

Insights into Li/Ni Ordering and Surface Reconstruction during Synthesis of Ni-rich Layered Oxides

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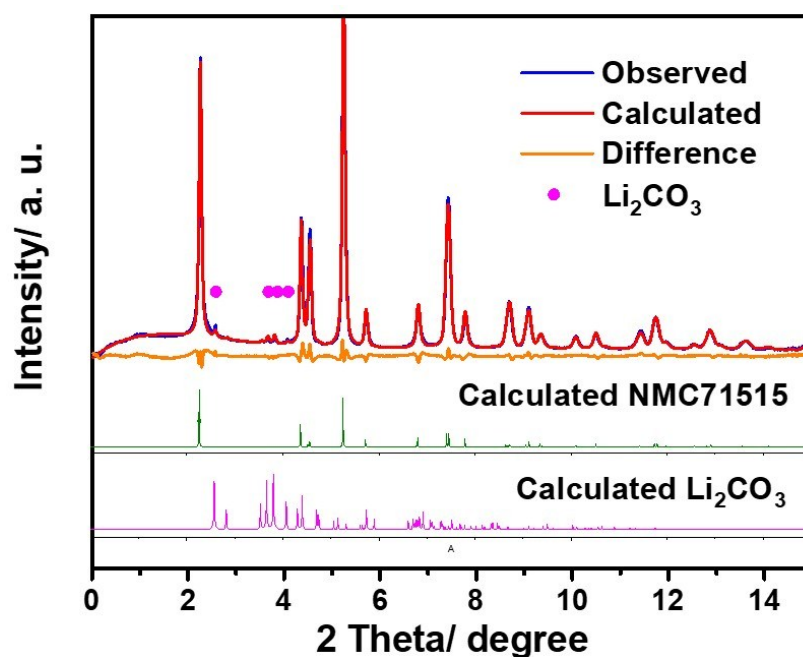


Figure S1. Rietveld refinement results of synchrotron X-ray patterns for NMC71515 after pretreatment at 500 °C for 10 h (R_{wp} =6.94 %).

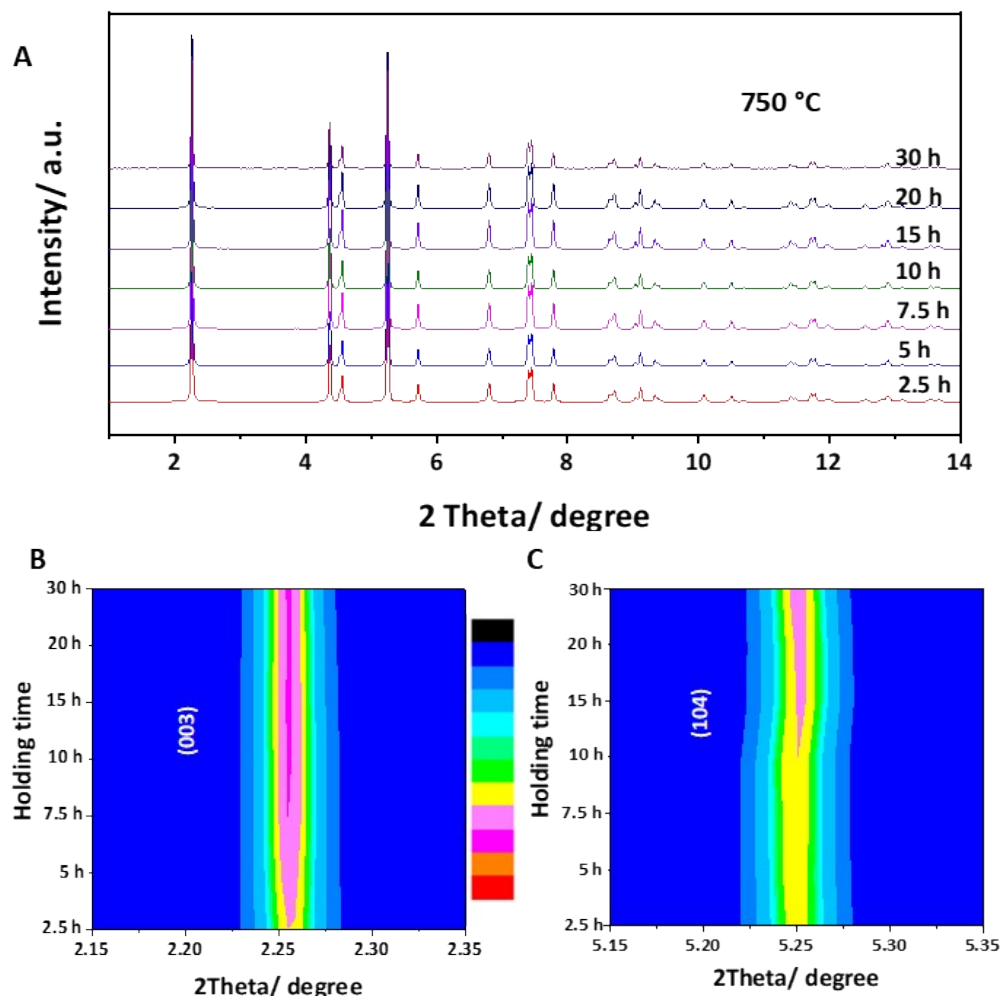


Figure S2. *Ex-situ* high-energy X-ray diffraction patterns for NMC71515 after heat treatment at 750 °C for different holding times (A). Contour plots in the selected 2θ regions containing (003) peak (B) and (104) peak (C).

