Electronic supporting information (ESI)

Improving the structural and cyclic stability of P2-type $Na_{0.67}MnO_2$ cathode material *via* Cu and Ti co-substitution for sodium ion batteries

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Experiments

Material synthesis

$Na_{0.67}Mn_{0.7}Cu_{0.15}Ti_{0.15}O_2$ (NMCT) and $Na_{0.67}MnO_2$ (NM) were synthesized by solid state methods. Stoichiometric amounts of Na_2CO_3 (Sigma-Aldrich), Mn_2O_3 (Aladdin), CuO (Aladdin) and TiO_2 (Aladdin) powders were mixed using a ball mill and pressed into pellets. These were heated in air at 900℃ for 15h followed to room temperature in the furnace and stored under ambient condition.

Material characterization

All the XRD patterns were collected on a D8 Advance diffractometer (Bruker) with Cu Kα radiation (λ = 1.5418 Å). Rietveld refinement of the XRD data were performed with general structural analysis system (GSAS).[1] The morphology of powder was observed by scanning electron microscopy (SEM, Hitachi SU8010) and high-resolution transmission electron microscopy (HRTEM, FEI TECNAI F20). The distribution of each element was tested by the energy dispersive spectroscopy (EDS) mapping. The accurate elementary composition of the sample was measured by inductively coupled plasma-absorption emission spectrometry (ICP-AES). X-ray photoelectron spectroscopy (XPS) were conducted on a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer.

Electrochemical measurements

The cathode consist of NMCT/MN: acetylene black: polyvinylidene fluoride (PVDF) with the ratio of 75:20:5 onto a clean Al foil. And then the electrode was placed in a vacuum oven at 120 ºC for 5h. Sodium half-cells were assembled in an Ar-filled glove box using a NC-061 type electrolyte (DoDoChem.). The electrochemical properties were carried out on a Land BT2000 battery tester in Na half-cells at the galvanostatic mode. The operando XRD data was collected at 0.1 C by Chronopotentiometry (CP) test. EIS tests were detected by solartron 1260-1287.

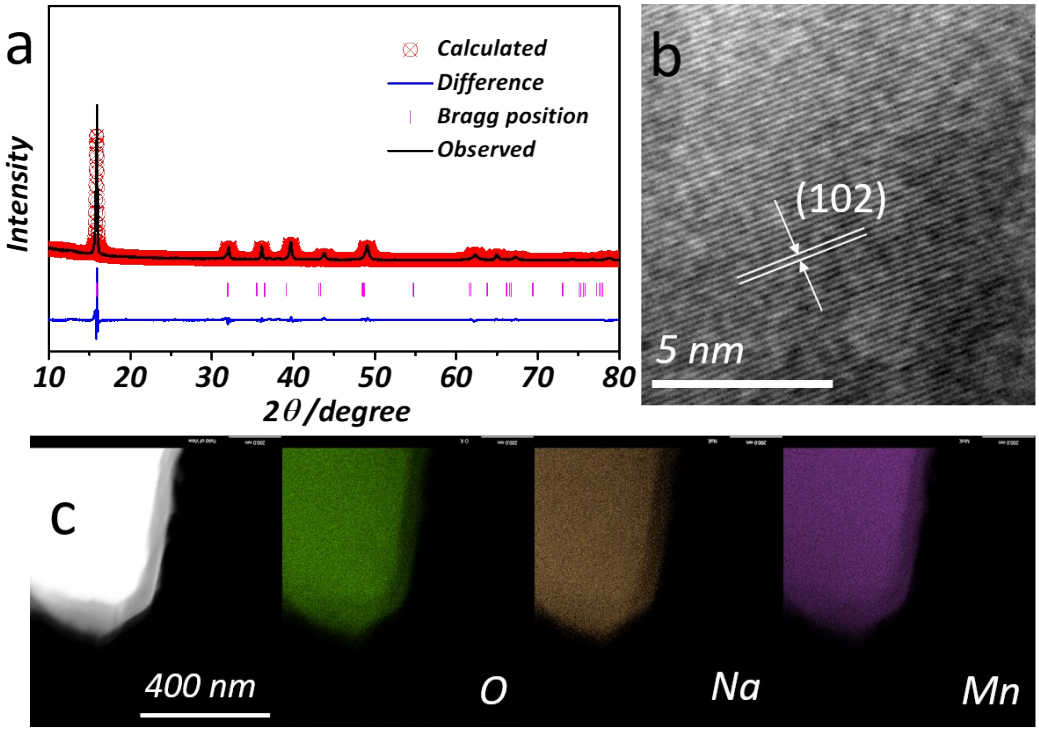

Fig. S1. (a) XRD spectra (b)TEM images and (c)mapping of NM.

