Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Eldfellite-type Cathode Material, $NaV(SO_4)_2$, for Na-ion Batteries

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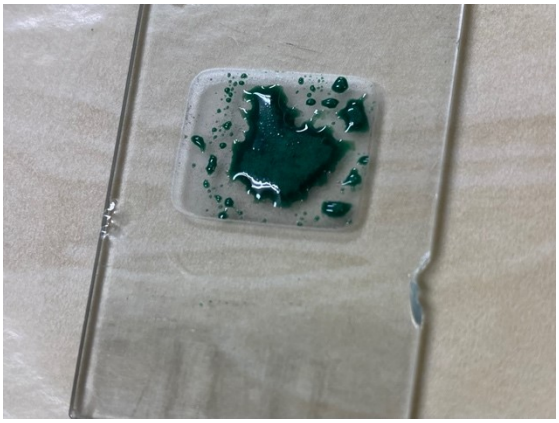

Fig. S1 $NaV(SO_4)_2$ which was left in the atmosphere overnight. It has become soaked because it has absorbed moisture from the atmosphere.

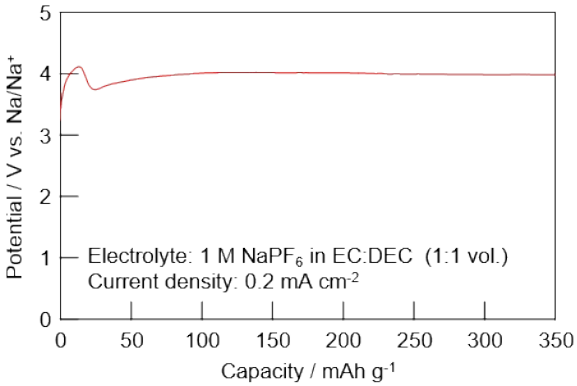

Fig. S2 Charging curves for $NaV(SO_4)_2$ after charging (desodiation) toward high potentials at the first cycle; the electrolyte was 1 M $NaPF_6$ in EC:DEC (1:1 by volume).

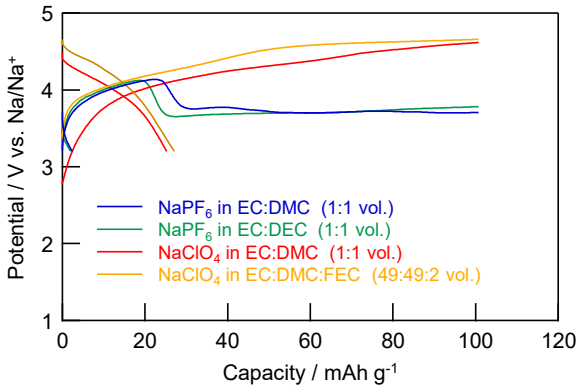

Fig. S3 Charge–discharge curves of $NaV(SO_4)_2$ for the first cycle in cells constructed using four different electrolytes. The charge capacity was regulated to 101 mAh g^{-1}, and the cutoff voltage and current density were set as 3.2–4.8 V and 0.1 mA cm^{-2}, respectively.

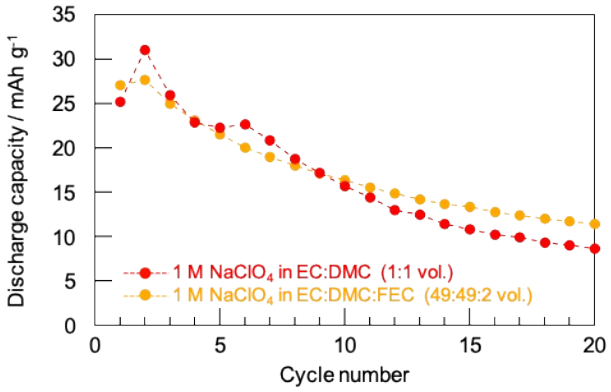

Fig. S4 Cycle performance of $NaV(SO_4)_2$ using 1 M $NaClO_4$ in EC:DMC (1:1 by volume) and 1 M $NaClO_4$ in EC:DMC:FEC (49:49:2 by volume) as the electrolyte. The charge capacity was regulated to 101 mAh g^{-1}, and the cutoff voltage and current density were set as 3.2–4.8 V and 0.1 mA cm^{-2}, respectively.

