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

Electronic Supporting Information

Intrinsic enhancement of the rate capability and suppression of the phase transition via p-type doping in Fe-Mn based P2-type cathodes used for sodium ion batteries

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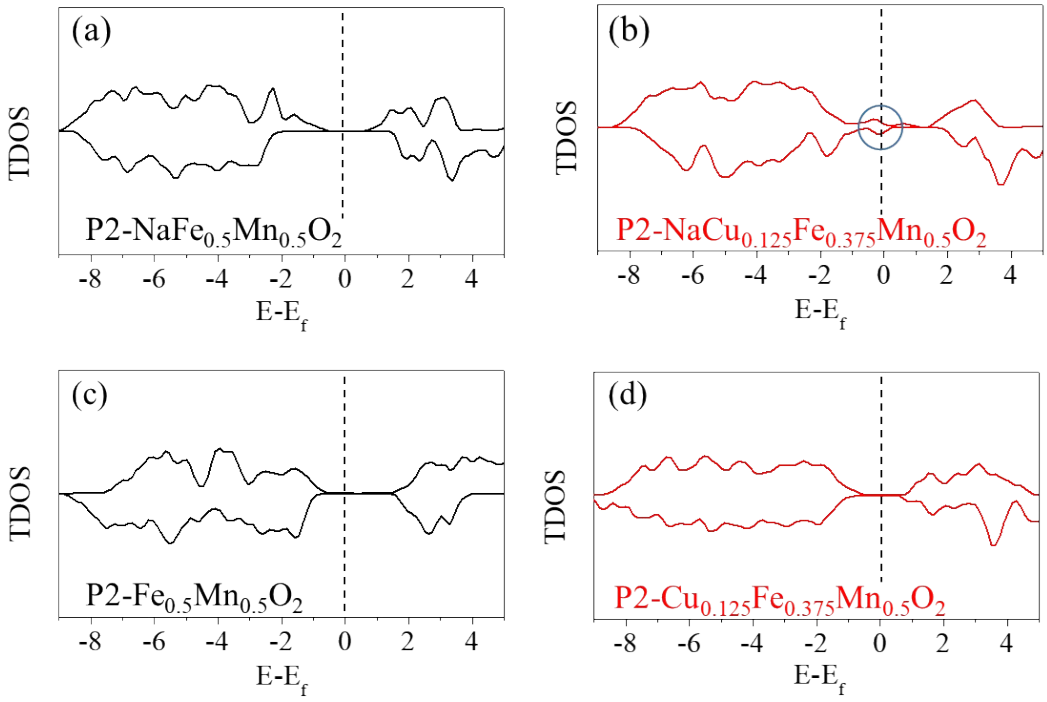

Fig. S1 TDOS of (a) P2-$NaFe_{0.5}Mn_{0.5}O_2$, (b) P2-$NaCu_{0.125}Fe_{0.375}Mn_{0.5}O_2$, (c) P2-$Fe_{0.5}Mn_{0.5}O_2$, and (d) P2-$Cu_{0.125}Fe_{0.375}Mn_{0.5}O_2$ with HSE06 hybrid functional (dotted line indicates the Fermi level).