Tab. S1. Refinement results of NMCT and NM samples.

Sample		NMCT		NM
Phase		P2-type		P2-type
Space Group		P63/mmc		P63/mmc
	a (Å)	2.92239(2)	*a* (Å)	2.86877(4)
	b (Å)	2.92239(2)	*b* (Å)	2.86877(4)
	c (Å)	11.23782(1)	*c* (Å)	11.16545(2)
Cell Parameters	*α* (°)	90.000	*α* (°)	90
	β (°)	90.000	*β* (°)	90
	γ (°)	120.000	*γ* (°)	120
	Volume (Å^3)	82.91(7)	Volume (Å^3)	79.57(9)
	R_{wp} (%)	10.81	R_{wp} (%)	14.41
Agreement Factors	R_p (%)	6.85	R_p (%)	10.46
	CHI*2	7.345	CHI*2	7.106

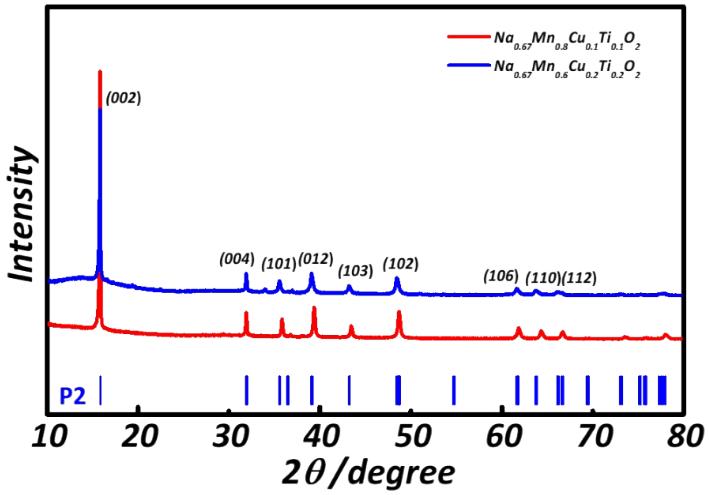

Fig. S2. XRD data of $Na_{0.67}Mn_{0.8}Cu_{0.1}Ti_{0.1}O_2$ and $Na_{0.67}Mn_{0.6}Cu_{0.2}Ti_{0.2}O_2$.

Tab. S2. ICP results of transition metals for NMCT and NM samples.

Sample	Mn	Cu	Ti
NM	1	0	0
NMCT	0.70	0.16	0.14

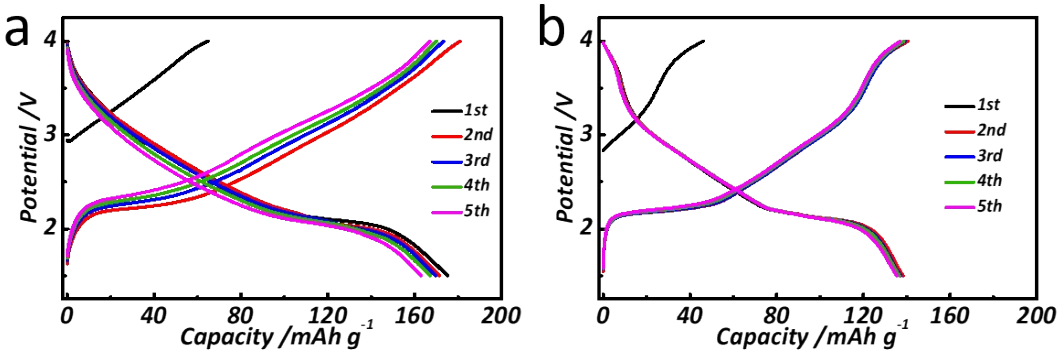

Fig. S3. The charge/discharge curves of (a) $Na_{0.67}Mn_{0.8}Cu_{0.1}Ti_{0.1}O_2$ and (b)$Na_{0.67}Mn_{0.6}Cu_{0.2}Ti_{0.2}O_2$.

