First Exploration of Na-ion Migration Pathways in NASICON $Na_3V_2(PO_4)_3$

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Experimental Section

Synthesis and characterization of $Na_3V_2(PO_4)_3$

NVP was prepared by solution-based carbothermal reduction method (S-CTR) using a solvation-based precursor. Stoichiometric amounts of analytical purity Na_2CO_3, NH_4H_2PO4, V_2O_5 and acetylene black powders (5 wt.% excess acetylene black would be used as conductive agent while these as reducer for the reaction should match the stoichiometric ration) were mixed and stirring in distilled water and dried under 50 ºC by forced-air drying. The precursor was ground and preheated at 350 ºC in flow argon for 4h, and reground before being re-fired at 650 ºC in argon atmosphere for 8h.

The crystallographic structure of the as prepared material was studied by X-ray powder diffraction (XRD) using a Bruker D8 diffractometer with monochromatic Cu Kα radiation (λ=1.5406 Å), and the diffraction data was recorded in the 2θ range of 10–60 º with a scan rate of 8 º/min. The infrared (IR) spectra was obtained using an FT-IR Spectrometer (Jasco, FT/IR-4100, Japan) under transmission mode based on the KBr pellet method in the range of 500-2000 cm^{-1}. The particle morphology of the composite was investigated by a FEI Quanta 200 scanning electron microscopy (SEM). The thermogravimetric analysis (TG) of the samples was carried on a Diamond TG thermo-analyzer.

Electrochemical measurements

NVP/NaClO4/Na system was employed into a sodium-ion battery to be investigated in this work. The cathode electrode was fabricated with the active material, acetylene black, and binder (Polyvinylidene Fluoride, PVDF) in a weight ratio of 8:1:1 by using NMP as solvent and an aluminum foil as current collector (~

4.5 mg/cm^2), followed by drying in vacuum at 110 ºC for 24 h. The R2016 coin cell was assembled in an argon-filled glove box using alkali foil (lithium or sodium) as anode, Celgard 2500 membrane as separator. The electrolyte was 1 M $NaClO_4$ dissolved in polycarbonate (PC). The and NVP/$LiPF_6$/Li cell could be constructed by using the relative components above, respectively.

Cyclic voltammetry (CV) and galvanostatic charge/discharge cycling tests were carried out in a setting voltage range by using an electrochemical workstation (CHI660C) and a CT2001A LAND battery tester, respectively. Electrochemical impedance spectroscopy (EIS) was studied using a Modulab (Solartron Analytical) with the amplitude of 5 mV in the frequency range from 1 MHz to 10 mHz. All electrochemical tests were carried out at room temperature.

Computation

All calculations on $Na_3V_2(PO_4)_3$ were performed with the spin-polarized Generalized Gradient Approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation parameterization to Density Functional Theory (DFT) using CASTEP program. A plane-wave basis with a kinetic energy cutoff of 330 eV was used, and size of standard grid was 1.5. BFGS optimization method was used and the geometry optimization parameters of total energy convergence, max ionic force, max ionic displacement and max stress component tolerance were 0.2×10^{-4} eV/atom, 0.5×10^{-1} eV/ Å, 0.2×10^{-2} Å and 0.1GPa respectively. The electronic convergence thresholds parameters of total energy and eigen-energy were 0.2×10^{-5} eV and 0.5638×10^{-6} eV. All calculations were conducted in a unit cell of $[Na_3V_2(PO_4)_3]_2$.

Table S1. Bond population of O-Na in the optimized cell.

