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"Al-doped High Voltage Cathode of $Na_4Co_3(PO_4)_2P_2O_7$ Enabling a Highly Stable 4V Full Sodium-Ion Batteries"

By

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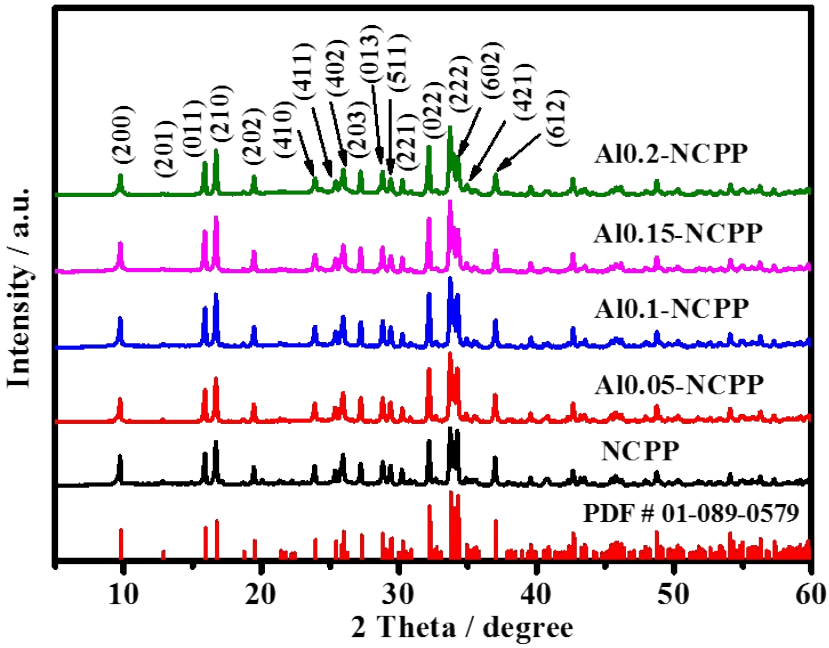

Fig. S1 XRD patterns of $Na_{4-x}Co_{3-x}Al_x(PO_4)_2P_2O_7$ samples with various Al contents (x=0, 0.05, 0.1, 0.15, 0.2).

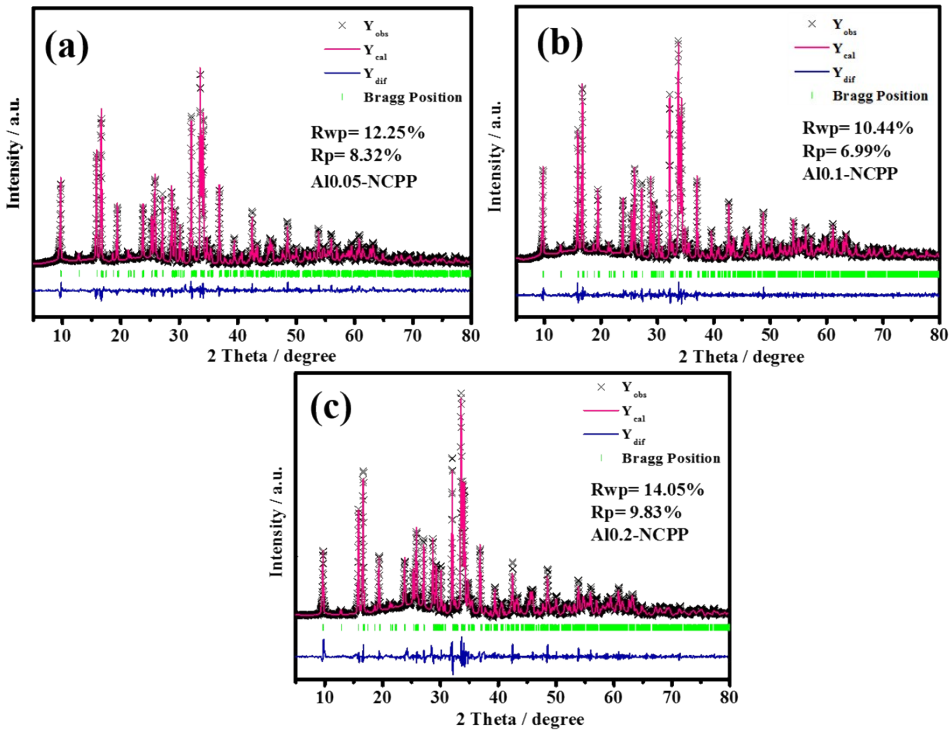

Fig. S2 Rietveld Refinement patterns of $Na_{4-x}Co_{3-x}Al_x(PO_4)_3P_2O_7$ (a) x = 0.05, (b) x = 0.1, (c) x = 0.2.

