## Supplementary File

# Potassium doping towards enhanced Na-ion diffusivity in fluorophosphate cathode for sodium-ion full cell

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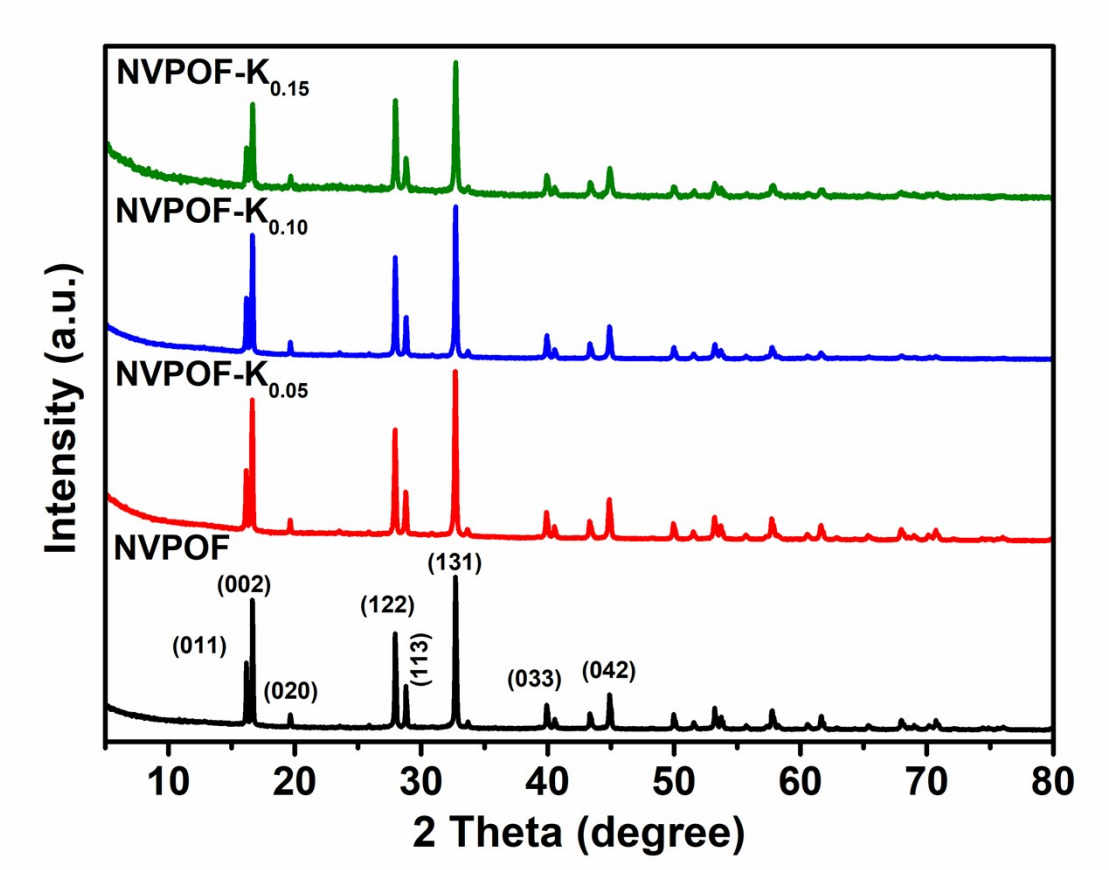


