Supporting Information

Copper-Substituted $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ Cathode Materials for Sodium-Ion Batteries with Suppressed P2-O2 Phase Transition

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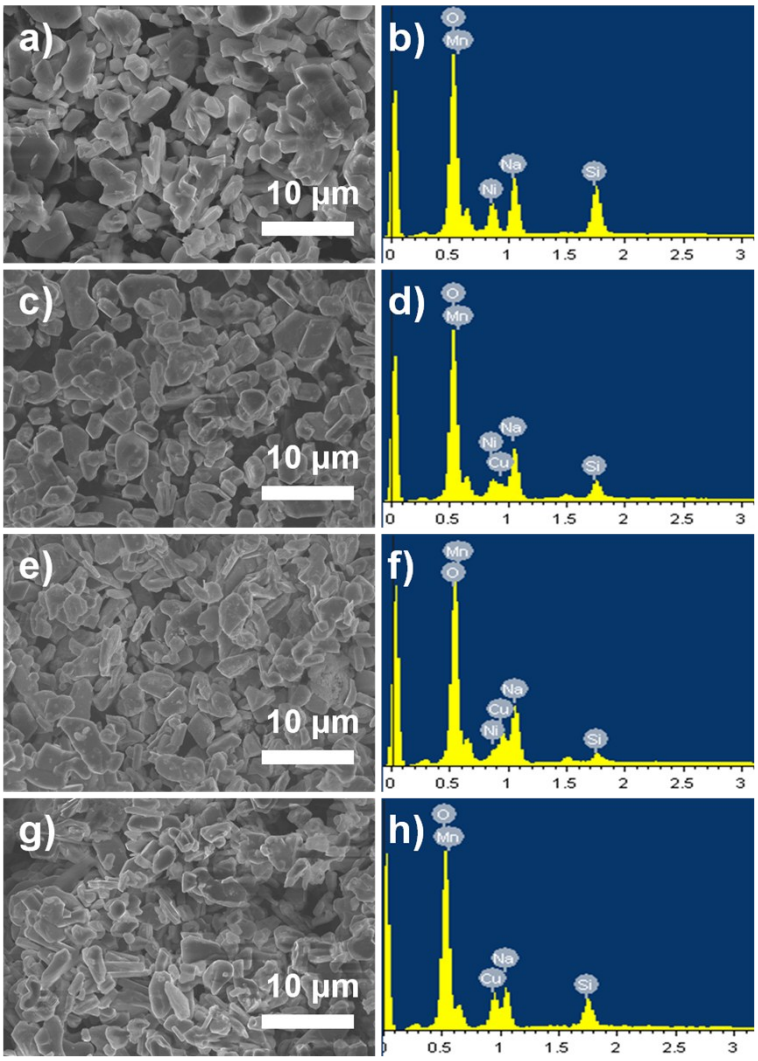

Figure S1 The Scanning electron microscopy (SEM) images of $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ (x=0, 0.1, 0.2 and 0.3) and the corresponding energy dispersive spectroscopy (EDS). a) and b) is for $Na_{0.67}Ni_{0.3}Mn_{0.7}O_2$; b) and b) is for $Na_{0.67}Ni_{0.2}Cu_{0.1}Mn_{0.7}O_2$; e) and f) is for $Na_{0.67}Ni_{0.1}$ $Cu_{0.2}Mn_{0.7}O_2$; g) and h) is for $Na_{0.67}Cu_{0.3}Mn_{0.7}O_2$;

Table S1 Summary of refined structural parameters of $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ (x=0, 0.1, 0.2 and 0.3).

