Exploration of A$_2$VO(SO$_4$)$_2$ (A = Li, Na) as Electrode for Li-ion and Na-ion Batteries

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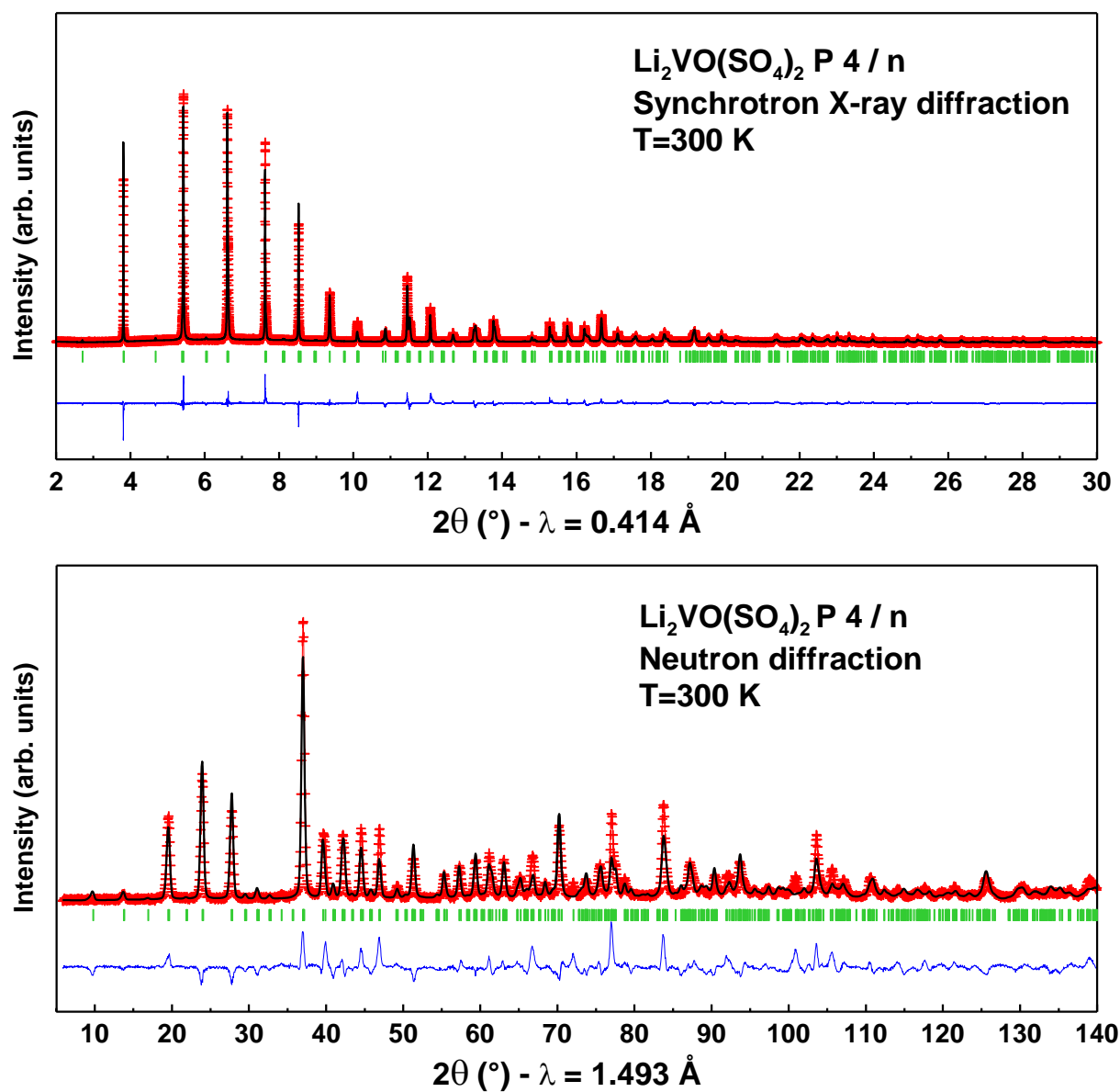
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SUPPORTING INFORMATION

