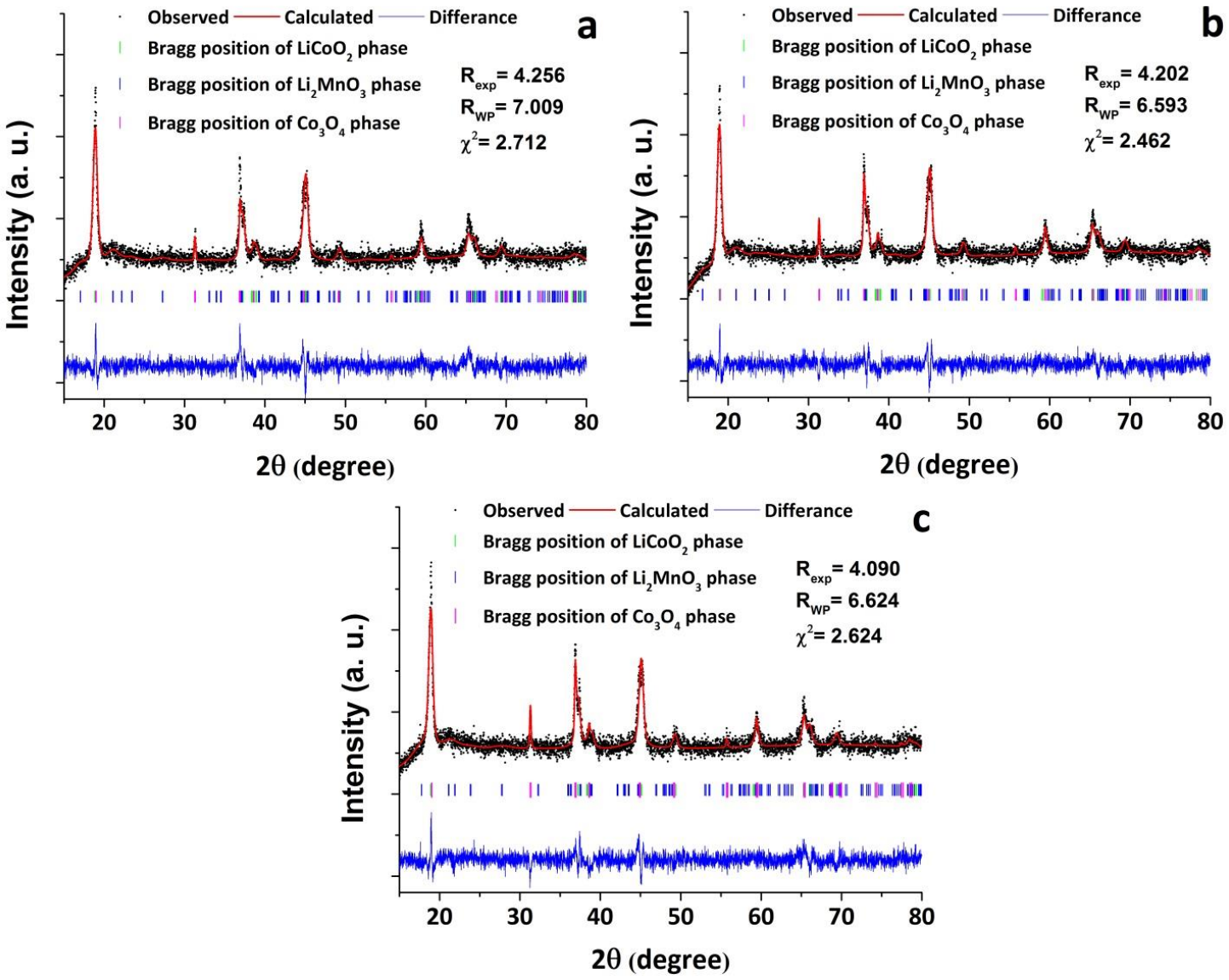


**Figure S5**. Examples of Rietveld refinement results of the HR5AC (a), HR2AC (b), and HR5SC (c) samples.

The prepared samples contained Co and Mn, contributing to the high background signals of the diffraction patterns owing to the fluorescent effect. This led to rather low R factors. To improve these R factors, 80% of the background signals were removed without a significant effect on the refined lattice parameter values.