Synthesized samples	structural parameters			
	a (Å)	c (Å)	Cell volume ($Å^3$)	R_p (%)
x=0	2.8834(4)	11.1774(1)	80.4816(1)	6.71
x=0.1	2.8848(4)	11.1992(3)	80.7168(9)	6.43
x=0.2	2.8867(5)	11.2162(8)	80.9467(3)	7.57
x=0.3	2.8914(7)	11.2116(1)	81.1780(9)	9.44

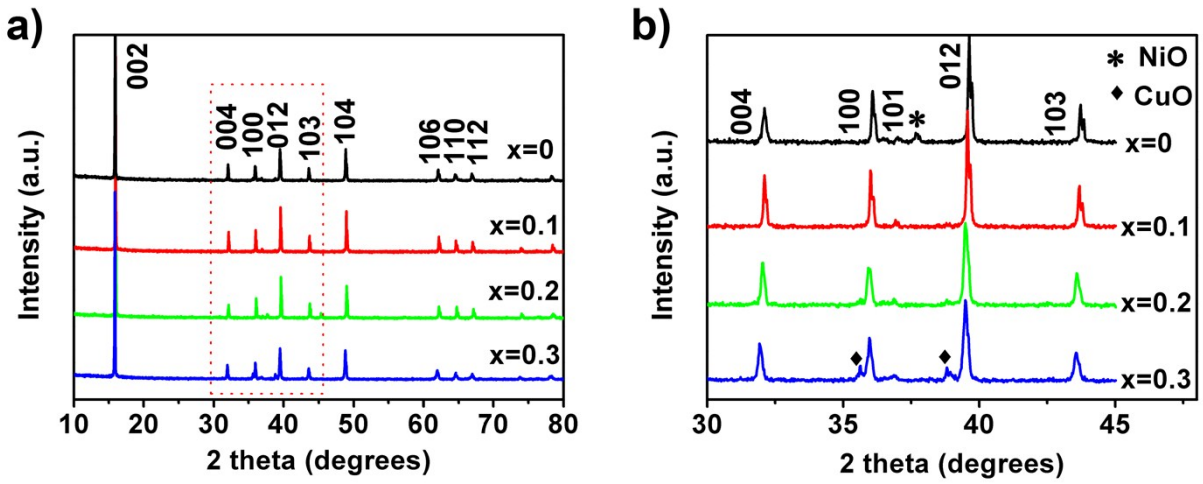

Figure S2 XRD analysis for $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ (x=0, 0.1, 0.2 and 0.3). a) 2θ is between 10°and 80°; b) 2θ is between 30°and 45°. A trace amount of a NiO and CuO impurity are observed in $Na_{0.67}Ni_{0.3}Mn_{0.7}O_2$ and $Na_{0.67}Cu_{0.3}Mn_{0.7}O_2$.

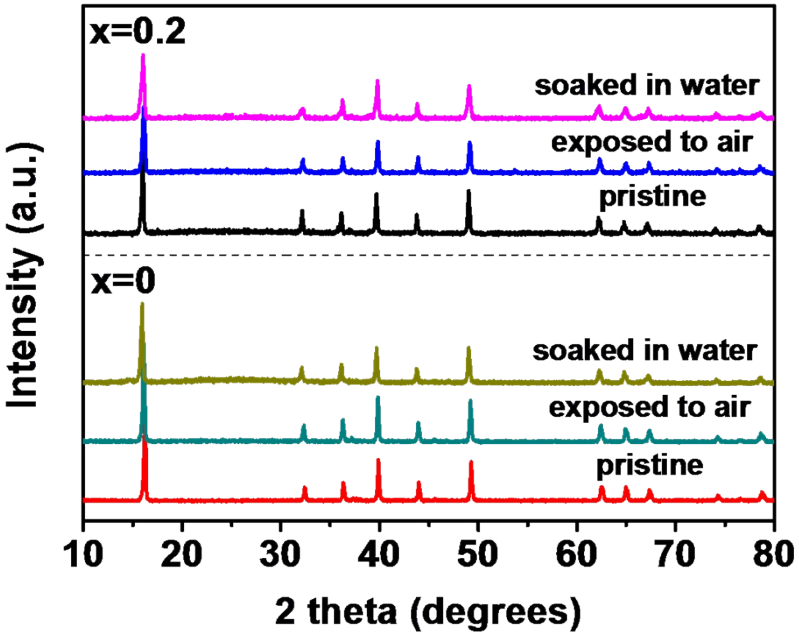

Figure S3 XRD analysis for as-synthesized $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ (x=0 and 0.2) electrodes after exposed to air and soaked in water for a month.