Table S1. Structural parameters for $Na_2VO(SO_4)_2$ deduced from the Rietveld refinement of the synchrotron X-ray diffraction patterns at 300 K.

| $Na_2VO(SO_4)_2$	Space Group: $P\,2_1\,2_1\,2_1$					
a= 6.310020(13) Å, b = 6.807419(13)Å, c= 16.69296(3) Å						
V= 717.045(3) Å³, density= 2.826 g/cm³, Z= 4						
Atom	Wyckoff site	X	y	z	Occupancy	B(Å²)
Na1	4a	0.6744(4)	0.1511(4)	0.59123(17)	1	3.12(6)
Na2	4a	0.3706(3)	0.1083(4)	0.23909(13)	1	1.54(5)
V	4a	0.53277(17)	0.14911(14)	0.91053(6)	1	0.71(2)
S1	4a	0.0340(2)	0.0853(2)	0.93224(9)	1	0.99(3)
S2	4a	0.8567(2)	0.1042(2)	0.25017(9)	1	0.88(3)
O1	4a	0.2166(5)	0.2001(4)	0.9056(2)	1	0.21(7)
O2	4a	0.5236(6)	0.4012(5)	0.97815(19)	1	1.01(7)
O3	4a	0.5104(6)	0.3592(5)	0.81536(20)	1	0.93(7)
O4	4a	0.8505(5)	0.1931(5)	0.8969(2)	1	0.92(7)
O5	4a	0.5157(5)	-0.0493(5)	0.8226(2)	1	0.94(7)
O6	4a	0.5374(5)	-0.0099(4)	0.9815(2)	1	1.19(8)
O7	4a	0.0478(5)	-0.1130(5)	0.9078(2)	1	1.46(8)
O8	4a	0.2722(6)	-0.2274(5)	0.2331(2)	1	0.84(8)
O9	4a	-0.2747(5)	-0.0647(5)	0.22501(19)	1	0.51(7)