**Fig. S1** XRD patterns of NVPOF, NVPOF-$K_{0.05}$, NVPOF-$K_{0.10}$ and NVPOF-$K_{0.15}$ samples.

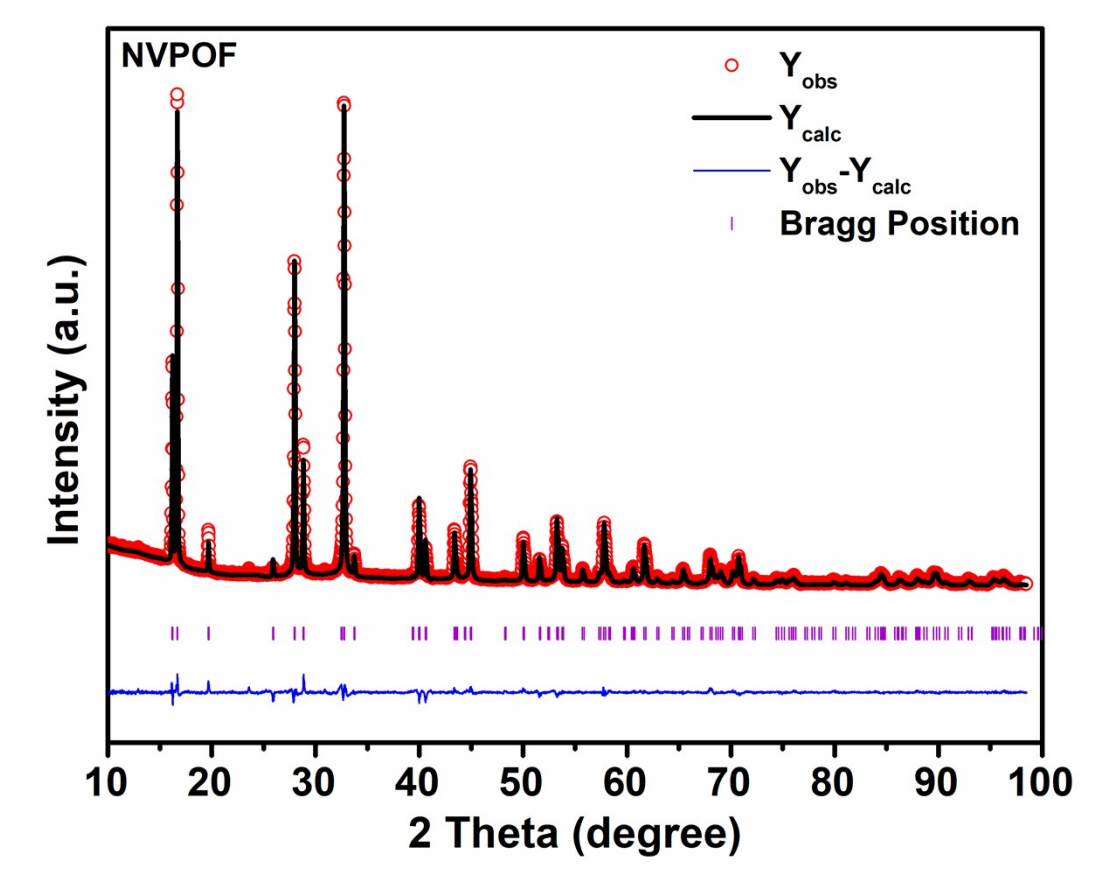


