Supplementary Information

Unveiling a High Capacity Multi-redox ($Nb^{5+}/Nb^{4+}/Nb^{3+}$) NASICON-$Nb_2(PO_4)_3$ Anode for Li- and Na-ion Batteries

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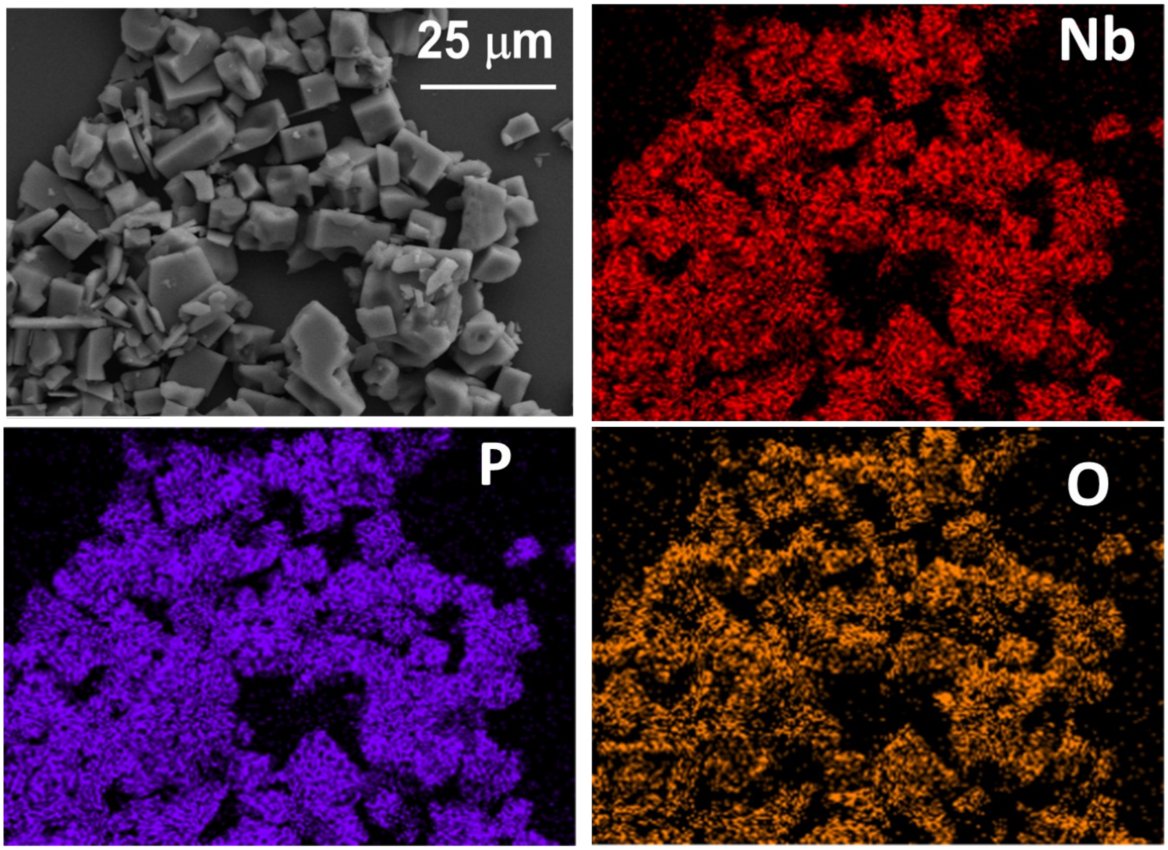

Figure S1. FESEM images and EDS mapping of $Nb_2(PO_4)_3$ anode.

