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

The effect of cation mixing controlled by thermal treatment duration on electrochemistry stability of lithium transition-metal oxide

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Table S1 The refined crystal sites and atom occupancies of NMC-0 using the Rietveld method

Atom	Site	x	y	z	Occupancy
Li	3b	0	0	0.5	0.923
Ni	3b	0	0	0.5	0.077
Li	3a	0	0	0	0.077
Ni	3a	0	0	0	0.256
Co	3a	0	0	0	0.333
Mn	3a	0	0	0	0.334
O	6c	0	0	0.2420	1.000

Table S2 The refined crystal sites and atom occupancies of NMC-5 using the Rietveld method

Atom	Site	x	y	z	Occupancy
Li	3b	0	0	0.5	0.944
Ni	3b	0	0	0.5	0.056
Li	3a	0	0	0	0.056
Ni	3a	0	0	0	0.277
Co	3a	0	0	0	0.333
Mn	3a	0	0	0	0.334
O	6c	0	0	0.2426	1.000

Table S3 The refined crystal sites and atom occupancies of NMC-9 using the Rietveld method

Atom	Site	x	y	z	Occupancy
Li	3b	0	0	0.5	0.979
Ni	3b	0	0	0.5	0.021
Li	3a	0	0	0	0.021
Ni	3a	0	0	0	0.3112
Co	3a	0	0	0	0.333
Mn	3a	0	0	0	0.334
O	6c	0	0	0.2422	1.000