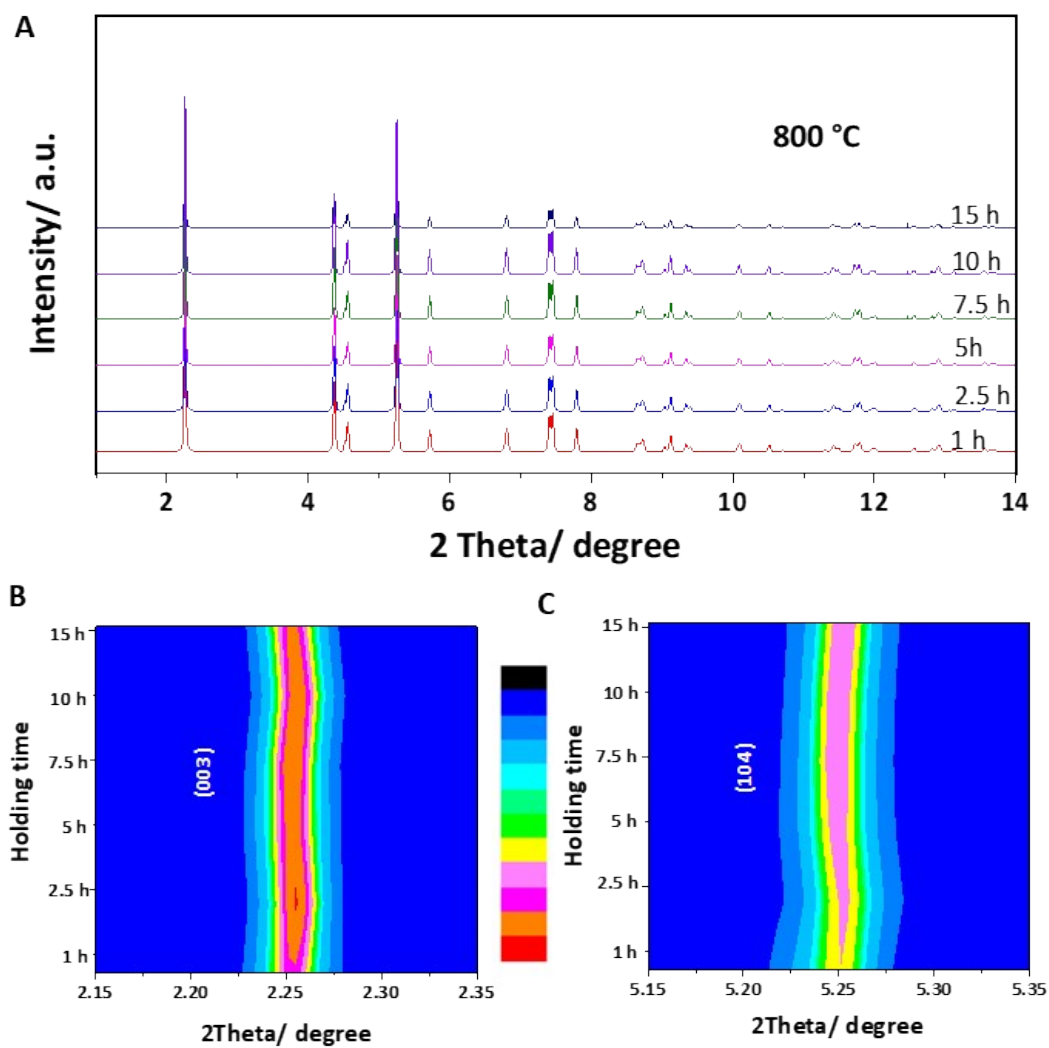


Figure S3. (A) *Ex-situ* high-energy X-ray diffraction patterns for NMC71515 after heat treatment at 800 °C for different holding times. Contour plots in the selected 2θ regions containing (003) peak (B) and (104) peak (C).

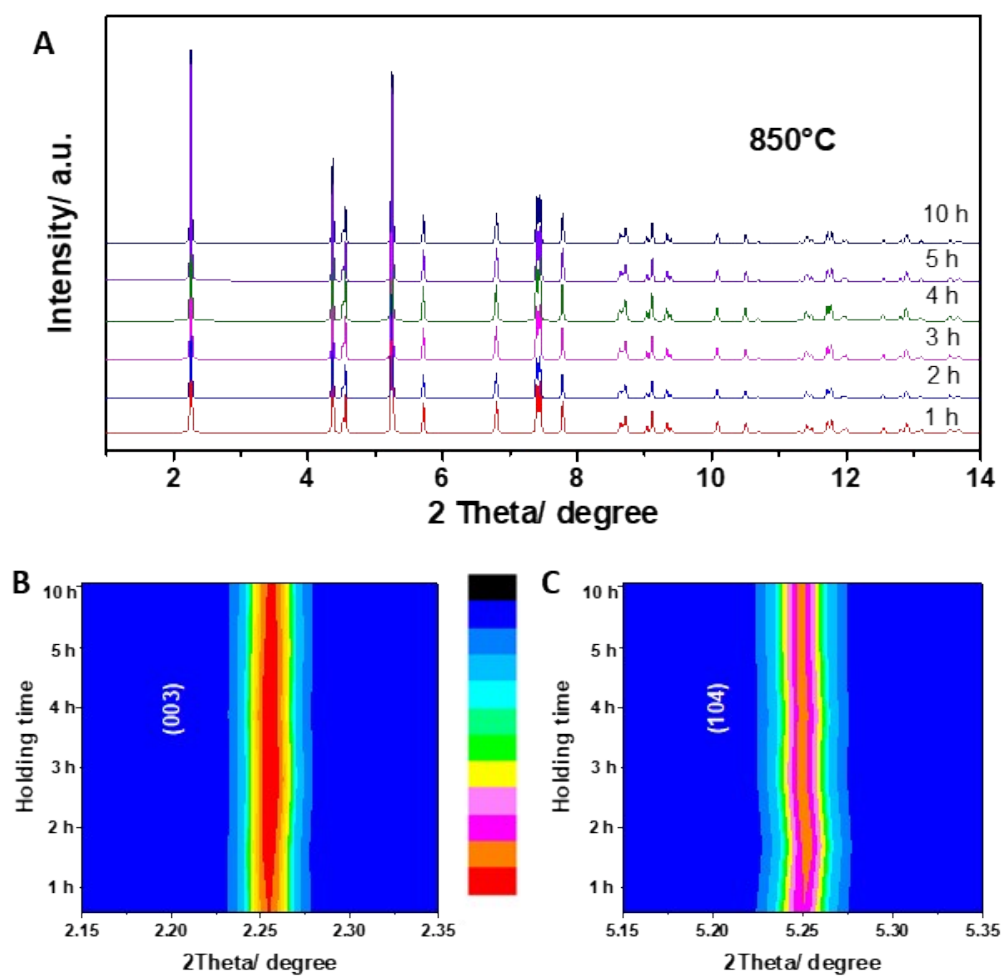


Figure S4. (A) *Ex-situ* high-energy X-ray diffraction patterns for NMC71515 after heat treatment at 850 °C for different holding times. Contour plots in the selected 2θ regions containing (003) peak (B) and (104) peak (C).