Reliability parameters: χ^2= 5.96; Bragg R-factor= 5.64%

Figure S1. *Unsatisfactory* Rietveld refinement of synchrotron and neutron diffraction patterns obtained for $Li_2VO(SO_4)_2$ (T=300 K) using the structure model of $Li_4VO(PO_4)_2$ (space group: $P\ 4/n$). The red crosses, black continuous line and bottom blue line represent the observed, calculated, and difference patterns, respectively. Vertical green tick bars mark the Bragg reflections.
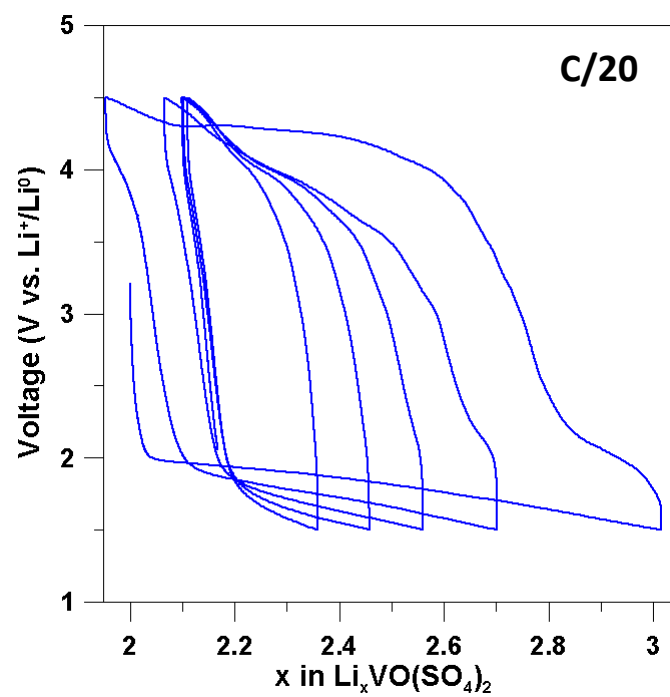
Figure S2. Voltage – composition curve for $Li_2VO(SO_4)_2$ upon discharge with 1 Li^+ fixed to be inserted in the first cycle.
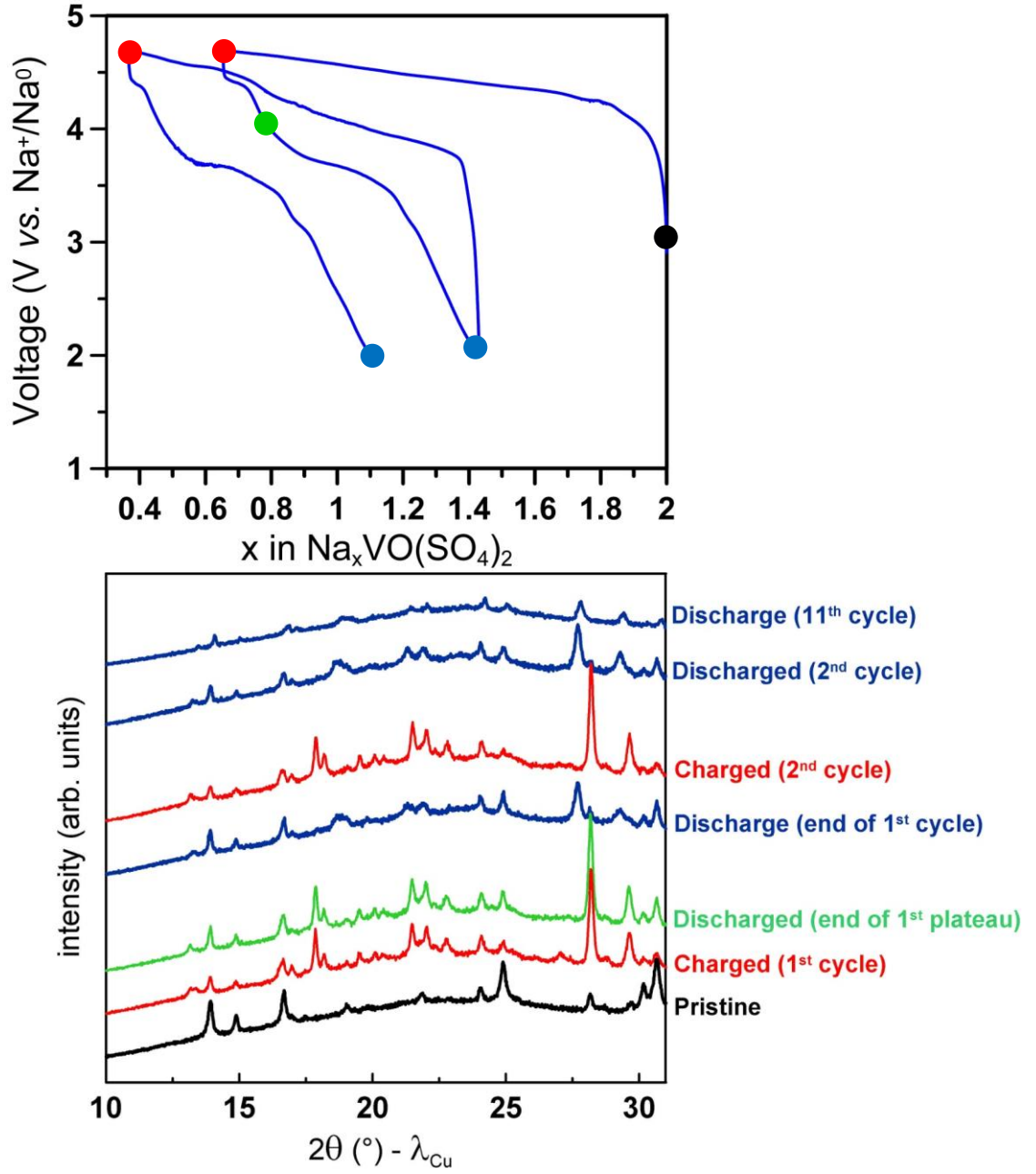
Figure S3. In situ XRD patterns recorded for a $Na_2VO(SO_4)_2$/Na cell behind a Be window while the cell is charged to 4.7 V (lower panel), the voltage–composition curve is shown (upper panel). The black pattern corresponds to the pristine phase, the red one refers to the fully oxidized sample (for both 1st and 2nd