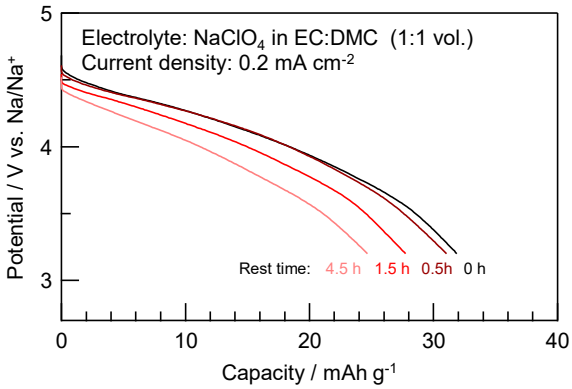

Fig. S5 Discharge curves of $NaV(SO_4)_2$ after charging (desodiation) for 101 mAh g^{-1} toward high potentials at the first cycle of cells constructed using 1 M $NaClO_4$ in EC:DMC (1:1 by volume) as the electrolyte. The rest time was varied from 0 h to 4.5 h.

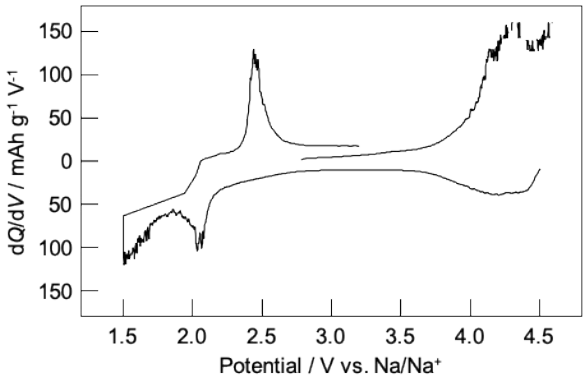

Fig. S6 dQ/dV curves obtained from the initial charge-discharge measurement provided from Fig. 3e.

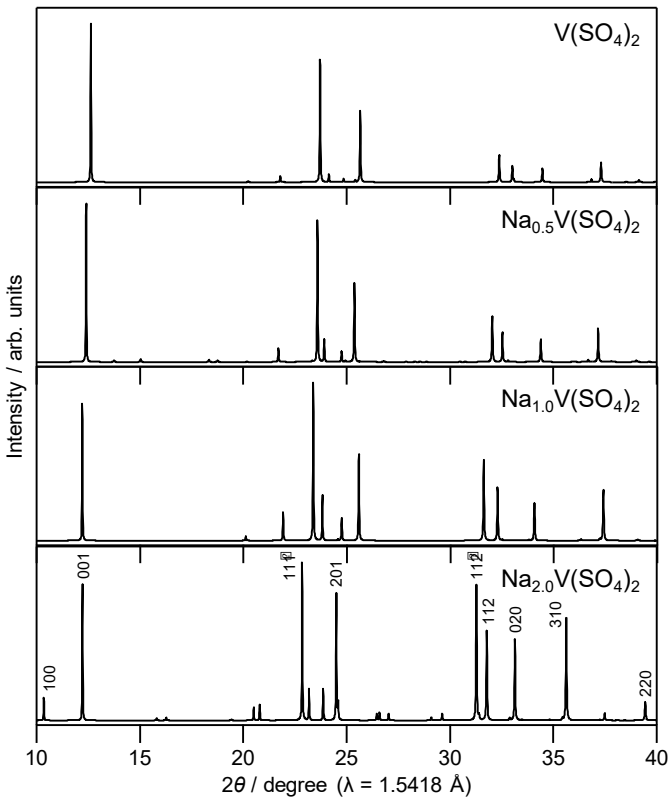

Fig. S7 Calculated XRD patterns for each Na^+ content (x) in $Na_xV(SO_4)_2$. The stabilized crystal structures were obtained using DFT calculations, and the XRD patterns based on the DFT-calculated structure were exported using the VESTA software.[1]

