Supporting Information

Mitigating P2-O2 Transition and Na^+/Vacancy Ordering in $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ by Anion/Cation Dual-Doping for Fast and Stable Na^+ Insertion/Extraction

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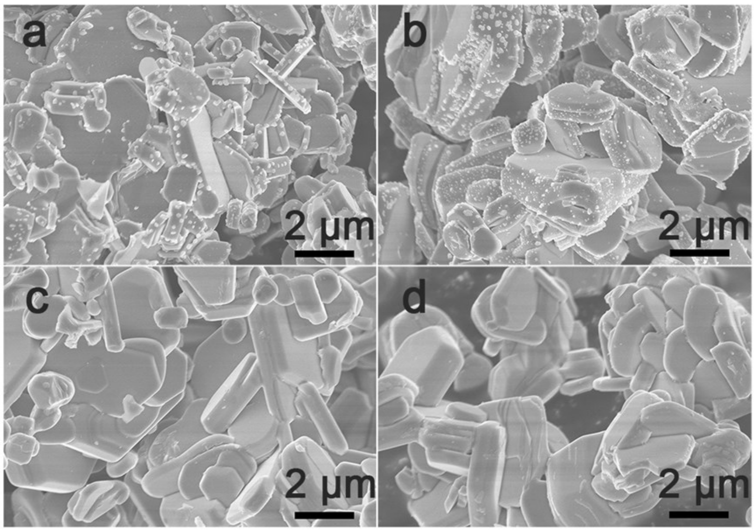

Fig. S1 SEM images of $Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$ samples (a) x = 0, (b) x = 0.01, (c) x = 0.03 and (d) x = 0.05.

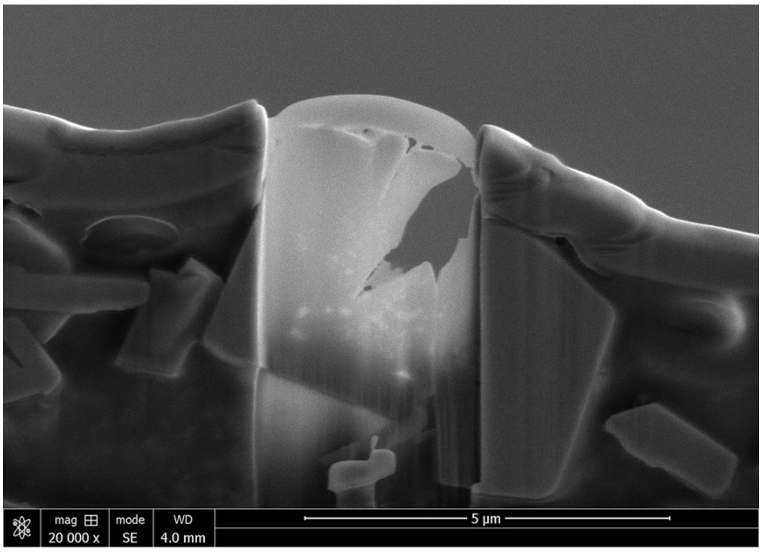

Fig. S2 FIB-cut image of TEM specimen.

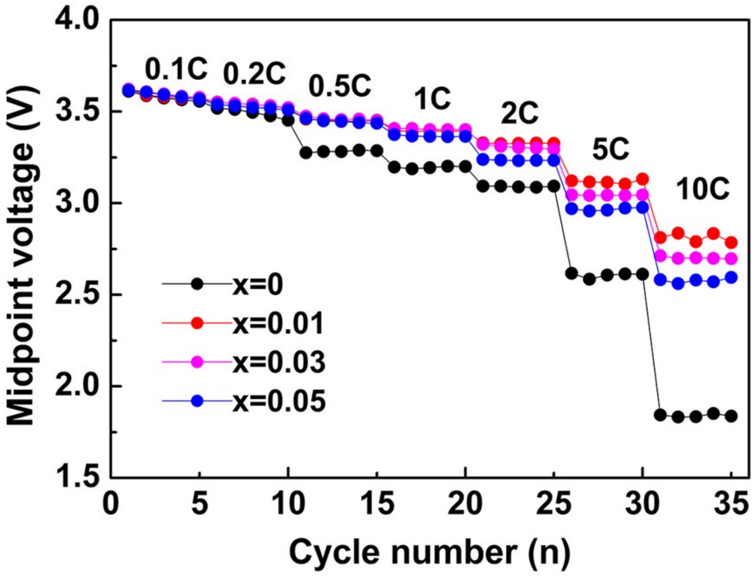

Fig. S3 Midpoint voltage of $Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$ (x = 0, 0.01, 0.03 and 0.05) at various current densities.

