

Fig.S1 Rietveld refined XRD patterns of KLS0/0.01/0.03/0.05/0.07/0.1-NVP (a-f) and the XRD patterns of all samples (g)

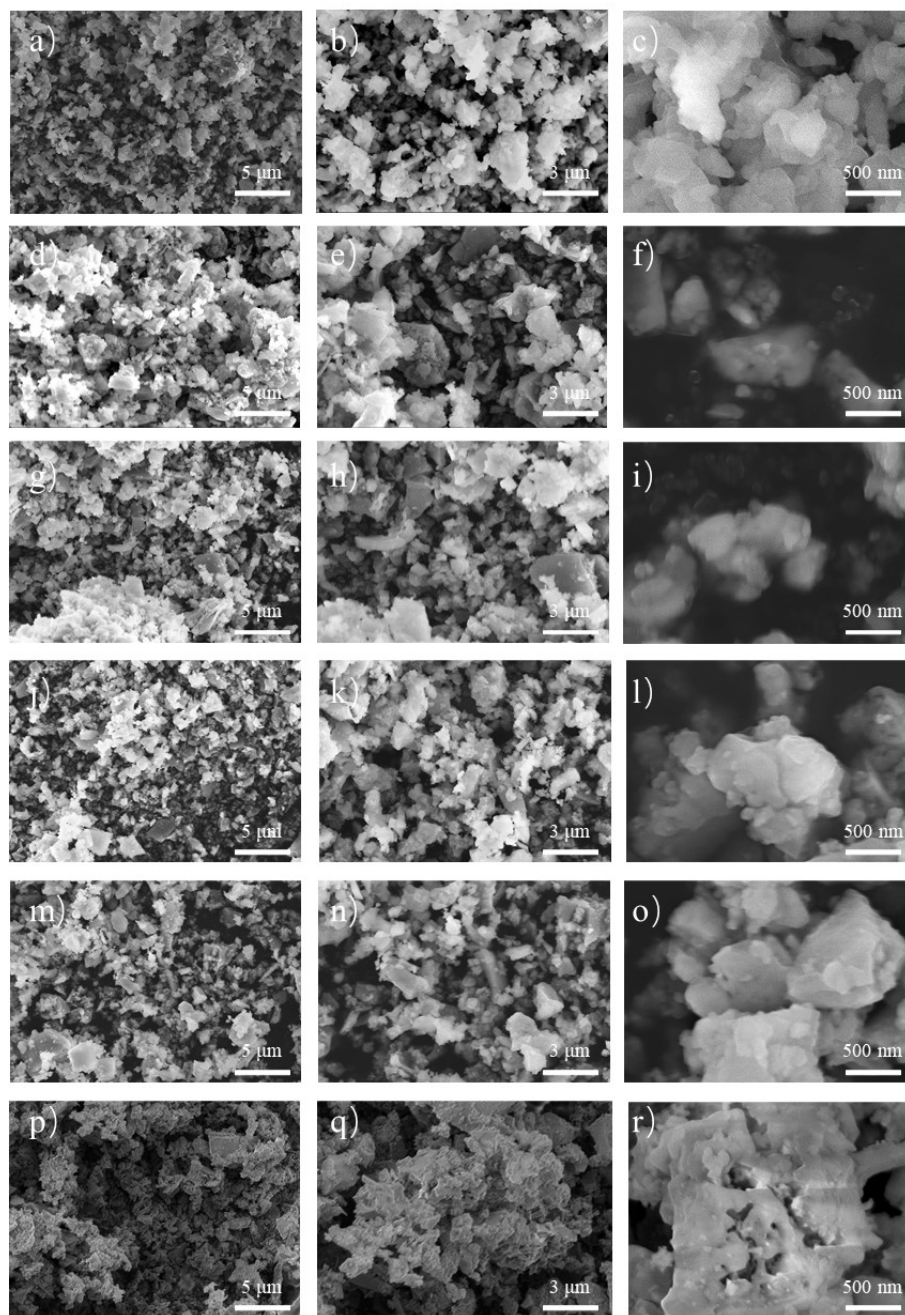


Fig.S2 Different magnification times at 5000/15000/50000 of NVP (a-c), KLS0.01 (d-f), KLS0.03 (g-i), KLS0.05 (j-l), KLS0.07 (m-o) and KLS0.1 (p-r).