Table S2 ICP-AES results of $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ (x=0, 0.1, 0.2 and 0.3).

Synthesized samples	Measured atomic ratio			
	Na	Cu	Ni	Mn
x=0	0.659	0	0.273	0.653
x=0.1	0.655	0.089	0.192	0.667
x=0.2	0.662	0.185	0.095	0.665
x=0.3	0.665	0.266	0	0.664

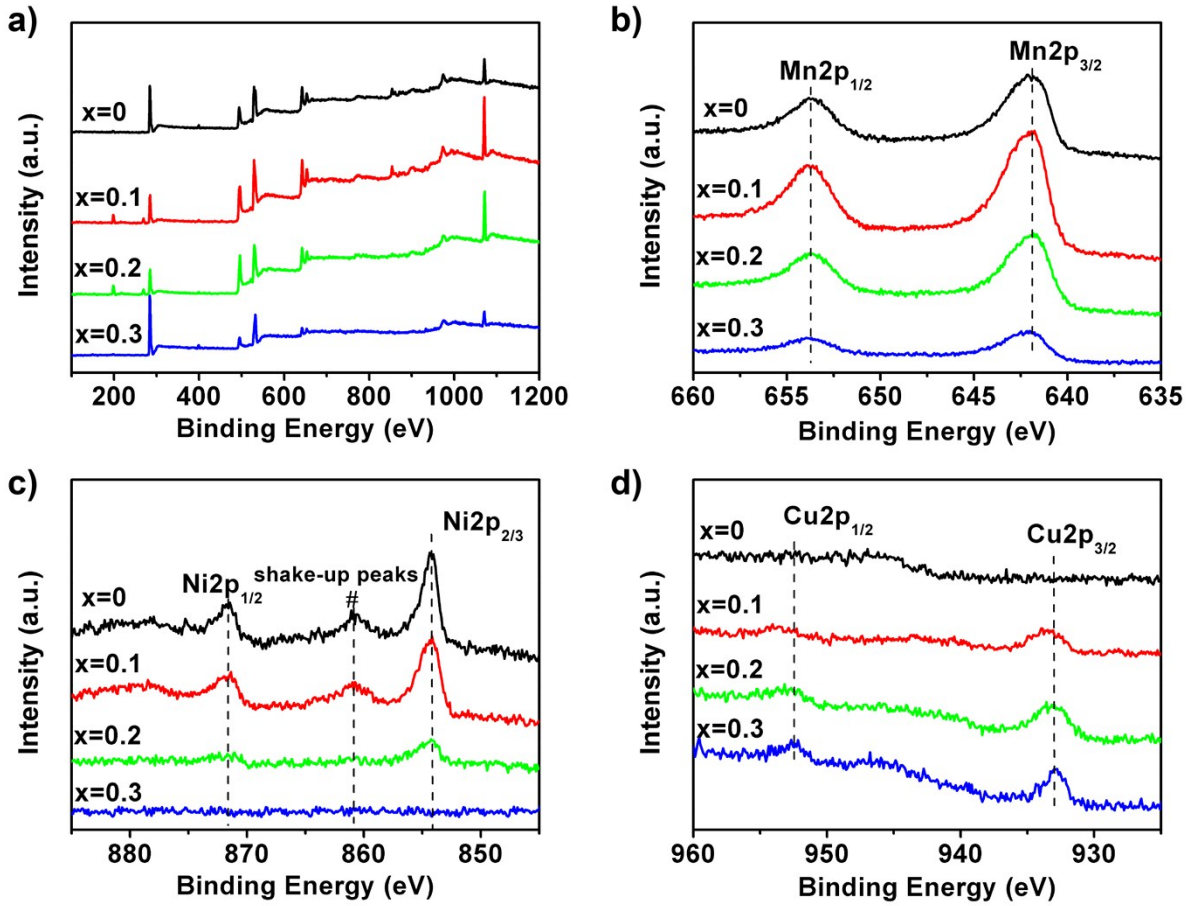

Figure S4 XPS survey for $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ (x=0, 0.1, 0.2 and 0.3). a) XPS spectra of as-synthesized electrodes; The high resolution XPS spectra of b) Mn 2p, c) Ni 2p and d) Cu 2p.