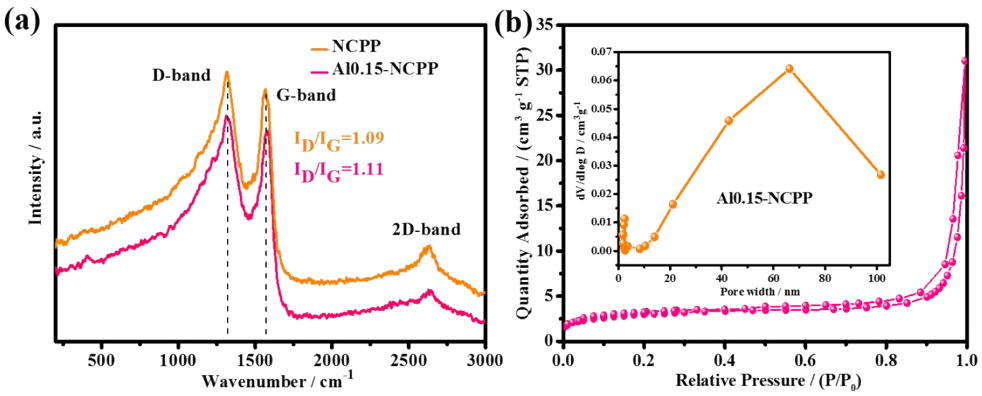

Fig. S3 (a) Raman spectra of NCPP and Al0.15-NCPP, (b) N_2-sorption isotherms of Al0.15-NCPP.

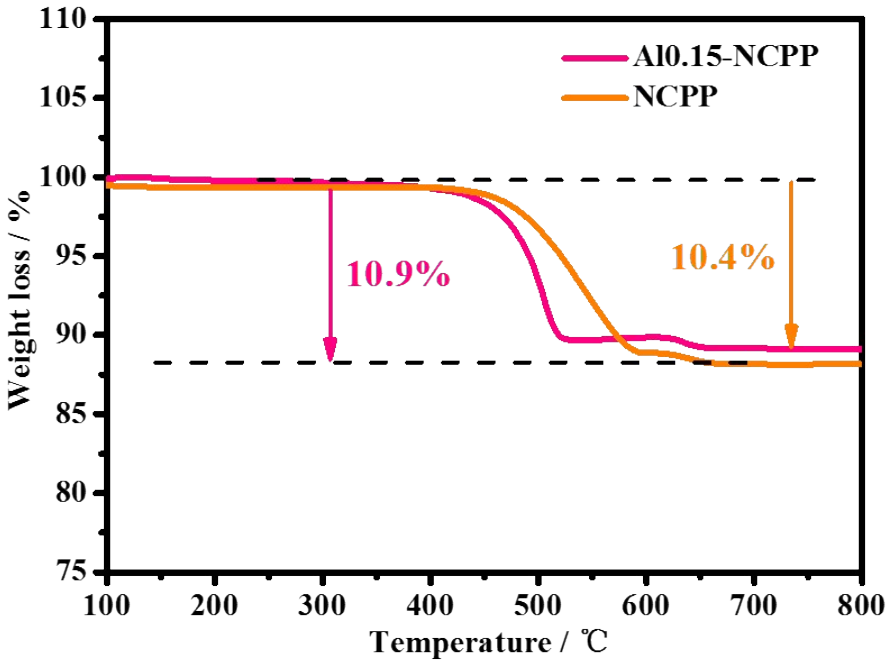

Fig. S4 TGA curves of the Al0.15-NCPP and NCPP.