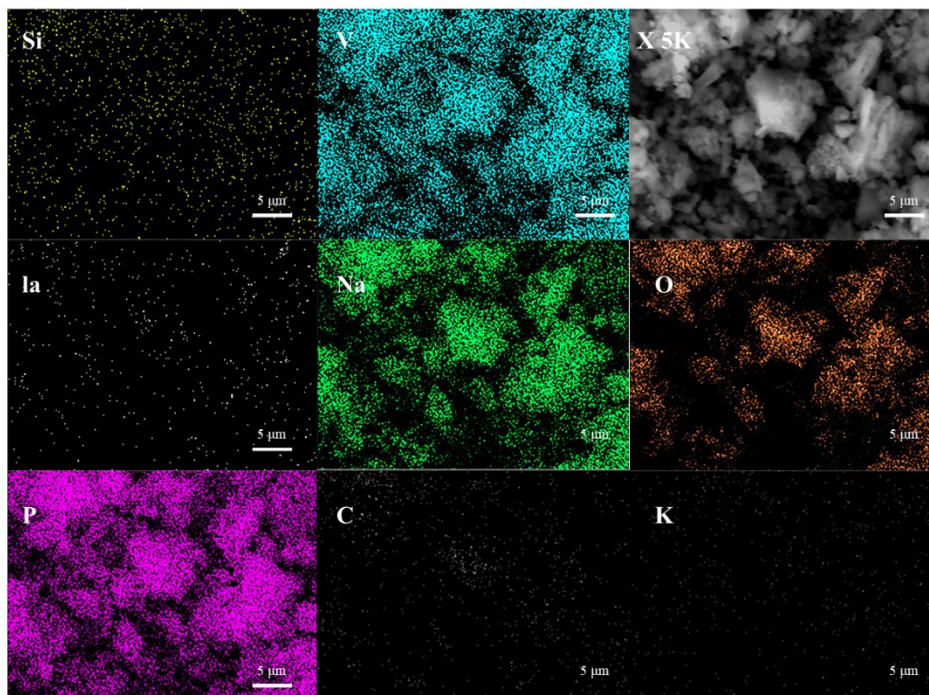


Fig.S3 The EDS spectrum of KLS0.07 with original image and every dispersed states of elements

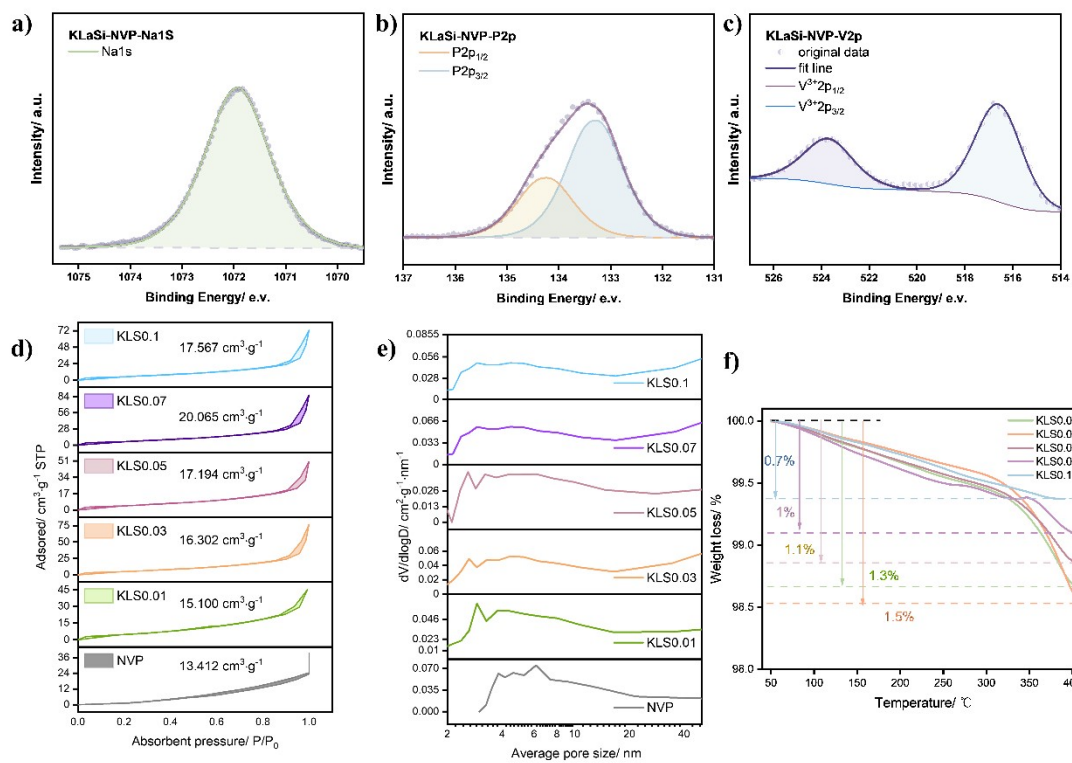


Fig.S4 The XPS testing results of Na 1s (a), V 2p (b), P 2p (c) and the BET curves (d), BJH broken lines (e) and TG curves of KLS samples (f).