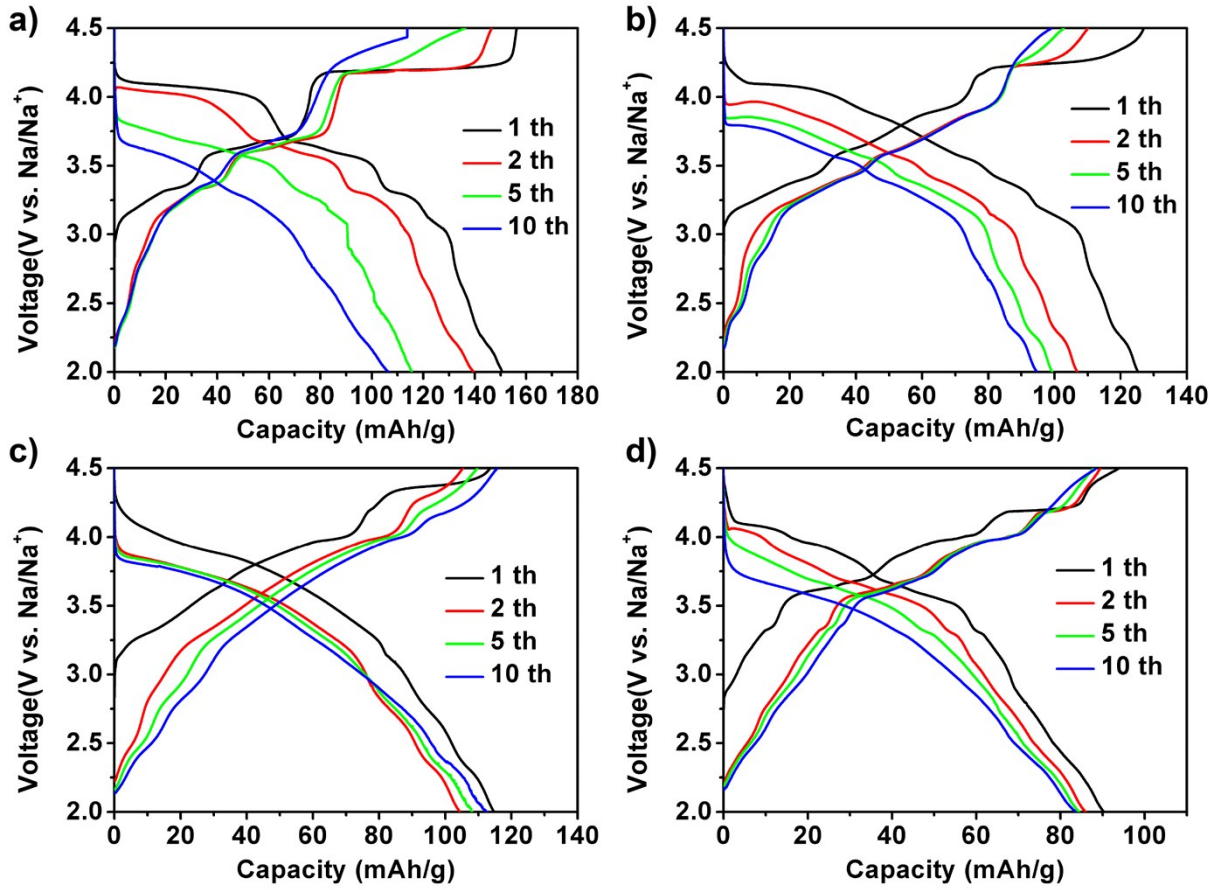

Figure S5 The typical Galvanostatic discharge/charge curves of a) $Na_{0.67}Ni_{0.3}Mn_{0.7}O_2$, b) $Na_{0.67}Ni_{0.2}Cu_{0.1}Mn_{0.7}O_2$, c) $Na_{0.67}Ni_{0.1}Cu_{0.2}Mn_{0.7}O_2$ and d) $Na_{0.67}Cu_{0.3}Mn_{0.7}O_2$ from 1^{th} cycle to 10^{th} cycle at 0.1C between 2.0-4.5V.

