

## Support

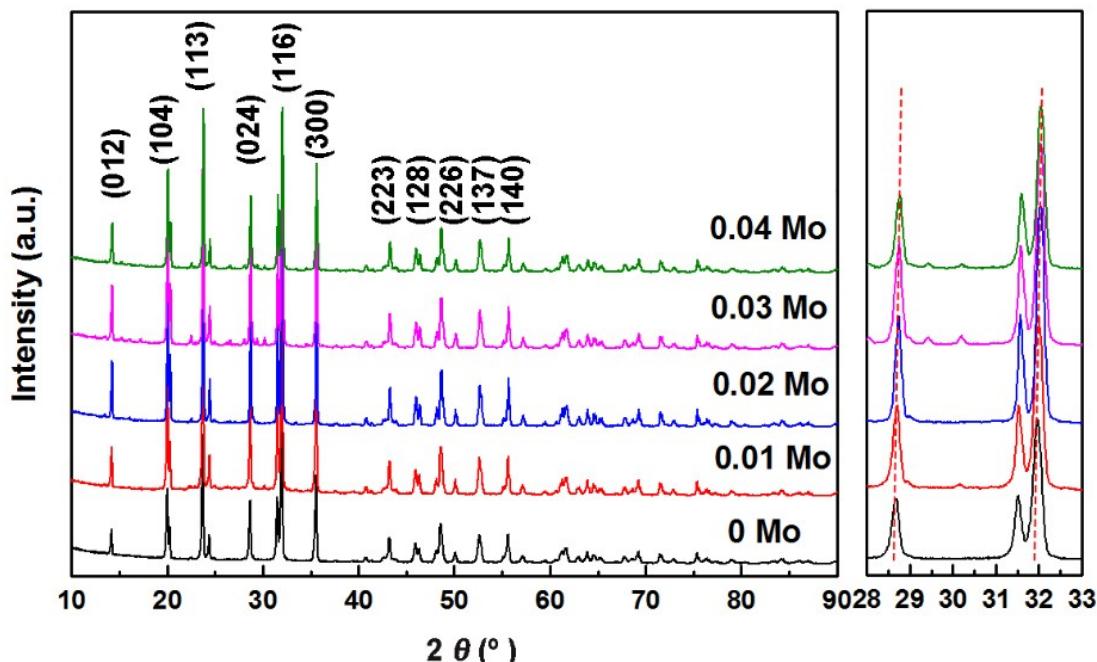


Fig. S1 XRD patterns of  $\text{Na}_{3-5x}\text{Mo}_x\text{V}_{2-x}(\text{PO}_4)_3$  ( $x=0 - 0.04$  ).