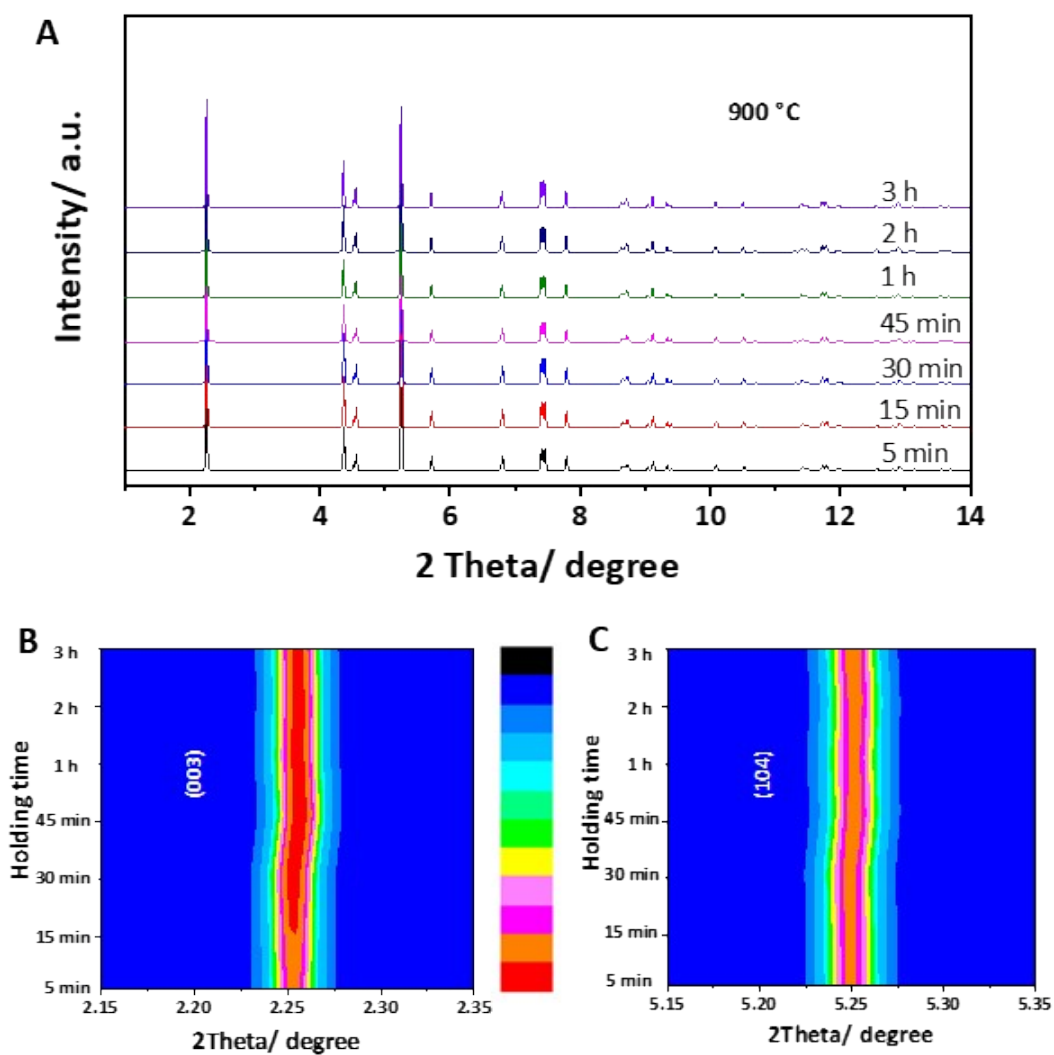


Figure S5. (A) *Ex-situ* high-energy X-ray diffraction patterns for NMC71515 after heat treatment at 900 °C for different holding times. Contour plots in the selected angle regions containing (003) peak (B) and (104) peak (C).

Table S1. Refined structural parameters of $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ at different sintering temperatures with various holding times.

NMC71515 (wt%=89.22)

a(Å)	c(Å)	c/a	Ni(3b)	Li-slab	Li-O (Å)	TM-O (Å)	Zo	C.S. (nm)
2.8789	14.220	4.939	0.135	2.128	2.1113	1.9743	0.2415	26.4

Li_2CO_3 (wt%=10.78)

a(Å)	b(Å)	c(Å)	C.S.(nm)
8.3414(9)	4.9796(8)	6.1987(2)	20.1

Table S2. Refined structural parameters of XRD patterns collected at 750 °C with different holding times.

	a(Å)	c(Å)	c/a	Ni(3b)	Li-slab	Li-O(Å)	TM-O (Å)	Zo	C.S. (nm)
2.5h	2.8717(4)	14.207(8)	4.9475	0.046(2)	2.136(1)	2.1067(2)	1.9731(2)	0.2418(6)	80.9
5h	2.8715(2)	14.207(8)	4.9478	0.043(4)	2.136(3)	2.1072(0)	1.9730(6)	0.2418(5)	88.8
7.5h	2.8715(3)	14.208(5)	4.9480	0.043(2)	2.136(6)	2.1076(5)	1.9727(3)	0.2418(0)	95.8
10h	2.8717(7)	14.208(0)	4.9475	0.042(5)	2.136(9)	2.1079(5)	1.9725(3)	0.2418(7)	100.2
15h	2.8722(6)	14.209(9)	4.9473	0.045(4)	2.138(1)	2.1080(6)	1.9728(0)	0.2418(6)	107.3
20h	2.8722(9)	14.209(9)	4.9473	0.047(0)	2.136(9)	2.1079(1)	1.9729(6)	0.2419(0)	115.7
30h	2.8730(4)	14.212(2)	4.9468	0.050(7)	2.134(7)	2.1077(7)	1.9734(4)	0.2417(7)	125.3

Table S3. Refined structural parameters of XRD patterns collected at 775 °C with different holding times.

	a(Å)	c(Å)	c/a	Ni(3b)	Li-slab	Li-O(Å)	TM-O(Å)	Zo	C.S. (nm)
1h	2.8719(0)	14.208(6)	4.9474	0.031(3)	2.135(9)	2.1079(5)	1.9718(1)	0.2418(3)	98.9
2.5h	2.8717(4)	14.209(8)	4.9482	0.030(7)	2.138(6)	2.1081(2)	1.9716(9)	0.2419(2)	132.6

5h	2.8715(7)	14.210(2)	4.9486	0.028(9)	2.139(3)	2.1086(0)	1.9716(1)	0.2419(4)	143.8
7.5h	2.8717(2)	14.211(4)	4.9488	0.026(4)	2.139(9)	2.1090(5)	1.9714(3)	0.2419(5)	159.2
10h	2.8721(6)	14.212(3)	4.9483	0.027(5)	2.139(2)	2.1089(9)	1.9715(3)	0.2419(2)	170.2
15h	2.8726(6)	14.211(7)	4.9473	0.029(0)	2.138(7)	2.1088(6)	1.9726(9)	0.2419(1)	189.8
20h	2.8732(1)	14.213(0)	4.9468	0.031(8)	2.138(0)	2.1087(7)	1.9737(3)	0.2418(8)	216.7
25h	2.8740(2)	14.216(0)	4.9464	0.036(4)	2.136(7)	2.1086(2)	1.9745(3)	0.2418(2)	230.3

Table S4. Refined structural parameters of XRD patterns collected at 800 °C with different holding times.

