Supporting Information

Enhancing the rate capability of $Na_4Fe_3(PO_4)_2(P_2O_7)$ by partial co-substitution of V^{3+} and Al^{3+} for Fe^{2+}

Shu Zhao, Hao Li, Shuo Shi, Chao Wang* and X. S. Zhao*

Institute of Materials for Energy and Environment, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, P. R. China

*Corresponding authors and email addresses: wangc@qdu.edu.cn (CW), chezxs@qdu.edu.cn (XSZ)

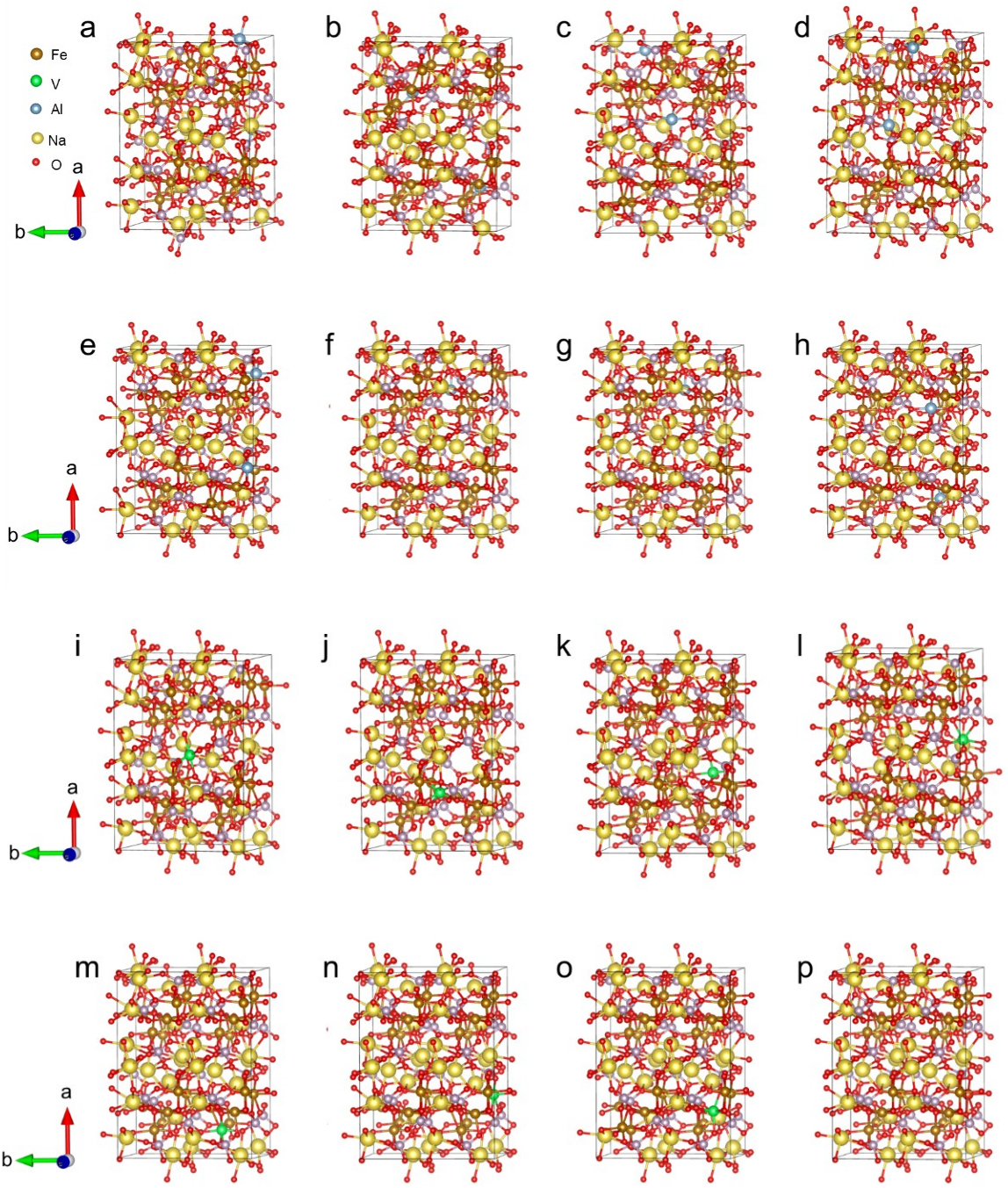

Fig. S1 Schematic illustration of the models used in the computation showing substitution of Al^{3+} for Na^{+} or Fe^{2+} at (a) Na1, (b) Na2, (c) Na3, (d) Na4, (e) Fe1, (f) Fe2, (g) Fe3 and (h) Fe2 without Na vacancy locations, and V^{3+} for Na^{+} or Fe^{2+} at (i) Na1, (j) Na2, (k) Na3, (l) Na4, (m) Fe1, (n) Fe2, (o) Fe3 and (p) Fe2 without Na vacancy locations.