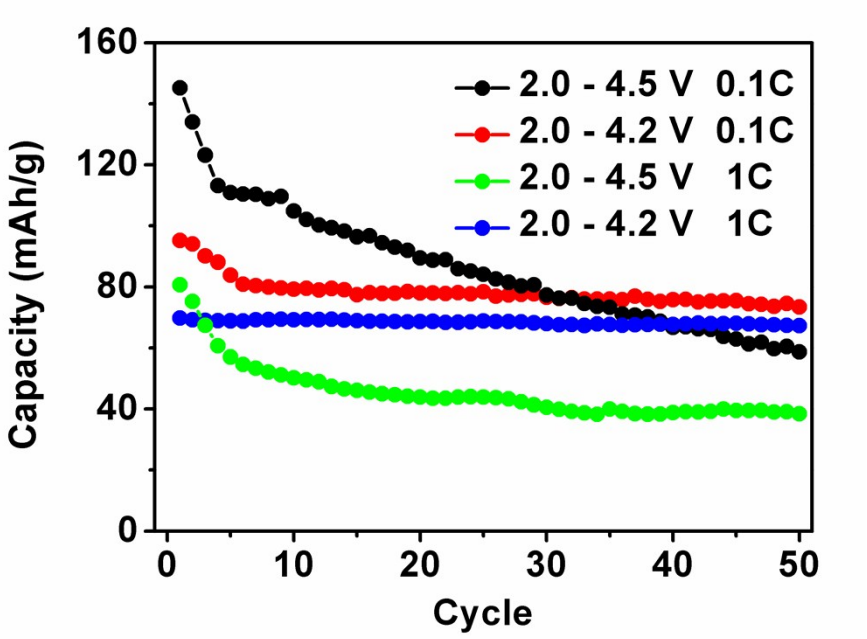

Figure S6 Cycle retentions of the Cu-free $Na_{0.67}Ni_{0.3}Mn_{0.7}O_2$ electrode at different current density with different cut-off voltage.

Table S3 Electrochemical properties of current cathode materials.