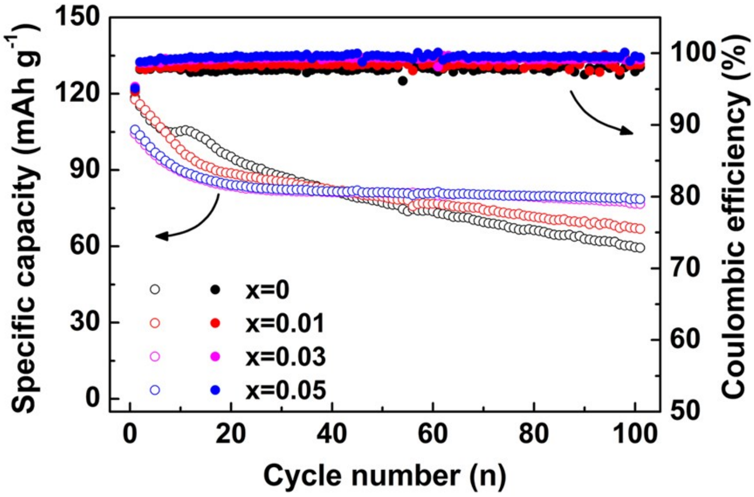

Fig. S4 Cycling performance of $Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$ (x = 0, 0.01, 0.03 and 0.05) cycled at 0.2C in the voltage range of 2.0-4.3 V.

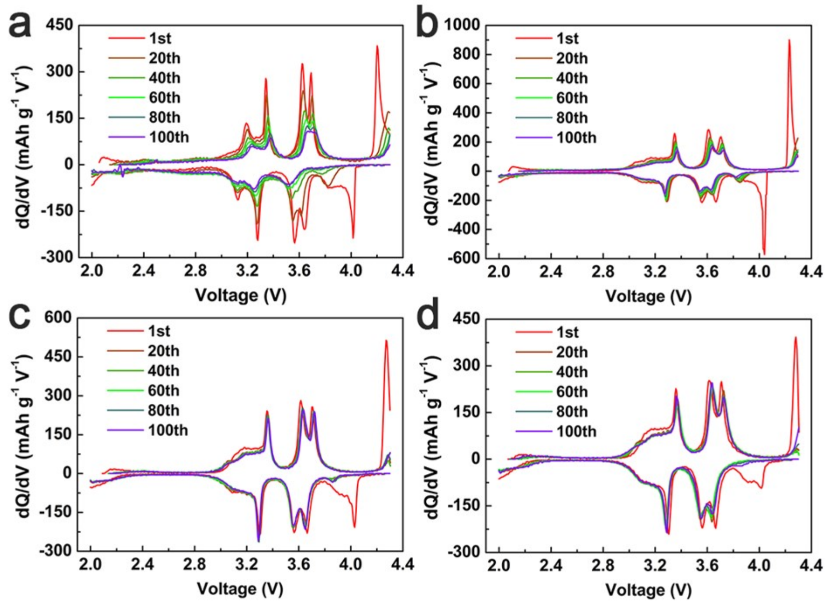

Fig. S5 The dQ/dV plots of $Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$ (a) x = 0, (b) x = 0.01, (c) x = 0.03 and (d) x = 0.05 at 0.2C.