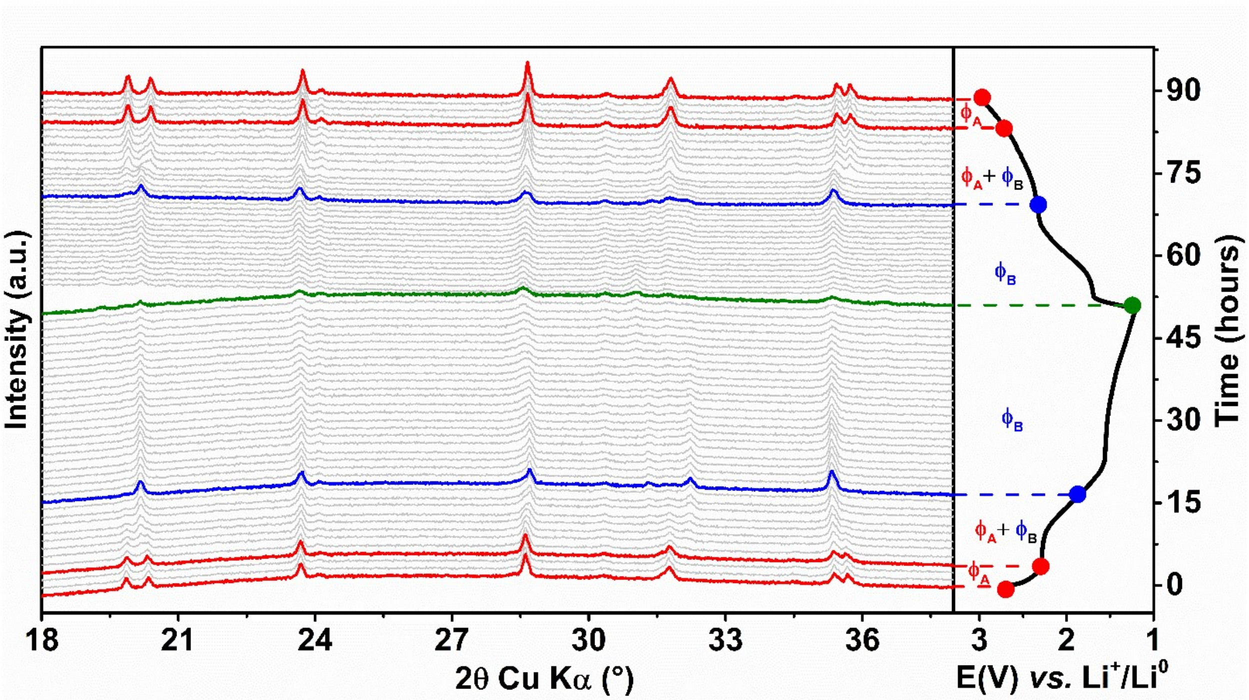

Figure S2. *In-situ* XRD patterns of $Nb_2(PO_4)_3$/Li cell collected during 2nd cycle.