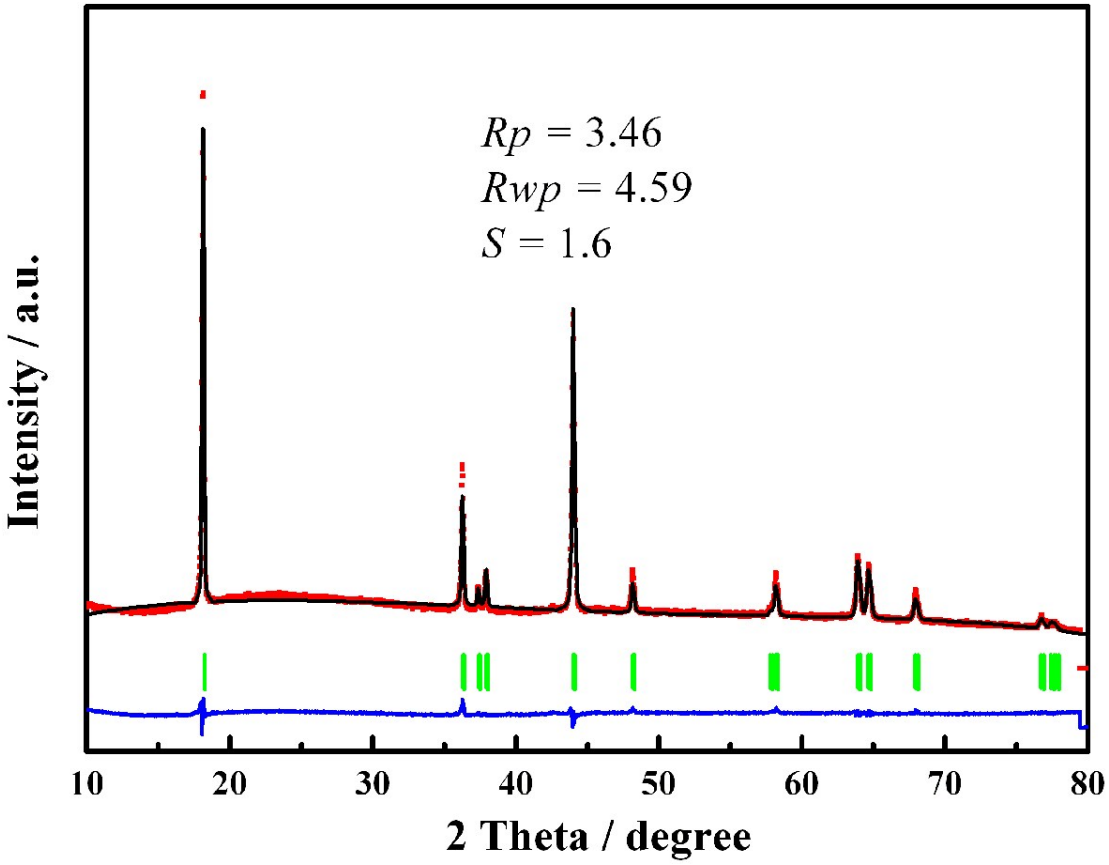

Figure S1 Observed refinement results of the as-prepared material NCM-3.

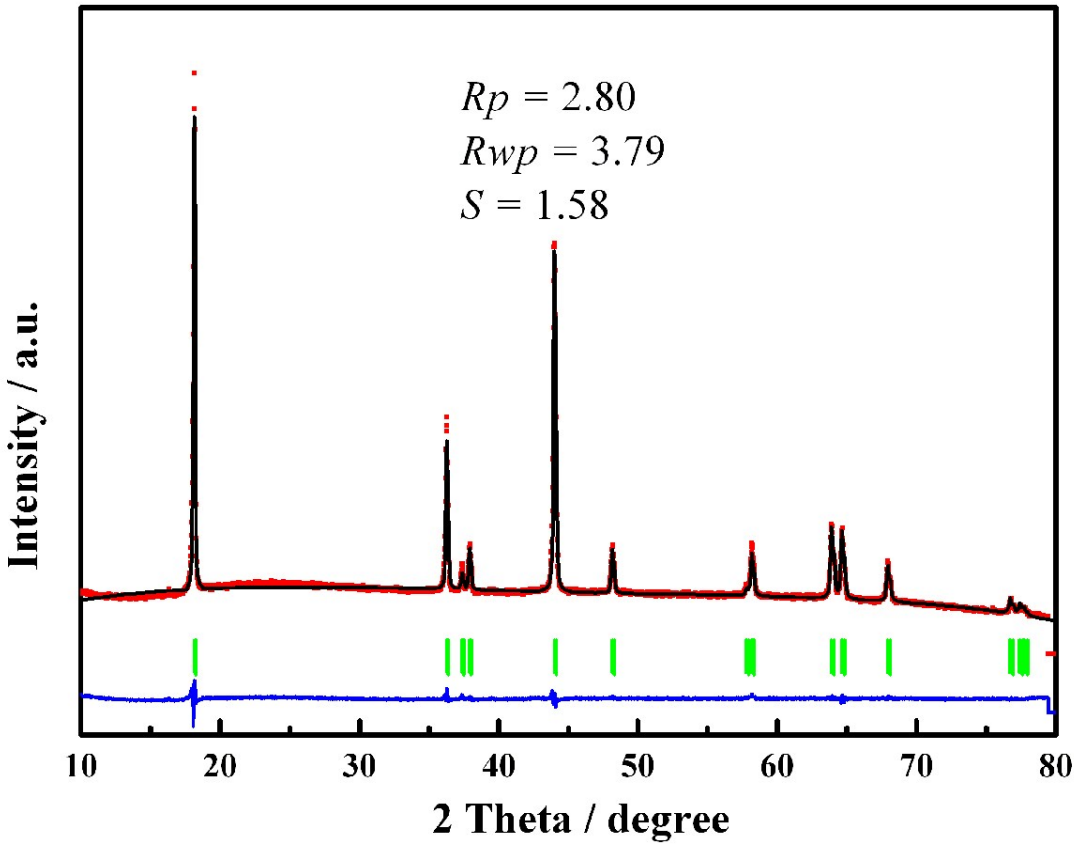

Figure S2 Observed refinement results of the as-prepared material NCM-7.