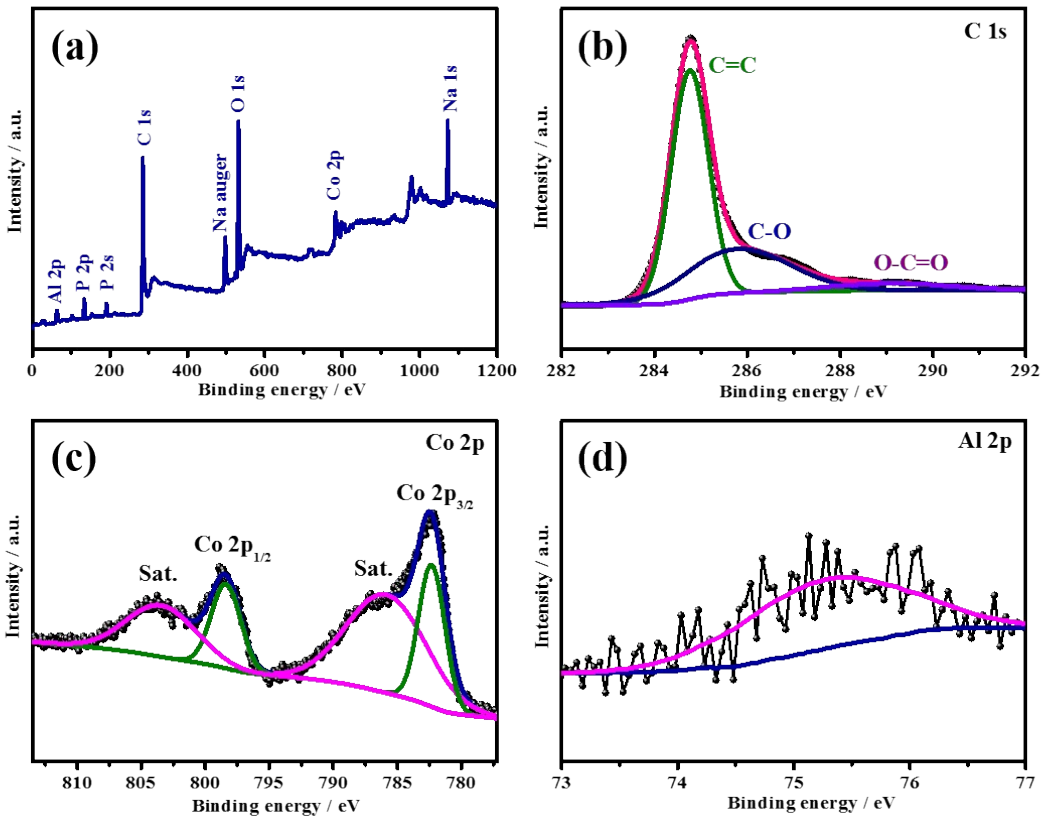

Fig. S5 (a) XPS spectrum, (b) High-resolution C1s spectrum, (c) Co2p spectrum, (d) Al2p spectrum of Al0.15-NCPP.