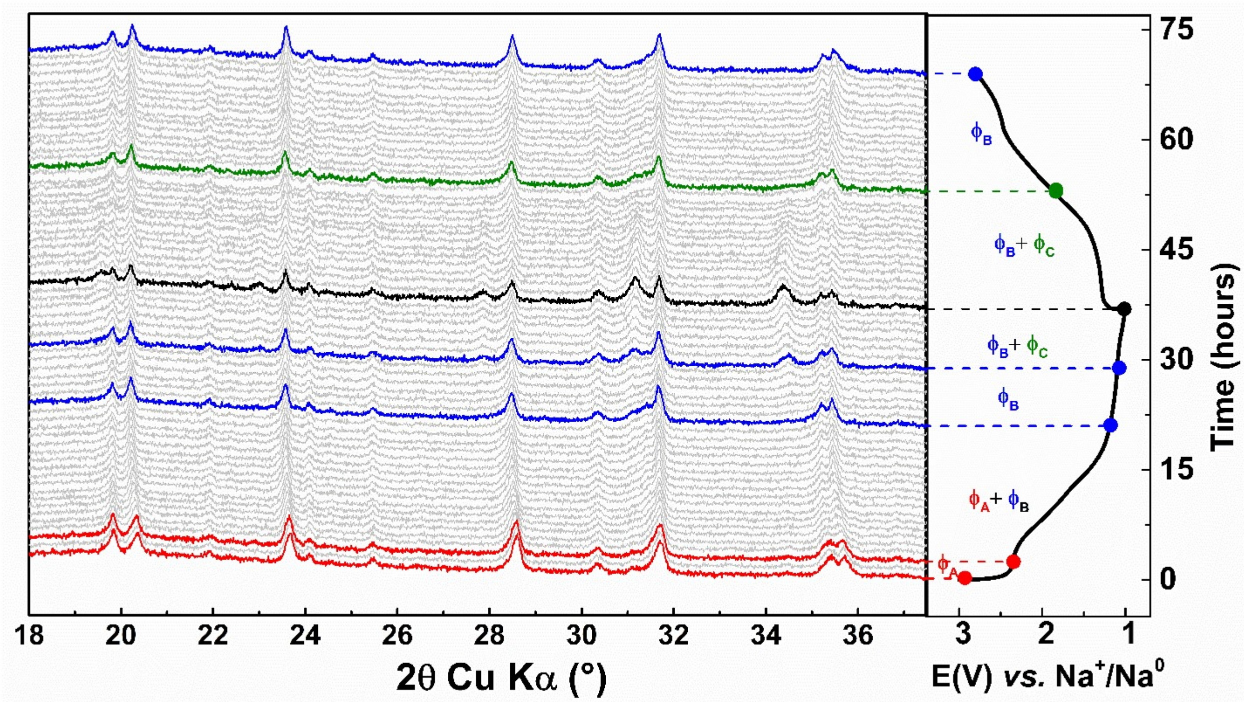

Figure S3. *In-situ* XRD patterns of $Nb_2(PO_4)_3$/Na cell collected during 2nd cycle.

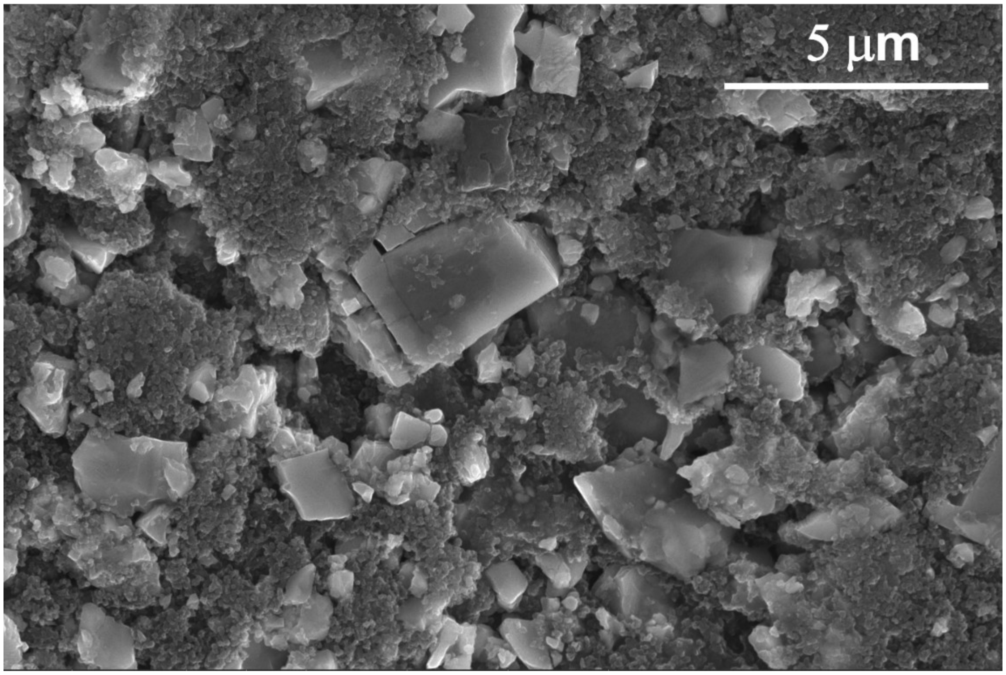

Figure S4. SEM images of as-prepared $Nb_2(PO_4)_3$ electrode.