**Fig. S2** XRD pattern and Rietveld refinement plot for NVPOF material.

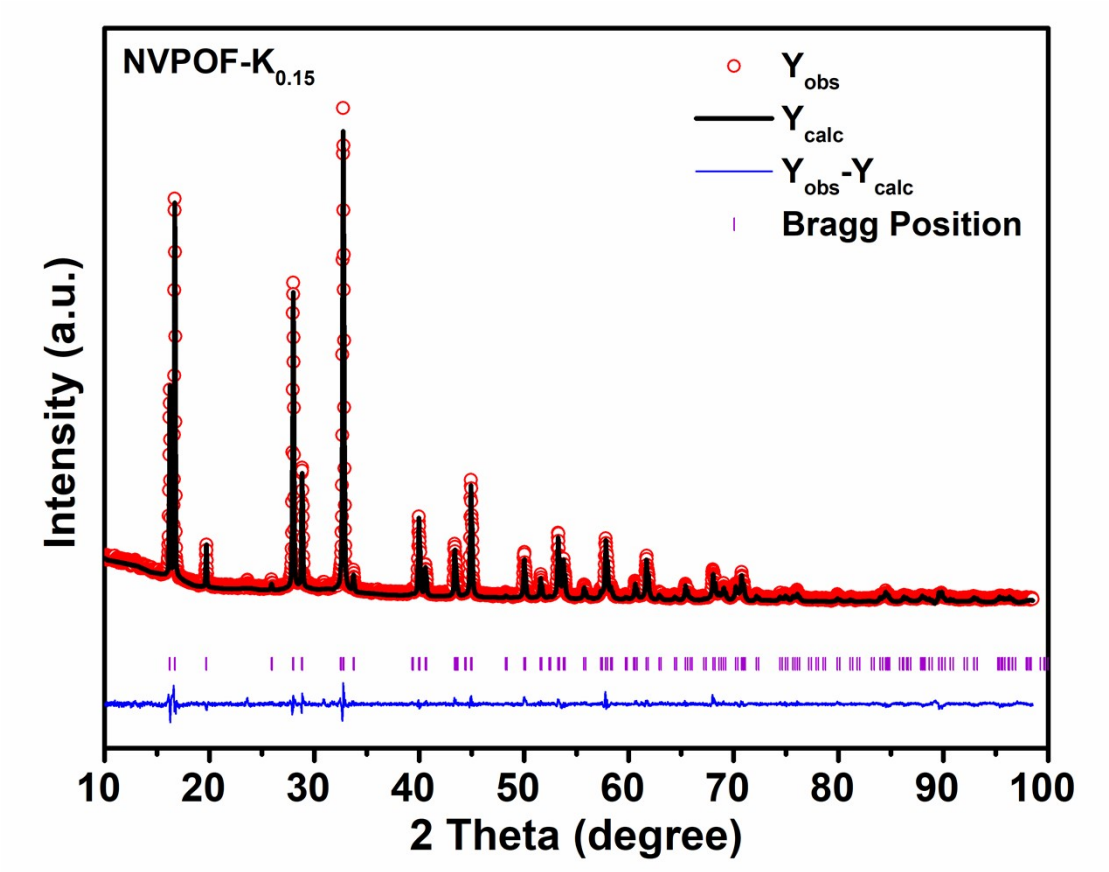


**Fig. S3** XRD pattern and Rietveld refinement plot for NVPOF-$K_{0.15}$ material.