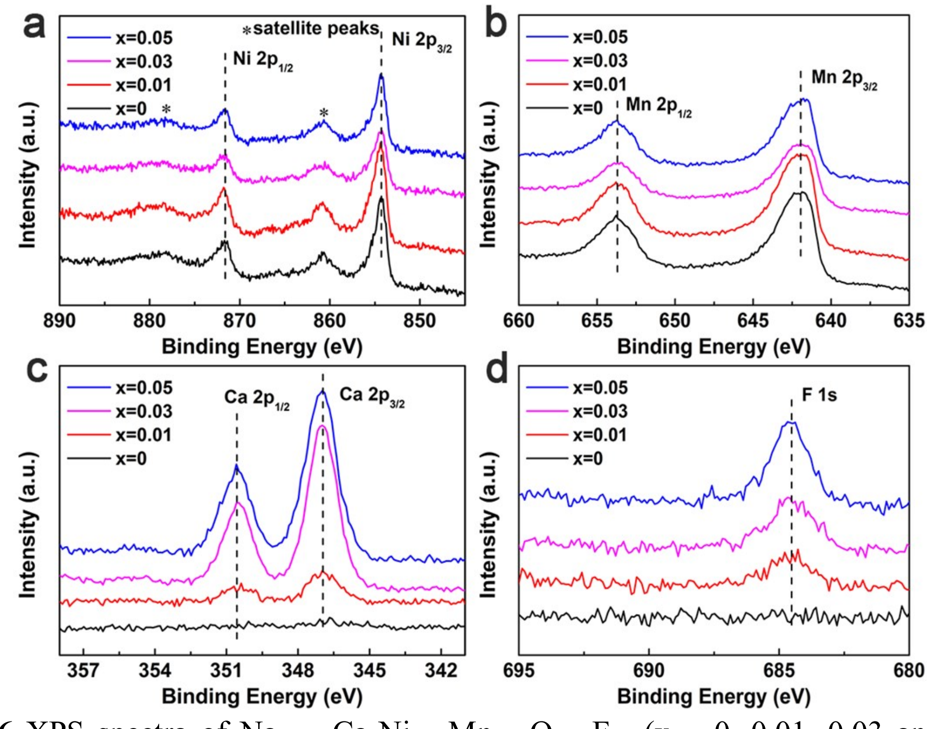

Fig. S6 XPS spectra of $Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$ (x = 0, 0.01, 0.03 and 0.05) powders for (a) Ni 2p, (b) Mn 2p, (c) Ca 2p and (d) F 1s.

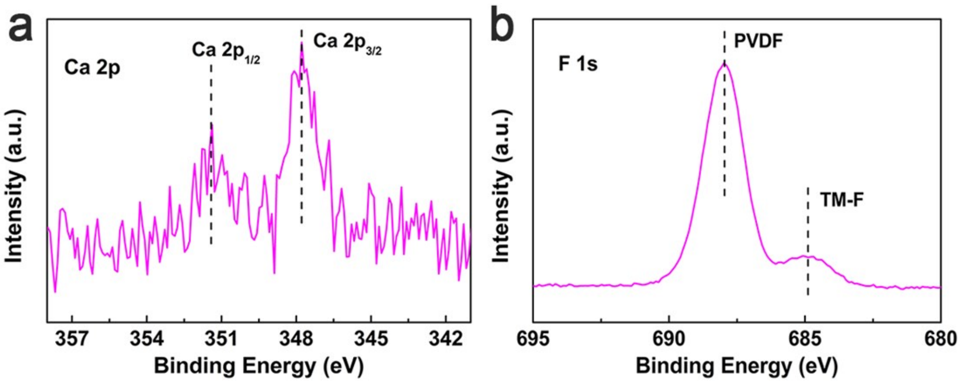

Fig. S7 XPS spectra of $Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$ (x = 0.03) cathode charged to 4.3 V for (a) Ca 2p and (b) F 1s.