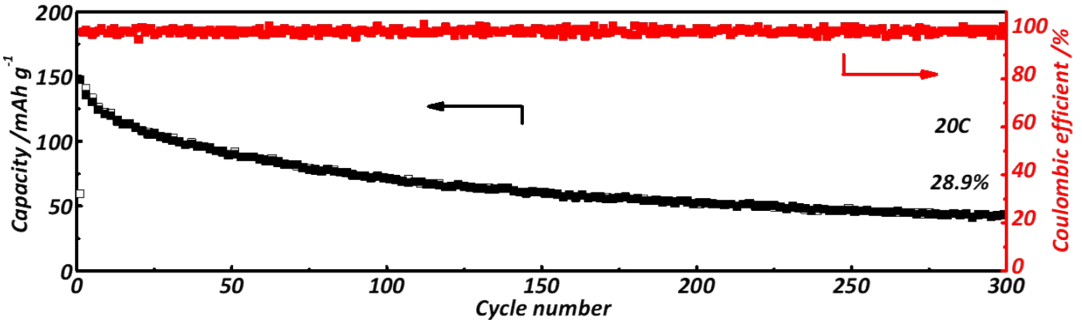

Fig. S4. The cycling performance with the Coulombic efficiency at 20C for NM.

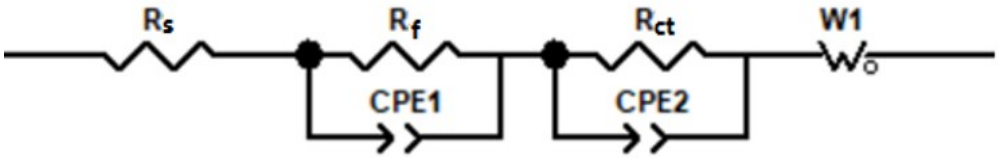

Fig. S5. The equivalent circuit of fitted EIS data for NMCT and NM.

Tab. S3. EIS parameters of the equivalent circuits of NMCT and NM after different cycles.

Sample		NM	NMCT
After 1 cycle	R_s/Ω	6.975	6.79
	R_f/Ω	513.4	530.14
	R_{ct}/Ω	680.9	681.7
After 100 cycles	R_s/Ω	5.827	5.269
	R_f/Ω	217.5	232.2
	R_{ct}/Ω	1751	1177

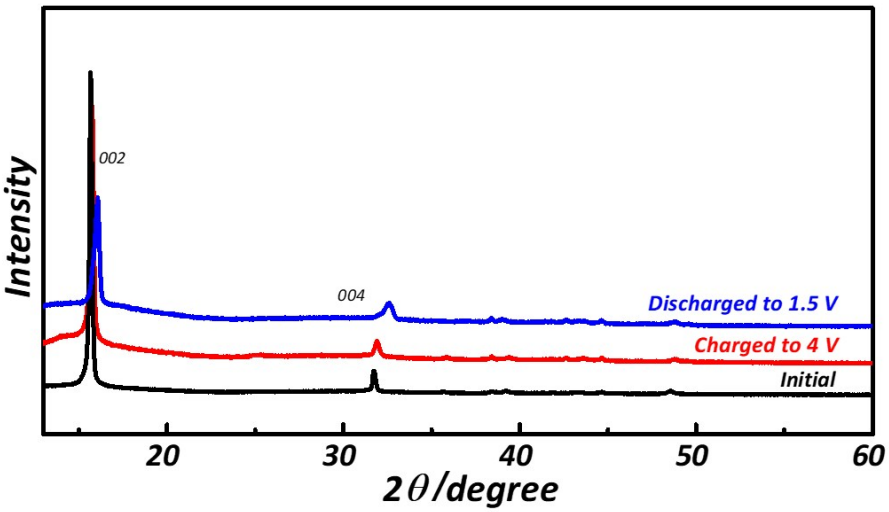

Fig. S6. Ex-situ XRD patterns of NMCT electrodes. (a)initial, (b)charged to 4 V and (c)discharged to 1.5 V.