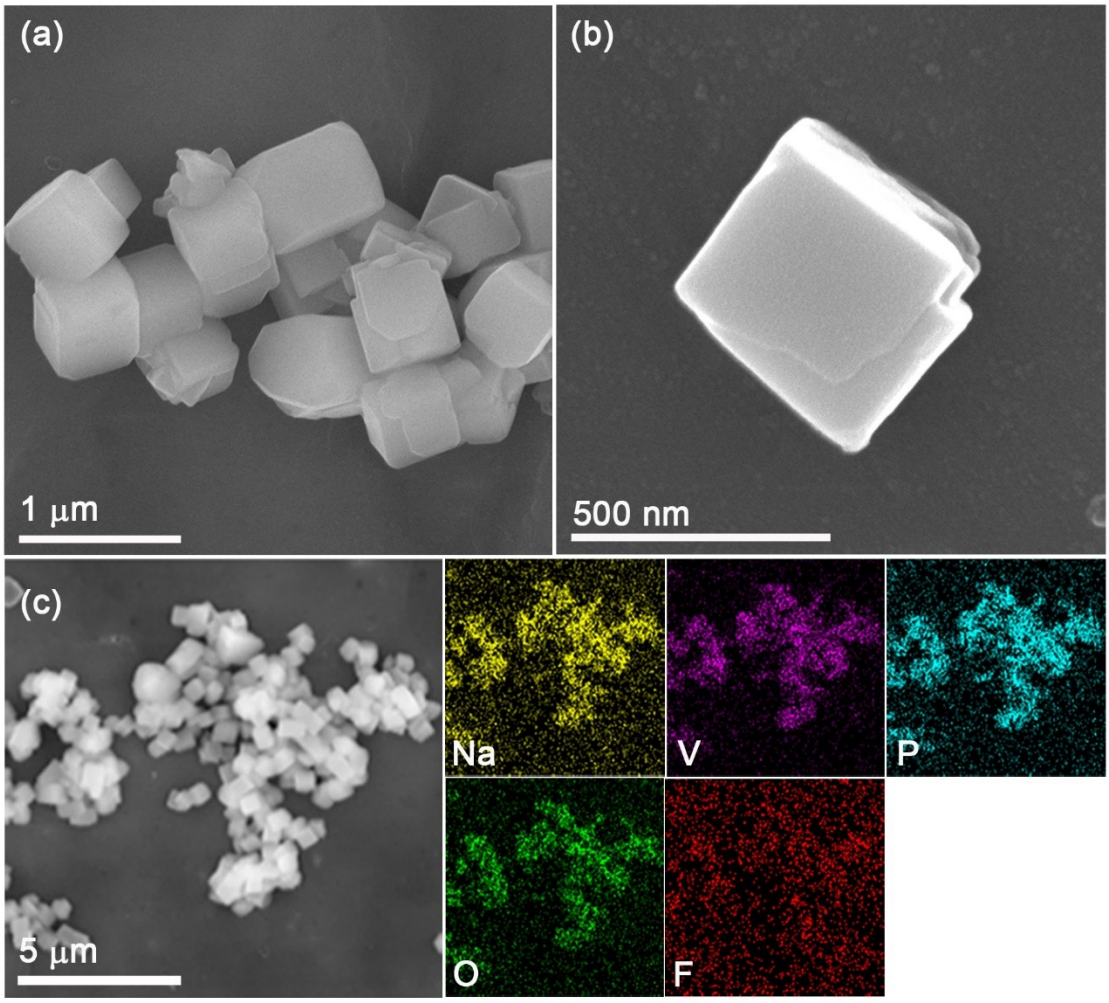


**Fig. S4** FESEM images and corresponding EDX elemental mapping of NVPOF material.