**Table S1.** The lattice parameters and agreement indices obtained from Reitveld refinement of XRD patterns of HR5AC, HR2AC, and HR5SC samples.

| Conditions | Lattice parameters | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $Li_2MnO_3$ (C2/m) $\alpha = \gamma = 90°$ | | | | | $LiCoO_2$ ($R\bar{3}m$) $\alpha = \beta = 90°$ and $\gamma = 120°$ | | |
| | a (Å) | b (Å) | c (Å) | β(°) | Unit cell volume (Å$^3$) | a and b (Å) | C (Å) | Unit cell volume (Å$^3$) |
| HR5AC | 4.9295 ±0.0001 | 8.5569 ±0.0002 | 4.9529 ±0.0009 | 109.5359 ±0.0050 | 197.1429 | 2.8259 ±0.0004 | 14.0811 ±0.0021 | 97.3829 |
| HR2AC | 4.9234 ±0.0006 | 8.5383 ±0.0003 | 4.9390 ±0.0008 | 109.8551 ±0.0011 | 197.2621 | 2.8281 ±0.0005 | 14.0681 ±0.0050 | 97.4375 |
| HR2SC | 5.0261 ±0.0005 | 8.4261 ±0.0005 | 4.9453 ±0.0006 | 109.4681 ±0.0004 | 197.4593 | 2.8243 ±0.0004 | 14.0741 ±0.0003 | 97.2034 |