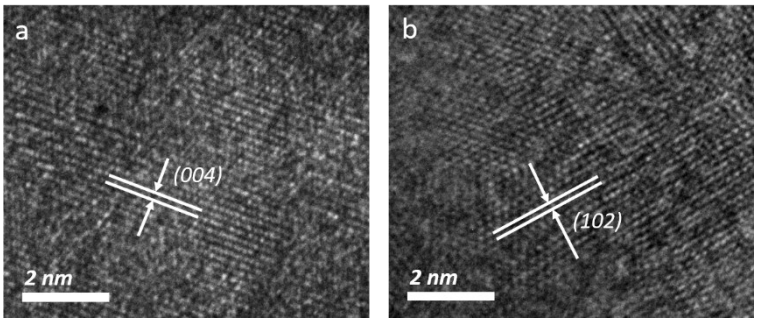

Fig. S7. TEM images of NMCT electrodes for charged to 4 V (a) and discharged to 1.5 V (b).

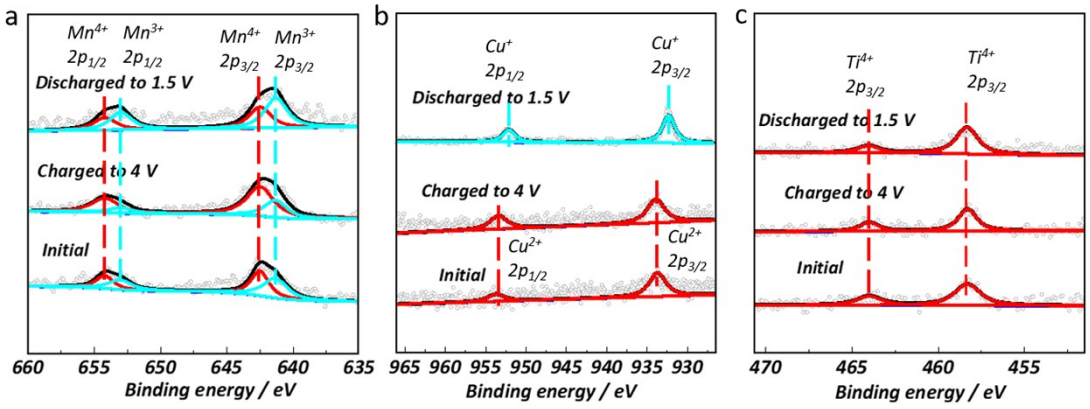

Fig. S8. XPS of Mn 2p(a), Cu 2p(b) and Ti 2p(c) of NMCT electrodes for the initial electrode, charged to 4 V and discharged to 1.5 V, respectively.

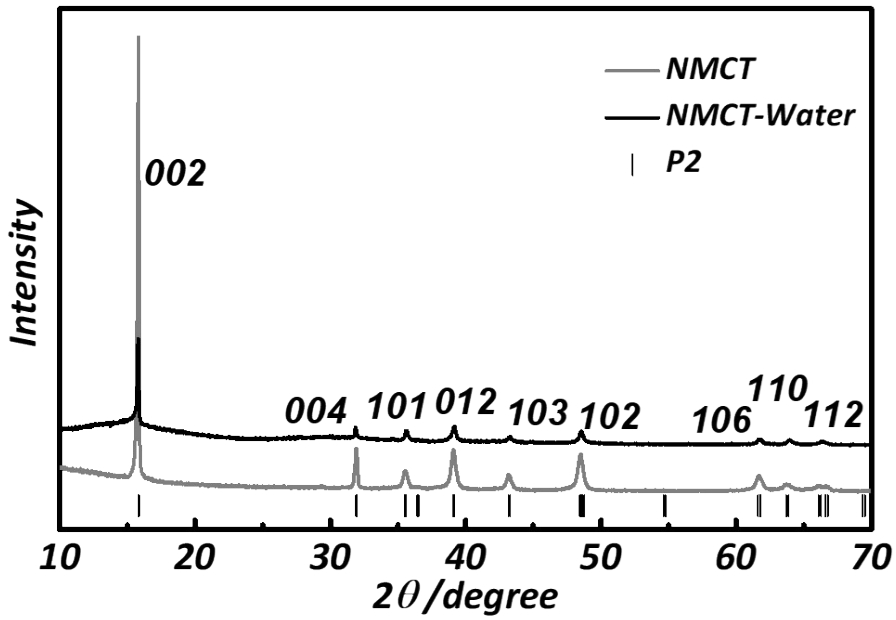

Fig. S9. XRD patterns of NMCT and the water-soaked NMCT.

References

1. Larson, A. C. and Von Dreele, R. B. GSAS: General Structure Analysis System (LANSCE, MS-H805, Los Alamos, NM, 1994).