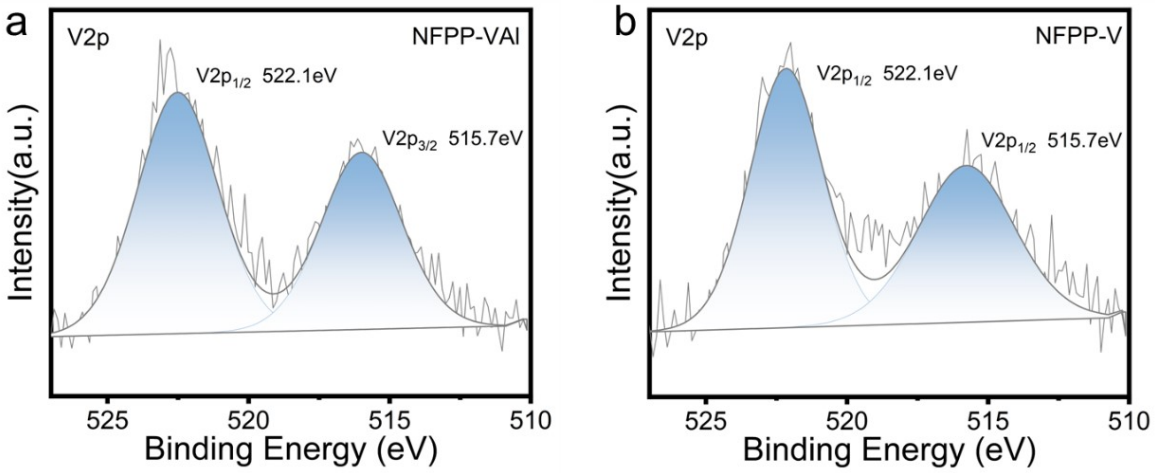

Fig. S2 V2p XPS spectra of NFPP-VAl (a) and NFPP-V (b).

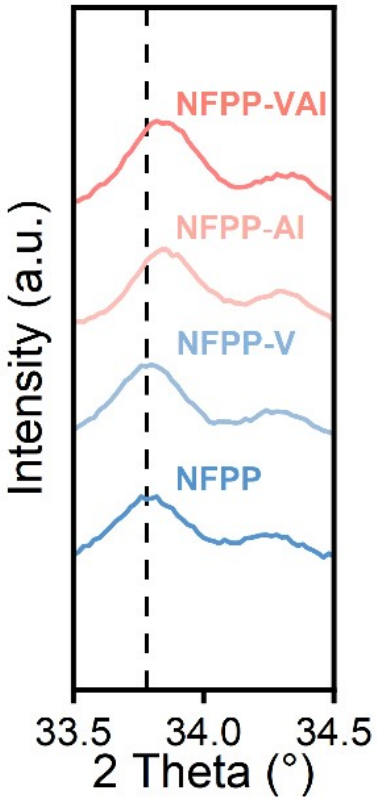

Fig. S3 XRD patterns of samples between 33.5 and 34.5 degrees two theta.