	a(Å)	c(Å)	c/a	Ni(3b)	Li-slab	Li-O(Å)	TM-O(Å)	Zo	C.S. (nm)
1h	2.8718(4)	14.210(7)	4.9482	0.037(2)	2.135(5)	2.1075(7)	1.9717(8)	0.2418(0)	111.3
2.5h	2.8715(2)	14.209(6)	4.9484	0.032(0)	2.136(8)	2.1081(6)	1.9717(9)	0.2418(5)	132.8
5h	2.8717(3)	14.210(6)	4.9484	0.028(0)	2.139(9)	2.1085(8)	1.9716(9)	0.2419(6)	159.0
7.5h	2.8717(3)	14.211(6)	4.9487	0.027(9)	2.139(6)	2.1087(8)	1.9716(1)	0.2419(4)	167.6
10h	2.873(1)	14.216(4)	4.9481	0.033(2)	2.138(1)	2.1088(2)	1.9719(1)	0.2418(6)	172.6
15h	2.8736(2)	14.215(9)	4.9470	0.038(6)	2.137(1)	2.1087(4)	1.9735(5)	0.2418(3)	190.1

Table S5. Refined structural parameters of XRD patterns collected at 850 °C with different holding times

	a(Å)	c(Å)	c/a	Ni(3b)	Li-slab	Li-O(Å)	TM-O(Å)	Zo	C.S. (nm)
1h	2.8717(4)	14.208(8)	4.9478	0.035(0)	2.135(4)	2.1075(9)	1.9725(3)	0.2418(1)	302.6
2h	2.8716(9)	14.210(0)	4.9483	0.028(8)	2.137(3)	2.1080(9)	1.9724(3)	0.2418(7)	368.9
3h	2.8719(4)	14.211(6)	4.9484	0.028(1)	2.138(3)	2.1083(6)	1.9722(2)	0.2418(9)	380.3
4h	2.8723(7)	14.214(3)	4.9486	0.027(0)	2.139(6)	2.1085(4)	1.9719(3)	0.2419(2)	398.5
5h	2.8728(3)	14.215(7)	4.9483	0.031(5)	2.137(7)	2.1084(4)	1.9732(8)	0.2418(5)	403.0
10h	2.8741(8)	14.216(9)	4.9464	0.055(0)	2.137(0)	2.1084(0)	1.9759(0)	0.2418(2)	436.3

Table S6. Refined structural parameters of XRD patterns collected at 900 °C with different holding times.

	a(Å)	c(Å)	c/a	Ni(3b)	Li-slab	Li-O(Å)	TM-O(Å)	Zo	C.S. (nm)
5min	2.8718(4)	14.20888	4.9469	0.040(0)	2.132(2)	2.1080(4)	1.9733(3)	0.2417(0)	395.0
15min	2.8718(6)	14.21008	4.9471	0.035(5)	2.132(9)	2.1081(7)	1.9734(3)	0.2417(3)	485.4
30min	2.8718(2)	14.21168	4.9472	0.033(0)	2.132(3)	2.1083(8)	1.9730(5)	0.2417(0)	514.8
45min	2.8718(5)	14.21438	4.9479	0.031(5)	2.136(7)	2.1085(4)	1.9721(9)	0.2418(5)	582
1h	2.8718(5)	14.21578	4.9485	0.033(0)	2.138(9)	2.1085(5)	1.9721(1)	0.2419(2)	600
2h	2.8719(4)	14.21698	4.9484	0.044(9)	2.137(3)	2.1084(8)	1.9724(1)	0.2418(6)	640.1
3h	2.8725(8)	14.20888	4.9473	0.049(9)	2.137(4)	2.1084(6)	1.9729(0)	0.2418(6)	687.6

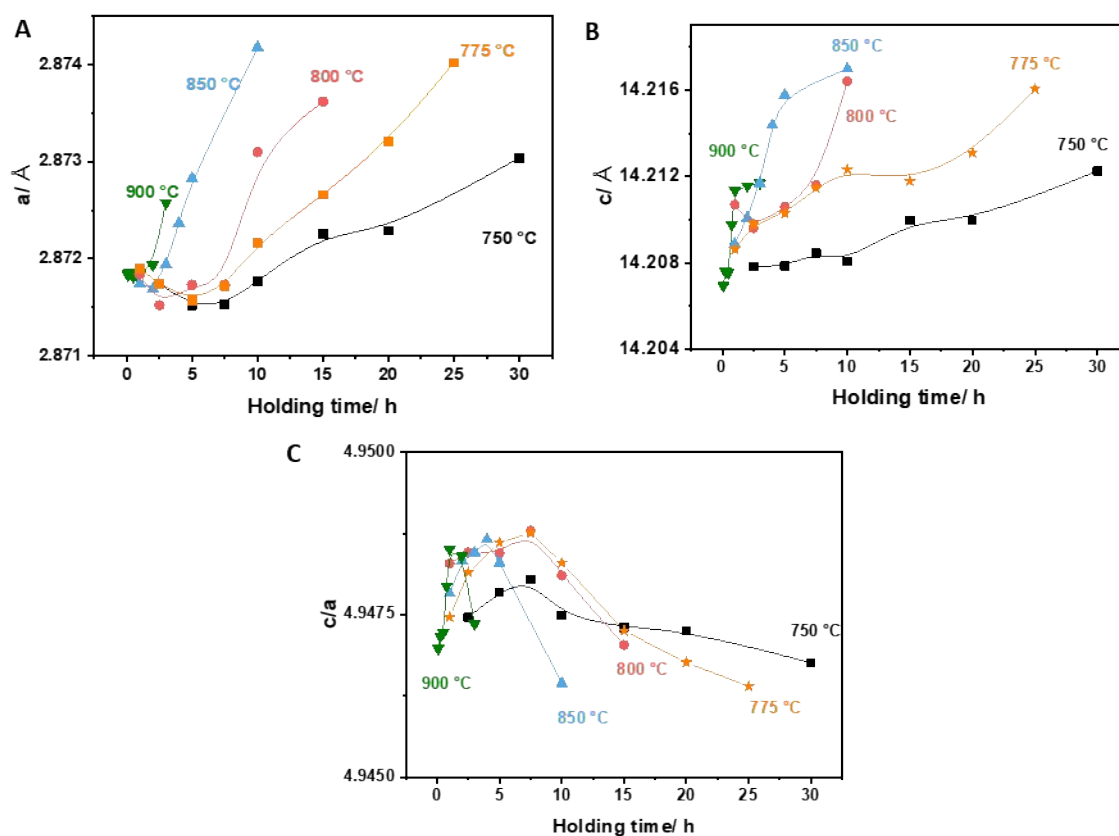


Figure S6. Evolution of lattice parameters (A) *a* and (B) *c* and (C) *c/a* for NMC71515 at 750 °C, 800 °C, 850 °C, 900 °C as function of holding time.