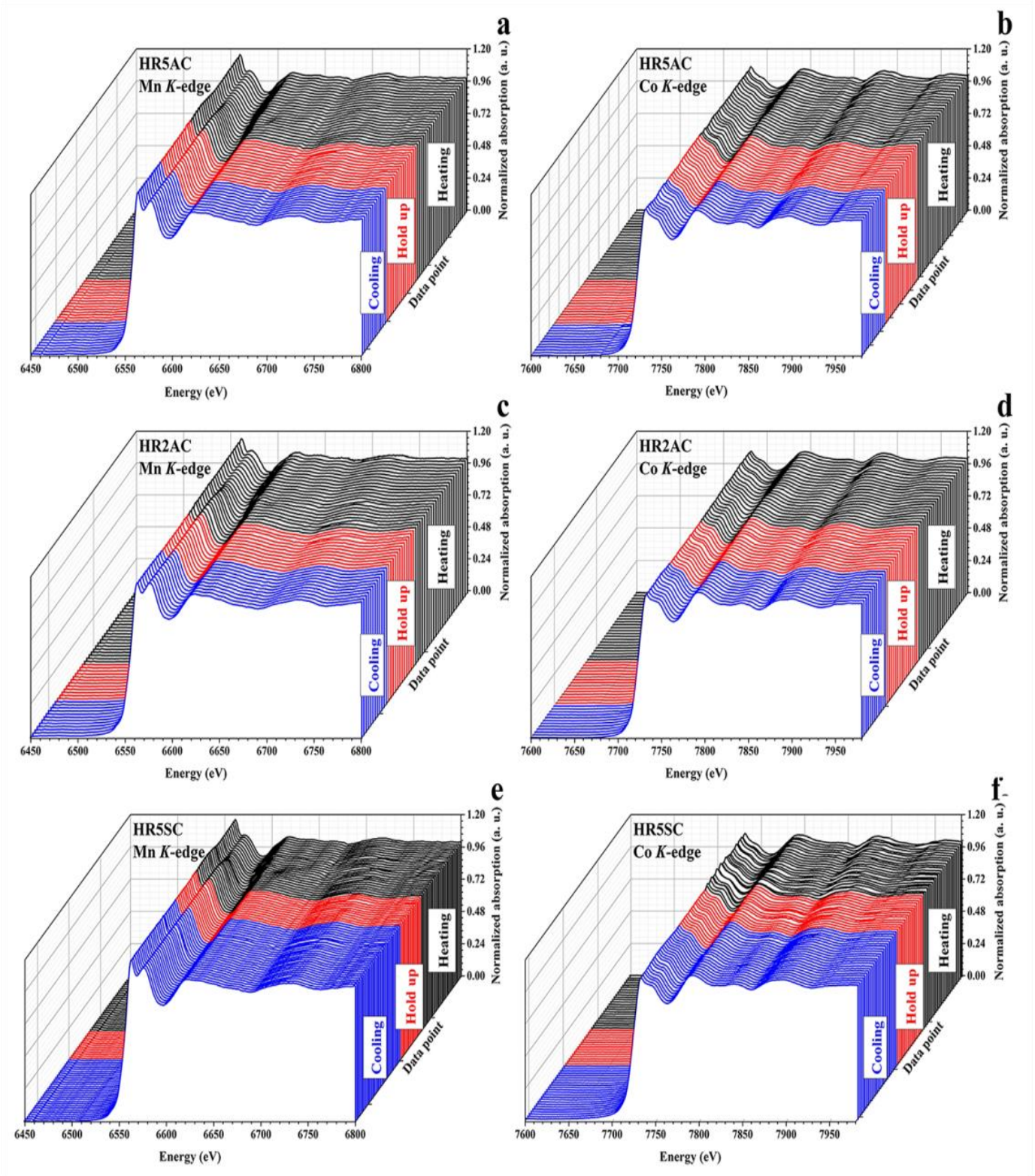


**Figure S6.** XAS spectra of the HR5AC (a), HR2AC (b), and HR5SC (c) samples measured during heating processes with various heating and cooling rates.

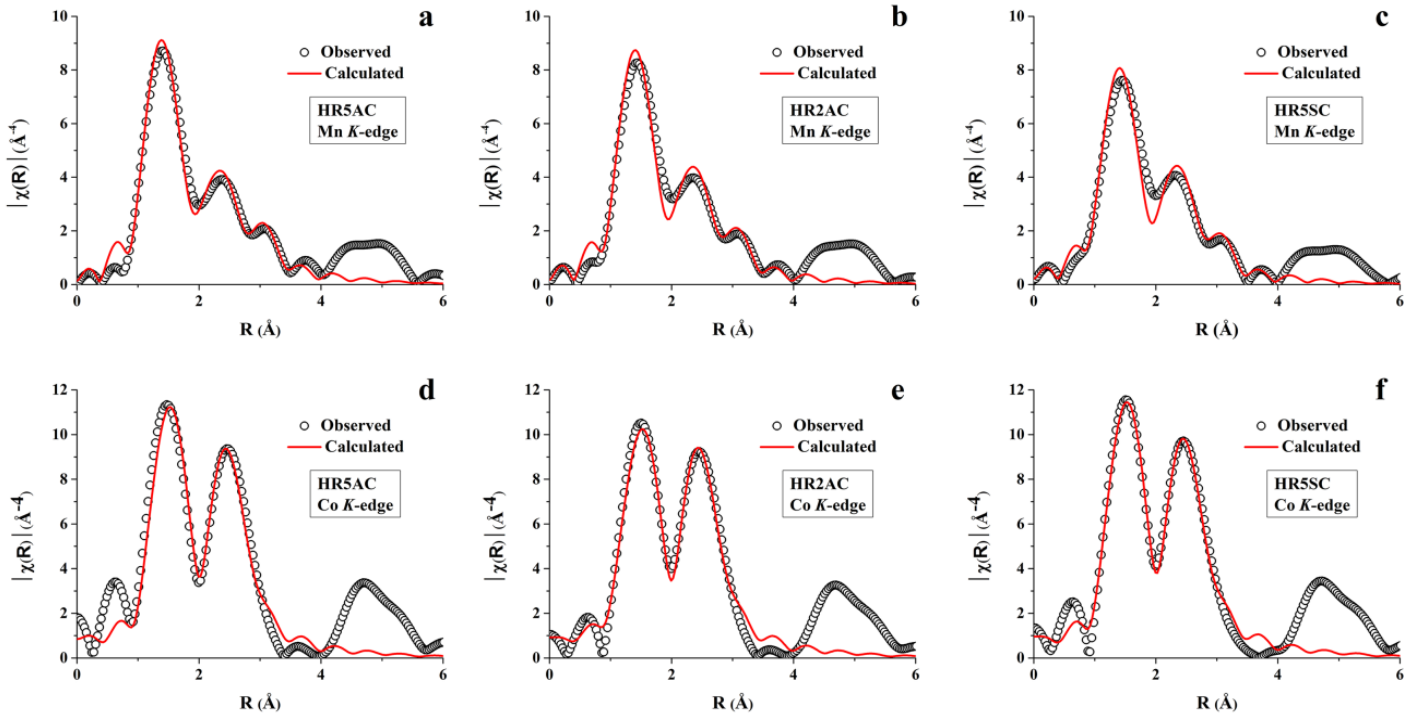


**Figure S7.** EXAFS fitting of the HR5AC (a), HR2AC (b), and HR5SC (c) samples synthesized using various heating and cooling rates.