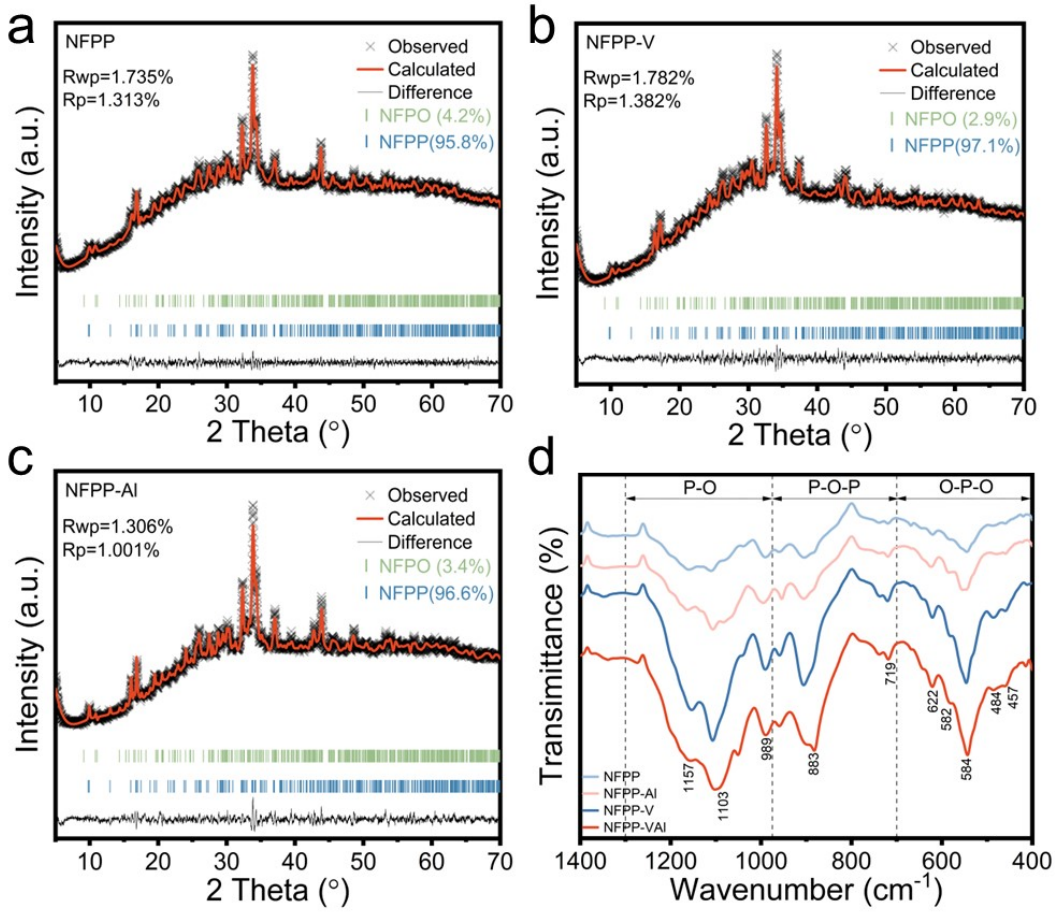

Fig. S4 Rietveld refinement results of XRD patterns for NFPP (a), NFPP-V (b) and NFPP-Al (c). (d) FTIR spectra of NFPP, NFPP-Al, NFPP-V and NFPP-VAl.

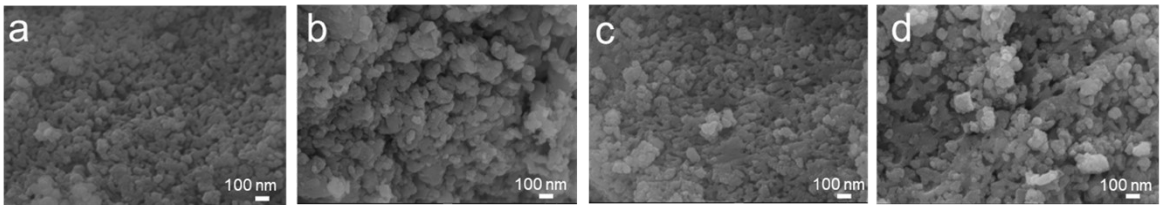

Fig. S5 FESEM images of NFPP-Val (a), NFPP-Al (b), NFPP-V (c) and NFPP (d).

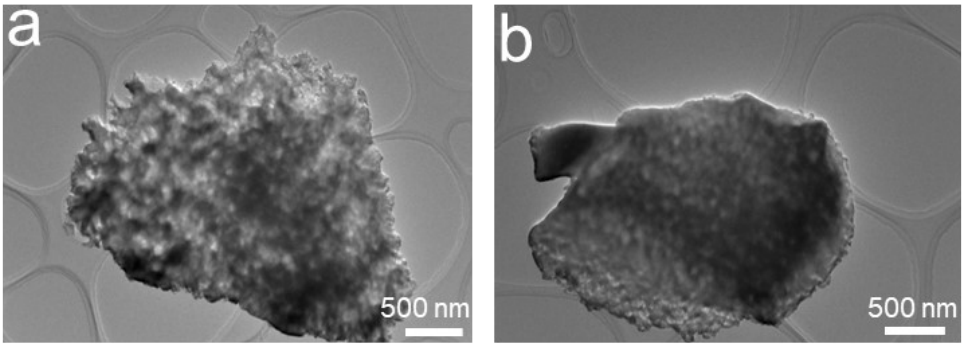

Fig. S6 TEM images of NFPP-Al (a) and NFPP-Al (b).