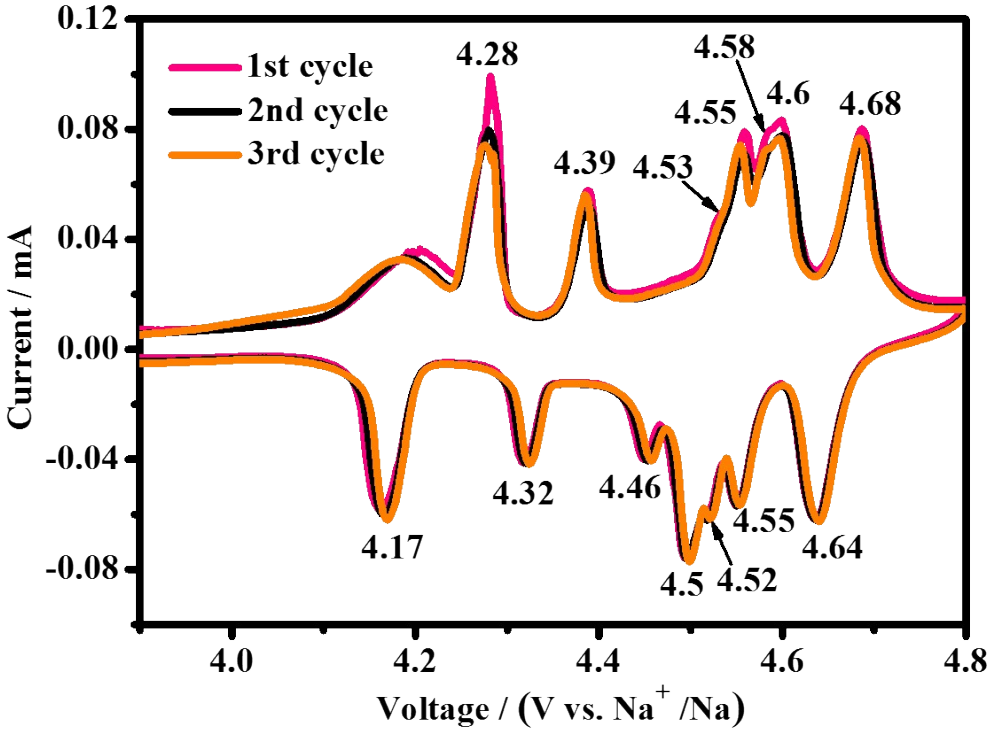

Fig. S6 CV curves of the first 3 cycles at a scan rate of 0.05 mV s^{-1} for Al0.15-NCPP.

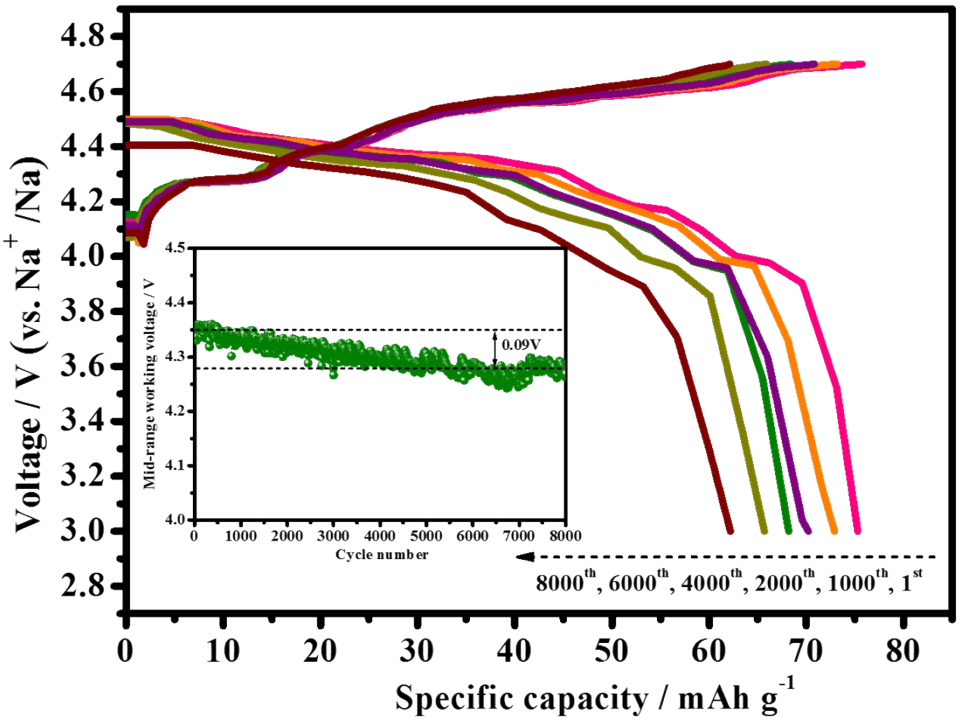

Fig. S7 The charge and discharge curves of Al0.15-NCPP at different cycle numbers (30 C). The inset is the mid-range working voltage retention within 8000 cycles.

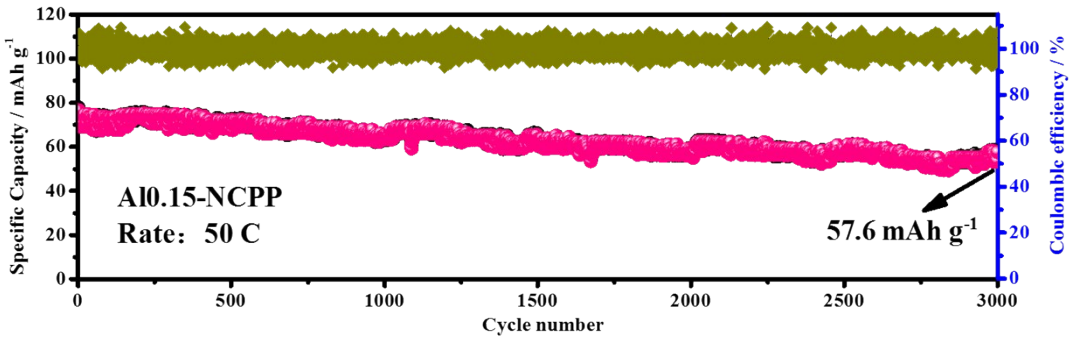

Fig. S8 Long-term cycling performance of Al0.15-NCPP at 50 C.

