Supporting information

Ultrafast Biphasic $Na_5V_3(PO_4)_2(P_2O_7)_2$/C composite cathode for Sodium-Ion Batteries

Experimental Section

Material Synthesis: The series of $Na_{3+2x}V_{2+x}(PO_4)_{3-x}(P_2O_7)_{2x}$ ($0 \leq x \leq 2$) materials were synthesized with a traditional sol-gel approach. Firstly, 1 mmol of V_2O_5 (99.5%, Aladdin) and 3 mmol of $H_2C_2O_7$ (99.5%, RHAWN)were dissolved in distilled water under magnetic stirring at 60°C for 2 h, followed by adding soichiometric other raw materials (CH_3COONa (99.9%, Aladdin) and $NH_4H_2PO_4$ (99.9%, Aladdin)) and droping graphene oxide solution (60 mg GO in 30 ml H_2O) as carbon resource. Secondly, the solvent was evaporated at 80℃ until a gel was obtained. The gel was sufficiently dried in a vacuum oven at 100 ℃ for 12 h. After being uniformly mixed, the gel power was preheated at 450°C for 4h and sintered at 750°C for 8h, to obtain the final products.

Material characterization: X-ray diffraction (X′Pert Powder, Cu Ka rays) was used to confirm the crystal structure, and XRD patterns were collected in the 10°-80°range at a scanning rate of $8°min^{-1}$. FTIR spectroscopy (Thermo Nicolet iS10) was used to investigate microstructural properties of the materials in the wave number range of 400-1200 cm^{-1}. The elemental composition and valence states were examined using an X-ray photoelectron spectrometer (AXIS-ULTRA DLD, Al kα radiation source). The morphology was observed using a scanning electron microscope (JSM-7500F, operating voltage 5.0 KeV) and a transmission electron microscope (JEM-2100).

Electrochemical testing: The working electrode was made by mixing 70 wt% active material, 20 wt% conductive agent (Super P), and 10 wt% binder (PVDF). A CR2032 coin-type cell was assembled in an argon-filled glove box (H_2O, O_2 < 0.1 ppm) with a working electrode, a sodium sheet as the counter electrode, glass fiber (Whatman, GF/F) as the diaphragm, and 1 M $NaClO_4$/EC-PC (1:1, 5 wt% FEC) as the electrolyte. The mass loading of the working electrodes was about 2.0 mg cm^{-2}. Constant current charge/discharge measurements were performed on a Neware test system with a potential range of 2.0-4.2 V (vs Na^+/Na).