cycle), the green pattern refers to reduced sample at the end of 1st plateau, and the blue patterns were recorded at the subsequent discharge states (for all the 1st, 2nd, and 11th cycles). It indicates a reversible cycling from the 2nd cycle of this process.
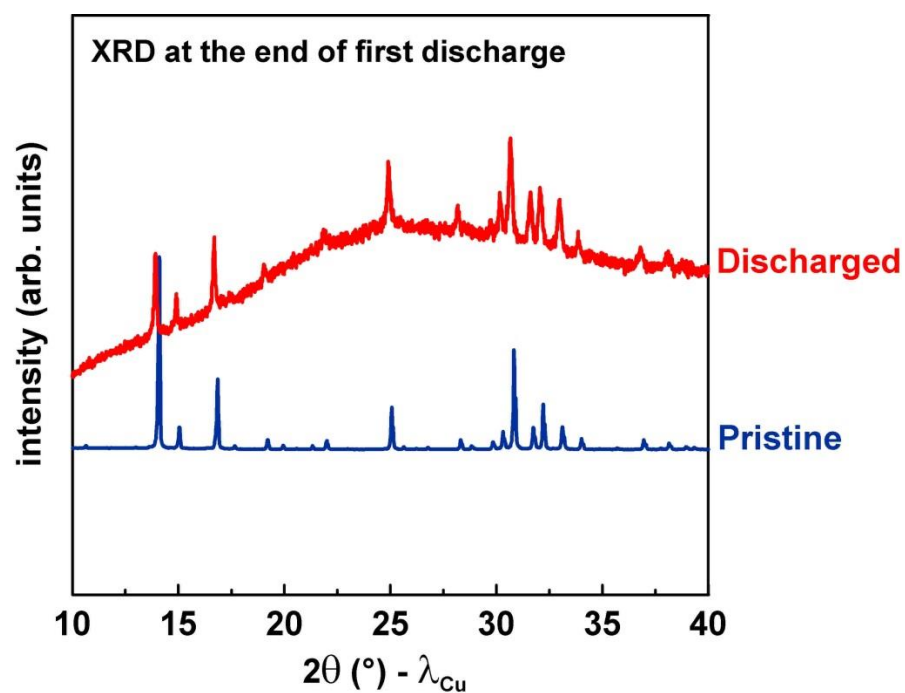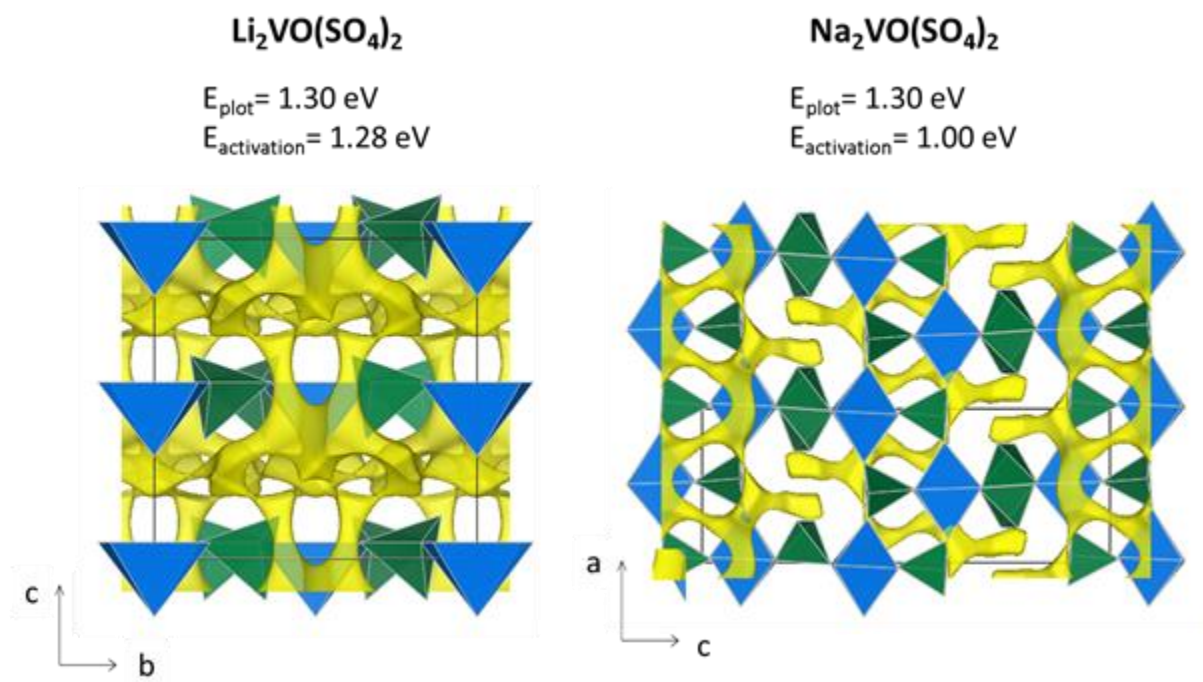
Figure S4. X-ray diffraction patterns collected at the end of first discharge of $Na_2VO(SO_4)_2$/Li cell compared to the pristine phase of $Na_2VO(SO_4)_2$. Their similar profiles suggest that the $Na_2VO(SO_4)_2$ structural framework is preserved through the cycling process.
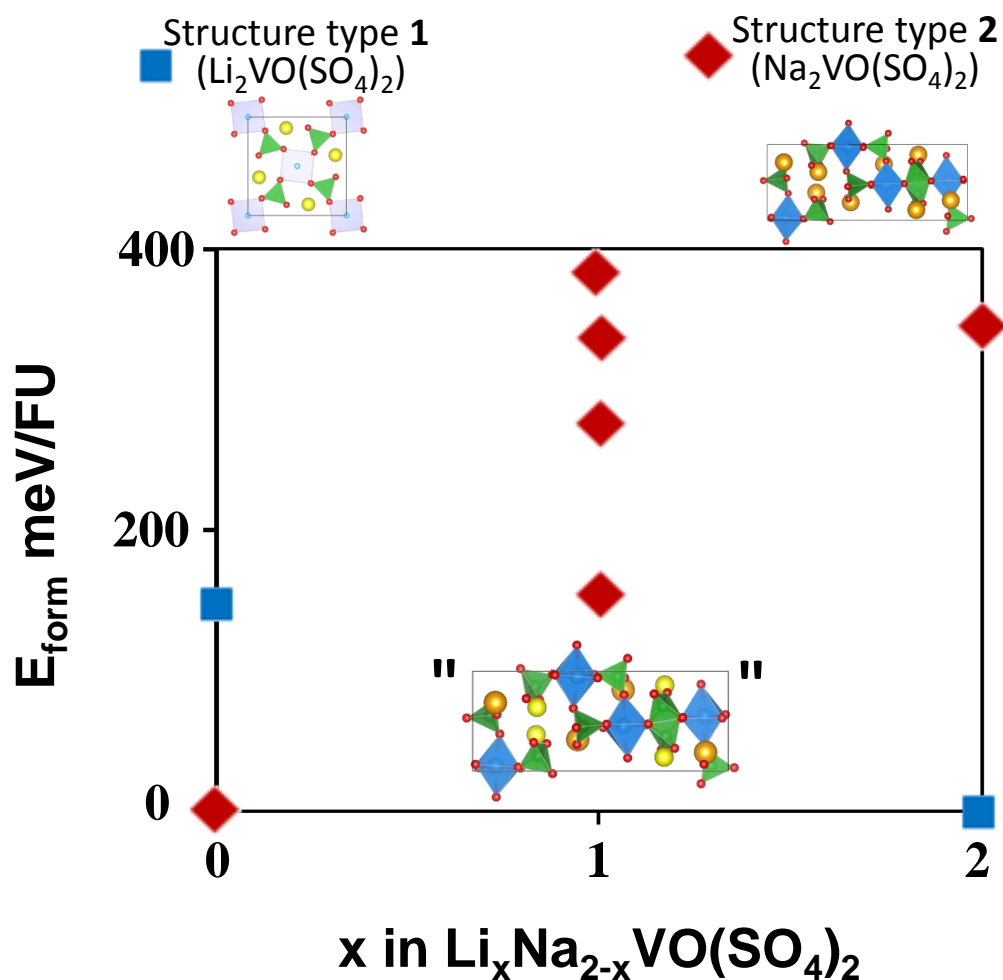
Figure S5. We investigate the thermodynamic stability of the Li/Na substitution in the two $A_2VO(SO_4)_2$ (A=Li, Na) structural type. x=0 and x=2 on the x-axis refer to the stoichiometry $Na_2VO(SO_4)_2$ and $Li_2VO(SO_4)_2$ phases that adopts structure type 2 and 1, respectively. As expected, for x=0 (corresponding to the stoichiometry $Na_2VO(SO_4)_2$), the polymorph of structural type 2 (red) is found far more stable than the polymorph of structural type 1 (blue) where all Li where substituted by Na. Similarly, for x=2 this is the opposite, the polymorph of structural type 1 is found far more stable than the polymorph of structural type 2 where all Na where substituted by Li. Going to intermediate stoichiometry (x=1) that is $NaLiVO(SO_4)_2$, the 4 different configurations inequivalent by symmetry, obtained by exchanging Na by Li in the structure type 2, where tested (since this was shown to be experimentally feasible). In all cases we obtain polymorphs having a formation energy above the energy of a "phase segregation" (the 0 reference). Among the 4 polymorphs tested the one close to stabilization is shown. Overall, this suggests that no solid solution is expected thermodynamically for this $NaLiVO(SO_4)_2$ stoichiometry. The energy of zero reference is defined here in as

