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Electronic Supporting Information

General synthesis of three-dimensional alkali metal vanadates aerogels

with superior lithium storage properties

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Figures and Captions



Fig. S1 SEM images of (a and b) the precursor, and (c) NaV₃O₈ materials without freeze-drying, (d) XRD pattern of NaV₃O₈ materials without freeze-drying.



Fig. S2 Nitrogen adsorption-desorption isotherms of (a) NaV₃O₈ aerogel and (b) NaV₃O₈ materials without freeze-drying; Inset: the corresponding pore size distributions.



Fig. S3 Electrochemical performances for NaV_3O_8 materials without freeze-drying. (a) Cycling performance at 50 mA g⁻¹, (b) Rate capability.



Fig. S4 Ex-situ Raman spectroscopies after different cycles at 100 mA g⁻¹ of NaV₃O₈ cathodes.

The Ex-situ Raman spectroscopies after different cycles at 100 mA g⁻¹ of NaV₃O₈ cathodes are indicated in **Fig. S4**. After various cycles, a typical translational mode at 166 cm⁻¹ reflecting the long range order of layered structure and a bond bending vibration mode at 307 cm⁻¹, a typical Raman peak at 795 cm⁻¹ for NaV₃O₈ have no change, indicating that the structure of NaV₃O₈ is almost stable during cycling. Three modes are weaken at 266, 688, and 725 cm⁻¹ after cycling. Several modes are shifted toward higher wavenumber: from 132 to 140 cm⁻¹; from 425 to 438 cm⁻¹; from 479 to 481 cm⁻¹; from 549 to 554 cm⁻¹; from 990 to 995 cm⁻¹. R. Baddour-Hadjean et al. have reported that Raman bands shifting are strongly affected by more lithium ions insertion into the β -Na_{0,33}V₂O₅ host.¹ The result demonstrates that, to some extent, lithium ions insertion in NaV₃O₈ would generate tiny changes for host structure, as discussed before. Fortunately, it does not damage the structure of NaV₃O₈ and the Raman spectrums with various cycles are consistent, which is benefit for the cyclic stability.



Fig. S5 SEM images of (a) NaV₆O₁₅ aerogel precursor, (b) NaV₆O₁₅ aerogel, (c) K_{0.25}V₂O₅ aerogel precursor, and (d) K_{0.25}V₂O₅ aerogel. Both aerogels show nanofiber-in-networks morphology, which consists of cross-linked ultra-long nanofibers.



Fig. S6 TEM images of (a and b) NaV_6O_{15} aerogel, and (c and d) $K_{0.25}V_2O_5$ aerogel.



Fig. S7 Structural characterization and electrochemical performances for NaV₆O₁₅ aerogel. (a) XRD pattern, (b) Raman spectrum, (c) The initial five cyclic voltammetry curves at a scan rate of 0.1 mV s⁻¹ and (d) Rate capability.

The Raman spectrum recorded for NaV₆O₁₅ (Fig. S7b) exhibits 13 modes located at 122, 147, 197, 269, 287, 314, 370, 510, 552, 688, 808, 850, and 1006 cm⁻¹, which agrees with the previous report of β -Na_{0.33}V₂O₅.¹ The highest frequency mode at 1006 cm⁻¹ represents the V-O stretching vibration. The phonon modes in medium-frequency region, such as 510, 552, 688, 808, and 850 cm⁻¹, are due to the O-V-O and V-O-V bending vibrations. And the low-frequency modes below 400 cm⁻¹ correspond to the bond bending vibrations.^{2, 3} For example, the typical translational mode located at 147 cm⁻¹ reflects the long range order in the plane of the NaV₆O₁₅ sheets.² The CV curves is indicated in **Fig. S7c**, the cathodic peaks observed at 3.62, 3.22, 2.80, 2.34, and 1.92 V (vs. Li⁺/Li) belong to the multiple-step intercalation of lithium ions into the NaV₆O₁₅ (Na_{0.33}V₂O₅) phase. And the anodic peaks for deintercalation of lithium ions are located at 2.17, 2.95, 3.10, 3.40, and 3.69 V (vs. Li⁺/Li). NaV₆O₁₅ (Na_{0.33}V₂O₅) is a typical of β -vanadium bronze, which contains tunnels formed by the association of VO₆ and VO₅ frameworks along the *b*-axis, and Na ions are located

inside the tunnels, in half of four interstitial equivalent sites per unit cell along the *b*-axis, named M_{1} .⁴ The two additional tunnel sites for Li intercalation are four eight-coordinated sites (M_2) and four tetrahedral sites (M_3) per unit cell.⁴ During cathodic process before 3.22 V, the lithium ions began to occupy the M_3 sites, and the second process at 2.80 V corresponds to the half occupancy of the M_2 sites. When discharging to 2.34 V, the remaining M_1 , M_2 , and M_3 sites were assigned by the Li ions. According to lithium-ion insertion into V_2O_5 , the cathodic peak below 2.0 V would be ascribed to the formation of irreversible phase.⁵ For our NaV₆O₁₅, fortunately, the peak at 1.92 V in the subsequent scans is consistent, demonstrating good reversibility of NaV₆O₁₅ electrodes. This result also indicates that doping small amount of element (such as Ag⁺, Na⁺, K⁺, etc.) into V₂O₅ interlayers can stable its structure, thus realize the good cycling stability. It can also exhibit a good rate capability (**Fig. S7d**). At various rates of 50, 100, 200, and 500 mA g⁻¹, the electrode exhibits high discharge capacities of 244, 229, 211, and 163 mA h g⁻¹, respectively. Even at the rate of 1000 mA g⁻¹, it still retains a high value of 107 mA h g⁻¹.