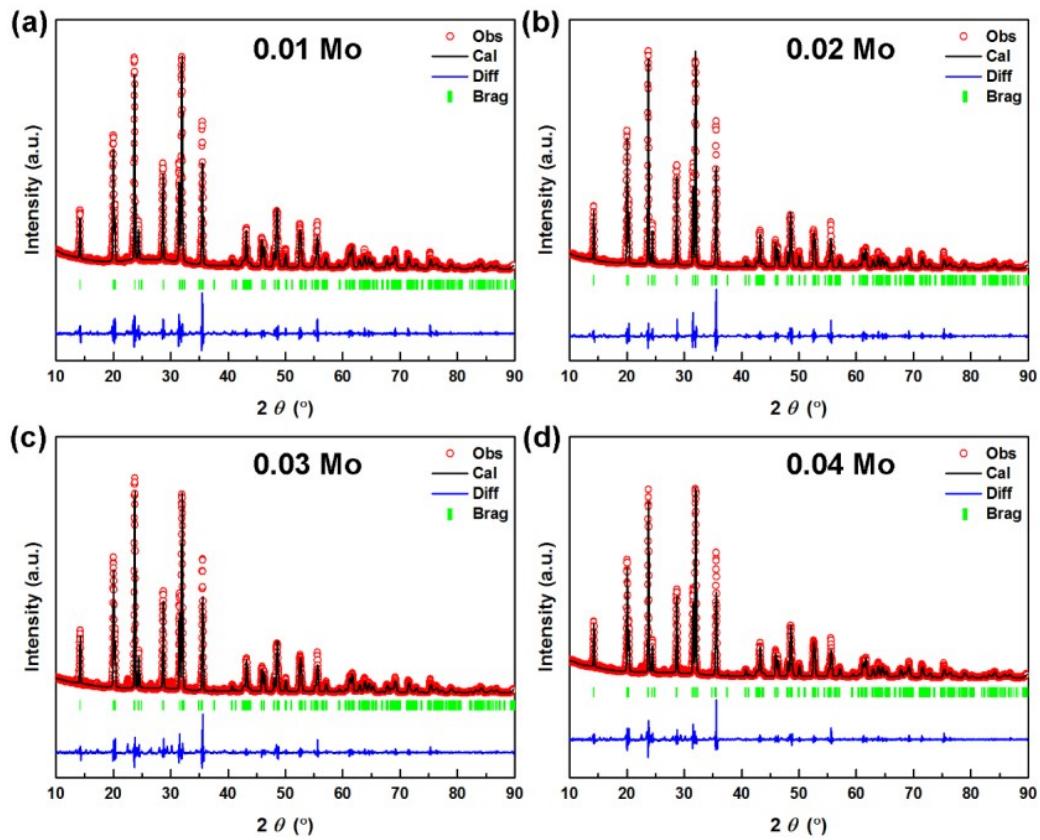


Fig. S2 Rietveld Refinement patterns of  $\text{Na}_{3.5x}\text{Mo}_x\text{V}_{2-x}(\text{PO}_4)_3$

(a)  $x = 0$ ; (b)  $x = 0.01$ ; (c)  $x = 0.03$ ; (d)  $x = 0.04$ .

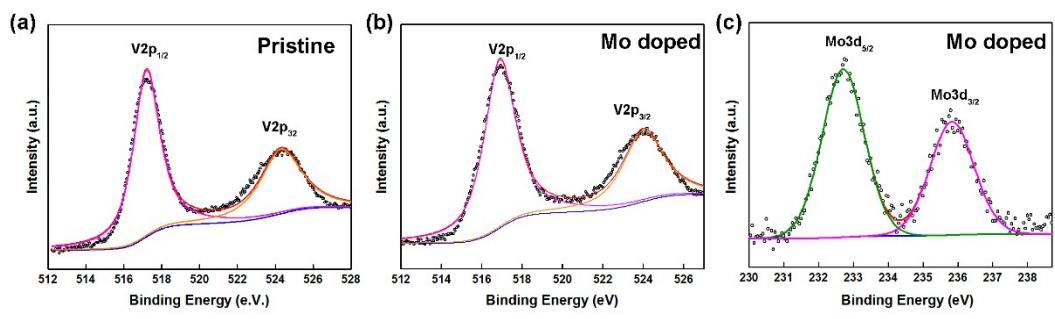


Fig. S3 High resolution X-ray photoelectron spectra of pristine NVP and Mo doped NVP: (a) V 2p, V 2p (a) and Mo 3d (b).

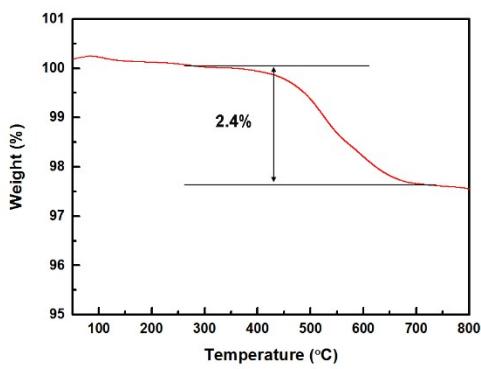


Fig. S4 Thermogravimetry patterns of the NVP/C.

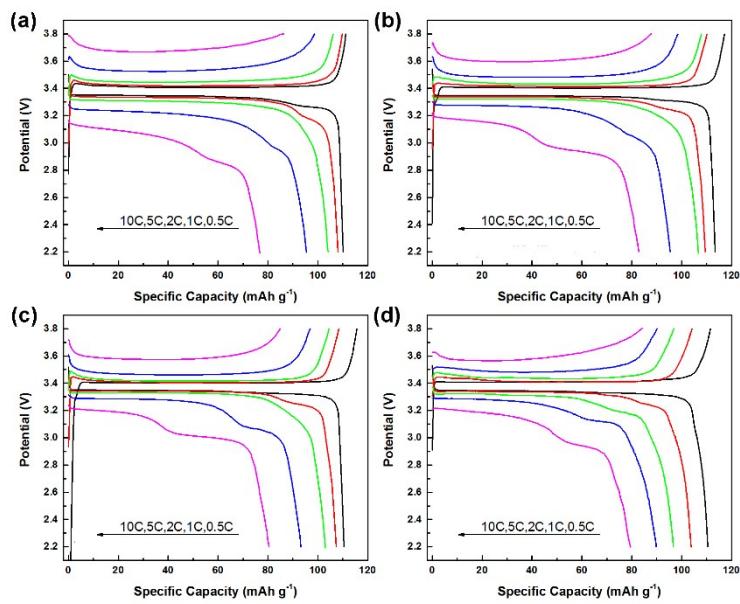


Fig. S5 Charge/Discharge curves of different rate from 0.5C to 10C

(a)  $x = 0$ ; (b)  $x = 0.01$ ; (c)  $x = 0.03$ ; (d)  $x = 0.04$ .