$E = x/2$ (E_f of $Li_2VO(SO_4)_2$) + $(2-x)/2$ (E_f of $Na_2VO(SO_4)_2$).

Li$_2$VO(SO$_4$)$_2$

E$_{plot}$= 1.30 eV
E$_{activation}$= 1.28 eV

Na$_2$VO(SO$_4$)$_2$

E$_{plot}$= 1.30 eV
E$_{activation}$= 1.00 eV

Figure S6. Bond valence energy landscape (BVEL) deduced for (a) Li$_2$VO(SO$_4$)$_2$ and (b) Na$_2$VO(SO$_4$)$_2$. These BVEL were created using the BondStr program available in the FullProf suite,[1] using soft bond valence sum parameters developed by S. Adams.[2] BVEL are obtained from soft-BVS parameters by transforming them valence into energy units, using a Morse-type potential for the attractive part and a screened Coulomb potential for the repulsive part.[3] The probing ion, in our case Li$^+$ for Li$_2$VO(SO$_4$)$_2$ and Na$^+$ for Na$_2$VO(SO$_4$)$_2$, is placed in all points of the unit cell and its interaction energy, using the above mentioned potential, is calculated up to a common distance of 10 Å. In the figure, SO$_4$ are coloured in green, VO$_n$ polyhedra in blue, and the yellow domains correspond to the migration paths for Li/Na in the structures, both plotted using an iso-surface value of 1.30 eV over the minimum energy. The energies leading to an infinitely connected path for Li in Li$_2$VO(SO$_4$)$_2$ or Na in Na$_2$VO(SO$_4$)$_2$ are 1.28 eV and 1.00 eV, respectively (these energies are denoted "activation energies" in the paper).

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3   S. Adams, in Bond Valences, eds. I. D. Brown and K. R. Poeppelmeier, Springer Berlin Heidelberg, 2013, pp. 91–128.