Fig. S8 Structural characterization and electrochemical performances for K_{0.25}V₂O₅ aerogel. (a) XRD pattern, (b) Raman spectrum, and cycling performances at (c) 100 mA g⁻¹ and (d) 500 mA g⁻¹.

The Raman spectrum recorded for $K_{0.25}V_2O_5$ (Fig. S8b) exhibits 14 modes located at 152, 262, 321, 349, 371, 399, 425, 504, 559, 702, 777, 874, 949, and 974 cm⁻¹. $K_{0.25}V_2O_5$ is isomorphic to β -Na_{0.33}V₂O₅, which contains 3D tunnels composed by the association of VO₆ and VO₅ frameworks with zigzag double chains along the b axis. However, the phonon modes of $K_{0.25}V_2O_5$ are quite different from that of NaV₆O₁₅ (Na_{0.33}V₂O₅). For instance, the strong phonon modes in medium-frequency for $K_{0.25}V_2O_5$ is from 702 to 874 cm⁻¹, while for NaV₆O₁₅ exhibits from 510 to 688 cm⁻¹. On the contrary, the V-O stretching modes of $K_{0.25}V_2O_5$ are weak and shifted toward lower wavenumber compared to NaV₆O₁₅. These changes demonstrate that K-O chemical bands are formed and K ions make the layer spacing larger,¹ which facilities ion diffusion. $K_{0.25}V_2O_5$ electrodes exhibit excellent stability with no capacity fading over 50 cycles at 100 mA g⁻¹ and 95% capacity retention over 100 cycles at 500 mA g⁻¹ (Fig. S8c and d).

Electrode material	Theoretical capacity /mA h g ⁻¹	Current density /mA g ⁻¹	Capacity/mA h g ⁻¹ (Cyclic number)	Cyclic number (retention/%)	High rate capability /mA h g ⁻¹
NaV ₃ O ₈	318	50	220 (1)	50 (95.9%)	96 (1000 mA g ⁻¹)
		500	155 (1)	400 (85.8%)	
		1000	105 (1)	600 (no fading)	
NaV ₆ O ₁₅		50	244 (1)		
	377	100	222 (1)	30 (96%)	107 (1000 mA g ⁻¹)
		500	161 (1)	200 (93%)	
$K_{0.25}V_2O_5$	384	100	198 (2)	50 (no fading)	· 144 (1000 mA g ⁻¹)
		500	164 (2)	100 (95%)	

Table S1. Comparisons of the electrochemical properties between the three aerogel materials reported in this work.

The three aerogel materials can be regarded as pre-insertion of Na⁺ and K⁺ cations into vanadium pentoxide (V₂O₅) host framework and their theoretical capacity is different. As known, V₂O₅ has a high theoretical capacity of 442 mA h g⁻¹ at the discharge voltage range from 4.0 to 1.5 V (vs. Li⁺/Li) when 3 Li⁺ intercalated into the V₂O₅ host according to the Faraday theory capacity formula:

$$C = \frac{n \cdot F}{3.6 \cdot M} \left(mA \ h \ g^{-1} \right)$$

Where *C* is theoretical capacity, *n* is the molar number of electron exchange, *F* is Faraday constant (~96485 C/mol), *M* is the molar mass of electrode material. NaV₃O₈ can be seen as 0.66 Na⁺ ions intercalated into V₂O₅, abbreviated as Na_{0.66}V₂O₅ and these Na⁺ ions are situated at octahedral sites and link strongly the adjacent vanadium oxygen layers to form a 2D layered structure.^{6, 7} Therefore, when discharged at 4.0-1.5V, theoretically there are (3-0.66) Li⁺ ions intercalated into Na_{0.66}V₂O₅ and its theoretical capacity is calculated as 318 mA h g⁻¹. For NaV₆O₁₅ (Na_{0.33}V₂O₅), 0.33 Na⁺ ions pre-inserted into V₂O₅ host framework to construct 3D network along the *b* axis contains open intercalation sites for about (3-0.33) Li⁺ ions intercalated at 4.0-1.5V,^{1, 4} namely, its theoretical capacity of 384 mA h g⁻¹ according to Faraday theory capacity formula. The above mentioned capacity of each material is based on the theoretical calculation.

Electrode material	Current density /mA g ⁻¹	Cyclic number (retention/%)	Ref.
NaV ₃ O ₈	1000	600 (without fading)	
NaV ₆ O ₁₅	500	200 (93%)	This work
$K_{0.25}V_2O_5$	500	100 (95%)	
Na _{1.1} V ₃ O _{7.9}	1500	200 (95%)	8
nanobelts	2000	200 (72%)	
Na _{1.08} V ₃ O ₈ nanosheets	1000	200 (without fading)	9
Na _{1.25} V ₃ O ₈ nanobelts	200	450 (94%)	10
Na _{1.25} V ₃ O ₈ nanowire arrays	50	50 (85.4%)	11
Na ₂ V ₆ O ₁₆ ·0.14H ₂ O nanowires	300	200 (76.9%)	12
Mesoporous β -Na _{0.33} V ₂ O ₅	50	50 (60.2%)	13
Na _{0.33} V ₂ O ₅ -graphene hybrids	4500	400 (87.4%)	14
highly crystalline β -Na _{0.33} V ₂ O ₅		70 (89%)	4
K-V-O nanowires	1000	900 (76%)	15
Book-like K _{0.23} V ₂ O ₅	50	100 (76%)	16
K _{0.25} V ₂ O ₅	500	500 (88.5%)	17
$K_{0.5}V_2O_5$ nanorods	C/10	70 (87%)	18

Table S2. Comparisons of cyclic stability of sodium and potassium vanadates cathodes.

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