## Supplementary Information

## **Robust Vanadium Pentoxide Electrodes for Sodium and Calcium Ion**

## **Batteries: Thermodynamic and Diffusion Mechanical Insights**

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Section 1: The effect of U values on the energetic and electronic properties of  $V_2O_5$ . Three U values (U = 2.45<sup>1</sup>, 3.1<sup>2</sup> and 4.0 eV<sup>3</sup>) were taken into consideration. The calculated formation energies for Ca<sub>x</sub>V<sub>2</sub>O<sub>5</sub> by using these three U values are very similar (Fig. S1). Previous theoretical calculations<sup>5</sup> predicted that  $\delta$ -CaV<sub>2</sub>O<sub>5</sub> is about 0.27 eV per formula unit more stable than  $\alpha$ -CaV<sub>2</sub>O<sub>5</sub>, in agreement with the fact that  $\alpha$ -CaV<sub>2</sub>O<sub>5</sub> can be synthesized experimentally<sup>6, 7</sup>. However, the energy difference between  $\alpha$ -CaV<sub>2</sub>O<sub>5</sub> and  $\delta$ -CaV<sub>2</sub>O<sub>5</sub> by PBE+vdW+U are quite similar with the relatively large U values (U = 3.1 and 4.0 eV). On the other hand, the calculated band gap with U = 2.45 eV is 2.05 eV (Fig. S2), which is smaller than the experimental value of ~2.35 eV<sup>4</sup>. As the value of U increases to 4.0 eV, the band gap becomes 2.31 eV, which is more close to the experimental value. Thus, a Hubbard U correction of 4.0 eV is added on the vanadium *d*-electrons to obtain the energetic properties in our study.



**Fig. S1** The formation energies  $(\Delta_f E_x)$  as a functional of Ca concentration, which were calculated by PBE+vdW+U, where (a) U = 2.45 eV, (b) U = 3.1 eV, (c) U = 4.0 eV, as well as by (d) PBE+U (4.0 eV). The blue and yellow solid lines indicate the formation energies of the  $\alpha$ -phase and  $\delta$ phase, respectively. The same numbers in (c) and (d) indicate the same Ca-intercalation configurations calculated by vdW correction and non-vdW correction, respectively.



Fig. S2 The total density of states (DOS) of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> calculated by PBE+vdW+U with (a) U=2.45 eV, (b) U=3.1 eV and (c) U=4.0 eV, respectively. The band energies are obtained by aligning the orbital energies with respect to the vacuum level.

Section 2: Na/Ca-V<sub>2</sub>O<sub>5</sub> ground state hull. Since the intercalation ordering would vary for different Na/Ca concentrations, some strategies were followed to explore the structural evolution of  $\alpha$ - and  $\delta$ -V<sub>2</sub>O<sub>5</sub> in the intercalation process. Here we take Na in  $\alpha$ -V<sub>2</sub>O<sub>5</sub> as an example, the supercell with 84 (V<sub>24</sub>O<sub>60</sub>) atoms was used to explore the structural evolution, and six positions (A1, A2, A3 and B1, B2, B3) could be found for Na/Ca intercalated in a single channel (Fig. S3). Thus, with the consideration of point group symmetry, one (One atom intercalation,  $A_x$  or  $B_x$ , x=1, 2, 3), three (Two atoms intercalation, A<sub>1</sub>+A<sub>2</sub>, A<sub>1</sub>+B<sub>1</sub>, A<sub>1</sub>+B<sub>2</sub>), three (Three atoms intercalation, A<sub>1</sub>+A<sub>2</sub>+A<sub>3</sub>,  $A_1+A_2+B_1$ ,  $A_1+A_2+B_2$ ), three (Four atoms intercalation, the same as the case of two atom intercalation), one (Five atoms intercalation, the same as the case of one atom intercalation) and one (Full occupation) different configurations could be found for Na/Ca intercalation into a single channel at the concentration of 0.083, 0.167, 0.25, 0.333, 0.417 and 0.5, respectively. The most stable configurations of Na/Ca to intercalated into a single channel at each of the concentrations was determined. For this, only different ways of stacking with the fixed minimum energy arrangements in each channel were calculated to explore the most stable configuration of Na/Ca-ions intercalated into all galleries. As a result, 43 configurations were used to study the process of Na intercalation into  $\alpha$ -V<sub>2</sub>O<sub>5</sub>, as the blue squares shown in Fig. S4a. Ultimately, the above procedure was also employed for Na intercalation into  $\delta$ -V<sub>2</sub>O<sub>5</sub> and Ca intercalation into  $\alpha$ - and  $\delta$ -V<sub>2</sub>O<sub>5</sub>. A total of 172 configurations were calculated to explore the  $\alpha$ - and  $\delta$ -Na<sub>x</sub>/Ca<sub>x</sub>V<sub>2</sub>O<sub>5</sub> ground state hulls in our study, as shown in Fig. S4.