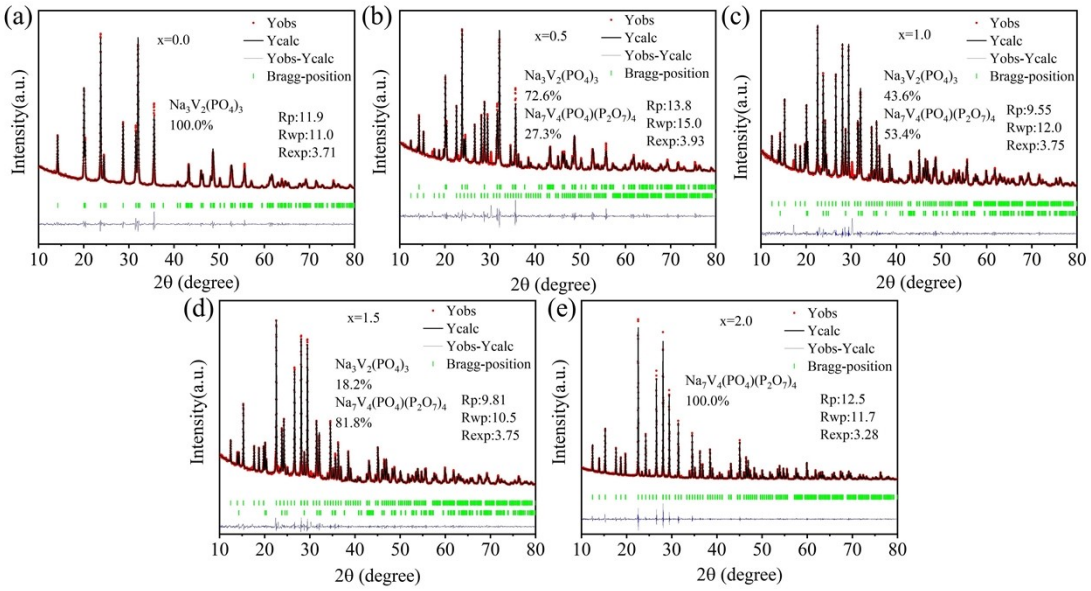

Figure S1 Rietveld refinement XRD pattern of $Na_{3+2x}V_{2+x}(PO_4)_{3-x}(P_2O_7)_{2x}$ ($0 \le x \le 2$) compositions.

Table S1 Detailed structural information of the $Na_{3+2x}V_{2+x}(PO_4)_{3-x}(P_2O_7)_{2x}$ (x=1) composition from the Rietveld refinement.

$Na_5V_3(PO_4)_3(P_2O_7)_2$

46.59% $Na_3V_2(PO_4)_3$, a=b=8.7286, c=21.8050

53.41% $Na_7V_4(P_2O_7)_4PO_4$, a=b=14.2234, c=6.3674

Atom	site	x	y	z
V1	12c	0.3333	0.6667	0.0189
V2	8e	0.8143	0.1214	0.1275
Na1	6b	0.3333	0.6667	0.1667
Na2	18e	0.6667	0.9550	0.0833
Na3	2a	0.0000	0.0000	0.5000
Na4	4d	0.0000	0.5000	0.8228
Na5	8e	0.9158	0.2652	0.6105
P1	18e	-0.0623	0.3333	0.0833
P2	2a	0.0000	0.0000	0.0000
P3	8e	0.6201	0.2547	0.1366
P4	8e	0.9571	0.3030	0.1028
O1	36f	0.1368	0.4930	0.0780
O2	36f	0.5237	0.8292	-0.0202

O3	8e	0.1462	0.1695	0.1923
O4	8e	0.7000	0.1935	0.0949
O5	8e	0.9325	0.0513	0.1614
O6	8e	0.5375	0.1881	0.2010
O7	8e	0.5902	0.3091	0.9415
O8	8e	0.0057	0.2547	0.9186
O9	8e	0.9232	0.3996	0.0721
O10	8e	0.8910	0.2456	0.204

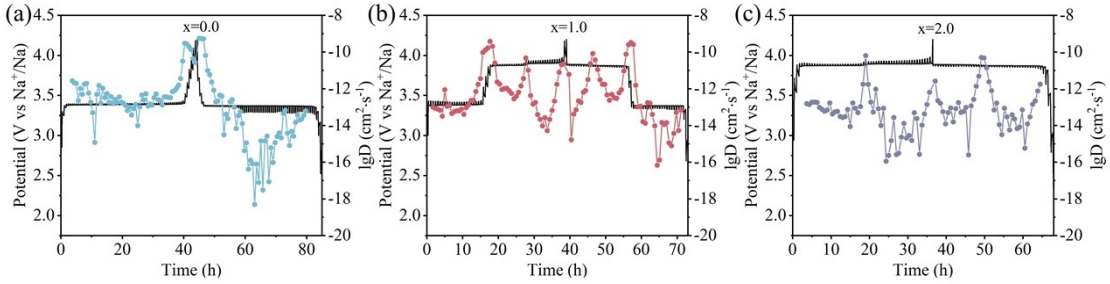

Figure S2 Apparent diffusion coefficients of Na^+ ions of $Na_{3+2x}V_{2+x}(PO_4)_{3-x}(P_2O_7)_{2x}$ (a) x=0, (b) x=1, and (c) x=2 compositions.