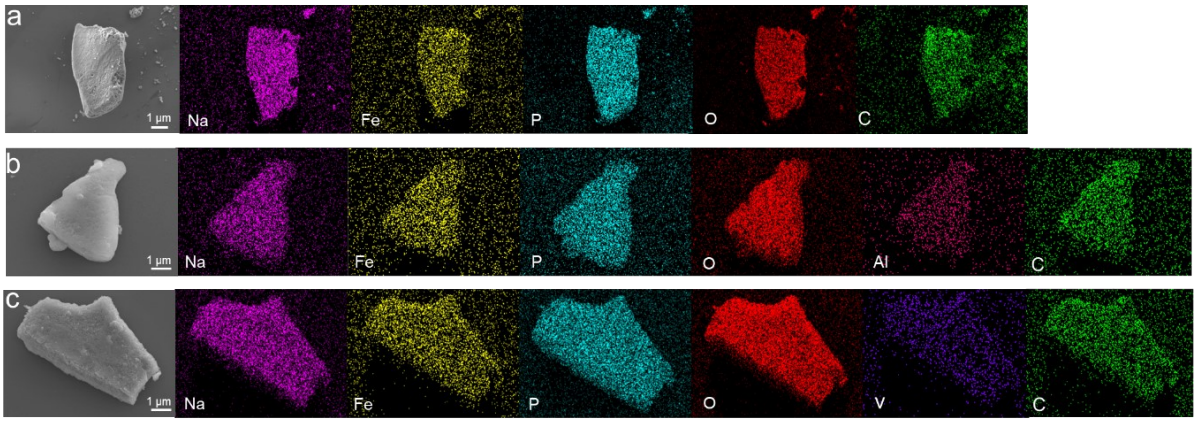

Fig. S7 EDS elemental mapping images of NFPP (a), NFPP-Al (b) and NFPP-V (c).

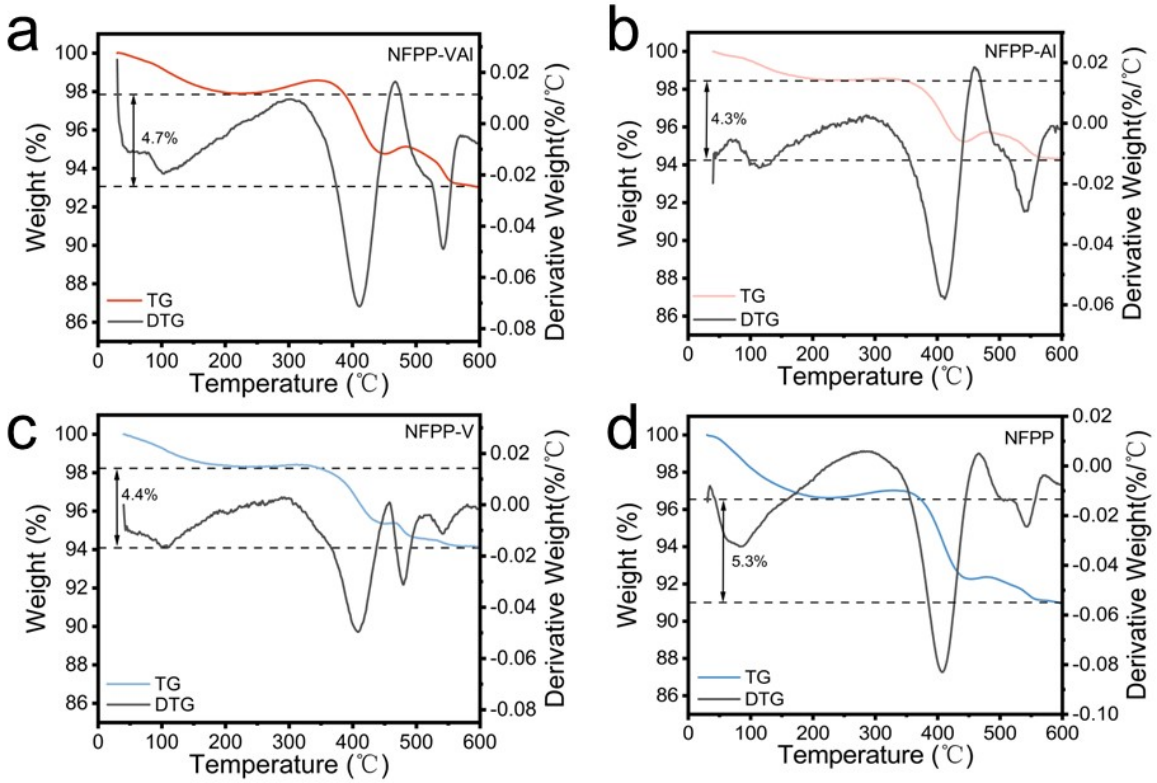

Fig. S8 TG and DTG curves of NFPP-VAl (a), NFPP-Al (b), NFPP-V (c) and NFPP (d).