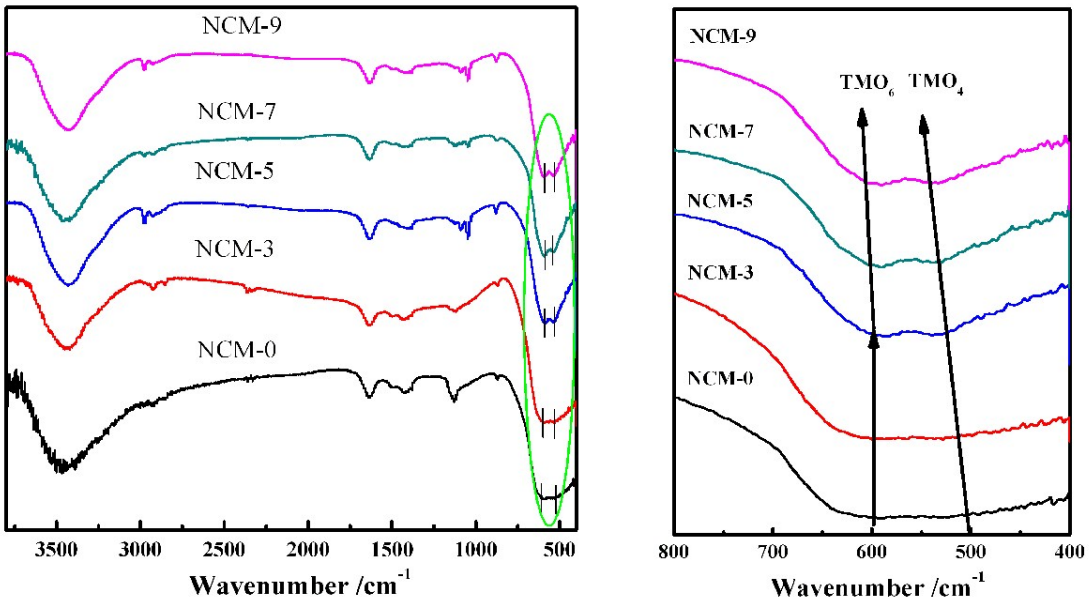

Figure S3 FTIR spectra of the NCM-0, 3, 5, 7 and 9 samples.

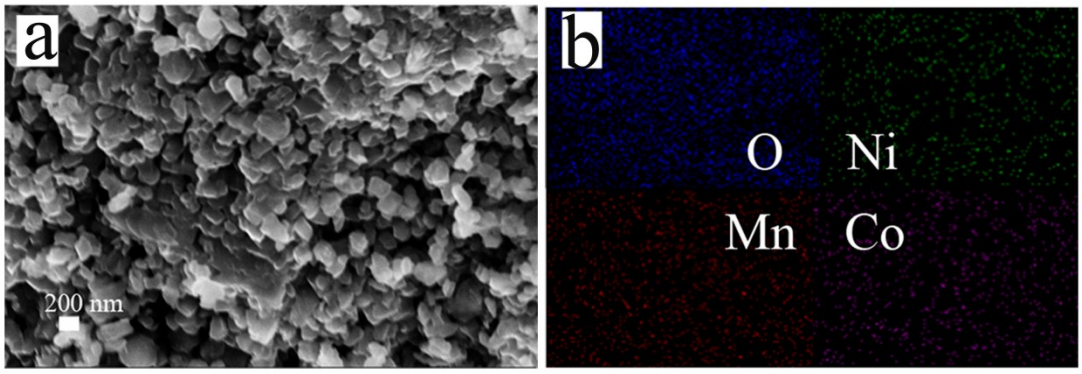

Figure S4 SEM images of NCM-5 (a) and (b) EDS mapping images of the NCM-5.