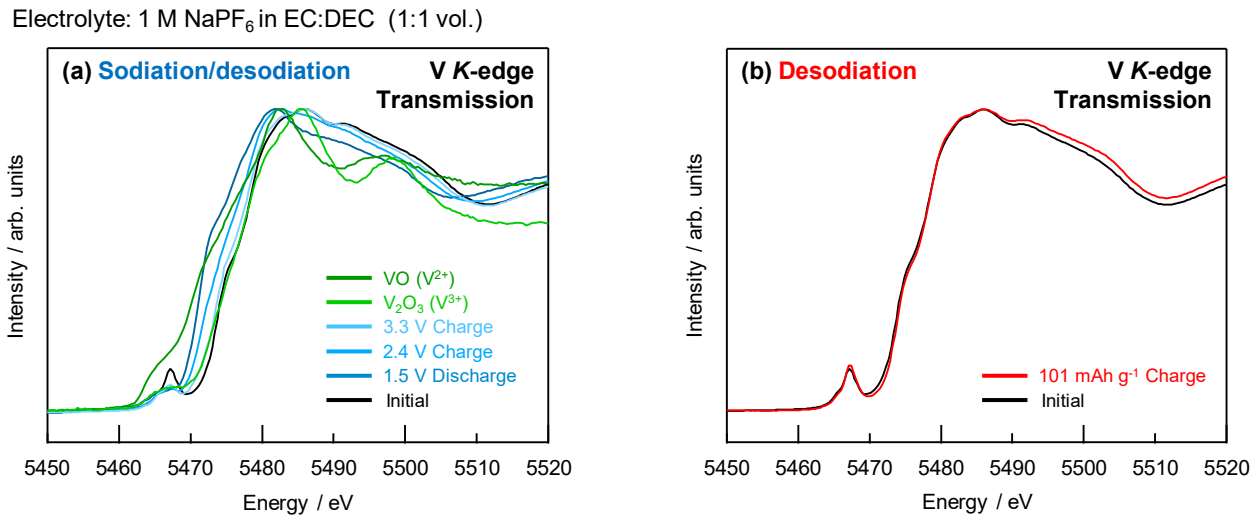

Fig. S8 V K-edge XANES spectra of $NaV(SO_4)_2$ at the different charge–discharge states during the first cycle for (a) the sodiation/desodiation process and (b) desodiation process from the initial composition in cells constructed using 1 M $NaPF_6$ EC:DEC (1:1 by volume) electrolyte. Transmission mode was used for the measurements with hard X-rays.

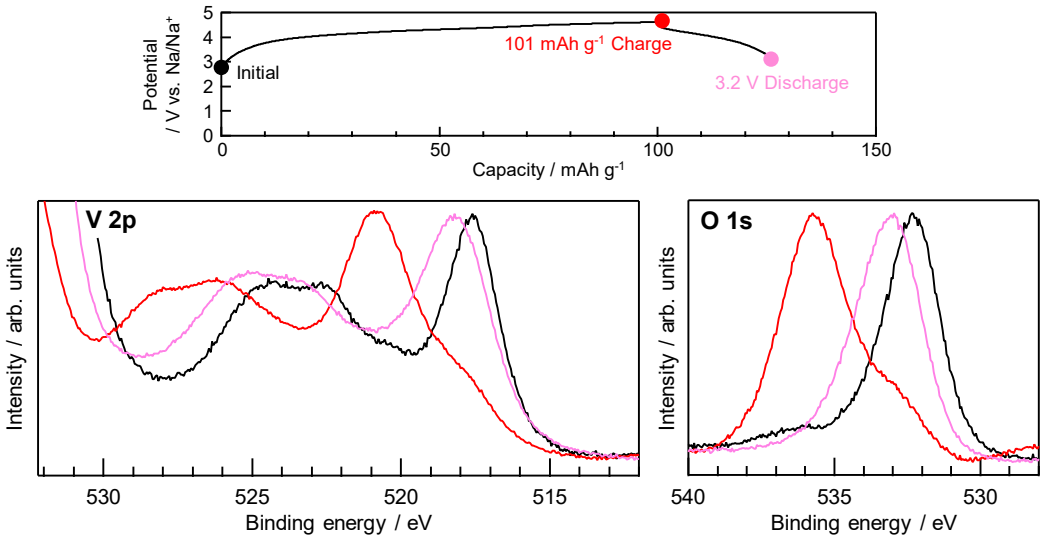

Fig. S9 *Ex-situ* XPS spectra of $NaV(SO_4)_2$ at different charge–discharge states during the first cycle of cells constructed using 1 M $NaClO_4$ in EC:DMC (1:1 by volume) as the electrolyte. The measured samples were obtained from the disassembled coin cells after they were washed with DMC. To eliminate the mismatch resulting from sample charging, the binding energy values were corrected on the basis of the binding energy of the adventitious carbon compared with the standard binding energy of carbon.