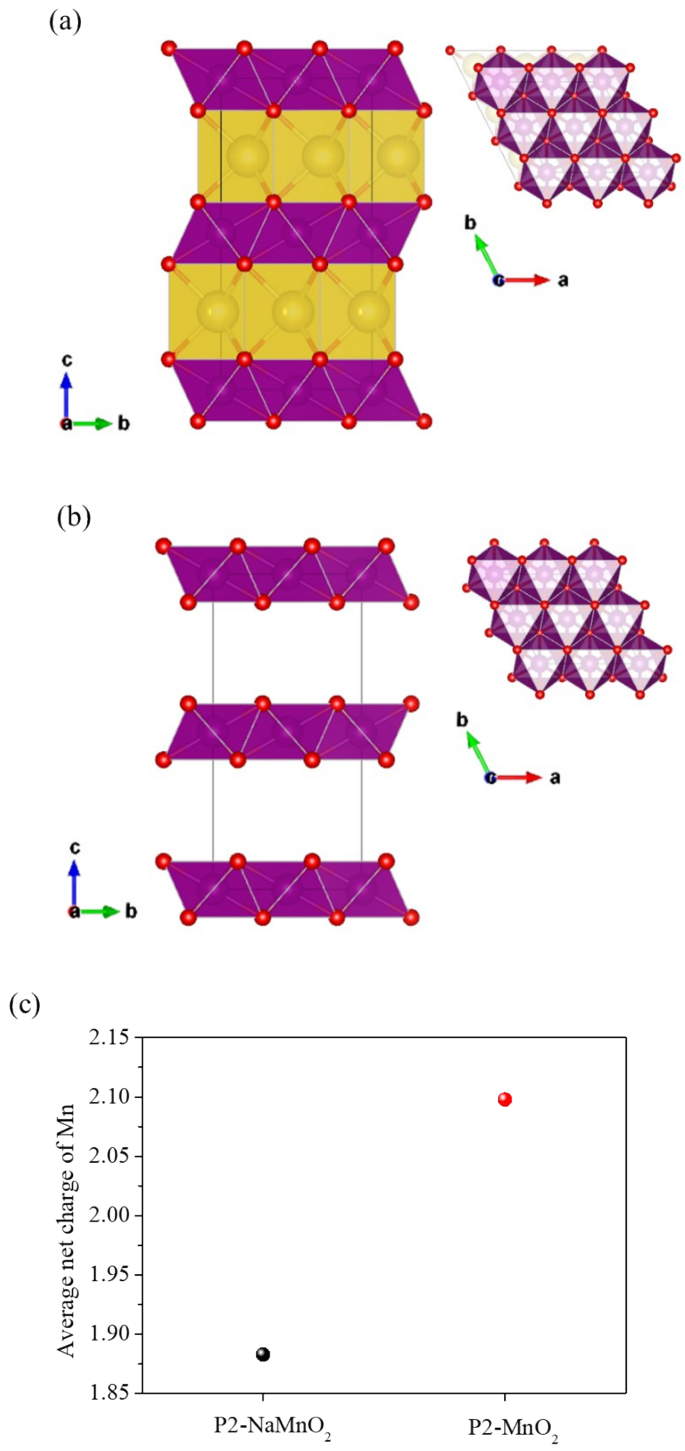

Fig. S2 (a, b)Atomic structures and (c)Average net charges of Mn in P2-$NaMnO_2$ and P2-MnO_2.

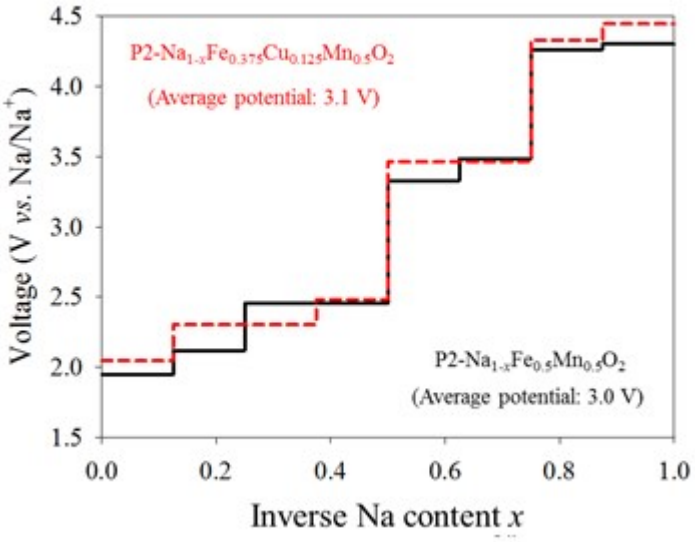

Fig. S3 Calculated electrochemical potential with respect to the inverse Na content x in P2-$Na_{1-x}Fe_{0.5}Mn_{0.5}O_2$ (black) and P2-$Na_{1-x}Cu_{0.125}Fe_{0.375}Mn_{0.5}O_2$ (red).