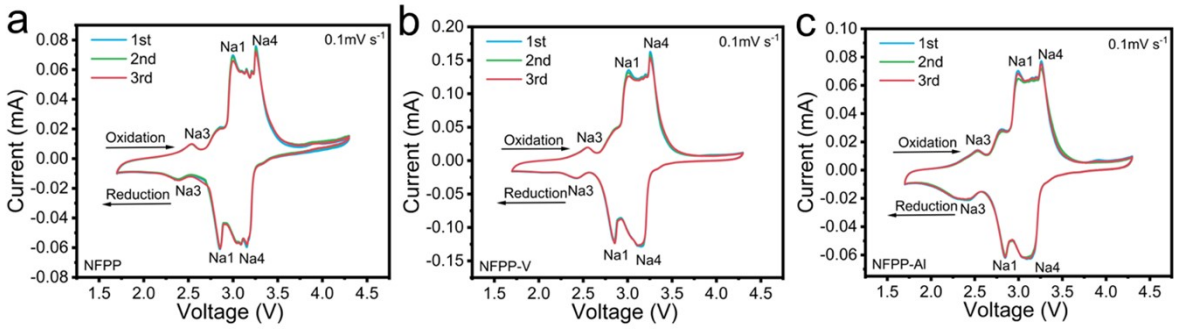

Fig. S9 CV curves of NFPP (a), NFPP-V (b) and NFPP-Al (c) measured at 0.1 mV s^{-1}.