Cathode materials	Average voltage/voltage range (V)	Initial capacity (mAh g^{-1})	Cycle	Ref.
$Na_{2/3}Ni_{1/3}Mn_{5/9}Al_{1/9}O_2$	3.2 / 1.6-4.0	118 / 0.1C	77.5% (100 cycle)	1
$Na_{0.5}[Ni_{0.23}Fe_{0.13}Mn_{0.63}]O_2$	3.2 / 1.5-4.6	200 / 15 mA g^{-1}	75% (70 cycle)	2
$Na_{0.66}Li_{0.18}Mn_{0.71}Ni_{0.21}Co_{0.08}O_{2+d}$	3.2/ 1.5-4.5	185 / 20 mA g^{-1}	84% (50 cycle)	3
$Na_{0.67}Mn_{0.67}Ni_{0.28}Mg_{0.05}O_2$	3.7/ 2.5-4.35V	123 / 17 mA g^{-1}	85% (50 cycle)	4
$Na_{0.67}Mn_{0.8}Ni_{0.1}Mg_{0.1}O_2$	<3.0 / 1.5-4.2V	171 / 12 mA g^{-1}	81% (50 cycle)	5
$Na_{0.66}Ni_{0.33-x}Zn_xMn_{0.67}O_2$	3.6 / 2.2-4.25V	131 / 12 mA g^{-1}	89% (30 cycle)	6
$Na_{2/3}Ni_{1/3}Mn_{1/2}Ti_{1/6}O_2$	3.7 / 2.5-4.5V	127 / 12 mA g^{-1}	86% (20 cycle)	7
$Na[Ni_{0.60}Co_{0.05}Mn_{0.35}]O_2$	<3.0 / 1.5-4.1V	157 / 15 mA g^{-1}	80% (100 cycle)	8
$Na_{0.8}[Li_{0.12}Ni_{0.22}Mn_{0.66}]O_2$	3.2 / 2.0-4.4V	133 / 12 mA g^{-1}	86% (50 cycle)	9
$Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O_2$	3.2 / 2.5-4.05V	98 / 10 mA g^{-1}	97% (100 cycles)	10
$Na_{0.67}Mn_{0.7}Ni_{0.3-x}Cu_xO_2$	3.5 / 2.0-4.5V	115 / 17 mA g^{-1}	90% (50 cycle)	This Work

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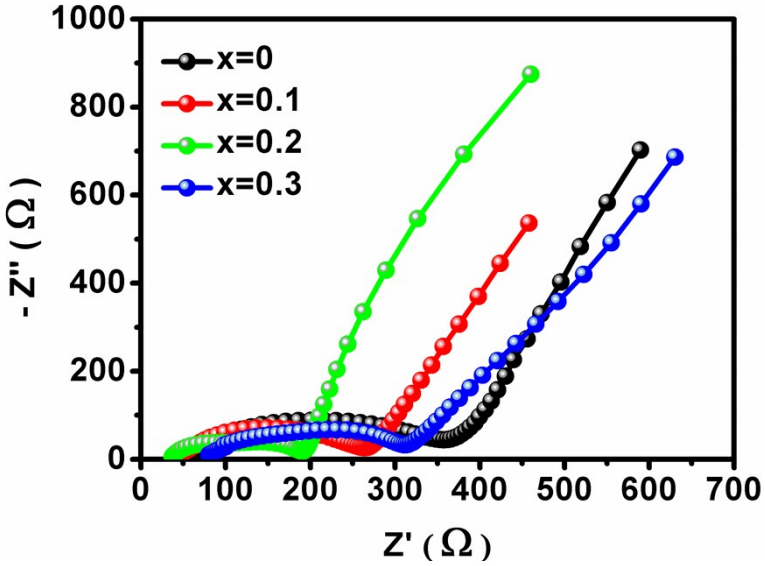

Figure S7 The Nyquist plots gathered by electrochemical impedance spectroscopy (EIS) measurements for $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ (x=0, 0.1, 0.2 and 0.3) electrodes after one cycle between 0.1 and 100k Hz.