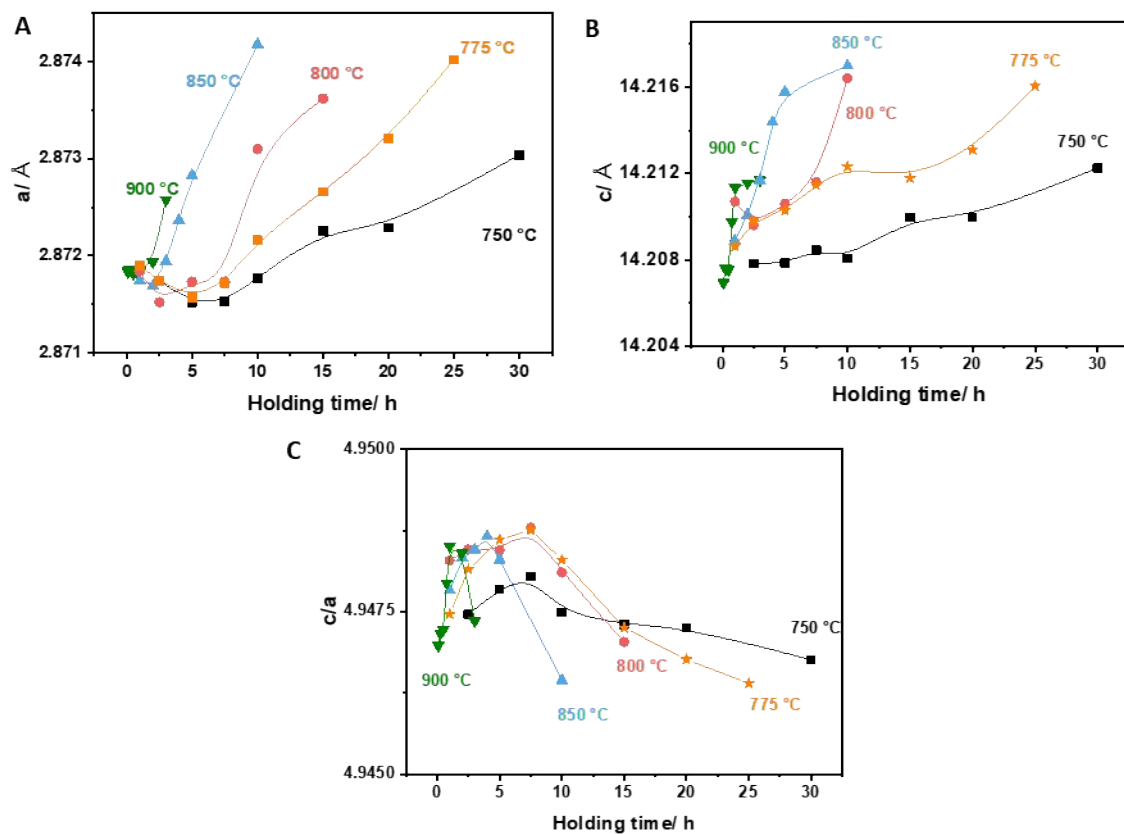


Figure S7. Bond length of (A) Li-O and (B) TM-O (bottom) and (C) Li slab with holding time.

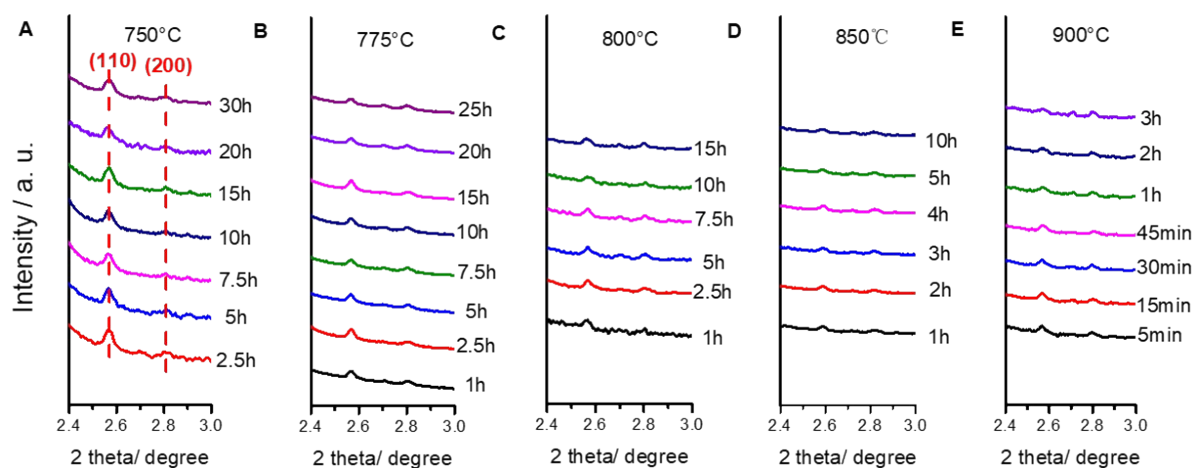


Figure S8. *Ex-situ* high-energy X-ray diffraction patterns in the selected 2θ regions containing Li₂CO₃ (110) and (200) peaks.