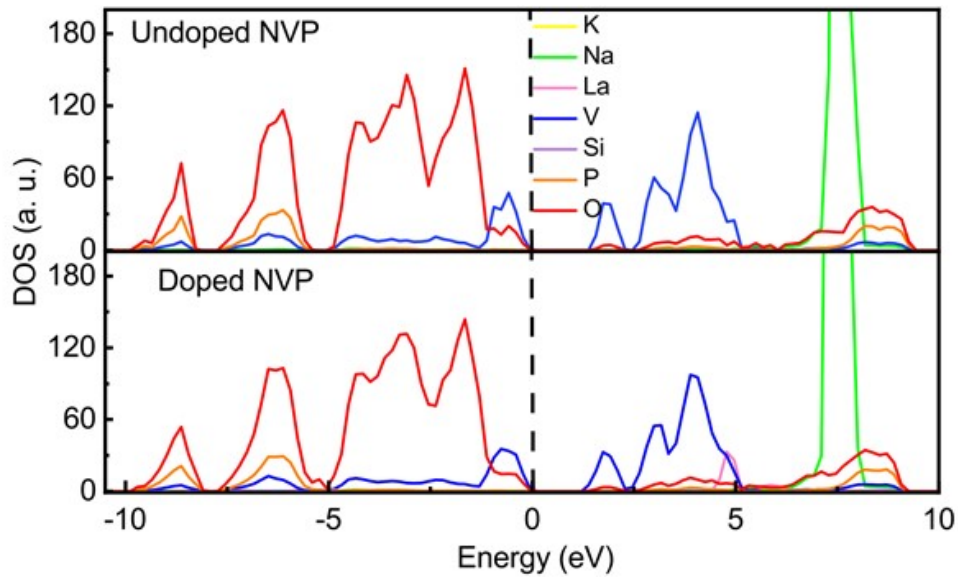


Fig.S5 Specific DOS mapping of all the elements in NVP before and after doping.

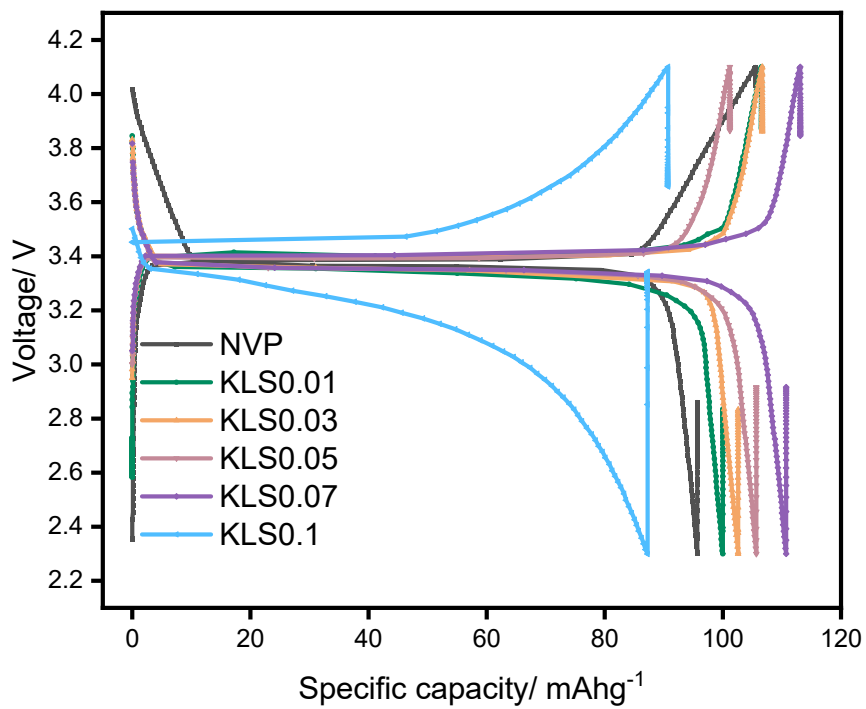


Fig.S6 Initial charging and discharging profiles at 1C of all the samples.