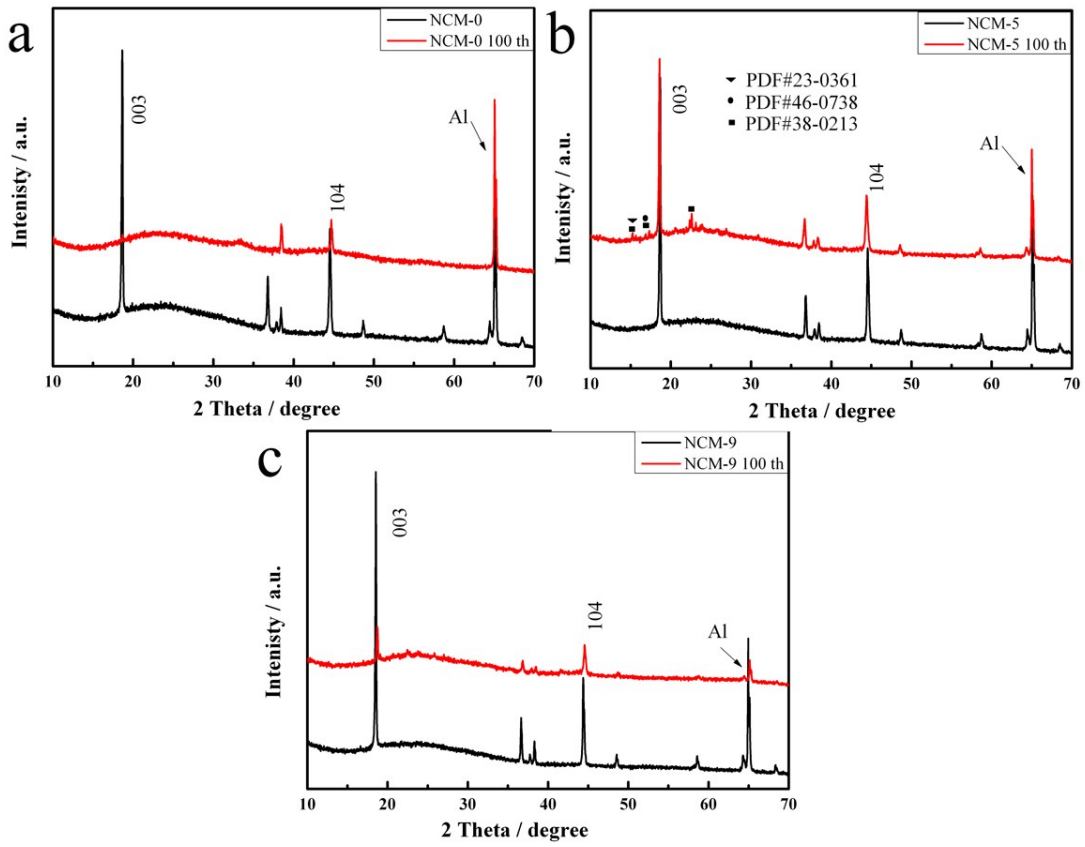

Figure S5 XRD patterns of electrode before and after 100th cycles between 2.5-4.8 V. (a) NCM-0, (b) NCM-5, (c) NCM-9.

After being cycled between 4.8 and 2.5 V, one can see that some minor impurity peaks form XRD pattern of the NCM-5 electrode. We speculate that this phenomenon may arise for two reasons: (1) the electrode material reacts with the electrolyte, (2) the structure of the electrode material changes. We find that those minor impurity peaks regarding $Li_6P_6O_{18}$ (PDF#38-0213), $LiMnO_2$ (PDF#23-0361) and Li_2NiO_2 (PDF#46-0738) appear in the pattern of NCM-5 electrode. We think that the layer cathode materials reacts with $LiPF_6$ in the electrolyte, and several types of compounds are created on the surface of electrode with the test going on. And the structure of materials on the surface undergoes a phase change, and some new phases are formed.