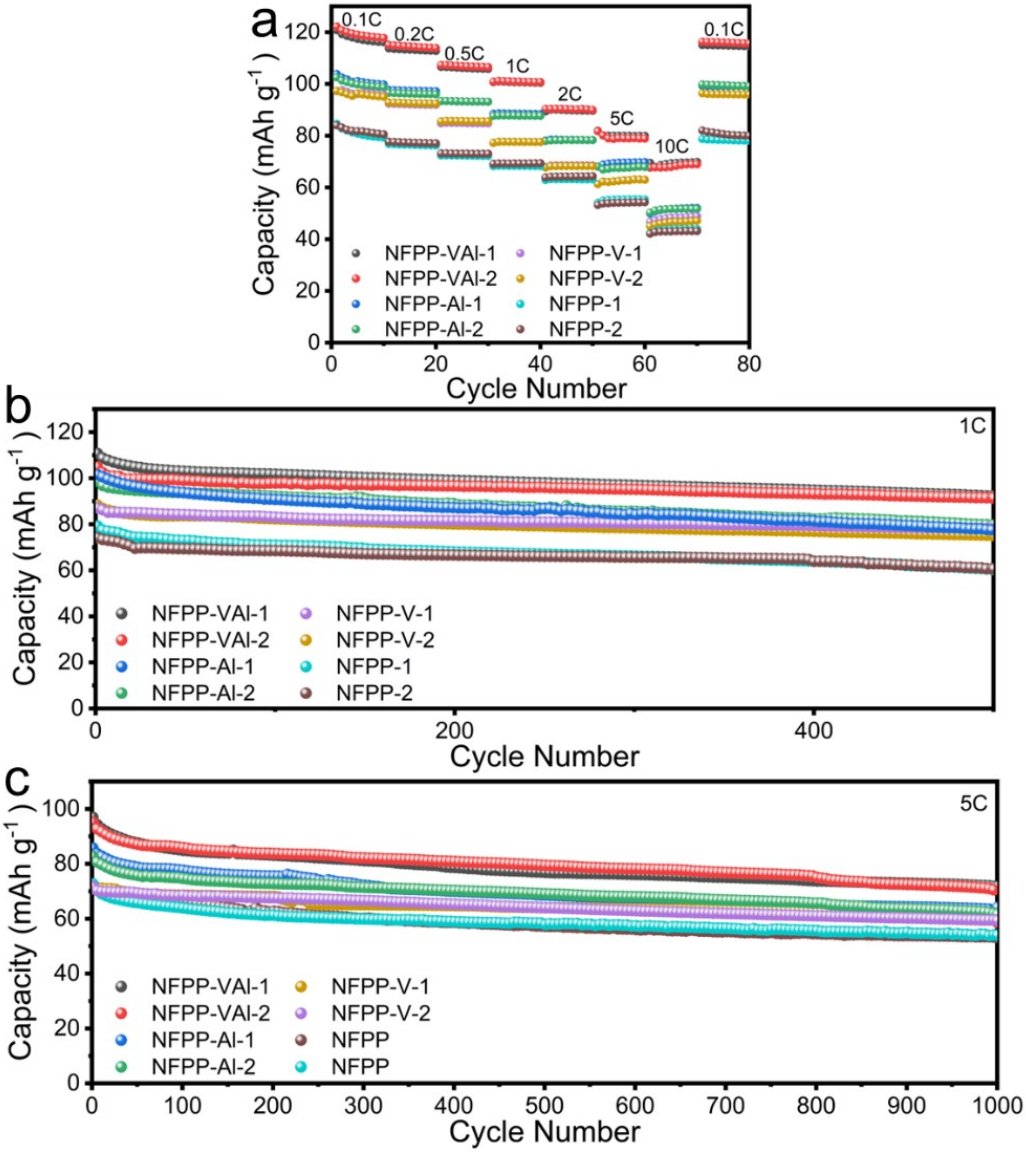

Fig. S10 Parallel measurement data for the four electrode materials to ensure data reliability: rate performance data (a) and cycling stability measured at 1C (b) and 5C (c). The numbers of 1 and 2 behind each sample represent Set 1 and Set 2 data, respectively.

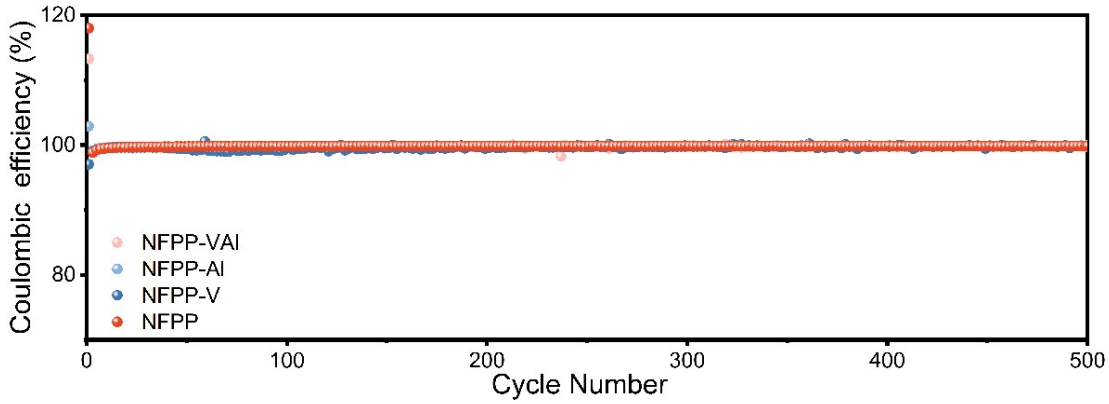

Fig. S11 Coulombic efficiency of electrode materials measured at 1C.

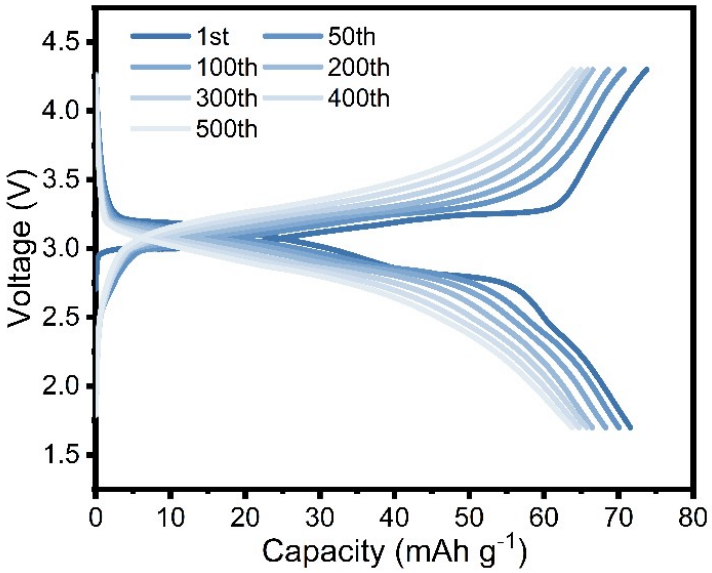

Fig. S12 GCD profiles of NFPP for different cycles measured at 1C.