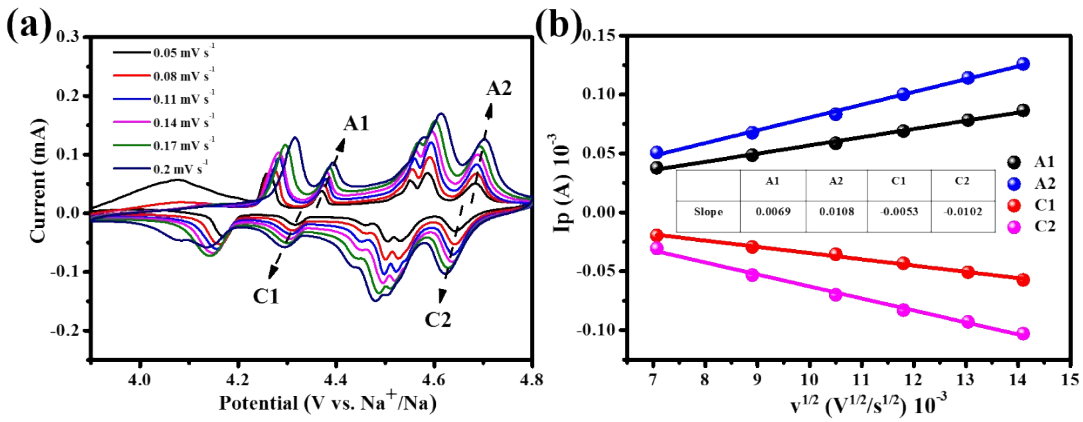

Fig. S9 (a) Cyclic voltammograms of NCPP at different scanning rates (0.05, 0.08, 0.11, 0.14, 0.17 and 0.2 mV s^{-1}), (b) Linear fitting results of the peak current (Ip) versus the square root of the scan rate ($v^{1/2}$) curves from the redox peaks in CV curves for NCPP.