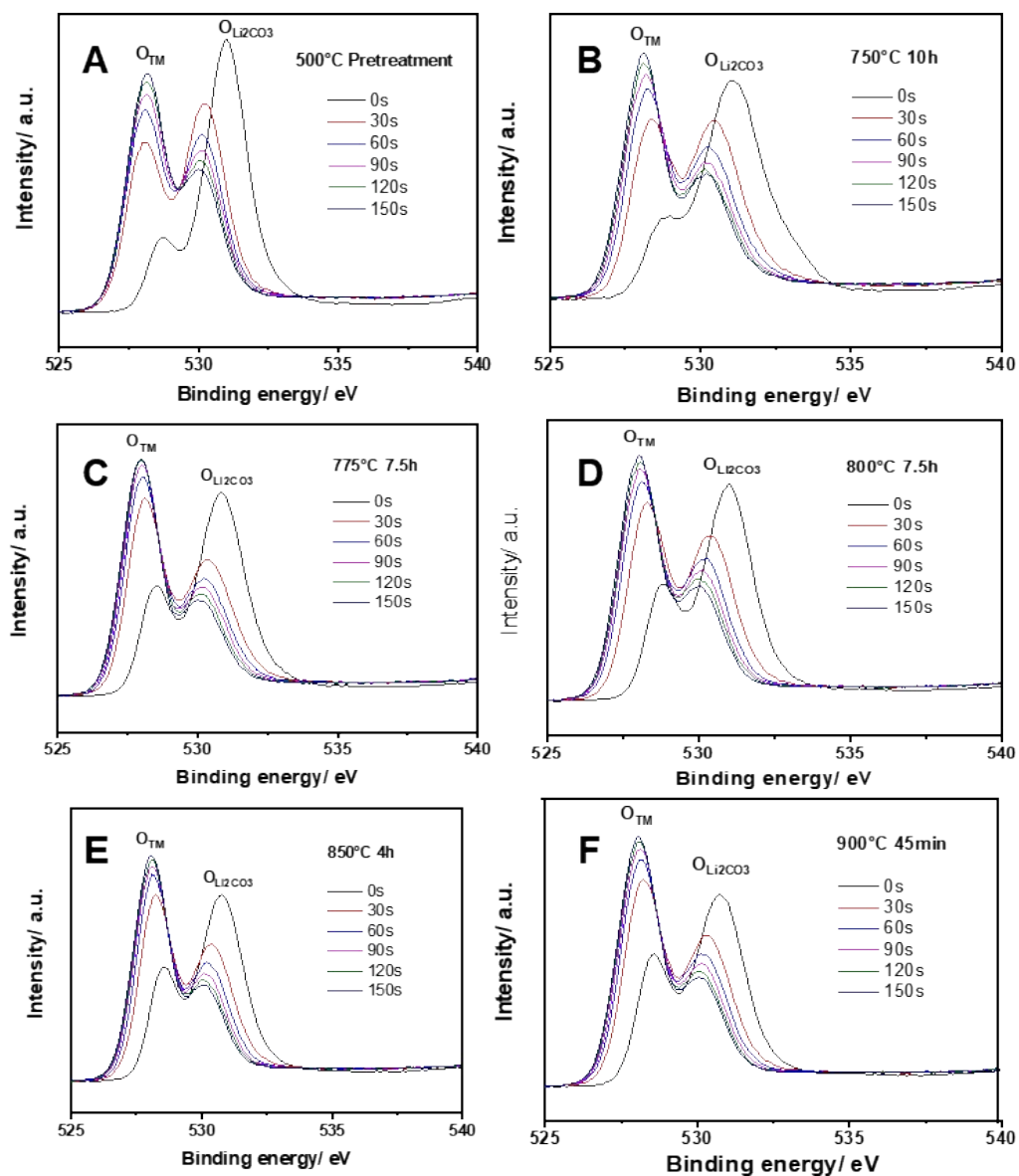


Figure S9. O 1s XPS spectra of various samples at different etching times.

Table S7. Binding energy (eV) and peak area (A.U.) of O element assigned in Figure S9 and surface Li₂CO₃ content.

		CO ₃ ²⁻		TM-O		Surface Li ₂ CO ₃ content
		B. E.	Peak Area	B. E.	Peak Area	
500°C 10h	0s	531.1	97825	528.67	10269	0.90
	30s	530.49	65114	528.33	42813	0.60
	60s	530.36	49851	528.21	52958	0.48
	90s	530.31	41389	528.14	59909	0.41
	120s	530.28	37010	528.1	62505	0.38
	150s	530.27	33750	528.07	66142	0.35
750°C 10h	0s	530.99	120458	528.63	16932	0.88
	30s	530.22	86460	528.03	59149	0.59
	60s	530.16	69100	528.05	73779	0.48
	90s	530.14	61505	528.08	81680	0.43
	120s	530.13	53667	528.11	87949	0.37
	150s	530.11	48956	528.11	91475	0.34
775°C 7.5h	0s	530.83	106188	528.46	31110	0.77
	30s	530.4	67395	528.1	71413	0.51
	60s	530.29	52985	528.02	82925	0.41
	90s	530.25	44582	527.99	89944	0.36
	120s	530.2	39281	527.96	92634	0.32
	150s	530.19	35056	527.94	95534	0.29
800°C 7.5h	0s	530.96	113671	528.77	34684	0.77
	30s	530.39	80016	528.26	76470	0.49
	60s	530.21	62895	528.1	89610	0.39
	90s	530.15	53819	528.05	97146	0.33
	120s	530.11	48406	528.02	100614	0.3
	150s	530.08	43059	527.99	103828	0.27
850C 4h	0s	530.74	110626	528.51	36925	0.75
	30s	530.41	72673	528.23	77831	0.48
	60s	530.29	57335	528.14	89658	0.39
	90s	530.23	48397	528.09	97014	0.33
	120s	530.2	42112	528.07	101200	0.29
	150s	530.19	38613	528.05	104994	0.27
900°C 45min	0s	530.72	106758	528.54	43022	0.71
	30s	530.35	75332	528.21	84874	0.47
	60s	530.25	60996	528.13	96795	0.39
	90s	530.2	52546	528.09	103523	0.34
	120s	530.17	46488	528.06	108402	0.30
	150s	530.16	42451	528.04	111387	0.28

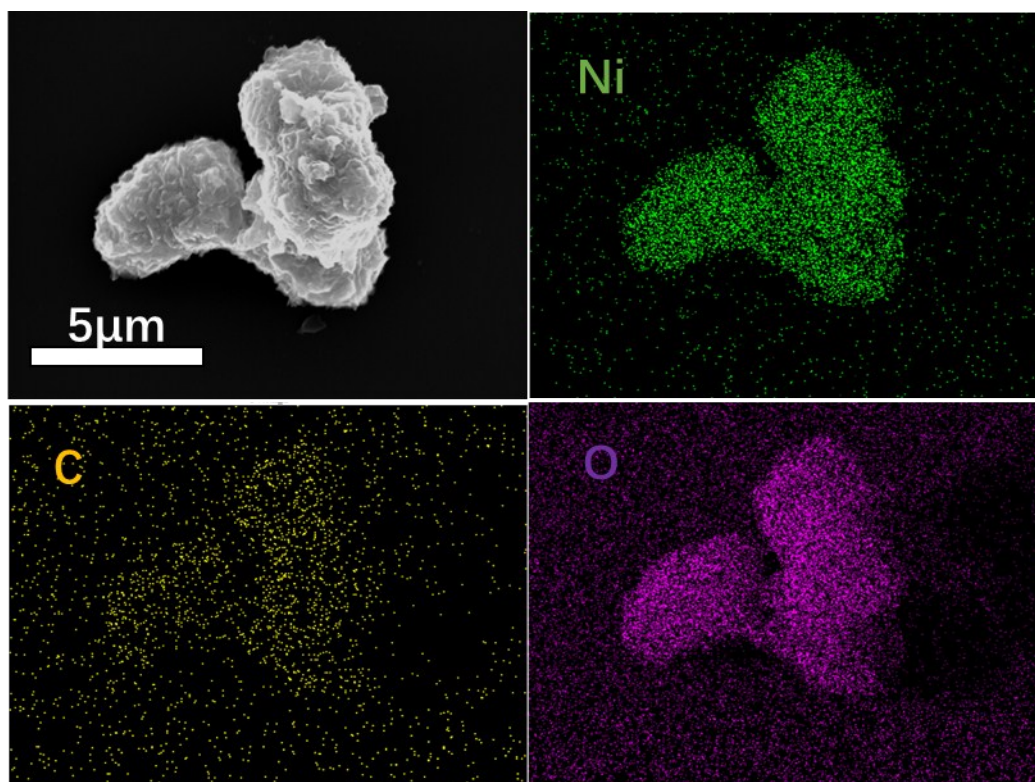


Figure S10. SEM-EDS elemental mapping images of NMC71515 pre-heated at 500 °C.