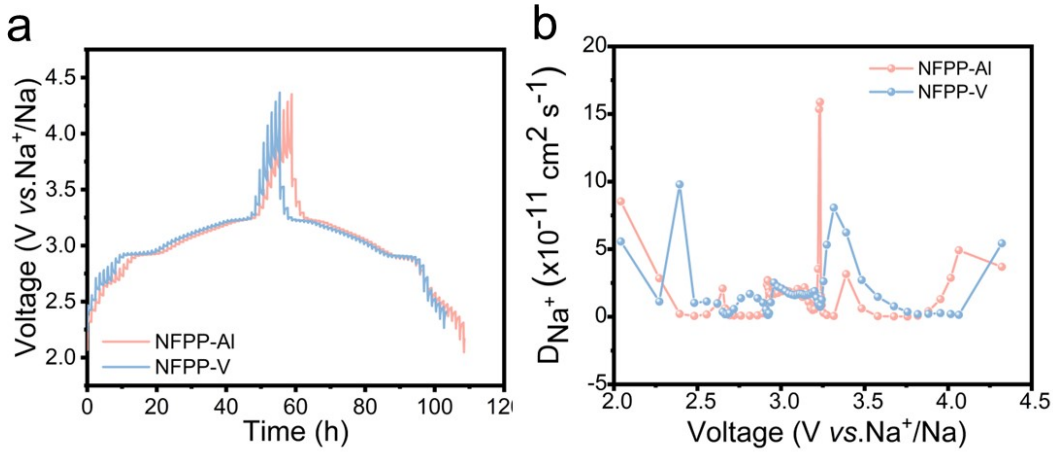

Fig. S13 (a) GITT plots measured at 0.1C; (b) Na^+ diffusion coefficients against voltage.

Table S1. Atomic ratio of Na:Fe:V:Al measured using the ICP-OES technique.

Sample	Na	Fe	V	Al
NFPP	3.91	2.91	0	0
NFPP-V	3.87	2.88	0.045	0
NFPP-Al	3.82	2.83	0	0.089
NFPP-VAl	3.74	2.77	0.047	0.093

Table S2. Structure information of NFPP-VAl from Rietveld refinement.

Atom	Mult	x	y	z	Occ
Fe1	4	0.348322	0.49671	0.099893	1
Fe2	4	0.139	0.4948	0.5901	0.85
Fe3	4	0.2429	0.7423	0.3226	1
P1	4	0.2925	0.5015	0.5985	1
P2	4	0.1791	0.4864	0.0881	1
P3	4	0.568	0.7368	0.4554	1
P4	4	0.4486	0.7275	0.1469	1
Na1	4	0.4934	0.9768	0.819	1
Na2	4	0.2955	0.7472	0.852	1
Na3	4	0.3941	0.2635	0.4281	1
Na4	4	0.462	0.541	0.6738	1
O1	4	0.247793	0.614471	0.533275	1
O2	4	0.333754	0.493164	0.429693	1
O3	4	0.351846	0.522215	0.762605	1
O4	4	0.207806	0.469576	0.551344	1
O5	4	0.232	0.6031	0.1137	1
O6	4	0.127	0.5122	0.0919	1
O7	4	0.234	0.3743	0.0548	1
O8	4	0.1351	0.4573	0.2829	1
O9	4	0.487	0.6978	0.3696	1
O10	4	0.5575	0.8628	0.5666	1
O11	4	0.6222	0.743	0.2804	1
O12	4	0.5839	0.6303	0.6058	1
O13	4	0.4566	0.8694	0.1119	1
O14	4	0.3687	0.6889	0.1714	1
O15	4	0.4904	0.6475	0.0032	1
V	4	0.139	0.4948	0.5901	0.05
Al	4	0.139	0.4948	0.5901	0.1

Table S3. Structure information of NFPP-Al from Rietveld refinement.

Atom	Mult	x	y	z	Occ
Fe1	4	0.3312	0.5044	0.0949	1
Fe2	4	0.1386	0.4955	0.5842	0.9
Fe3	4	0.2404	0.7443	0.3197	1
P1	4	0.29	0.5023	0.5881	1
P2	4	0.1795	0.4888	0.0782	1
P3	4	0.5706	0.734	0.4433	1
P4	4	0.4497	0.7279	0.1326	1
Na1	4	0.4939	0.9733	0.8079	1
Na2	4	0.2964	0.7486	0.842	1
Na3	4	0.3897	0.2621	0.4104	1
Na4	4	0.4606	0.5404	0.66	1
O1	4	0.233	0.6135	0.5507	1
O2	4	0.3402	0.4753	0.4056	1
O3	4	0.3372	0.5371	0.7775	1
O4	4	0.2369	0.3852	0.6194	1
O5	4	0.2369	0.6062	0.1035	1
O6	4	0.1266	0.5156	0.8971	1
O7	4	0.2257	0.3757	0.0451	1
O8	4	0.1354	0.4559	0.2739	1
O9	4	0.4895	0.696	0.3527	1
O10	4	0.5602	0.8607	0.5521	1
O11	4	0.6258	0.7408	0.2685	1
O12	4	0.5854	0.6259	0.5928	1
O13	4	0.4536	0.8723	0.1037	1
O14	4	0.3708	0.683	0.1581	1
O15	4	0.4909	0.6475	0.0032	1
Al	4	0.1386	0.4955	0.5842	0.1

Table S4. Structure information of NFPP-V after Rietveld refinement.