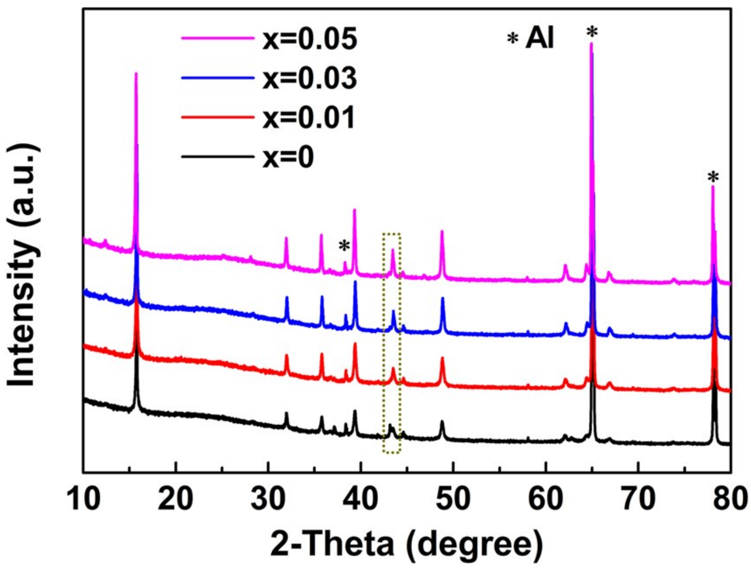

Fig. S8 Comparison of XRD patterns of $Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$ (x = 0, 0.01, 0.03 and 0.05) after 100 cycles at 0.2C.

Table S1. Crystallographic parameters of $Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$ (x = 0) refined by the Rietveld method.

Site	x	y	z	occ.
Na_f	0	0	0.25	0.3016
Na_e	0.3333	0.6667	0.75	0.3684
Ni	0	0	0	0.3260
Mn	0	0	0	0.6740
O	0.3333	0.6667	0.0890	1.0000
a = 2.886(5) Å	c = 11.151(3) Å	V = 80.45(3) $Å^3$	Rp = 4.96%	Rwp = 6.55%

Table S2. Crystallographic parameters of $Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$ (x = 0.03) refined by the Rietveld method.

Site	x	y	z	occ.
Na_f	0	0	0.25	0.2427
Na_e	0.3333	0.6667	0.75	0.3981
Ca_e	0.3333	0.6667	0.75	0.0292
Ni	0	0	0	0.3204
Mn	0	0	0	0.6796
O	0.3333	0.6667	0.0886	0.9400
F	0.3333	0.6667	0.0886	0.0600
a = 2.885(3) Å	c = 11.137(5) Å	V = 80.31(3) $Å^3$	Rp = 4.56%	Rwp = 5.74%

Table S3. Comparison of the electrochemical performance of $Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$ and other P2-Na-Ni-Mn-O type materials.

Material	Voltage window	Capacity retention	Reference
$Na_{2/3}Cu_{1/6}Ni_{1/6}Mn_{2/3}O_2$	2.5-4.4 V	97.0%, 30 cycles, 1C	1
$Na_{2/3}Ni_{1/4}Mn_{2/3}Cu_{1/12}O_2$	2.0-4.5 V	89.0%, 50 cycles, 0.05C	2
$Na_{0.67}Ni_{0.25}Mg_{0.05}Mn_{0.7}O_2$	2.0-4.5 V	91.5%, 50 cycles, 200 mA g^{-1}	3
$Na_{0.67}Mn_{0.65}Ni_{0.2}Co_{0.15}O_2$	2.0-4.3 V	62.0%, 100 cycles, 0.1C	4
$Na_{2/3}Ni_{1/3}Mn_{1/3}Ti_{1/3}O_2$	2.5-4.35 V	83.9%, 500 cycles, 1C	5
Al_2O_3-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$	2.5-4.3 V	73.2%, 300 cycles, 0.5C	6
$Na_{0.78}Al_{0.05}Ni_{0.33}Mn_{0.60}O_2$	2.0-4.5 V	83.9%, 50 cycles, 0.1C	7
$Na_{0.67}Fe_{0.20}Ni_{0.15}Mn_{0.65}O_2$	2.0-3.8 V	70.0%, 900 cycles, 1C	8
$Na_{2/3}[Ni_{0.3}Co_{0.1}Mn_{0.6}]O_2$	2.0-4.3 V	79.2%, 50 cycles, 0.1C	9
$Na_{2/3}Ni_{1/3}Mn_{7/12}Fe_{1/12}O_2$	2.0-4.4 V	85.0%, 300 cycles, 5C	10
$Na_{0.67-x}Ca_xNi_{0.33}Mn_{0.67}O_{2-2x}F_{2x}$	**2.0-4.3 V**	**87.2%, 500 cycles, 1C**	**This work**

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