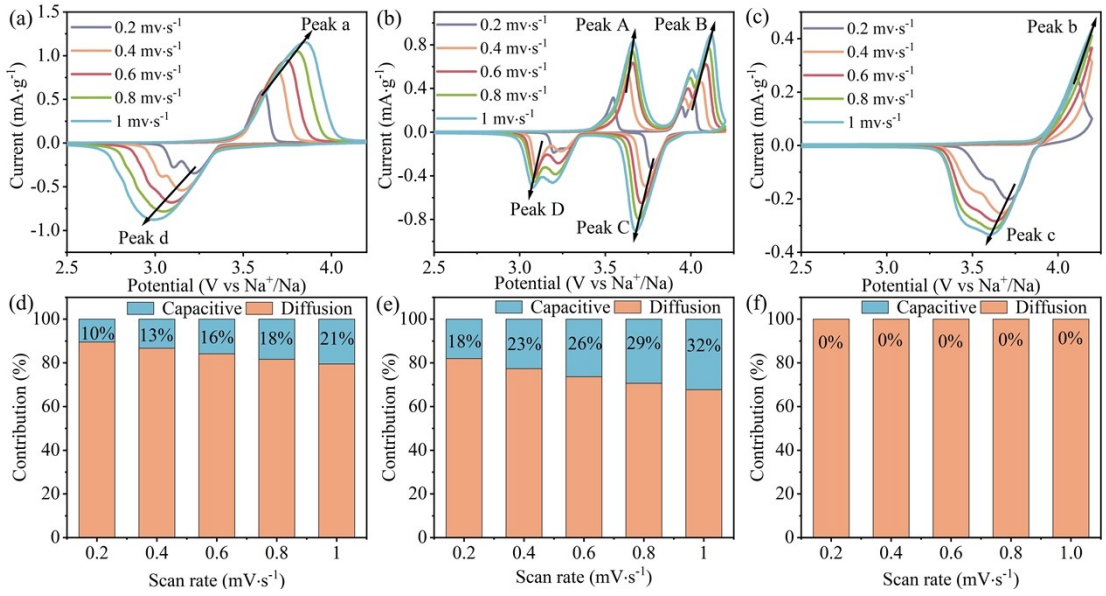

Figure S3 (a-c) CV curves of $Na_{3+2x}V_{2+x}(PO_4)_{3-x}(P_2O_7)_{2x}$ compositions (x=0, x=1, and x=2) at different scan rates; (d-f) Percentage of capacitance contribution of $Na_{3+2x}V_{2+x}(PO_4)_{3x}(P_2O_7)_{2x}$combinations (x=0, x=1, and x=2) at different scan rates.

Table S2 Comparison of cycling performance between the $Na_{3+2x}V_{2+x}(PO_4)_{3-x}(P_2O_7)_{2x}$ (x=1) composition and other cathodes of SIBs.

Sample	Cycle number	Rate	Capacity retention	Capacity loss per cycle
$Na_5V_3(PO_4)_3(P_2O_7)_2$	**1500**	**10C**	**88%**	**0.0069%**
$Na_3V_2(PO_4)_3$/GO	1000	5C	79%	0.0180%
Na_7V_4 $(P_2O_7)_4(PO_4)$/C	550	10C	73%	0.0424%
$Na_7V_3(P_2O_7)_4$	100	10C	92%	
$Na_4Fe_3(PO_4)_2(P_2O_7)$/C	2000	10C	79%	0.0101%
$Na_4[Mn_{1.5}Co_{1.5}](PO_4)_2(P_2O_7)$	300	2C	75%	
$Na_2FeP_2O_7$	100	1C	94.4%	0.0560%
$Na_2MnP_2O_7$	30	C/5	96%	0.1333%
$Na_3V(PO_3)_3N$	800	1C	91%	0.0112%
$NaVOPO_4$	1000	0.5C	67%	0.0330%
$Na_3MnZr(PO_4)_3$	500	0.5C	91%	0.0180%
$Na_3V_2O_2(PO_4)_2F$	1000	20C	90.2%	0.0098%