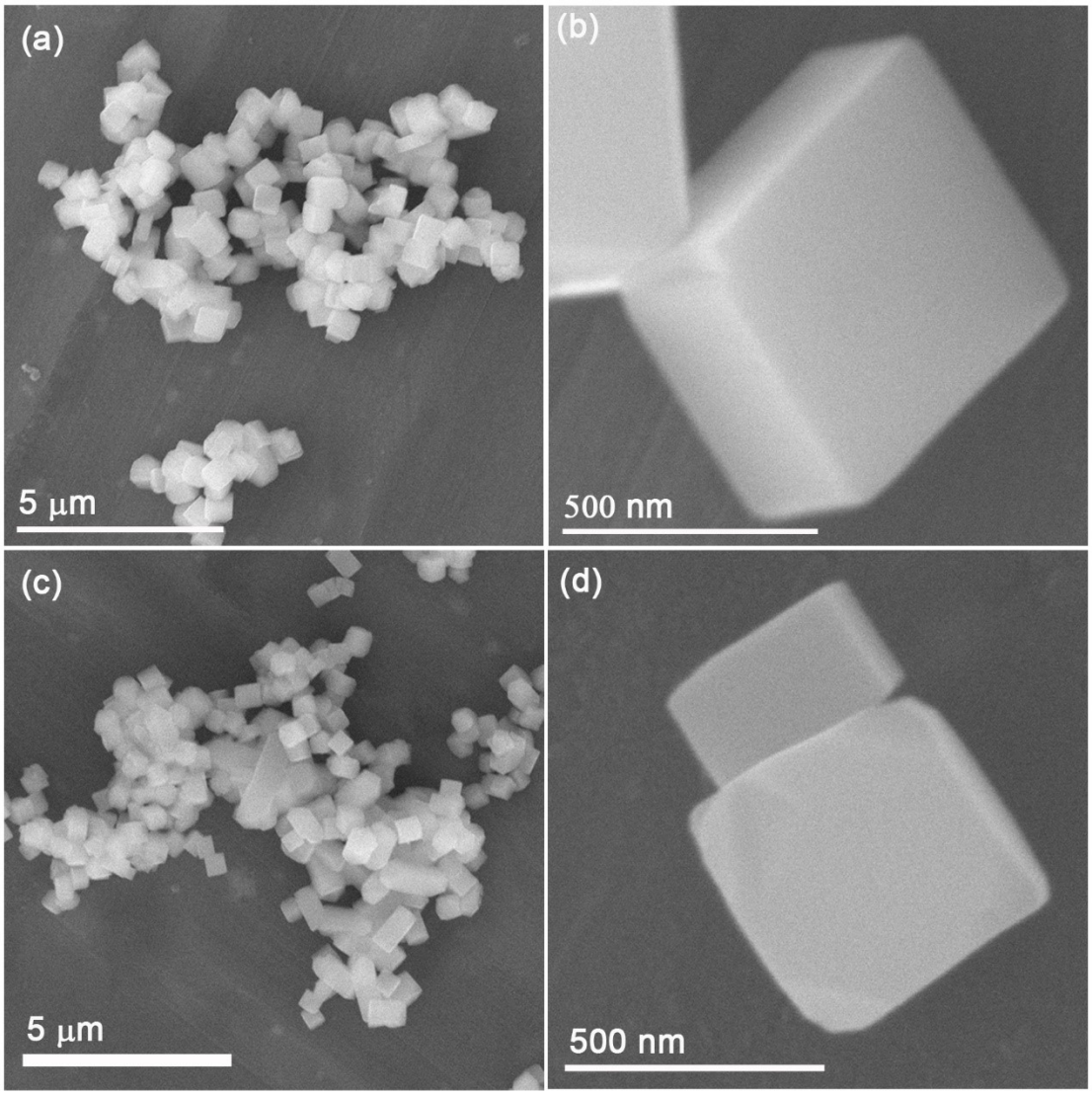


**Fig. S5** (a) and (b) FESEM images of NVPOF-$K_{0.10}$ and (c) and (d) FESEM images of NVPOF-$K_{0.15}$.

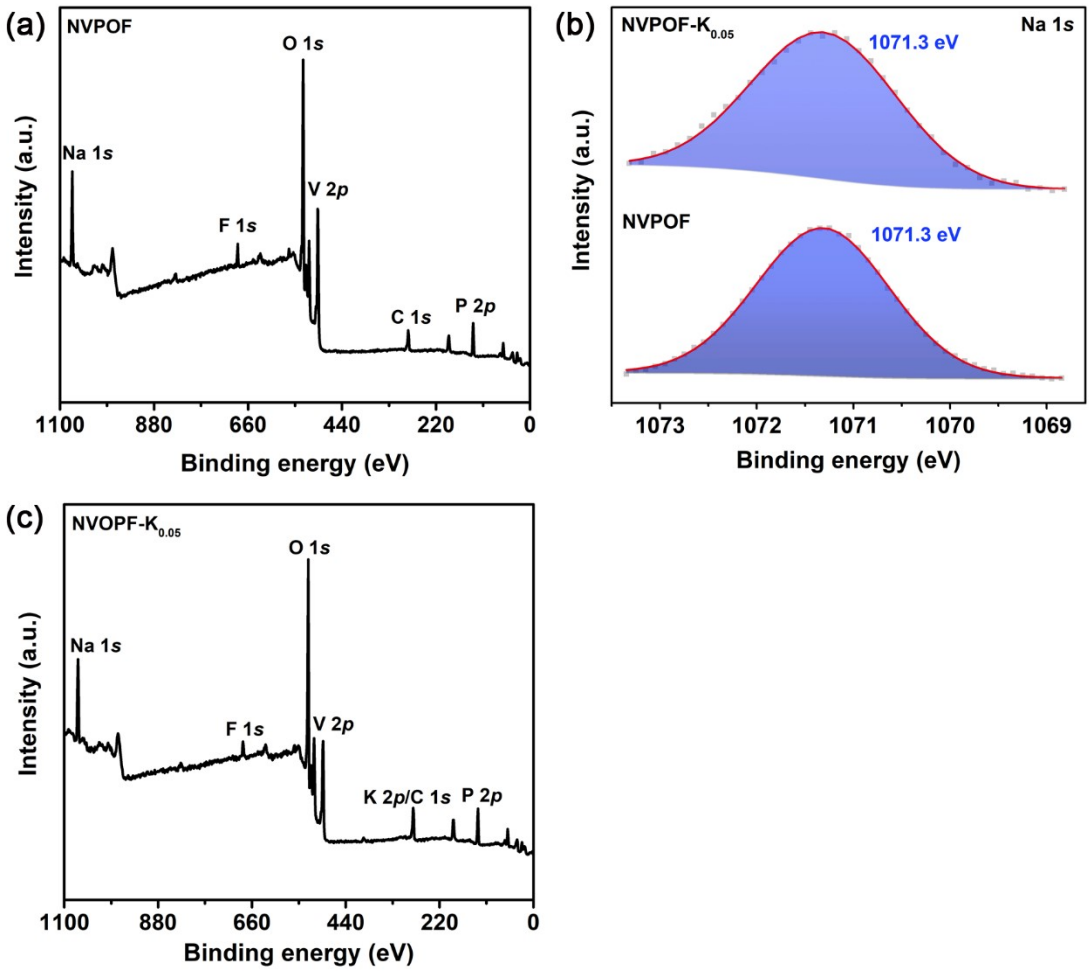


**Fig. S6** XPS results of NVPOF and NVPOF-$K_{0.05}$. Survey of (a) NVPOF and (c) NVPOF-$K_{0.05}$; (b) Na 1*s* of NVPOF and NVPOF-$K_{0.05}$.