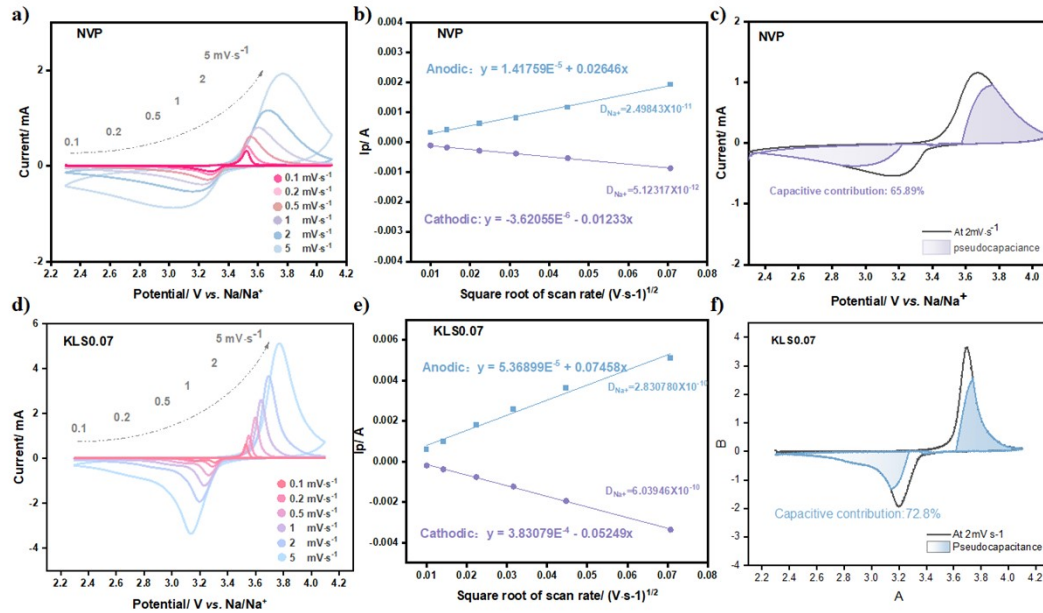


Fig.S7 Cyclic voltammogram (CV) curves of NVP and KLS0.07 at various scanning rates (a, d), the fit line between I_p and scan rate of NVP and KLS0.07 (b, e) and their corresponding pseudocapacitance (c, f).

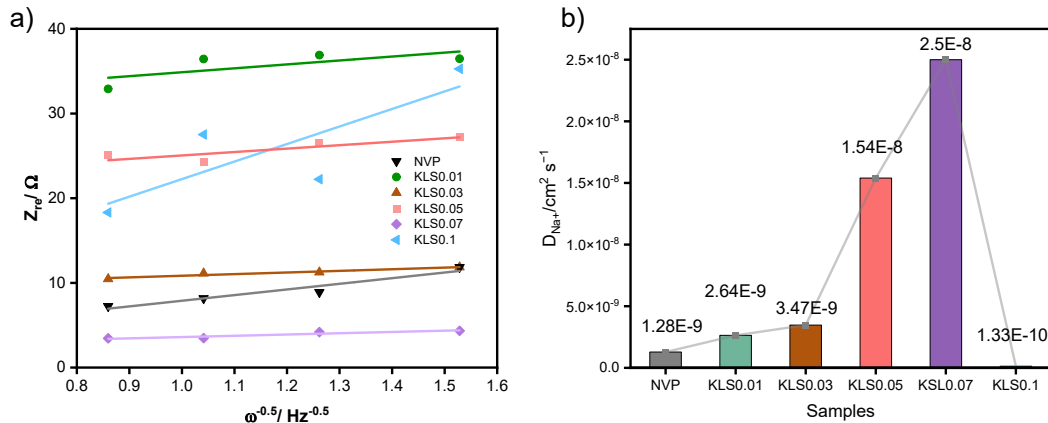


Fig.S8 The relationship for $\omega^{-1/2}$ and Z_{re} of all samples at 3.4 V (a), the corresponding diffusion coefficient of sodium ion of all samples.