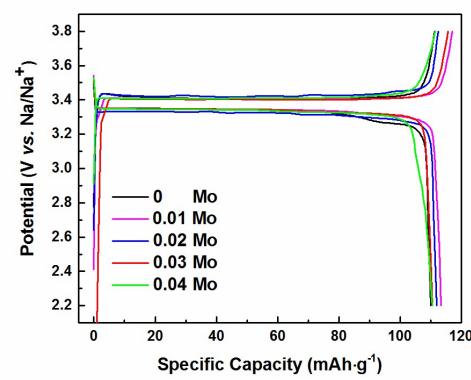


Fig. S6 Comparison charge/discharge curves of  $\text{Na}_{3.5x}\text{Mo}_x\text{V}_{2-x}(\text{PO}_4)_3$  at 0.5C

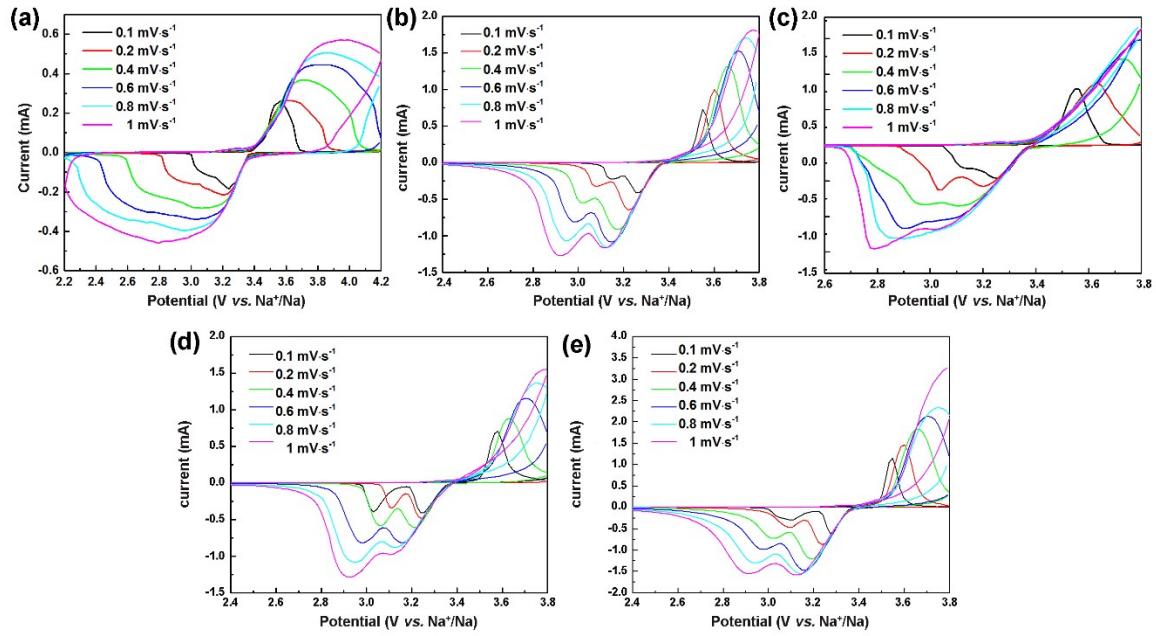


Fig. S7 CV curves of Na<sub>3.5x</sub>Mo<sub>x</sub>V<sub>2-x</sub>(PO<sub>4</sub>)<sub>3</sub>

(a)  $x = 0$ ; (b)  $x = 0.01$ ; (c)  $x = 0.02$ ; (d)  $x = 0.03$ ; (e)  $x = 0.04$ .