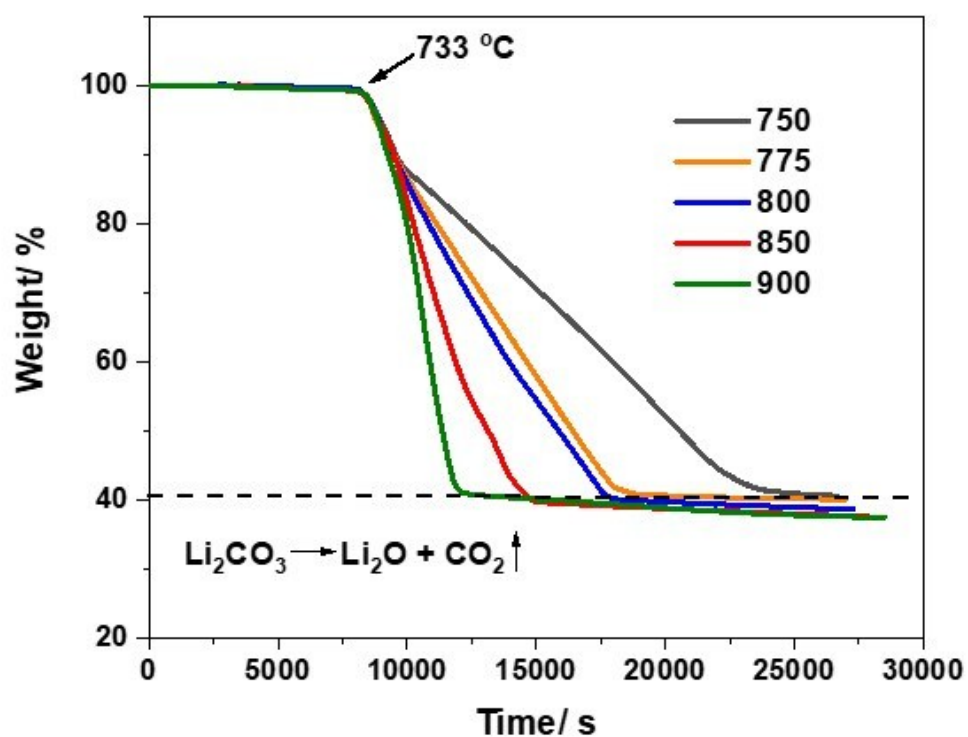


Figure S11. TGA results of Li_2CO_3 at different holding temperatures. The samples were heated at the rate of 5 K s^{-1} and held for 5 h at each temperature.

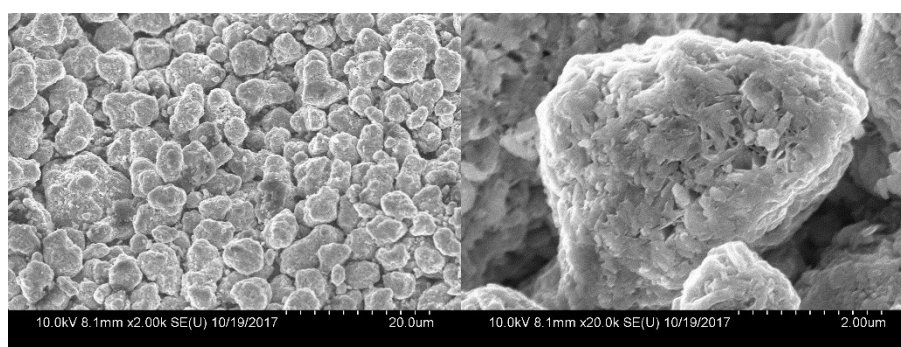
Table S8. Elemental composition of NMC71515 sintered at 900 °C for different durations.

	Ni	Co	Mn	Li	Weight loss
900°C, 45min	0.7500	0.1496	0.1510	1.010	0 %
900°C, 5h	0.7500	0.1498	0.1512	0.707	4.5%

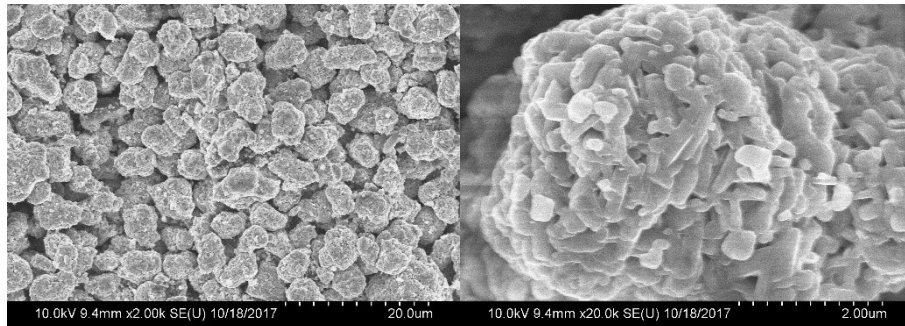
Table S9. Crystallite sizes of NMC71515 prepared under different sintering conditions.

Sintering temperature (°C)/ holding time (h)	Crystallite size/ nm
750/ 10	100.2
775/ 7.5	159.2
800/ 7.5	167.6
850/ 4	198.5
900/ 0.75	582.0