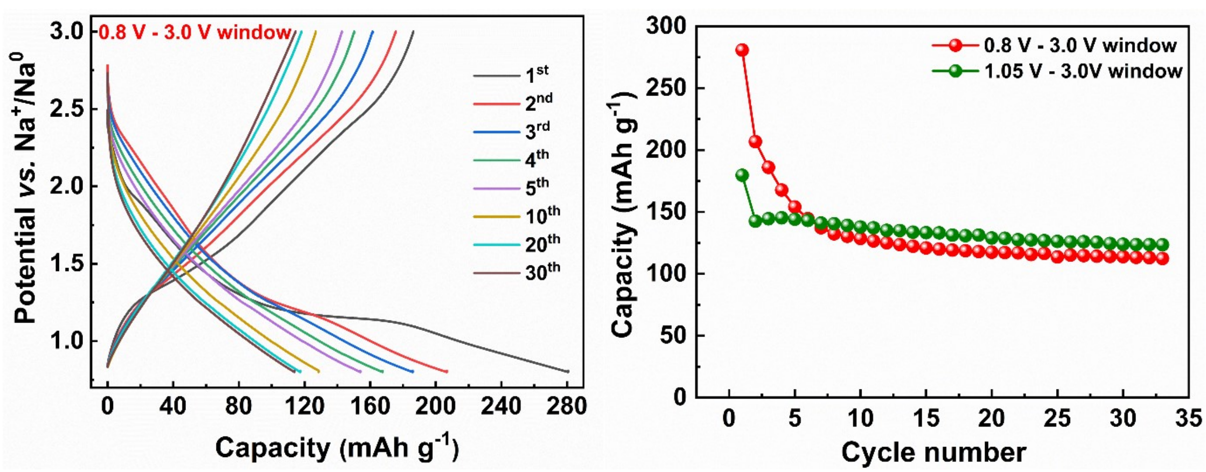

Figure S5. Comparison of cycling performances of $Nb_2(PO_4)_3$/Na cells with different cut-off voltages.