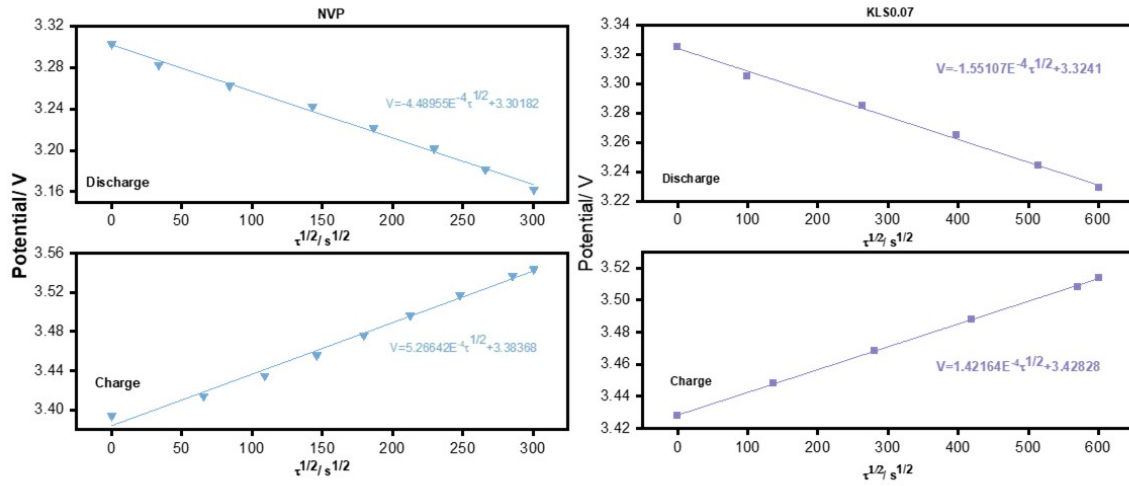


Fig.S9 The fitting condition between $\tau^{1/2}$ and V of NVP and KLS0.07 samples during dis/charge progress.

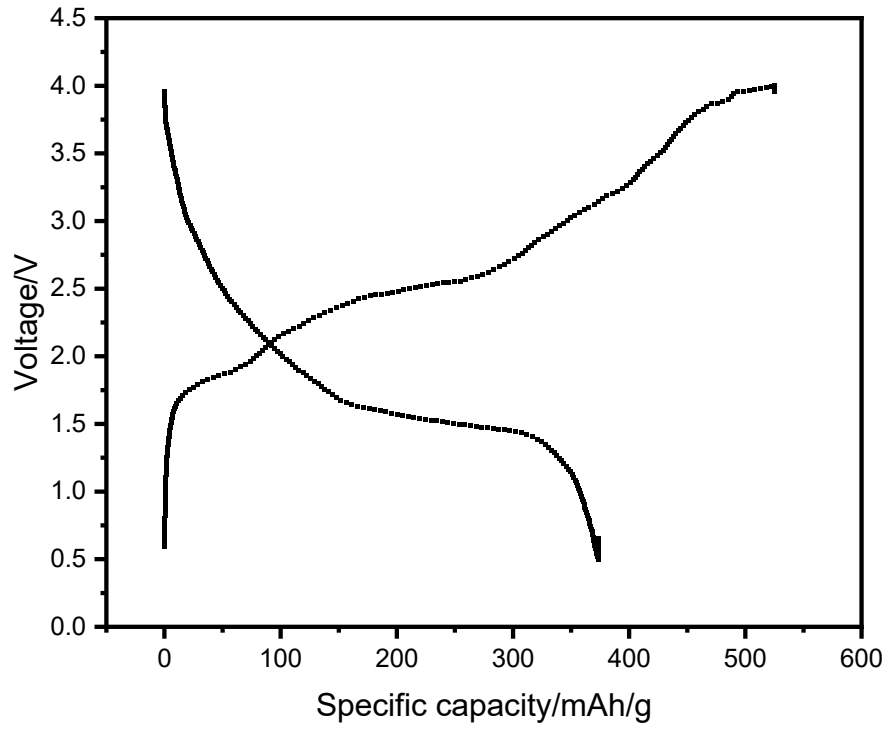


Fig.S10 The typical charge-discharge curves of full-cell KLS0.07//CoSe₂ at 1C.

Table.S1 Reaction material composition list of Na_{3.1-x}K_xV_{2-x}La_x(PO₄)_{2.9}(SiO₄)_{0.1} samples.