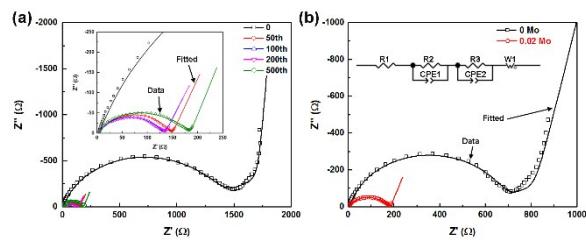


Fig. S8 The Nyquist plots circuit of  $\text{Na}_{2.9}\text{V}_{1.98}\text{Mo}_{0.02}(\text{PO}_4)_3$  at different cycles (a) and comparison of  $\text{Na}_{2.9}\text{V}_{1.98}\text{Mo}_{0.02}(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  after 500 cycles. (inset: equivalent circuit of  $\text{Na}_{2.9}\text{V}_{1.98}\text{Mo}_{0.02}(\text{PO}_4)_3$ ).

Table S1 parameters of  $\text{Na}_{3-5x}\text{V}_{2-x}\text{Mo}_x(\text{PO}_4)_3$  by Rietveld Refinement

	a=b(Å)	c(Å)	Volume(Å <sup>3</sup> )	R <sub>wp</sub>	R <sub>p</sub>
NVP	8.7142(1)	21.7908(5)	1433.04(4)	9.27%	6.85%
0.01 Mo	8.7281(1)	21.8194(5)	1439.51(4)	10.25%	7.45%
0.02 Mo	8.7374(1)	21.8423(4)	1444.10(3)	11.75%	8.53%
0.03 Mo	8.7403(1)	21.8588(5)	1446.13(4)	12.22%	9.08%
0.04 Mo	8.7517(1)	21.8895(5)	1451.95(4)	10.79%	7.81%

Table S2 Sodium ion diffusion coefficients (D) of samples (Unit:  $\text{cm}^2 \text{ s}^{-1}$ )

Sample	$D_{\text{Na}1}$	$D_{\text{Na}2}$
$\text{Na}_3\text{V}_2(\text{PO}_4)_3$		$7.1955\text{e}^{-13}$
$\text{Na}_{2.95}\text{V}_{1.99}\text{Mo}_{0.01}(\text{PO}_4)_3$	$1.1589\text{e}^{-11}$	$5.8044\text{e}^{-12}$
$\text{Na}_{2.9}\text{V}_{1.98}\text{Mo}_{0.02}(\text{PO}_4)_3$	$1.2202\text{e}^{-11}$	$6.0116\text{e}^{-12}$
$\text{Na}_{2.85}\text{V}_{1.97}\text{Mo}_{0.03}(\text{PO}_4)_3$	$1.188\text{e}^{-11}$	$3.3191\text{e}^{-12}$
$\text{Na}_{2.8}\text{V}_{1.96}\text{Mo}_{0.04}(\text{PO}_4)_3$	$1.7082\text{e}^{-11}$	$7.1728\text{e}^{-12}$

Table S3 EIS fitting results of  $\text{Na}_{3-5x}\text{V}_{2-x}\text{Mo}_x(\text{PO}_4)_3$  in different cycle

	0.02 Mo 0	0.02 Mo 50 <sup>st</sup>	0.02 Mo 100 <sup>th</sup>	0.02 Mo 200 <sup>th</sup>	0.02 Mo 500 <sup>th</sup>
R1	3.137	3.358	2.354	2.457	3.356
R2	1344	32.7	34.8	24.5	22.5
R3	-	108.9	92.9	102.9	151
CPE1-T	2.456E-6	6.036E-6	6.136E-6	6.236E-6	6.536E-6
CPE1-P	0.8505	0.7507	0.7371	0.7426	0.8678
CPE2-T	-	4.2432E-5	4.3576E-5	5.2441E-5	4.3441E-5
CPE2-P	-	0.7229	0.7134	0.7229	0.7183
W1-r	877	16.27	20.27	18.43	26.27
W1-t	1.037	0.086	0.113	0.123	0.155
W1-p	0.4497	0.3866	0.3776	0.3743	0.3998

Table S4 Electronic Conductivities of  $\text{Na}_{3-5x}\text{V}_{2-x}\text{Mo}_x(\text{PO}_4)_3$

	Mo 0	Mo 0.01	Mo 0.02	Mo 0.03	Mo 0.04
Powders	0.2 $\text{S}\cdot\text{m}^{-1}$	0.015 $\text{S}\cdot\text{m}^{-1}$	2 $\text{S}\cdot\text{m}^{-1}$	0.1 $\text{S}\cdot\text{m}^{-1}$	0.05 $\text{S}\cdot\text{m}^{-1}$
Electrode	300 $\text{S}\cdot\text{m}^{-1}$	800 $\text{S}\cdot\text{m}^{-1}$	1400 $\text{S}\cdot\text{m}^{-1}$	750 $\text{S}\cdot\text{m}^{-1}$	600 $\text{S}\cdot\text{m}^{-1}$