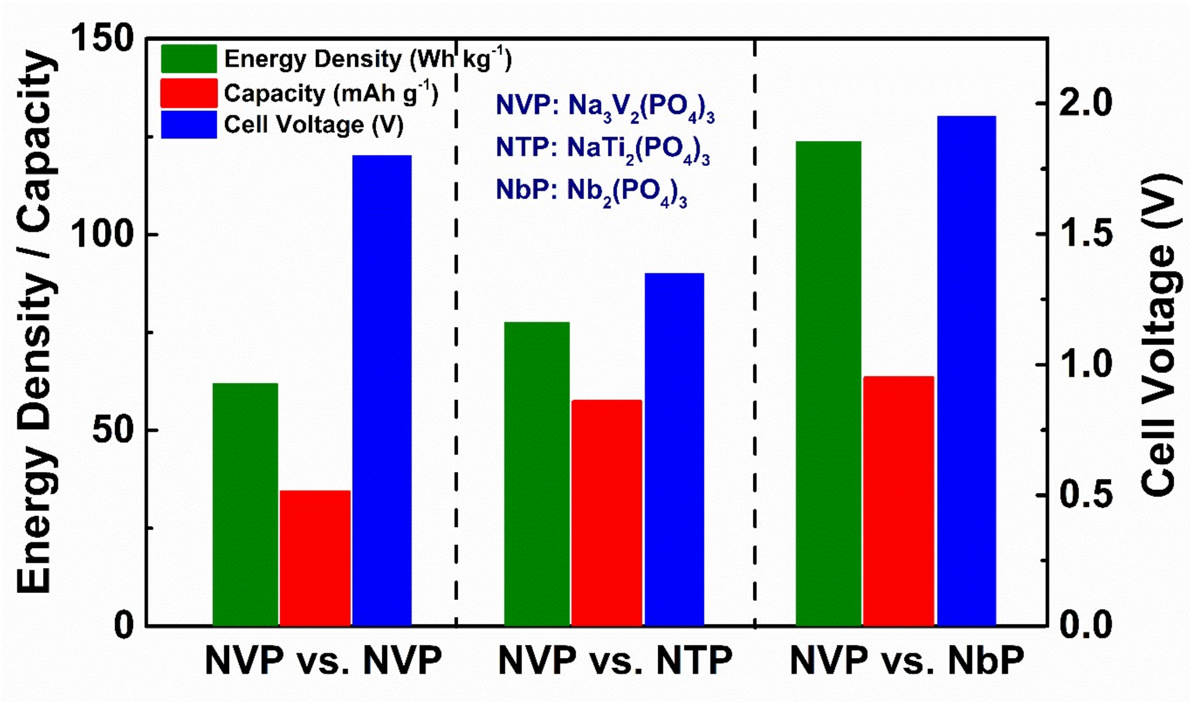

Figure S6. A comparison of energy densities of Na-ion cells comprising $Na_3V_2(PO_4)_3$ as the cathode and $Na_3V_2(PO_4)_3$ or $NaTi_2(PO_4)_3$ or $Nb_2(PO_4)_3$ as the anode.

The energy densities of Na-ion cells comprising $Na_3V_2(PO_4)_3$ as the cathode and $Na_3V_2(PO_4)_3$ or $NaTi_2(PO_4)_3$ or $Nb_2(PO_4)_3$ as the anode are calculated using the following formula:

Energy density (Wh $kg^{-1}_{(anode+cathode)}$) = average cell voltage x capacity (mAh $g^{-1}_{(anode+cathode)}$)

Capacity (mAh $g^{-1}_{(anode+cathode)}$) is calculated using the following formula:

$$\frac{1}{C_{anode\,+\,cathode}} = \frac{1}{C_{anode}} + \frac{1}{C_{cathode}}$$

The insertion potentials and capacities of NASICON compounds (at C/10 rate) are taken from the references.[1,2]

Table S1. Crystallographic parameters and atomic coordinates of NASICON-$Nb_2(PO_4)_3$

$Nb_2(PO_4)_3$						
S.G.: $R\bar{3}c$; Z = 6						Chi^2=4.56;
R_{bragg} = 2.33%; R_p = 8.23%; R_{wp} = 11.3%						
a = 8.6629(1) Å; c = 22.0627(6) Å.						
V =1433.92(5) $Å^3$;						
Average Nb-O Bond distance: (Nb-O1) × 3 = 1.975(3) Å; (Nb-O2) × 3 = 1.9368(2) Å						
Atom	Wyckoff site	X	Y	Z	B ($Å^2$)	Occ.
Nb1	12c	0	0	0.14122(2)	0.0049(2)	0.5
Nb2	12c	0	0	0.14122(2)	0.0049(2)	0.5
P	18e	0.283(2)	0	0.25	0.0145(1)	1.0
O1	36f	0.1684(2)	-0.0278(3)	0.1941(9)	0.0127(7)	1.0
O2	36f	0.1978(2)	0.1674(2)	0.0916(8)	0.0063(2)	1.0

Table S2. Refined parameters for the first shell of Nb K-edge EXAFS spectra collected on the pristine, discharged and charge $Nb_2(PO_4)_3$ anodes.

Sample	Coordination number	d(Nb-O) Å	E_0 (eV)	σ^2 $Å^2$	R-factor
Pristine	3 + 3	2.095(2) x 3 1.961(2) x 3	3.00	0.0001	0.0146
Discharge 1.0V	3.98 + 2.02	2.044(5) x 3.98 2.169(8) x 2.02	5.65	0.001(9)	0.0085
Charge 3.0V	3.3 + 2.7	2.104(5) x 2.7	3.57	0.0008	0.0193

		1.962(8) x 3.3			

References

1 M. K. Sadan, A. K. Haridas, H. Kim, C. Kim, G. B. Cho, K. K. Cho, J. H. Ahn and H. J. Ahn, *Nanoscale Adv.*, 2020, **2**, 5166–5170.

2 M. Wu, W. Ni, J. Hu and J. Ma, *Nano-Micro Lett.*, 2019, **11**, 1–36.