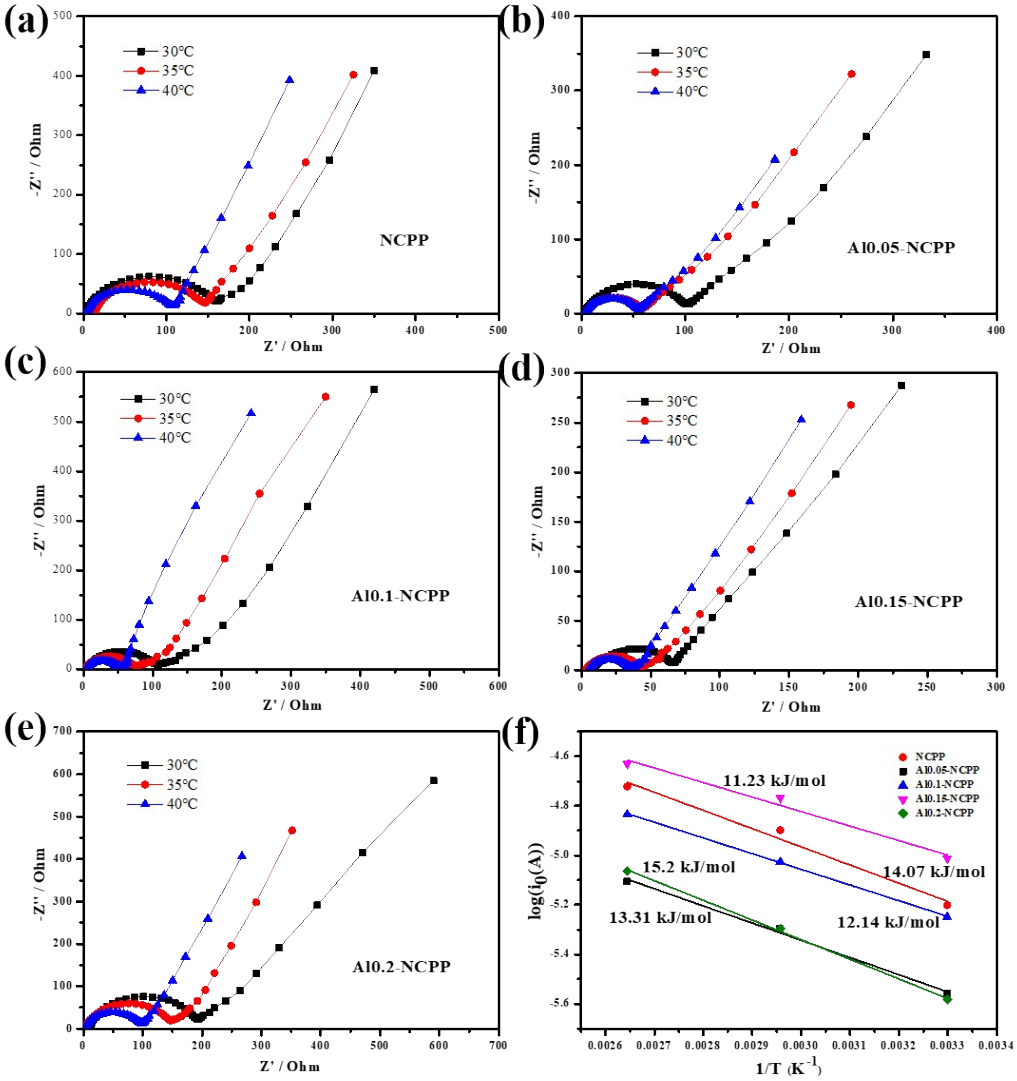

Fig. S10 (a-e) Nyquist plots of $Na_{4-x}Co_{3-x}Al_x(PO_4)_2P_2O_7$ electrodes with various Al contents (x=0, 0.05, 0.1, 0.15, 0.2) at a charged potential of 4.0 V (vs. Na^+/Na) at different temperatures from 100 kHz to 10 mHz, (f) Arrhenius plots of log i_0 versus 1/T for the electrodes of $Na_{4-x}Co_{3-x}Al_x(PO_4)_2P_2O_7$ electrodes with various Al contents (x=0, 0.05, 0.1, 0.15, 0.2) at a charged potential of 4.0 V (vs. Na^+/Na). The lines are the linear fitting results.

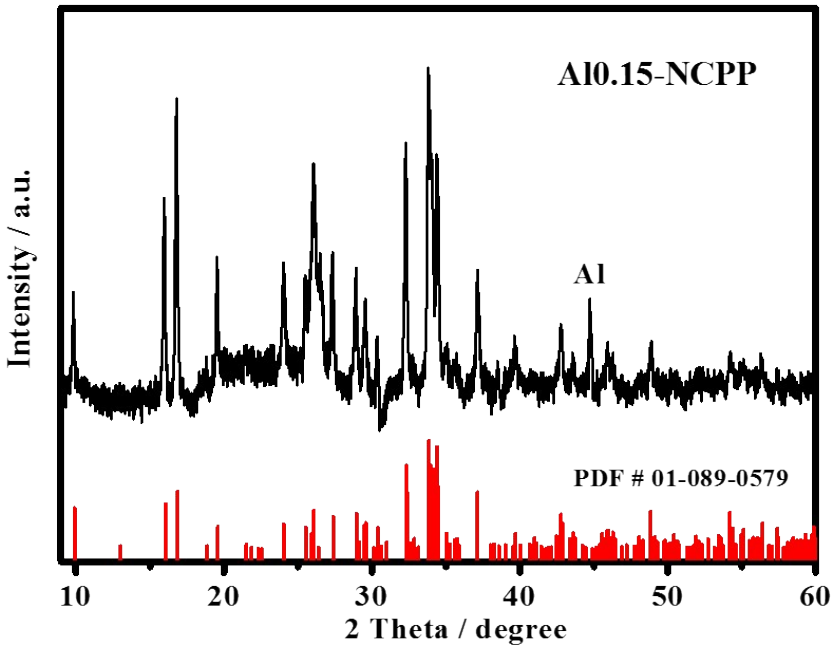

Fig. S11 The XRD of Al0.15-NCPP electrode after 800 cycles at 10 C.