Samples	NH ₄ VO ₃ /g	CH ₃ COONa/g	NH ₄ H ₂ PO ₄ /g	KH ₂ PO ₄ /g	LaN ₃ O ₉ /g	C ₈ H ₂₀ O ₄ Si/g
NVP	2.0537	2.1600	3.0290	/	/	/
KLS0.01	2.0299	2.2098	2.8982	0.0119	0.0378	0.1816
KLS0.03	2.0002	2.1856	2.8652	0.0354	0.1127	0.1808
KLS0.05	1.9710	2.1616	2.8324	0.0588	0.1871	0.1800
KLS0.07	1.9420	2.1378	2.7999	0.0819	0.2607	0.1792

KLS0.1 1.8991 2.1025 2.7518 0.1163 0.3700 0.1780

Table.S2 The position information of KLS0.07 ($\text{Na}_{3.03}\text{V}_{1.93}\text{La}_{0.07}(\text{PO}_4)_{2.9}(\text{SiO}_4)_{0.1}$) extracted from Rietveld refined XRD pattern by Fullprof software.

Atom	Mult.	x	y	z	Uiso	Occ.
Na1	12	0.333	0.667	-0.405	0.127	0.234
Na2	36	0.609	0.916	0.008	0.011	0.695
K1	12	0.333	0.667	-0.405	0.011	0.071
V1	12	0.333	0.666	0.010	0.945	0.931
La1	12	0.333	0.666	0.010	0.945	0.069
P1	18	0.233	0.578	0.222	0.008	0.906
Si1	18	0.233	0.578	0.222	0.008	0.094
O1	36	-0.003	0.376	0.099	0.004	1.000
O2	36	0.538	0.823	-0.037	0.013	1.000

Table.S3 The position information of KLS0.07 and extracted from Rietveld refined XRD pattern by XRD and DFT calculations, respectively.

Samples	Structural information		
	a=b/ Å	c/ Å	Volume/ Å ³
NVP(DFT)	8.90	21.85	1498.86
Doped NVP	8.95	22.08	1530.00

Table.S4 The comparison of calculated diffusion coefficients of Na⁺ for NVP and KLS0.07 by CV

Samples	D _{Na⁺-Anode,CV}	D _{Na⁺-Cathode,CV}
NVP	2.498x10 ⁻¹¹	5.123x10 ⁻¹²
KLS0.07	2.831x10 ⁻¹⁰	6.039x10 ⁻¹²

Table.S5 The charge transfer resistant (R_{ct}) of Na_{3.1-x}K_xV_{2-x}La_x(PO₄)_{2.9}(SiO₄)_{0.1} samples.

Samples	R _{ct} / Ω	σ	D _{Na⁺-EIS}
NVP	370.6	6.67	1.28x10 ⁻⁹
KLS0.01	531.2	4.64	2.64x10 ⁻⁹
KLS0.03	185.3	4.05	3.47x10 ⁻⁹

KLS0.05	156.0	1.92	1.54×10^{-8}
KLS0.07	116.7	1.51	2.50×10^{-8}
KLS0.1	230	20.71	1.33×10^{-10}

Table.S6 The comparison of calculated diffusion coefficients of Na^+ for NVP and KLS0.07 by GITT

Samples	$D_{\text{Na}^+\text{-Charge,GITT}}$	$D_{\text{Na}^+\text{-Discharge,GITT}}$
NVP	$0.5\text{-}1.8 \times 10^{-10}$	$1.4\text{-}3.7 \times 10^{-10}$
KLS0.07	$1.0\text{-}2.2 \times 10^{-10}$	$1.5\text{-}4.1 \times 10^{-10}$

Table.S7 The comparison of electrochemical performance between KLS0.07// CoSe_2 and other NVP-based full-cell.

Samples	Cycling performance	Rate performance	Ref.
KLS0.07// CoSe_2	95mAhg^{-1} at 1C after 100 cycles	100mAhg^{-1} at 5C	This work
HC//NVPF@rGO	100mAhg^{-1} at 1C after 100 cycles	60mAhg^{-1} at 50C	Ref.17
NVPMK//NVPMK	50mAhg^{-1} at 10C after 500 cycles	50mAhg^{-1} at 10C	Ref.38
HC//NVPSi0.05	90mAhg^{-1} at 1C after 140 cycles	102mAhg^{-1} at 1C	Ref.41
Zr0.1-NVP//Zr0.1-NVP	70mAhg^{-1} at 5C after 100 cycles	60mAhg^{-1} at 40C	Ref.43
BFCF-NVP//PGN/SiC	30mAhg^{-1} at 1C after 1600 cycles	52mAhg^{-1} at 1C	Ref.44