Notably, the previous theoretical calculations with PBE+U predicted that  $\delta$ -CaV<sub>2</sub>O<sub>5</sub> is more stable than  $\alpha$ -CaV<sub>2</sub>O<sub>5</sub>,<sup>5</sup> in agreement with the fact that  $\alpha$ -CaV<sub>2</sub>O<sub>5</sub> can be synthesized experimentally<sup>6, 7</sup>. Carrasco et al.<sup>8</sup> also suggested that that PBE+U could describe the right stability without the addition of vdW interactions, at the expense of precise lattice parameters. In order to check this, further calculations are performed. As shown in Figure S1(c) and (d), the PBE+U without including vdW shows that  $\alpha$ -

 $CaV_2O_5$  is about 0.207 eV per formula unit more stable than  $\delta$ -CaV<sub>2</sub>O<sub>5</sub>, consistent with other theoretical and experimental studies<sup>5-7</sup>. Thus, PBE+U could describe the right relative stability for the  $\alpha$ -CaV<sub>2</sub>O<sub>5</sub> and  $\delta$ -CaV<sub>2</sub>O<sub>5</sub>.



Fig. S3 Schematic illustration of different positions for Na/Ca storage in  $\alpha$ -V<sub>2</sub>O<sub>5</sub>



**Fig. S4** The ground state hull of (a) Na and (b) Ca in both  $\alpha$ - and  $\delta$ -V<sub>2</sub>O<sub>5</sub>. The formation energy per formula unit ( ${}^{\Delta}_{f}E_{x}$ ) has been plotted with respect to Na/Ca concentration.

Section 3: The effect of exchange-correlation functionals on the migration behavior of  $V_2O_5$ . We have investigated the Ca migration properties at the dilute concentration (charged state) by GGA+U functional, the calculated energy barriers were shown in Fig. S5. The results for different U (= 2.45, 3.1 and 4.0 eV) are quite

similar ( $\sim 0.85$  eV) with relatively less variation. This is significantly lower than the full intercalation state due to the high Coulomb repulsion between alkali-ions at high concentration. Ca migration in bulk  $\delta$ -V<sub>2</sub>O<sub>5</sub> has an even smaller barrier (about 0.2 eV) as reported by Gautam<sup>5</sup> and Rong<sup>9</sup>, this could be attributed to their different choice of NEB calculation method. It was suggested that the pronounced metastability of the electronic states along the ion migration path with DFT+U simulation would result in the poor computational convergence. Thus, the standard GGA was used for the NEB calculations in their work. For comparison we also calculate the Ca diffusion barrier using a standard GGA functional instead of the GGA+U functional. A barrier of 0.46 eV was found for Ca migration in bulk  $\delta$ -V<sub>2</sub>O<sub>5</sub> at the dilute concentration. This is comparable with the ~0.2 eV barrier reported by Gautam and Rong, and indicates more promising Ca migration in  $\delta$  phase than in the  $\alpha$  phase. The small difference could be attributed to the different vdW functional (vdW-DF was used in our work and vdW-DF2 was used in Gautam and Rong's work) and different Hubbard U correction (2.45 eV in our calculation and 3.1 eV in Gautam and Rong's work) used in the NEB calculations.



**Fig. S5** The energy barriers of dilute Ca diffusion in  $\delta$ -V<sub>2</sub>O<sub>5</sub> which is calculated by GGA (Red), GGA+U(=2.45 eV) (Blue), GGA+U(=3.1 eV) (Green) and GGA+U(=4.0 eV) (Yellow) functionals, respectively.

Section 4: The relativistic effect in V<sub>2</sub>O<sub>5</sub> systems. In order to account for relativistic effects in the systems, we have calculated the band gap of  $\alpha$ - and  $\delta$ -V<sub>2</sub>O<sub>5</sub> including the spin-orbit coupling (SOC), as shown in the figure and table below. The results for the  $\alpha$ - and  $\delta$ -V<sub>2</sub>O<sub>5</sub> phases are very similar. All the bands at the  $\Gamma$  and T points are spin split, where the spin-orbit splitting at the top of the VB (T point) was 117 meV for  $\alpha$ -V<sub>2</sub>O<sub>5</sub> and 202 meV for  $\delta$ -V<sub>2</sub>O<sub>5</sub>. The same splittings for the CB vary from 56 meV for  $\alpha$ -V<sub>2</sub>O<sub>5</sub> to 108 meV for  $\delta$ -V<sub>2</sub>O<sub>5</sub>, which are smaller than those of the VB, but definitely large enough so as to be observed. Despite this discrepancy, these two methods provide a similar electronic trend, *e.g.*, the spin-orbit splitting predicted by PBE+U+SOC methods are comparable in different V<sub>2</sub>O<sub>5</sub> are based on the PBE+U functional in our study.



Fig. S6 Electron energy band structures of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> calculated by PBE+U functional: a) bands calculated without SOC, b) bands calculated with SOC.

**Table S1** The spin-orbit splitting  $\Delta n$  (n labeled bands, see the above figure) at the CB and VB calculated for  $\alpha$ - and  $\delta$ -V<sub>2</sub>O<sub>5</sub> with the PBE+U+SOC.

Method		С	V	V-1	V-2
DFT/DFT+SOC	$\alpha$ -V <sub>2</sub> O <sub>5</sub>	56	117	-32	-19
$\Delta_n(\mathbf{K}) (\mathrm{meV})$					

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