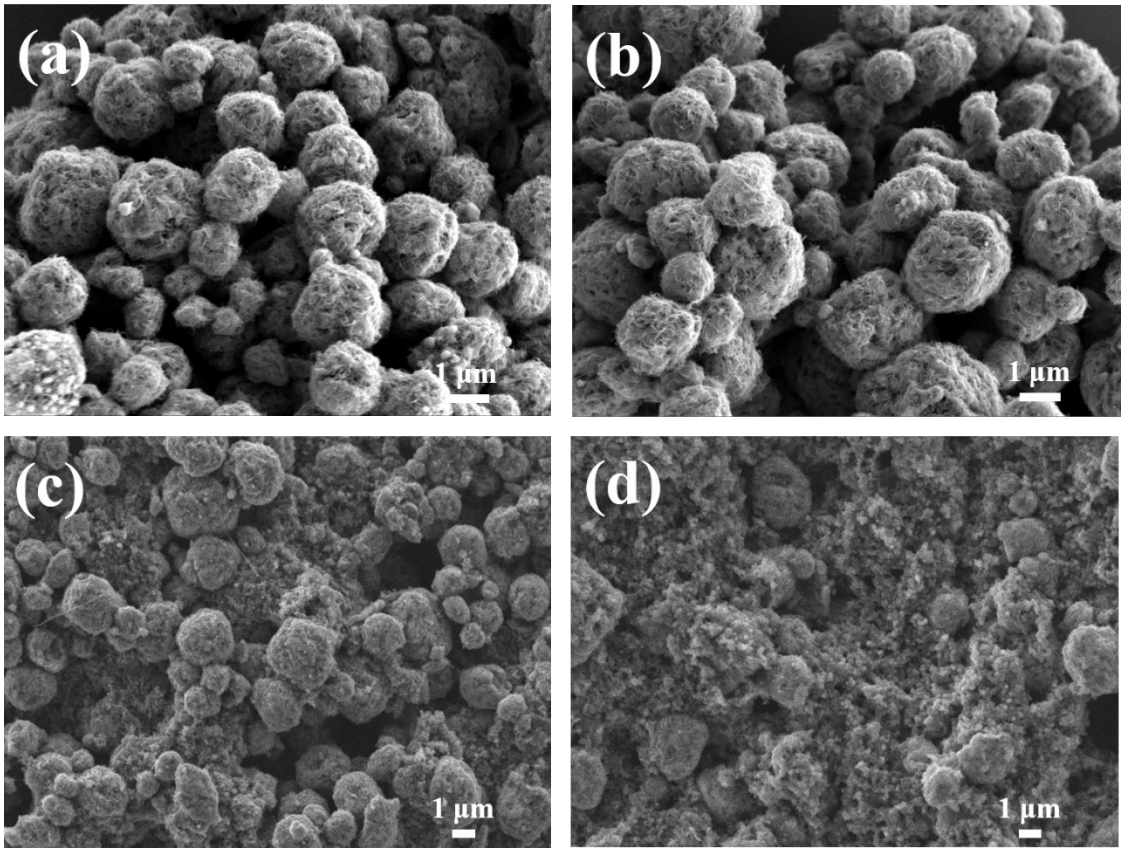

Fig. S12 SEM of Al0.15-NCPP and NCPP (a, b) before cycles, (c, d) after 800 cycles at 10 C.