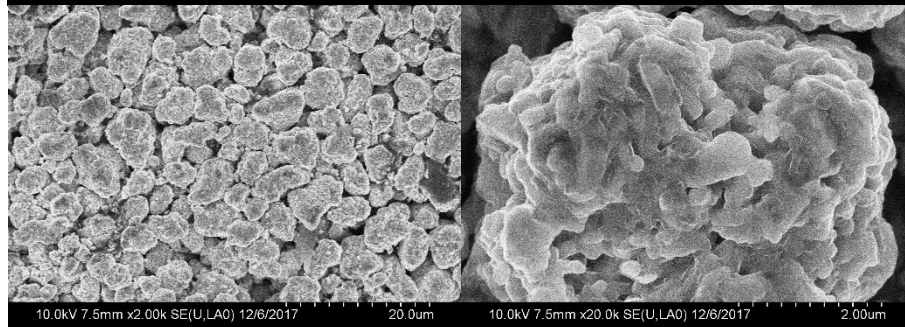
A



B



E



D

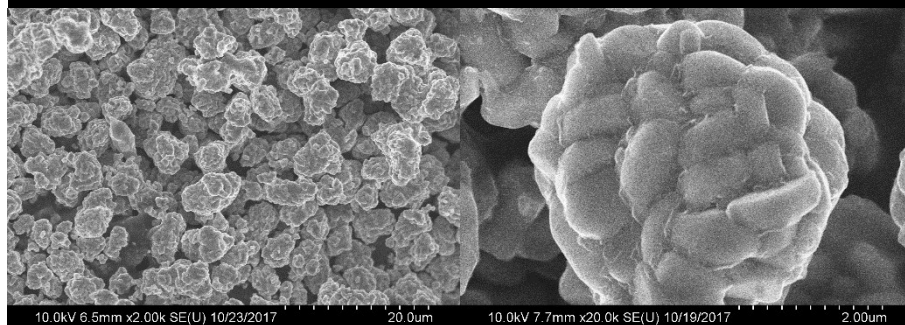
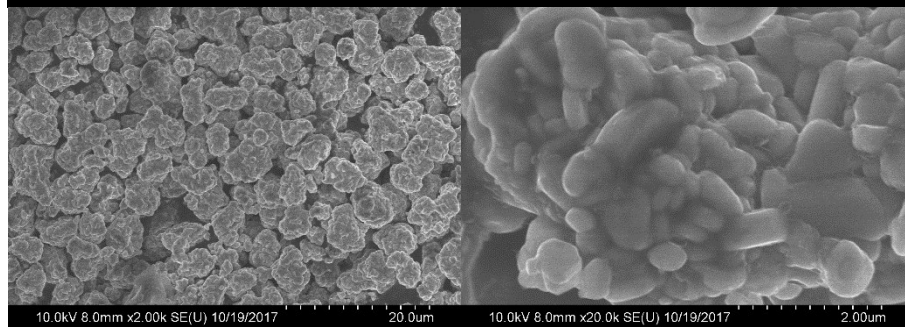
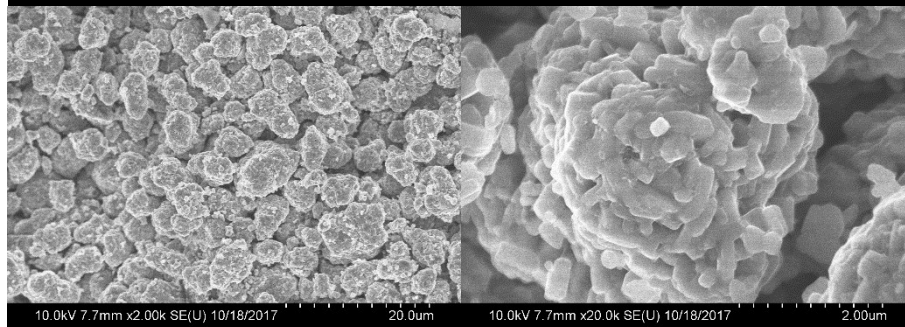


Figure S12. SEM images of NMC71515 sintered under different conditions: (A) pre-heated at 500 °C for 10h, (B) 750 °C for 10h, (C) 775 °C for 7.5 h, (D) 800 °C for 7.5h, (E) 850 °C for 4h, (F) 900 °C for 0.75h.

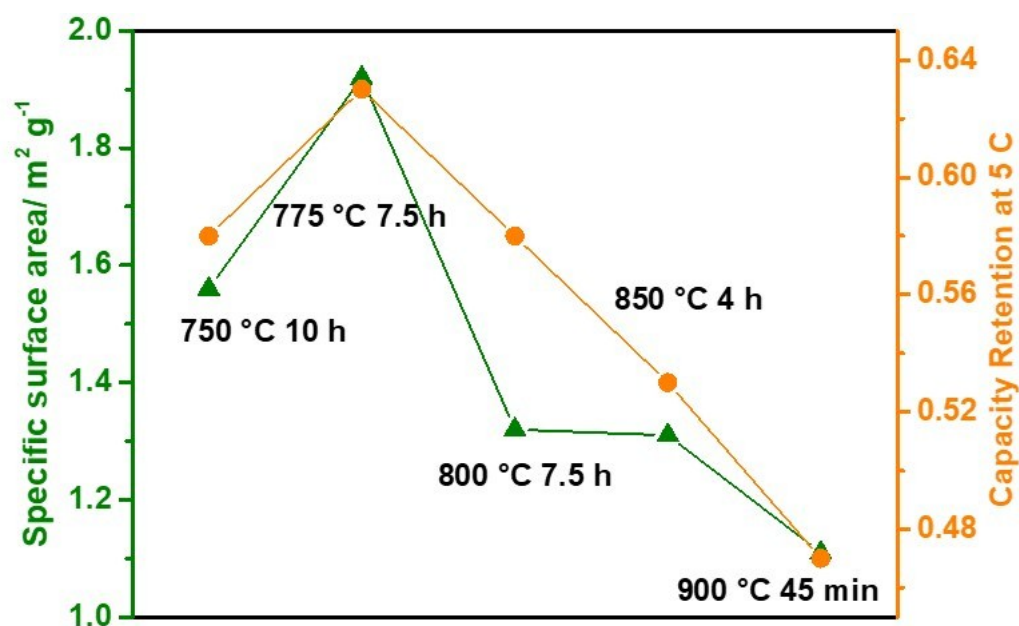


Figure S13. Correlation between specific surface area and capacity retention at rate of 5 C.

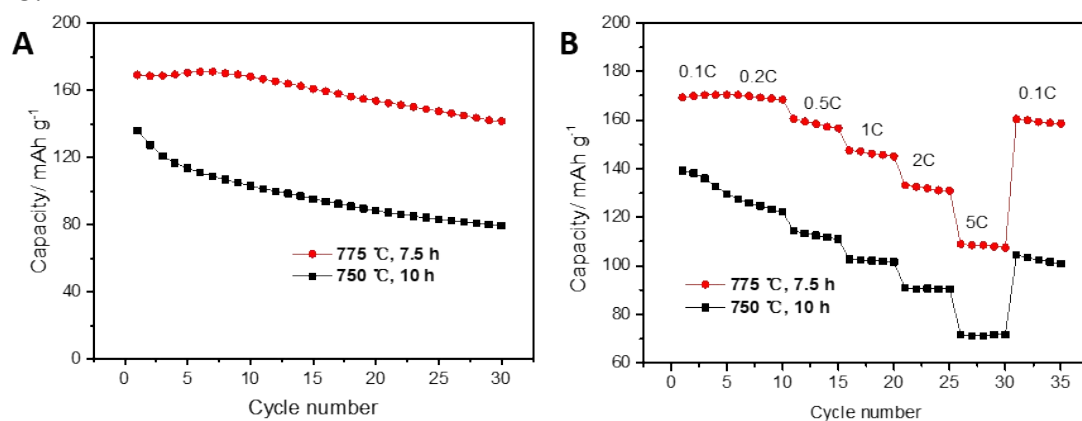


Figure S14. Cycling (0.5 C) and rate performances of different 71515 samples.