Bond		Population	Length (A)
O 018 --	Na 002	-0.04	2.48370
O 016 --	Na 001	-0.04	2.48385
O 014 --	Na 003	-0.04	2.48407
O 004 --	Na 004	-0.04	2.48438
O 002 --	Na 006	-0.04	2.48445
O 006 --	Na 005	-0.04	2.48470
O 010 --	Na 004	-0.04	2.48628
O 012 --	Na 006	-0.04	2.48637
O 008 --	Na 005	-0.04	2.48641
O 020 --	Na 002	-0.04	2.48662
O 022 --	Na 001	-0.04	2.48668
O 024 --	Na 003	-0.04	2.48707
O 020 --	Na 001	-0.02	2.50267
O 022 --	Na 003	-0.02	2.50268
O 008 --	Na 004	-0.02	2.50296
O 010 --	Na 006	-0.02	2.50297
O 024 --	Na 002	-0.02	2.50326
O 012 --	Na 005	-0.02	2.50386
O 006 --	Na 006	-0.02	2.50827
O 018 --	Na 003	-0.02	2.50893
O 004 --	Na 005	-0.02	2.50928
O 014 --	Na 001	-0.02	2.50930
O 002 --	Na 004	-0.02	2.50946
O 016 --	Na 002	-0.02	2.50957
O 004 --	Na 007	0.10	2.54606
O 002 --	Na 007	0.10	2.54623
O 008 --	Na 008	0.10	2.54666
O 014 --	Na 007	0.10	2.54672
O 012 --	Na 008	0.10	2.54717
O 016 --	Na 007	0.10	2.54728
O 010 --	Na 008	0.10	2.54732
O 020 --	Na 008	0.10	2.54734
O 006 --	Na 007	0.09	2.54752
O 024 --	Na 008	0.10	2.54822
O 022 --	Na 008	0.10	2.54831
O 018 --	Na 007	0.09	2.54841
O 023 --	Na 002	0.05	2.68173
O 011 --	Na 005	0.05	2.68278
O 013 --	Na 001	0.05	2.68454
O 009 --	Na 006	0.05	2.68547
O 021 --	Na 003	0.05	2.68549
O 017 --	Na 003	0.05	2.68624

O 019 --	Na 001	0.05	2.68680
O 001 --	Na 004	0.05	2.68710
O 007 --	Na 004	0.05	2.68711
O 015 --	Na 002	0.05	2.68723
O 005 --	Na 006	0.05	2.68904
O 003 --	Na 005	0.05	2.69034
O 003 --	Na 001	-0.04	2.97966
O 001 --	Na 003	-0.04	2.98022
O 015 --	Na 004	-0.04	2.98142
O 005 --	Na 002	-0.04	2.98164
O 007 --	Na 002	-0.04	2.98176
O 019 --	Na 005	-0.04	2.98232
O 013 --	Na 006	-0.04	2.98300
O 017 --	Na 005	-0.04	2.98328
O 011 --	Na 003	-0.04	2.98449
O 009 --	Na 001	-0.04	2.98449
O 021 --	Na 004	-0.04	2.98486
O 023 --	Na 006	-0.04	2.98539

Table S2. Bond population of O-Na in the optimized cell with six Na extraction. Notably, the Na001 and Na002 are the unextracted sodium ions at Na(1) sites.

Bond		Population	Length (A)
O 018 --	Na 001	-0.02	2.51793
O 012 --	Na 002	-0.02	2.51724
O 022 --	Na 002	-0.02	2.51729
O 020 --	Na 002	-0.02	2.51732
O 006 --	Na 001	-0.02	2.51766
O 016 --	Na 001	-0.02	2.51771
O 002 --	Na 001	-0.02	2.51773
O 014 --	Na 001	-0.02	2.51783
O 004 --	Na 001	-0.02	2.51788
O 010 --	Na 002	-0.02	2.51688
O 008 --	Na 002	-0.02	2.51690
O 024 --	Na 002	-0.02	2.51714

Table S3. Bond population of O-V in the optimized cell.

Bond		Population	Length (A)
O 021 --	V 004	0.36	2.02833
O 019 --	V 004	0.36	2.02840
O 003 --	V 001	0.36	2.02853
O 015 --	V 003	0.36	2.02855
O 009 --	V 002	0.36	2.02873
O 007 --	V 002	0.36	2.02880
O 023 --	V 004	0.36	2.02884

O 001 --	V 001	0.36	2.02896
O 013 --	V 003	0.36	2.02903
O 005 --	V 001	0.36	2.02903
O 017 --	V 003	0.36	2.02909
O 011 --	V 002	0.36	2.02929
O 018 --	V 003	0.30	2.15247
O 006 --	V 001	0.30	2.15328
O 016 --	V 003	0.30	2.15369
O 014 --	V 003	0.30	2.15399
O 024 --	V 004	0.30	2.15438
O 004 --	V 001	0.30	2.15441
O 002 --	V 001	0.30	2.15453
O 022 --	V 004	0.30	2.15470
O 010 --	V 002	0.30	2.15521
O 020 --	V 004	0.30	2.15530
O 012 --	V 002	0.30	2.15531
O 008 --	V 002	0.30	2.15604

Table S4. Bond population of O-V in the optimized cell with six Na extraction.