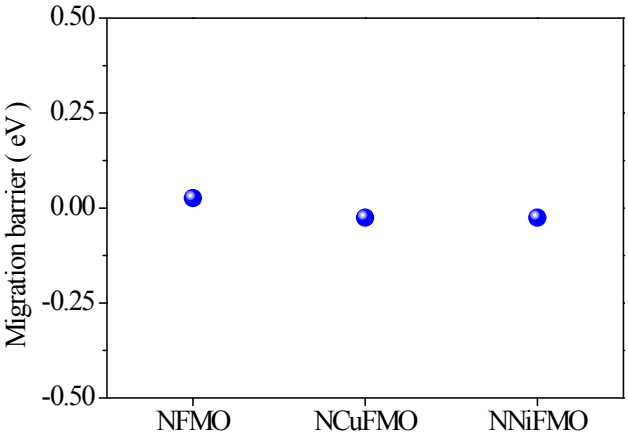

Fig. S4 Migration barrier from P2 to OP2.

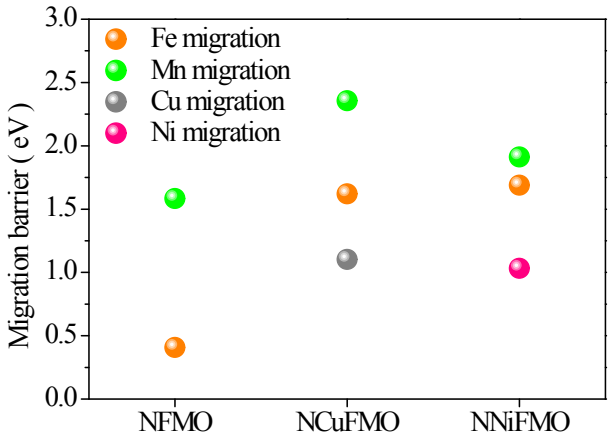

Fig. S5 Migration barrier from OP2 to Z.

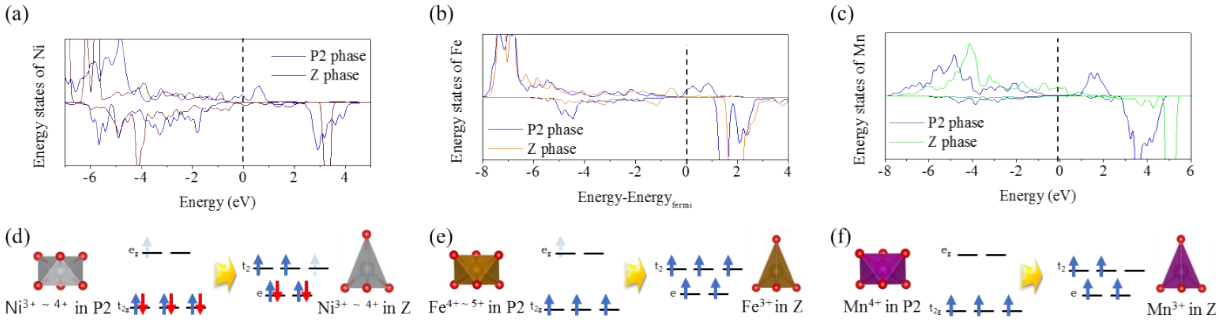

Fig. S6 (a-c) PDOS for (a)Ni, (b)Fe, (c)Mn and CFSDs of (d)Cu, (e)Fe, (f)Mn in NNiFMO. (Solid arrow : fully filled state, shaded arrow : partially filled state)