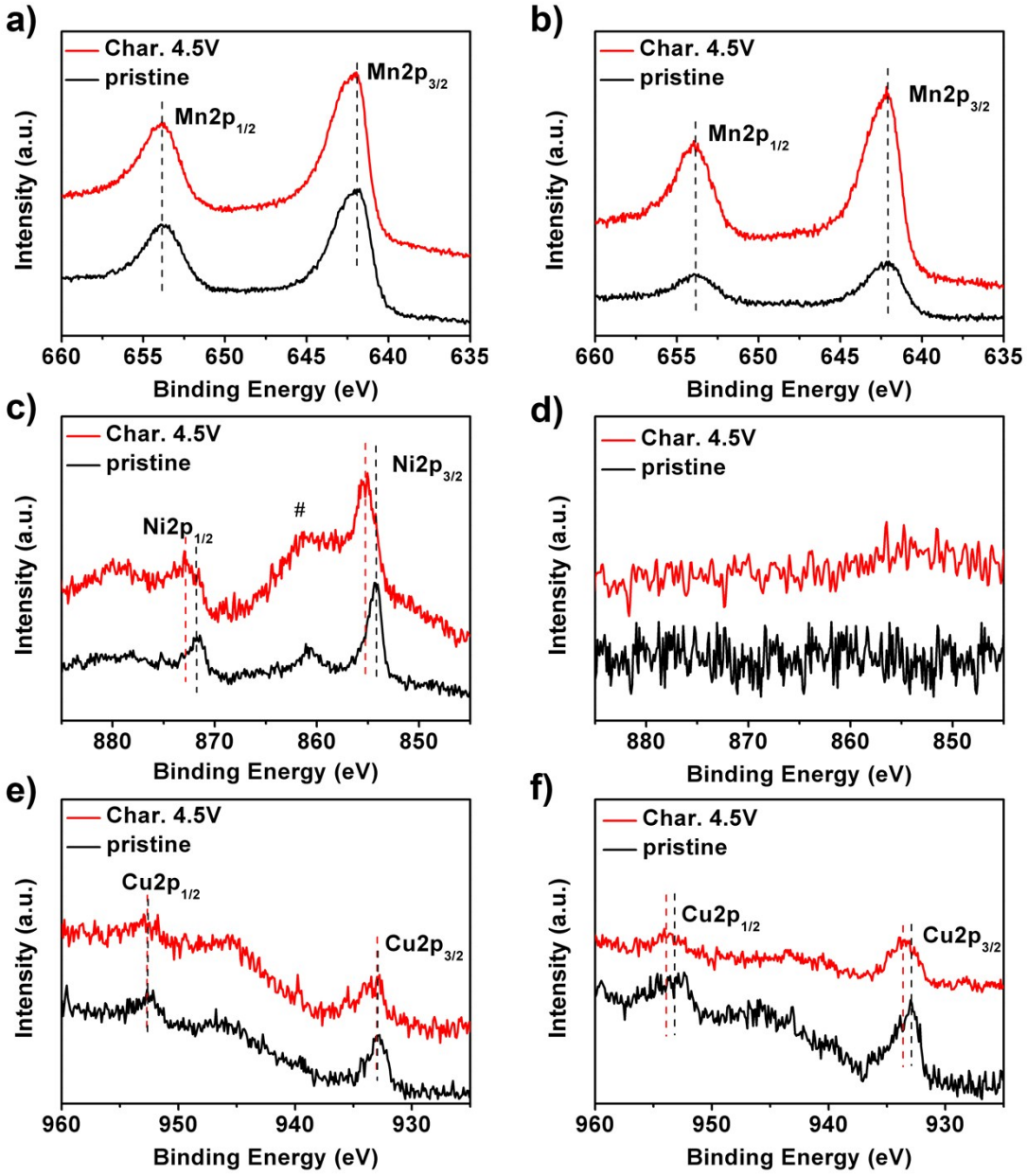

Figure S8 ex situ XPS spectra of $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ (x=0.1 and 0.3). The high resolution XPS spectra of a) Mn 2p, c) Ni 2p and e) Cu 2p in $Na_{0.67}Ni_{0.2}Cu_{0.1}Mn_{0.7}O_2$ electrode before and after charged to 4.5 V; The XPS spectra of b) Mn 2p, d) Ni 2p and f) Cu 2p in $Na_{0.67}Cu_{0.3}Mn_{0.7}O_2$ electrode before and after charged to 4.5 V. (# correspond to shake-up peaks)