Bond		Population	Length (A)
O 015 --	V 003	0.40	1.89271
O 005 --	V 001	0.40	1.89290
O 003 --	V 001	0.40	1.89294
O 023 --	V 004	0.40	1.89297
O 017 --	V 003	0.40	1.89303
O 011 --	V 002	0.40	1.89304
O 013 --	V 003	0.40	1.89318
O 001 --	V 001	0.40	1.89323
O 009 --	V 002	0.40	1.89332
O 021 --	V 004	0.40	1.89335
O 007 --	V 002	0.40	1.89351
O 019 --	V 004	0.40	1.89353
O 004 --	V 001	0.36	1.98342
O 016 --	V 003	0.36	1.98349
O 014 --	V 003	0.36	1.98394
O 024 --	V 004	0.36	1.98407
O 012 --	V 002	0.36	1.98411
O 002 --	V 001	0.36	1.98413
O 022 --	V 004	0.36	1.98414
O 010 --	V 002	0.36	1.98428
O 018 --	V 003	0.36	1.98429
O 020 --	V 004	0.36	1.98447
O 006 --	V 001	0.36	1.98451
O 008 --	V 002	0.36	1.98462

Table S5. Atomic population calculated by DFT of the optimized cell.

Species	Ion	s	p	d	f	Total	Charge (e)
O	1	1.83	5.11	0.00	0.00	6.94	-0.94
O	2	1.84	5.13	0.00	0.00	6.97	-0.97
O	3	1.83	5.11	0.00	0.00	6.94	-0.94
O	4	1.84	5.13	0.00	0.00	6.97	-0.97
O	5	1.83	5.11	0.00	0.00	6.94	-0.94
O	6	1.84	5.13	0.00	0.00	6.97	-0.97
O	7	1.83	5.11	0.00	0.00	6.94	-0.94
O	8	1.84	5.13	0.00	0.00	6.97	-0.97
O	9	1.83	5.11	0.00	0.00	6.94	-0.94
O	10	1.84	5.13	0.00	0.00	6.97	-0.97
O	11	1.83	5.11	0.00	0.00	6.94	-0.94
O	12	1.84	5.13	0.00	0.00	6.97	-0.97
O	13	1.83	5.11	0.00	0.00	6.94	-0.94
O	14	1.84	5.13	0.00	0.00	6.97	-0.97
O	15	1.83	5.11	0.00	0.00	6.94	-0.94
O	16	1.84	5.13	0.00	0.00	6.97	-0.97
O	17	1.83	5.11	0.00	0.00	6.94	-0.94
O	18	1.84	5.13	0.00	0.00	6.97	-0.97
O	19	1.83	5.11	0.00	0.00	6.94	-0.94
O	20	1.84	5.13	0.00	0.00	6.97	-0.97
O	21	1.83	5.11	0.00	0.00	6.94	-0.94
O	22	1.84	5.13	0.00	0.00	6.97	-0.97
O	23	1.83	5.11	0.00	0.00	6.94	-0.94
O	24	1.84	5.13	0.00	0.00	6.97	-0.97
Na	1	2.09	5.86	0.00	0.00	7.95	1.05
Na	2	2.09	5.86	0.00	0.00	7.95	1.05
Na	3	2.09	5.86	0.00	0.00	7.95	1.05
Na	4	2.09	5.86	0.00	0.00	7.95	1.05
Na	5	2.09	5.86	0.00	0.00	7.95	1.05
Na	6	2.09	5.86	0.00	0.00	7.95	1.05
Na	7	2.14	6.19	0.00	0.00	8.33	0.67
Na	8	2.14	6.19	0.00	0.00	8.33	0.67
P	1	0.96	2.02	0.00	0.00	2.98	2.02
P	2	0.96	2.02	0.00	0.00	2.98	2.02
P	3	0.96	2.02	0.00	0.00	2.98	2.02
P	4	0.96	2.02	0.00	0.00	2.98	2.02
P	5	0.96	2.02	0.00	0.00	2.98	2.02
P	6	0.96	2.02	0.00	0.00	2.98	2.02
V	1	2.29	6.47	3.42	0.00	12.18	0.82
V	2	2.29	6.47	3.45	0.00	12.21	0.79
V	3	2.29	6.47	3.44	0.00	12.21	0.79

V	4	2.29	6.47	3.43	0.00	12.19	0.81

Table S6. Atomic population calculated by DFT of the optimized cell with six Na extraction. Notably, the Na1 and Na2 are the unextracted sodium ions at Na(1) sites.