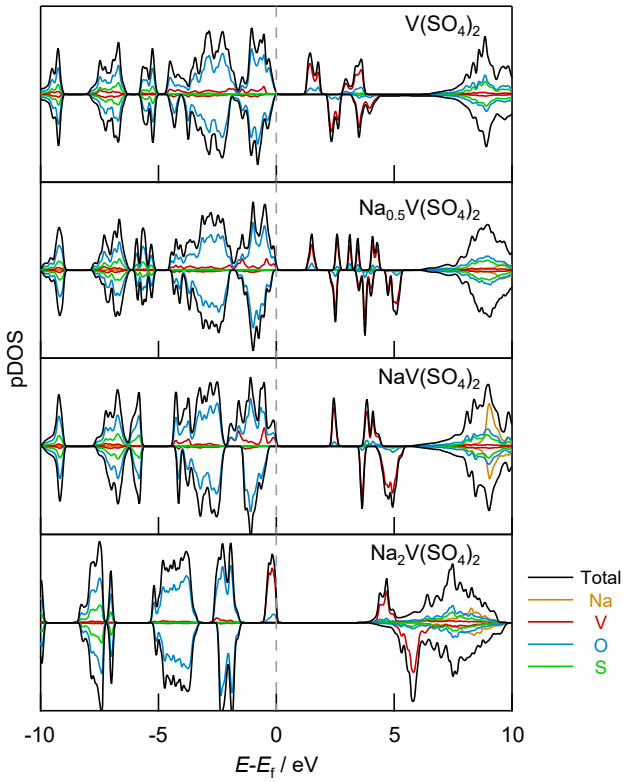

Fig. S10 Calculated partial density of states (pDOS) for $Na_xV(SO_4)_2$ (x = 0, 0.5, 1, 2), as obtained using DFT calculations. The dashed line is the Fermi energy level.

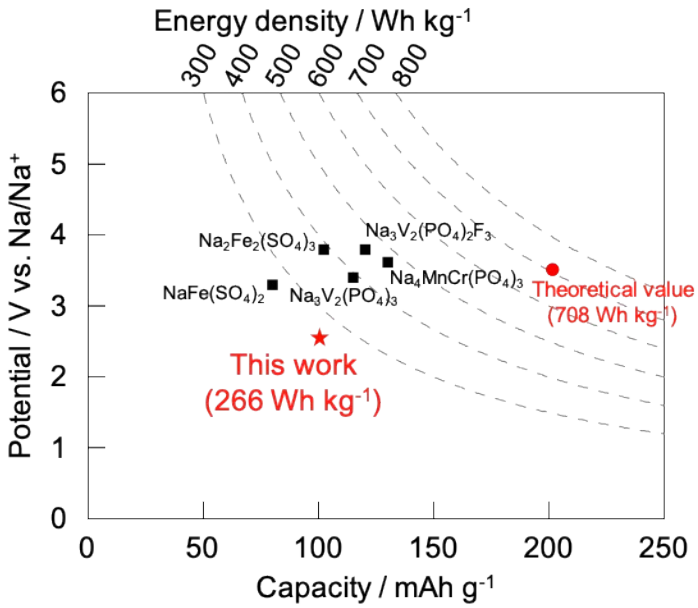

Fig. S11 Capacity and potential plots of competitive polyanionic cathode materials for Na-ion batteries.

Theoretical value of $NaV(SO_4)_2$ is also plotted.[2–6]

Table S1 Crystallographic parameters of as-synthesized $NaV(SO_4)_2$, as obtained by Rietveld refinement using the RIETAN-FP program.[7]

Chemical formula	$NaV(SO_4)_2$
Formula weight	266.056
Crystal system, space group	Monoclinic, *C*2/*m*
Temperature	~298 K (ambient)
a, *b*, *c* / Å	8.0289(16), 5.16063(10), 7.1370 (17)
α, *β*, *γ* / degrees	90, 91.870(12), 90
V / Å^3	295.56(11)
Z	2
Calculated density / g cm^{-3}	2.989
R_{wp}	6.16%
R_p	4.63%
R_e	4.76%
R_B	2.80%
R_F	1.58%
S	1.29
Goodness of fit	1.68
Radiation	Cu Kα

Atom	Wyckoff site	*x*	*y*	*z*	occ.	B_{iso} / Å^2
Na1	2c	0	0	1/2	1	2.03(6)
V1	2a	0	0	0	1	0.41(2)
S1	4i	0.3619(15)	0	0.2211(15)	1	1.06(3)
O1	4i	0.2351(3)	0	0.0605(3)	1	1.28(3)
O2	4i	0.2884(3)	0	0.4066(3)	1	1.28(3)
O3	8j	0.4686(18)	0.2343(3)	0.2005(19)	1	1.28(3)

Table S2 Magnetic moment and Bader charge on V and O sites in $Na_xV(SO_4)_2$ (x = 0, 0.5, 1, 2) structures.

	Magnetic moment / μ_B		Bader charge / e	
	V	O	V	O
$Na_2V(SO_4)_2$	2.752	0	1.574	−1.373
$NaV(SO_4)_2$	1.912	−0.004	2.024	−1.328
$Na_{0.5}V(SO_4)_2$	1.511	−0.013	2.139	−1.284
$V(SO_4)_2$	1.093	−0.018	2.244	−1.234

References

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