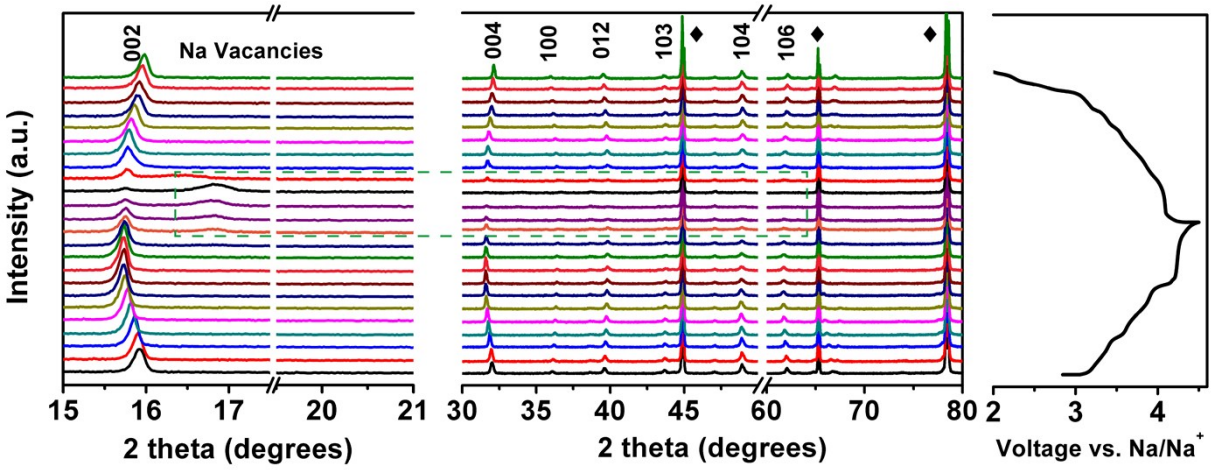

Figure S9 In situ XRD patterns collected during the first charge/discharge process of the $Na_{0.67}Ni_{0.2}Cu_{0.1}Mn_{0.7}O_2$ electrodes between 2.0 and 4.5 V under a current rate of 0.1 C.

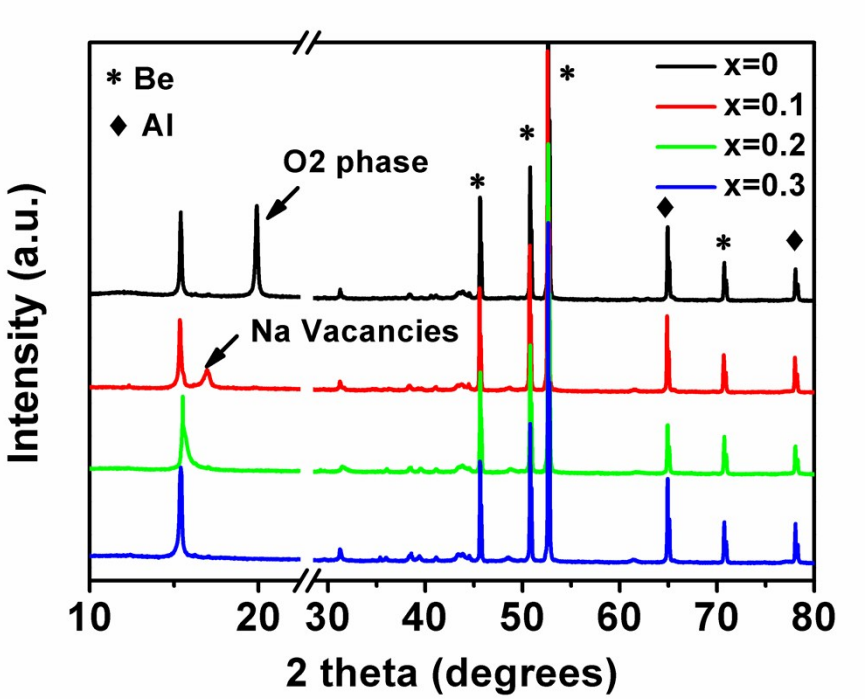

Figure S10 Ex situ XRD analysis for $Na_{0.67}Ni_{0.3-x}Cu_xMn_{0.7}O_2$ (x=0, 0.1, 0.2 and 0.3) electrodes. The patterns are collected after as-synthesized electrodes being charged to 4.5V and using Be as X-ray window.