Species	Ion	s	p	d	f	Total	Charge (e)
O	1	1.83	5.03	0.00	0.00	6.86	-0.86
O	2	1.84	5.08	0.00	0.00	6.92	-0.92
O	3	1.83	5.03	0.00	0.00	6.86	-0.86
O	4	1.84	5.08	0.00	0.00	6.92	-0.92
O	5	1.83	5.03	0.00	0.00	6.86	-0.86
O	6	1.84	5.08	0.00	0.00	6.92	-0.92
O	7	1.83	5.03	0.00	0.00	6.86	-0.86
O	8	1.84	5.08	0.00	0.00	6.92	-0.92
O	9	1.83	5.03	0.00	0.00	6.86	-0.86
O	10	1.84	5.08	0.00	0.00	6.92	-0.92
O	11	1.83	5.03	0.00	0.00	6.86	-0.86
O	12	1.84	5.08	0.00	0.00	6.92	-0.92
O	13	1.83	5.03	0.00	0.00	6.86	-0.86
O	14	1.84	5.08	0.00	0.00	6.92	-0.92
O	15	1.83	5.03	0.00	0.00	6.86	-0.86
O	16	1.84	5.08	0.00	0.00	6.92	-0.92
O	17	1.83	5.03	0.00	0.00	6.86	-0.86
O	18	1.84	5.08	0.00	0.00	6.92	-0.92
O	19	1.83	5.03	0.00	0.00	6.86	-0.86
O	20	1.84	5.08	0.00	0.00	6.92	-0.92
O	21	1.83	5.03	0.00	0.00	6.86	-0.86
O	22	1.84	5.08	0.00	0.00	6.92	-0.92
O	23	1.83	5.03	0.00	0.00	6.86	-0.86
O	24	1.84	5.08	0.00	0.00	6.92	-0.92
Na	1	2.02	5.78	0.00	0.00	7.80	1.20
Na	2	2.02	5.78	0.00	0.00	7.80	1.20
P	1	0.88	1.85	0.00	0.00	2.73	2.27
P	2	0.88	1.85	0.00	0.00	2.73	2.27
P	3	0.88	1.85	0.00	0.00	2.73	2.27
P	4	0.88	1.85	0.00	0.00	2.73	2.27
P	5	0.88	1.85	0.00	0.00	2.73	2.27
P	6	0.88	1.85	0.00	0.00	2.73	2.27
V	1	2.26	6.23	3.18	0.00	11.67	1.33
V	2	2.26	6.23	3.16	0.00	11.65	1.35
V	3	2.26	6.23	3.20	0.00	11.69	1.31
V	4	2.26	6.23	3.20	0.00	11.69	1.31

Table S7. Atom coordinates of $Na_3V_2(PO_4)_3$.

Site	Element	Wyckoff Symbol	Symmetry	x	y	z	Occupation
O1	O	36f	1	0.01714	0.20172	0.19119	1
O2	O	36f	1	0.18532	0.16658	0.08488	1
P1	P	18e	.2	0.29683	0	1/4	1
Na1	Na	18e	.2	0.63747	0	1/4	0.750
V1	V	12c	3.	0	0	0.14679	1
Na2	Na	6b	-3.	0	0	0	0.750

Table S8. Atom coordinates of $Na_2V_2(PO_4)_3$.

Site	Element	Wyckoff Symbol	Symmetry	x	y	z	Occupation
O1	O	36f	1	0.01714	0.20172	0.19119	1
O2	O	36f	1	0.18532	0.16658	0.08488	1
P1	P	18e	.2	0.29683	0	1/4	1
Na1	Na	18e	.2	0.63747	0	1/4	0.500
V1	V	12c	3.	0	0	0.14679	1
Na2	Na	6b	-3.	0	0	0	0.500