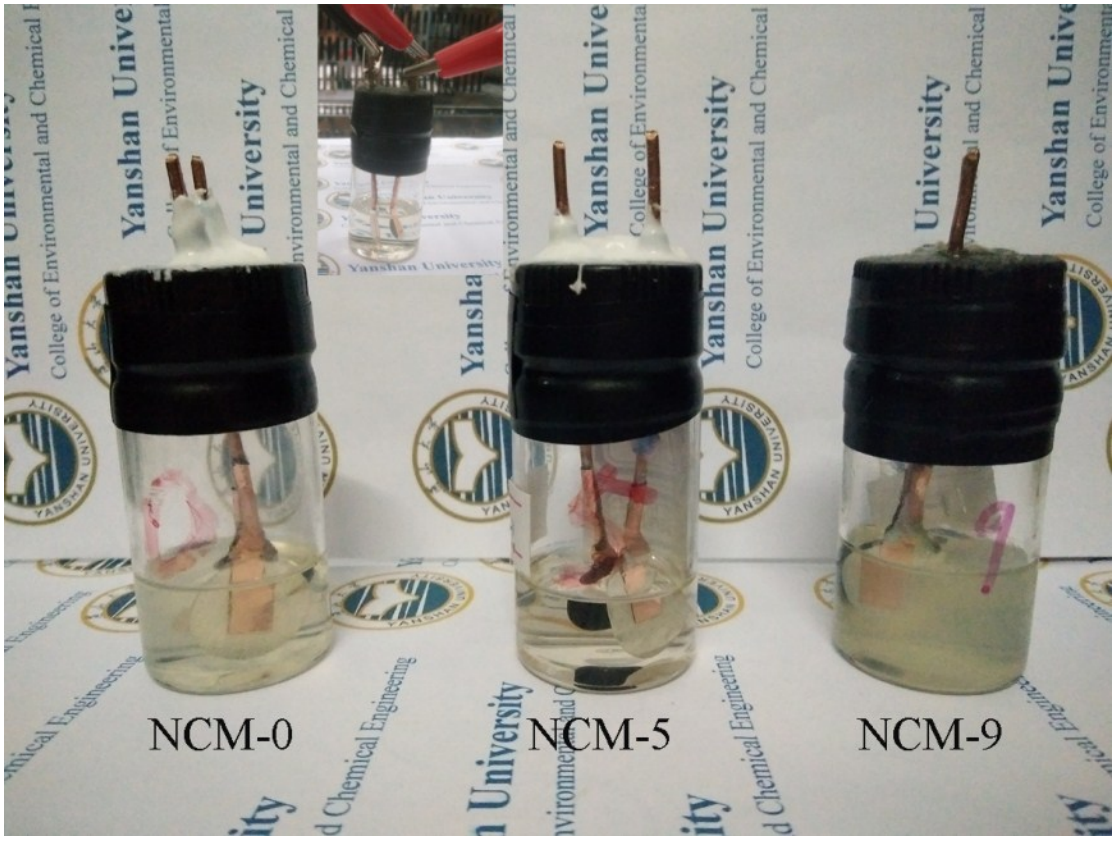

Figure S6 Digital image of NCM-0, 5 and 9 electrodes were charged-discharged at 0.05 C to 4.8 V with two cycles. (The electrolyte consisting of $LiPF_6$ (1 M) dissolved in ethylene carbonate, dimethyl carbonate, and diethyl carbonate mixed in a 1:1:1 volume ratio.)

All the three electrodes were charged-discharged at 0.05 C to 4.8 V in high voltage electrolyte with two cycles. From Figure S6, we can see that the electrolytes of NCM-0 and NCM-9 become turbid. There is no obvious change for the NCM-5 electrolyte. We think that the TM ions migrated out of the cathode materials and dissolve in the electrolyte, and the TM ions reacted with the electrolyte, causing the electrolyte to become turbid. The result again suggesting that the structure of NCM-5 electrode is more stable compared to other electrodes.