**Table S2**. The bond distances and agreement indices obtained from XAS spectra fitting of final XAS spectra of the HR5AC, HR2AC, and HR5SC samples.

| $Li_2MnO_3$ structure (Mn *K*- edge) | | | | | | |
|---|---|---|---|---|---|---|
| Samples | Shell | N (atoms) | R (Å) | $\sigma^2$ (Å$^2$) | R-factor | $E_0$ (eV) |
| HR5AC | O | 6 | 1.900 ±0.015 | 0.003 ±0.001 | 0.013 | -4.052 |
| | Mn | 3 | 2.866 ±0.021 | 0.004 ±0.002 | | |
| HR2AC | O | 6 | 1.909 ±0.018 | 0.003 ±0.001 | 0.020 | -3.091 |
| | Mn | 3 | 2.869 ±0.025 | 2.869 ±0.002 | | |
| HR5SC | O | 6 | 1.912 ±0.021 | 0.004 ±0.001 | 0.026 | -3.029 |
| | Mn | 3 | 2.866 ±0.028 | 0.004 ±0.002 | | |
| $LiCoO_2$ structure (Co *K*-edge) | | | | | | |
| Samples | Shell | N (atoms) | R (Å) | $\sigma^2$ (Å$^2$) | R-factor | $E_0$ (eV) |
| HR5AC | O | 6 | 1.901 ±0.022 | 0.003 ±0.002 | 0.012 | 9.434 |
| | Co | 6 | 2.832 ±0.02 | 0.005 ±0.002 | | |
| HR2AC | O | 6 | 1.911 ±0.027 | 0.005 ±0.003 | 0.016 | 9.427 |
| | Co | 6 | 2.837 ±0.027 | 0.004 ±0.002 | | |
| HR5SC | O | 6 | 1.909 ±0.025 | 0.004 ±0.002 | 0.013 | -3.359 |
| | Co | 6 | 2.851 ±0.029 | 0.006 ±0.002 | | |

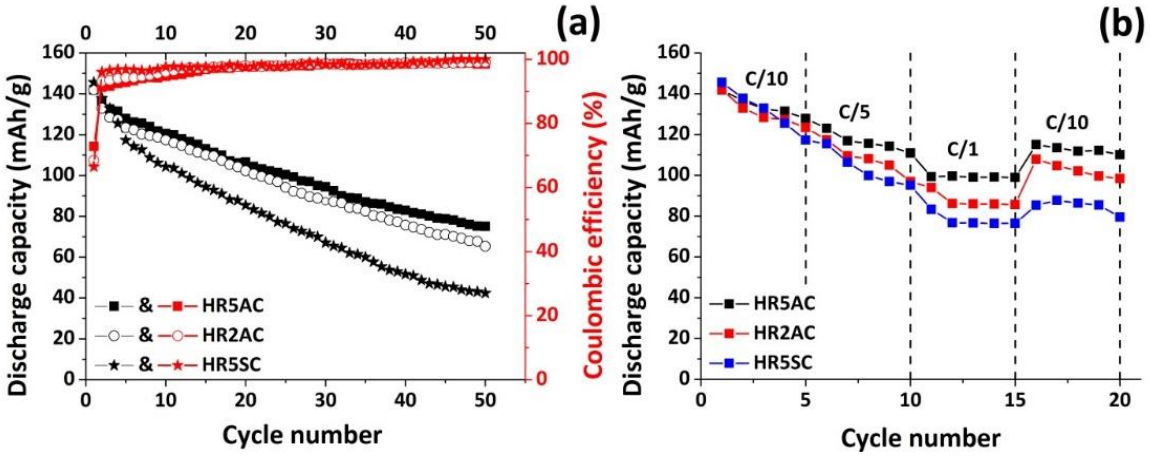


**Figure S8.** Cycling stabilities at C/10 (a) and rate performance (b) of the HR5AC, HR2AC, and HR5SC samples.