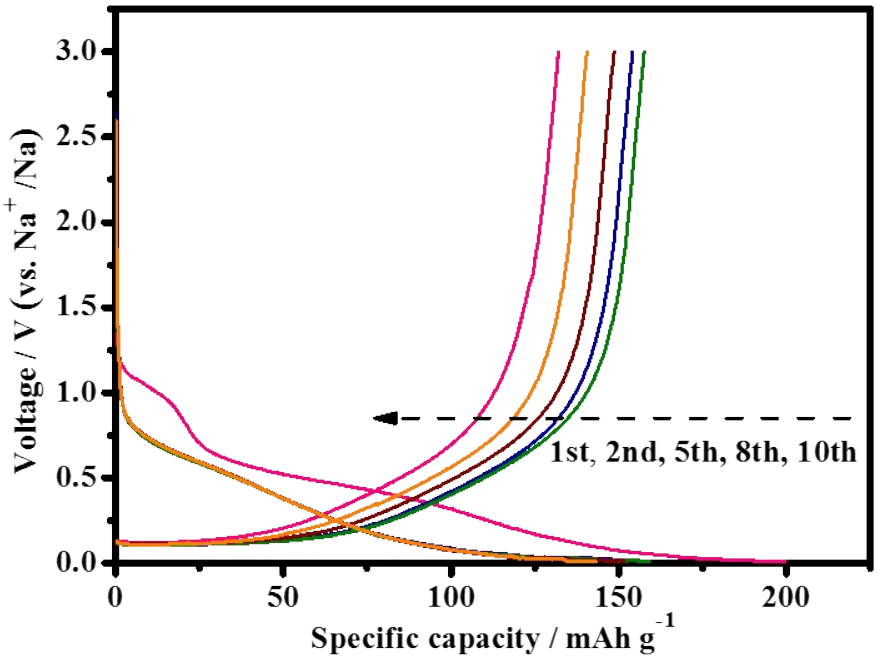

Fig. S13 Galvanostatic charge and discharge profiles at 50 mA g^{-1} of hard carbon (HC).

Table S1. Parameters of $Na_{4-x}Co_{3-x}Al_x(PO_4)_2P_2O_7$ by Rietveld Refinement

Samples	a(Å)	b(Å)	c(Å)	V(Å^3)
NCPP	18.0777(4)	6.5393(12)	10.5361(21)	1245.53(4)
Al0.05-NCPP	18.0886(4)	6.5511(10)	10.5577(20)	1251.09(4)
Al0.1-NCPP	18.0946(5)	6.5573(13)	10.5674(24)	1253.84(5)
Al0.15-NCPP	18.0981(4)	6.5601(12)	10.5691(22)	1254.82(4)
Al0.2-NCPP	18.1139(6)	6.5634(16)	10.5711(30)	1256.78(6)

Table S2. The calculated diffusion coefficients of the Na^+ ions (D_{Na^+}) of NCPP and Al0.15- NCPP

Samples	NCPP (D_{Na^+}) [cm^2 s^{-1}]	Al0.15-NCPP (D_{Na^+}) [cm^2 s^{-1}]
A1	5.83×10^{-13}	1.30×10^{-12}
A2	1.44×10^{-12}	3.01×10^{-12}
C1	3.44×10^{-13}	1.51×10^{-12}
C2	1.27×10^{-12}	1.86×10^{-12}

Table S3. The test value of R_s and R_{ct} for NCPP and Al0.15-NCPP samples after 100 cycles (charge state: 4.5 V)

Samples	R_s/Ω	$R_{[sf+ct]}/\Omega$
NCPP	4.441	120.6
Al0.15-NCPP	3.615	49.5

Table S4. A comparison of electrochemical performance of various mixed phosphate-based materials

Electrode materials	Method	Specific capacity	Cycle performance	Ref.
Al0.15-NCPP 1C=170 mA g^{-1}	Spray-drying	99.5 mAh g^{-1} at 0.5C, 73.4 mA h g^{-1} at 50C	96.3% after 900 cycles at 10C, 82.7% after 8000 cycles at 30C	**This work**
NCPP/VGCF 1C=170 mA g^{-1}	Sol-gel	95 mAh g^{-1} at 0.2C, 80 mAh g^{-1} at 25C	~95 mAh g^{-1} after 100 cycles at 0.2C	S1
NCoMnNiPP/VGCF 1C=170 mA g^{-1}	Sol-gel	106 mAh g^{-1} at 2C, 103 mAh g^{-1} at 5C	93% at2C and 88% at 5C after 10 cycles	S2
NMPP/C 1C=129.55 mA g^{-1}	Solid-state	109 mAh g^{-1} at 0.05C, 90 mAh g^{-1} at 1C	82% after 100 cycles at 0.2C	S3
NVPP/C 1C=92.8 mA g^{-1}	Sol-gel	92.1 mAh g^{-1} at 0.05C, 73mAh g^{-1} at 10C	95.2%after200 cycles at 0.05C, 92.6% after200 cycles at 0.5C	S4

NFPP@rGO 1C=129 mA g^{-1}	Spray-drying	128 mAh g^{-1} at 0.1C, 35 mAh g^{-1} at 200 C	62.3% after 6000 cycles at 10C	S5
NFPP/C 1C=129 mA g^{-1}	Template method	128.5 mAh g^{-1} at 0.2C, 79 mAh g^{-1} at 100C	63.5% after 4000 cycles at 10C	S6

References

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