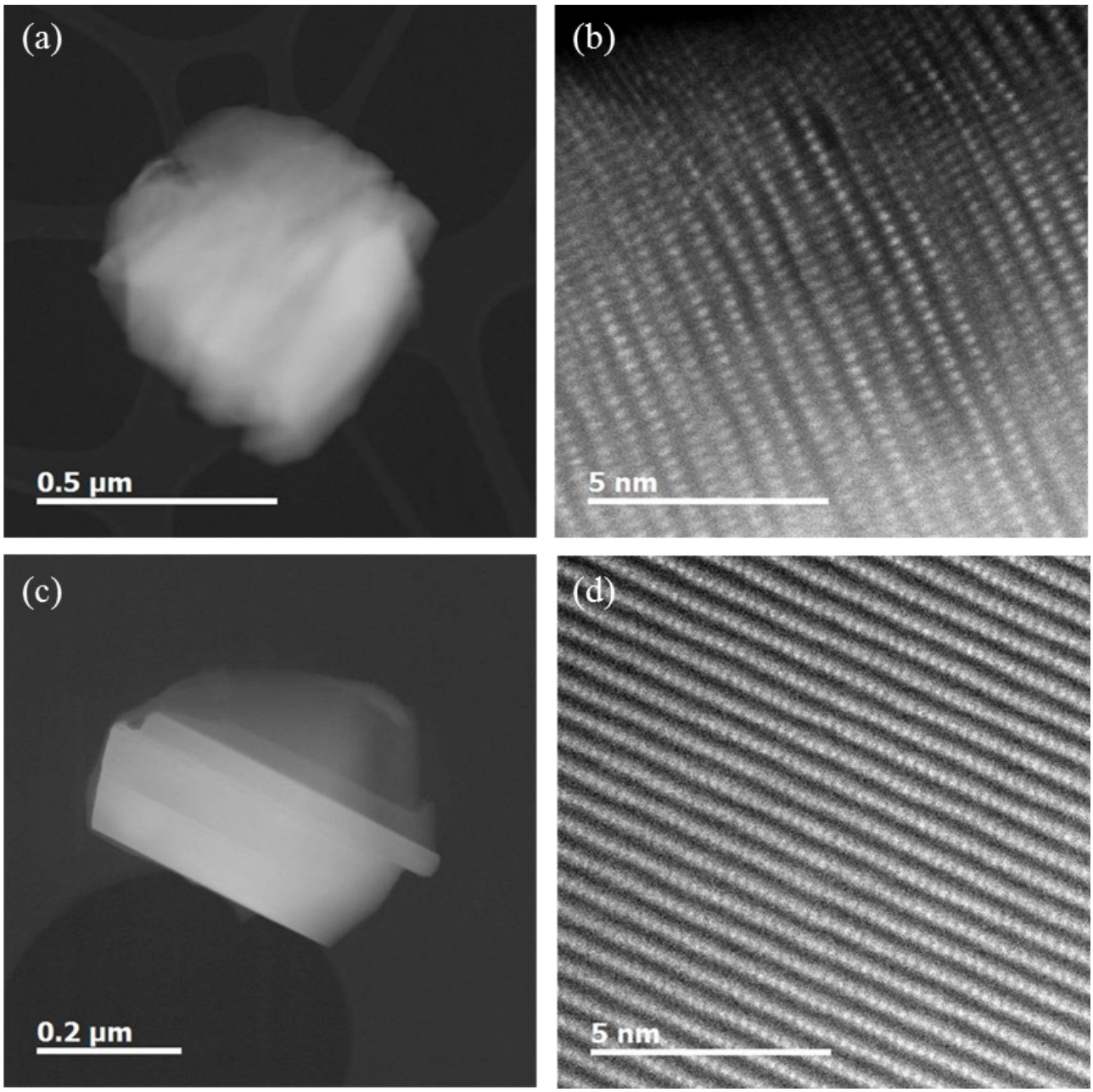

Fig. S7 STEM images of (a, b) P2-$Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$ and (c, d) P2-$Na_{0.67}Cu_{0.125}Fe_{0.375}Mn_{0.5}O_2$.