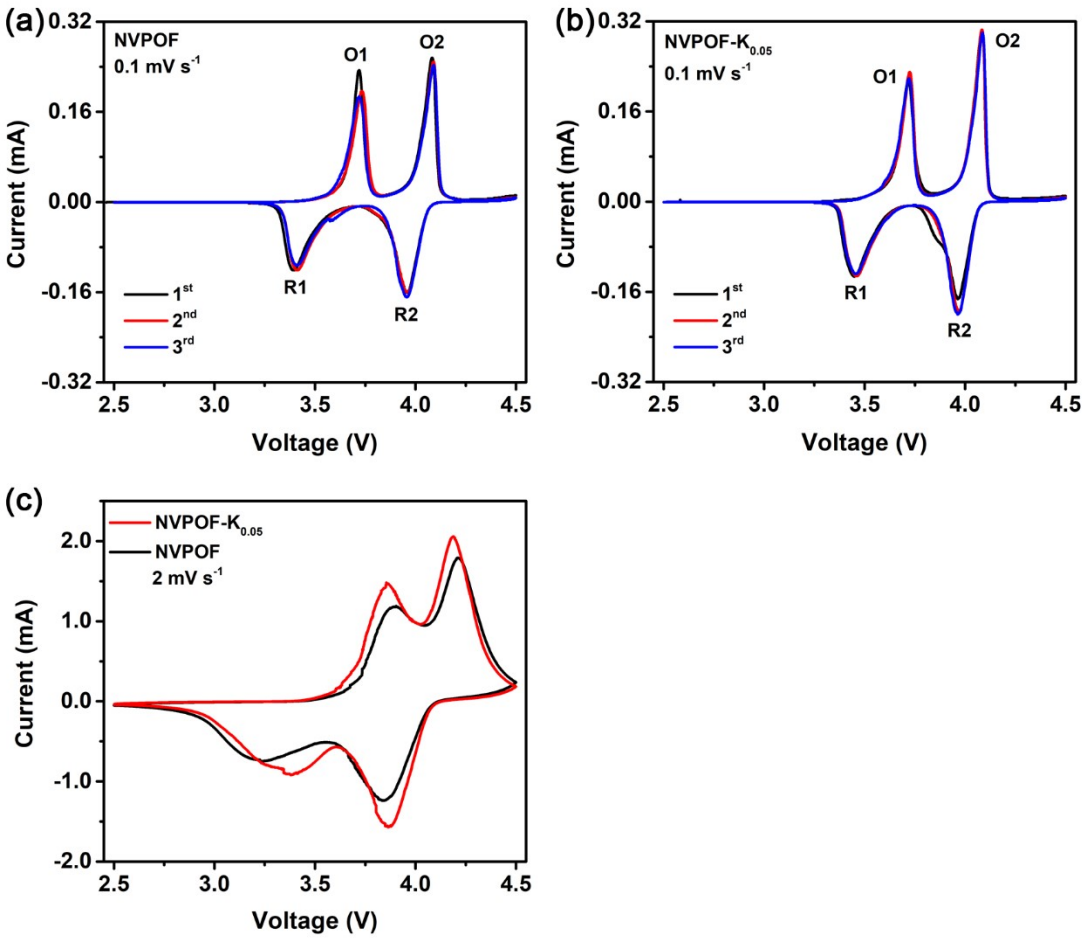


**Fig. S7** First three CV curves at 0.1 mV $s^{-1}$ of (a) NVPOF and (b) NVPOF-$K_{0.05}$. (c) Comparison of CV curve at 2 mV $s^{-1}$ of NVPOF and NVPOF-$K_{0.05}$.

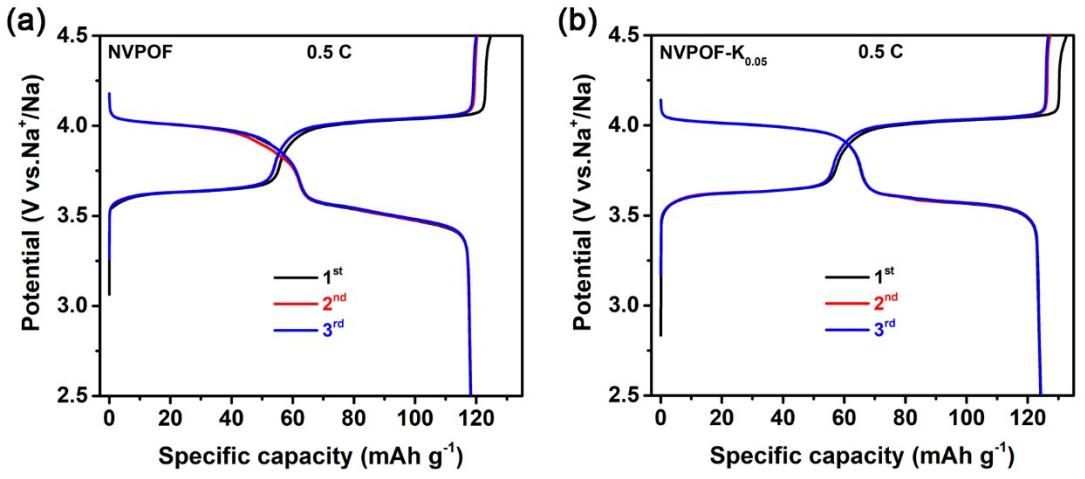


**Fig. S8** The first three GCD curves of (a) NVPOF and (b) NVPOF-$K_{0.05}$ cathodes at a current density of 0.5 C.

**Table S1** Chemical compositions of NVPOF and NVPOF-$K_{0.05}$ determined by ICP-OES

| Sample | Molar ratio of Na: V: (K) | | |
|---|---|---|---|
| | ICP-OES | ICP-OES（Na） | ICP-OES（V） |
| NVPOF | 2.960:1.876 | 1:0.634 | 1.578: 1 |
| NVPOF-$K_{0.05}$ | 3.358:2.151:0.018 | 1:0.640:0.005 | 1.561:1:0.008 |