Atom	Mult	x	y	z	Occ
Fe1	4	0.3246	0.4943	0.093	1
Fe2	4	0.1358	0.4856	0.5725	0.95
Fe3	4	0.2356	0.7294	0.3133	1
P1	4	0.2813	0.4872	0.5705	1
P2	4	0.1741	0.4741	0.0759	1
P3	4	0.5535	0.7120	0.43	1
P4	4	0.4362	0.7061	0.1286	1
Na1	4	0.4791	0.9441	0.7837	1
Na2	4	0.2875	0.7261	0.8167	1
Na3	4	0.3780	0.2542	0.3981	1
Na4	4	0.4468	0.5242	0.6402	1
O1	4	0.226	0.5951	0.5342	1
O2	4	0.33	0.461	0.3934	1
O3	4	0.3271	0.521	0.7542	1
O4	4	0.2298	0.3736	0.6008	1
O5	4	0.2298	0.588	0.1004	1
O6	4	0.1228	0.5001	0.8702	1
O7	4	0.218	0.3644	0.0437	1
O8	4	0.1313	0.4422	0.2657	1
O9	4	0.4748	0.67	0.3421	1
O10	4	0.5434	0.8349	0.5355	1
O11	4	0.607	0.718	0.2604	1
O12	4	0.5678	0.6071	0.575	1
O13	4	0.4412	0.8461	0.1006	1
O14	4	0.3597	0.6625	0.1534	1
O15	4	0.4762	0.6281	0.0031	1
V	4	0.1358	0.4856	0.5725	0.05

Table S5. Structure information of NFPP from Rietveld refinement.

Atom	Mult	x	y	z	Occ
Fe1	4	0.3444	0.5246	0.0987	1
Fe2	4	0.1441	0.5153	0.6076	1
Fe3	4	0.25	0.7741	0.3325	1
P1	4	0.3016	0.5224	0.6116	1
P2	4	0.1867	0.5084	0.0813	1
P3	4	0.5934	0.7634	0.461	1
P4	4	0.4677	0.757	0.1379	1
Na1	4	0.5137	1.0122	0.8402	1
Na2	4	0.3083	0.7785	0.8757	1
Na3	4	0.4053	0.2726	0.4268	1
Na4	4	0.479	0.562	0.6864	1
O1	4	0.2423	0.638	0.5727	1
O2	4	0.3538	0.4943	0.4218	1
O3	4	0.3507	0.5586	0.8086	1
O4	4	0.2464	0.4006	0.6442	1
O5	4	0.2464	0.6304	0.1076	1
O6	4	0.1317	0.5362	0.933	1
O7	4	0.2347	0.3907	0.0469	1
O8	4	0.1408	0.4741	0.2849	1
O9	4	0.5091	0.7238	0.3668	1
O10	4	0.5826	0.8951	0.5742	1
O11	4	0.6508	0.7704	0.2792	1
O12	4	0.6088	0.6509	0.6165	1
O13	4	0.4717	0.9072	0.1078	1
O14	4	0.3856	0.7103	0.1644	1
O15	4	0.5105	0.6734	0.0033	1

Table S6. Na-O bond length of NFPP and NFPP-VAl.

Bond	Bond length in NFPP (Å)	Bond length in NFPP-VAl (Å)
Na1-O6	2.471	2.493
Na1-O8	2.328	2.349
Na1-O10	2.527	2.532
Na1-O10	2.351	2.359
Na1-O13	2.309	2.315
Na1-O13	2.328	2.335
Na2-O1	2.619	2.628
Na2-O3	2.426	2.425
Na2-O4	2.421	2.427
Na2-O5	2.568	2.575
Na2-O7	2.429	2.435
Na2-O8	2.603	2.608
Na2-O14	2.546	2.556
Na3-O2	2.443	2.444
Na3-O6	2.710	2.710
Na3-O10	2.857	2.865
Na3-O11	2.324	2.324
Na3-O15	2.324	2.332
Na4-O2	2.780	2.797
Na4-O3	2.348	2.368
Na4-O9	2.638	2.643
Na4-O12	2.428	2.446
Na4-O15	2.453	2.459
Na4-O15	2.472	2.475
Average	2.487	2.496

Table S7. Values of R_{ct}, R_s, and Z_w fitted using the equivalent circuit model shown in Fig.3g.

	R_{ct} (Ω)	R_s (Ω)	Z_w (Ω)
NFPP	285	2.87	0.65
NFPP-V	168	2.75	1.06
NFPP-Al	157	2.68	1.00
NFPP-VAl	37	2.63	0.65