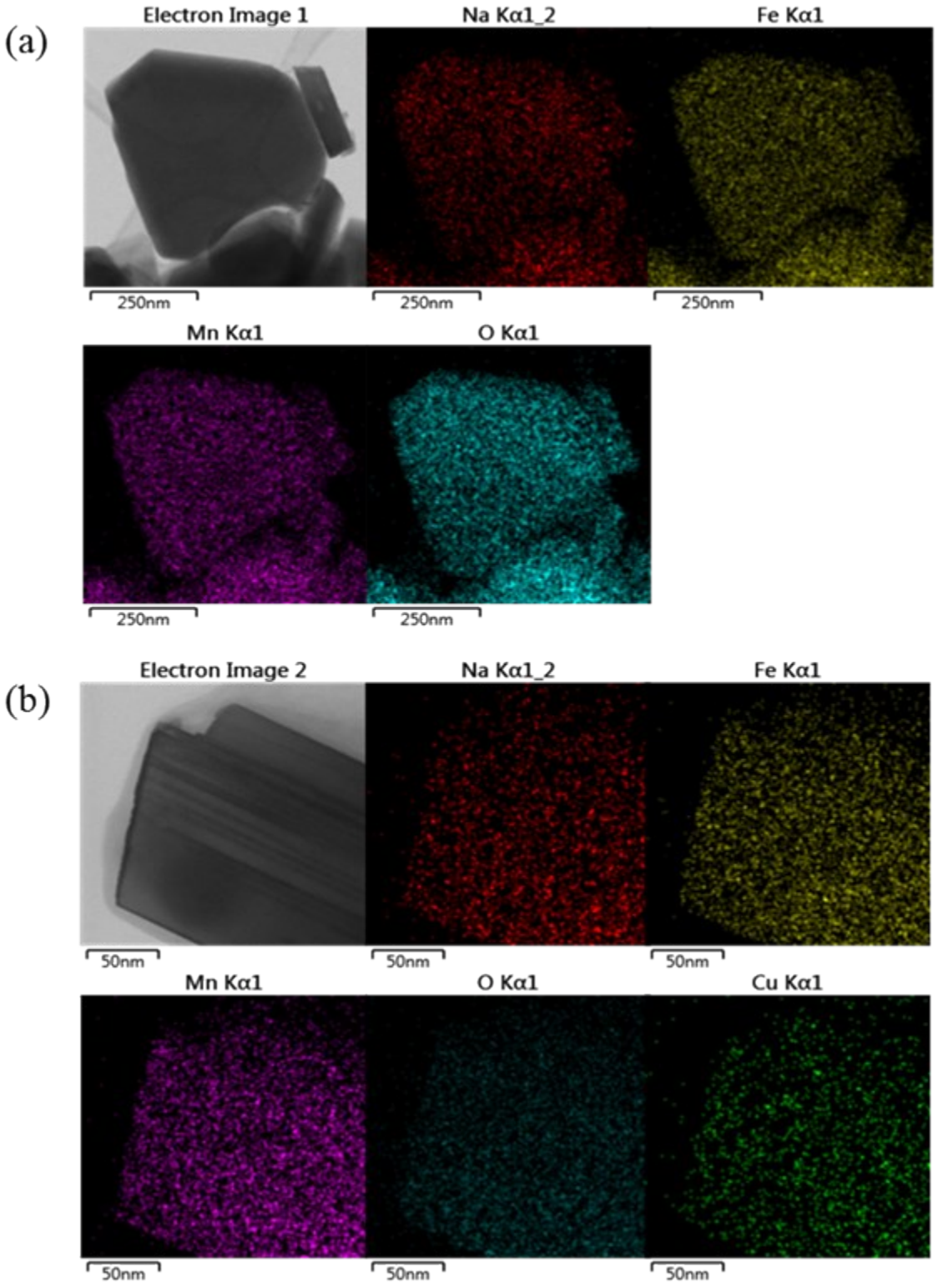

Fig. S8 Elemental distributions of Na (red), Fe (yellow), Mn (purple), O (cyan) and Cu (green) for (a) P2-$Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$ and (b) P2-$Na_{0.67}Cu_{0.125}Fe_{0.375}Mn_{0.5}O_2$ measured by HRTEM with EDS analysis.