**Table S2** Anodic and cathodic peak potentials of NVPOF and NVPOF-$K_{0.05}$ cathodes at different scan rates.

| Sample | Scan rate/ mV $s^{-1}$ | Anodic peak | | Cathodic peak | | Polarization | |
|---|---|---|---|---|---|---|---|
| | | O1/V | O2/V | R1/V | R2/V | (O1-R1)/mV | (O2-R2)/mV |
| NVPOF | 0.1 | 3.720 | 4.088 | 3.408 | 3.958 | 312 | 130 |
| | 2.0 | 3.903 | 4.211 | 3.229 | 3.836 | 674 | 375 |
| NVPOF-$K_{0.05}$ | 0.1 | 3.719 | 4.085 | 3.461 | 3.965 | 258 | 120 |
| | 2.0 | 3.855 | 4.185 | 3.383 | 3.869 | 472 | 316 |

**Table S3** A comparison of electrochemical performance of the NVPOF-$K_{0.05}$ cathode this work with the reported cathodes.

| Cathode materials | Rate capability | Cycle stability (C rate/cycle times/capacity retention) | Ref |
|---|---|---|---|
| NVPOF-MWCNT | ~60 mAh $g^{-1}$@20 C | 0.1 C/120/89% | [1] |
| NVPOF@C/G | 78.2 mAh $g^{-1}$@20 C | 2 C/200/92.9% | [2] |
| $Na_{2.94}Li_{0.06}V_2(PO_4)_2F_3$ | 65 mAh $g^{-1}$@20 C | -- | [3] |
| NKVPF@CNT | 50 mAh $g^{-1}$@50 C | 10 C/1600/90.9% | [4] |
| NVPOF-$K_{0.05}$ (this work) | 49.11 mAh $g^{-1}$@80 C | 10 C/500/100% | -- |

**Table S4** Resistances and apparent diffusion coefficients calculated from the EIS of NVPOF and NVPOF-$K_{0.05}$ cathode.

| Sample | $R_s$/Ω | $R_{ct}$/Ω | $\sigma_w$/Ω | $D$/$cm^2$ $s^{-1}$ |
|---|---|---|---|---|
| NVPOF | 7.14 | 273 | 3724.52 | $2.07 \cdot 10^{-15}$ |
| NVPOF-$K_{0.05}$ | 5.31 | 310 | 1800.00 | $8.85 \cdot 10^{-15}$ |

## Reference

[1] Kumar P R, Jung Y H, Wang J E, et al. $Na_3V_2O_2(PO_4)_2F$-MWCNT nanocomposites as a stable and high rate cathode for aqueous and non-aqueous sodium-ion batteries. Journal of Power Sources, 2016, 324, 421-427.

[2] Jin H, Liu M, Uchaker E, et al. Nanoporous carbon leading to the high performance of a $Na_3V_2O_2(PO_4)_2F$@carbon/graphene cathode in a sodium ion battery. CrystEngComm, 2017, 19(30), 4287-4293.

[3] Kosova N V, Rezepova D O. Mixed sodium-lithium vanadium fluorophosphates $Na_{3-x}Li_xV_2(PO_4)_2F_3$: The origin of the excellent high-rate performance. Journal of Power Sources, 2018, 408, 120-127.w

[4] Li L, Liu X, Tang L, et al. Improved electrochemical performance of high voltage cathode $Na_3V_2(PO_4)_2F_3$ for Na-ion batteries through potassium doping. Journal of Alloys and Compounds, 2019, 790, 203-211.