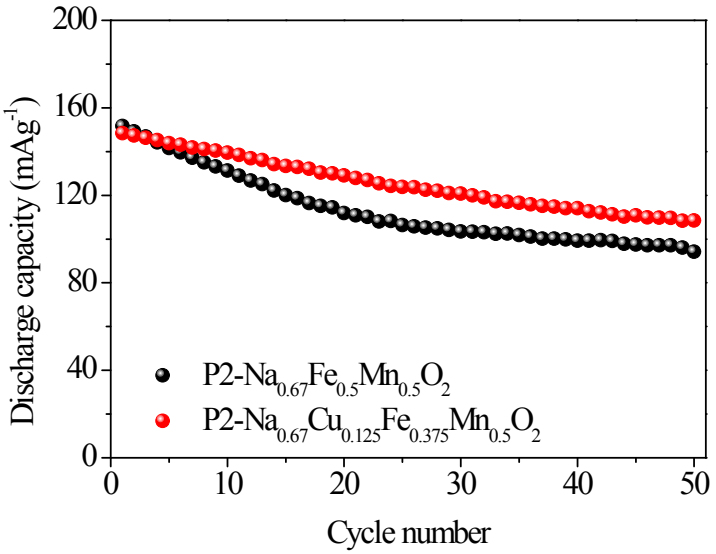

Fig. S9 Cycle performance of P2-$Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$ (black) and P2-$Na_{0.67}Cu_{0.125}Fe_{0.375}Mn_{0.5}O_2$ (red) at 100 mA g^{-1} in the range of 1.5 to 4.3 V *vs.* Na/Na^+.

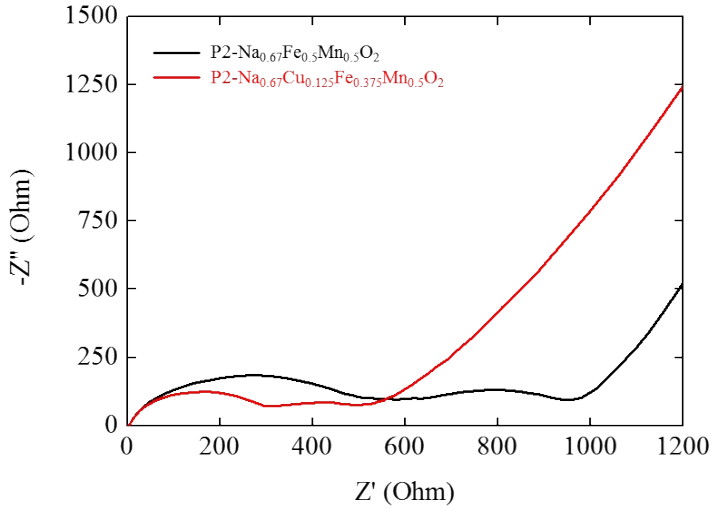

Fig. S10 Electrochemical impedance spectroscopy profiles of P2-$Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$ (black) and P2-$Na_{0.67}Cu_{0.125}Fe_{0.375}Mn_{0.5}O_2$ (red) at the OCV(Open circuit voltage) states.

Table. S1 Net charges of transition metal elements according to various migration states in NFMO, NCuFMO and NNiFMO.

		P2 phase	Z phase by Fe migration	Z phase by Mn migration	Z phase by Cu migration	Z phase by Ni migration
NFMO	Fe	1.99	1.92	1.95		
	Mn	2.11	2.11	1.78		
NCuFMO	Fe	2.03	1.93	2.03	2.03	
	Mn	2.10	2.12	1.84	2.11	
	Cu	1.28	1.28	1.29	1.29	
NNiFMO	Fe	2.03	1.93	2.03		2.03
	Mn	2.10	2.11	1.79		2.12
	Ni	1.42	1.49	1.44		1.36

Table. S2 *a* and *c* lattice parameters calculated by both XRD and DFT calculation of P2-$Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$ and P2-$Na_{0.67}Cu_{0.125}Fe_{0.375}Mn_{0.5}O_2$.

		a (Å)	*c* (Å)
XRD	P2-$Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$	2.917	11.294
	P2-$Na_{0.67}Cu_{0.125}Fe_{0.375}Mn_{0.5}O_2$	2.918	11.223
DFT calculation	P2-$Na_{0.63}Fe_{0.5}Mn_{0.5}O_2$	2.987	11.231
	P2-$Na_{0.63}Cu_{0.125}Fe_{0.375}Mn_{0.5}O_2$	2.96	11.225