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**Electronic Supplementary Information** 

# Better than crystalline: amorphous vanadium oxide for sodium-ion battery

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# **Experimental Procedure**

## Gel synthesis

The films synthesized and examined in this work were prepared *via* electrochemical deposition using a diluted vanadium pentoxide solution. In brief,  $V_2O_5$  powder (99.8%, Alfa Aesar) was added to deionized water and  $H_2O_2$  (30wt%, Sigma Aldrich) to yield a solution with a  $V_2O_5$  concentration ( $C_V$ ) of 0.3 M and with a  $H_2O_2$  to V ratio of 8.05:1. The resulting solution was stirred for 15 minutes, and then ultrasonicated for 10 minutes. Deionized water was added until the  $C_V$  concentration was 0.06 M, after which the solution was ultrasonicated for an additional 80 minutes.

## Deposition

The synthesized gel was further diluted to a  $C_V$  concentration of 7.5 mM in deionized water and stirred until the transparent solution was free of floculates. Electrochemical deposition was carried out using Ni-foil (0.125 mm thick, Sigma Aldrich) as the deposition substrate and Pt foil as the counter electrode. The distance between the two electrodes was kept constant at 1.5 cm and the deposition voltage was (-2.4) V. The deposition process was carried out for 30 minutes unless otherwise noted. After being dried at 50°C overnight the films were either annealed at 180°C under vacuum or 450°C in ambient for 3 hours.

## Characterization

The phase and crystallite size of the annealed  $V_2O_5$  films were studied using X-ray diffraction (XRD, D8 Bruker X-ray diffractometer) with Cu-K<sub>a</sub> radiation over the range of 10° to 70° (20), a step size of 0.02°, and an exposure time of 10 s. The accelerating voltage and current were 40 kV and 40 mA, respectively. Infrared absorption spectra were recorded using a Perkin Elmer 1640 Fourier Transform Infrared (FTIR, Perkin Elmer) Spectrophotometer with KBr pellets. X-ray photoelectron spectroscopy (XPS) was completed using a Surface Science Instruments S-probe spectrometer. The X-ray spot size was 800 x 800 µm and the take-off angle was 55°, corresponding to a sampling depth of approximately 50-70 Å. XPS data analysis was carried out using the Service Physics ESCA 2000-A analysis program (Service Physics, Bend, OR). X-ray absorption spectroscopy (XAS) was measured at the Advanced Photon Source, 13ID-E in transmission mode. Several layers of V<sub>2</sub>O<sub>5</sub> were dispersed on Kapton tape for the measurement to minimize the effect of thickness inhomogeneity, and the data sets were processed using the IFFEFIT software package. Microscopy investigations were carried out using a JEOL JSM-7000F scanning electron microscope (SEM) and FEI Tecnai G2 F20 transmission electron microscope (TEM) operating at 200 kV. The nitrogen sorption was performed using a Quantachrome NOVA 4200e. The specific surface area, micropore, and mesopore volumes were determined using multipoint Brunauer–Emmett–Teller (BET), t-method, and Barrett–Joyner–Halenda (BJH) desorption analyses, respectively. Thermogravimetric (TGA) analysis of the V<sub>2</sub>O<sub>5</sub> films were investigated from room temperature to 450°C (TGA 7, PerkinElmer) under nitrogen flow at a heating rate of 5°C min<sup>-1</sup>.

## **Electrochemical analysis**

For electrochemical analysis, 2016 type half-cells were assembled in a glove box (Mbraun) filled with high purity argon. Metallic sodium (Sigma Aldrich), 1 M NaClO<sub>4</sub> in propylene carbonate, and Celgard 2400 membrane were used as the counter/reference electrode, electrolyte, and separator, respectively. Lithium metal foil and a 1 M LiPF<sub>6</sub> ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v) solution were used as the counter/reference electrode and electrolyte, respectively, for the Li-ion half-cells. Cyclic voltammetry (CV) was completed using an electrochemical analyzer (CH Instruments, Model 605C) in the voltage range of 3.8-1.5 V (vs. Na/Na<sup>+</sup>) at scan rates ranging from 0.1 to 1.0 mV s<sup>-1</sup>. The current density and cycle stability performance of the V<sub>2</sub>O<sub>5</sub> films

were evaluated using an Arbin Battery Tester (BT-2000, Arbin Instruments) operating at room temperature. The half-cells were tested within the voltage range of 3.8-1.8 V vs. Na/Na<sup>+</sup> at various charging rates based on the weight of the active material alone, and assuming a 1 C current density of 236 mA g<sup>-1</sup>.

#### **Gel Reaction Pathway**

The method of gel preparation was adopted from previous work, and involved several parallel or sequential chemical reactions in association with the decomposition of excess hydrogen peroxide:

$$\begin{split} &V_2O_5 + 4H_2O_2 \rightarrow 2[VO(O_2)_2(OH_2)]^- + 2H^+ + H_2O \qquad (1) \\ &V_2O_5 + 2H^+ + 2H_2O_2 + 3H_2O \rightarrow 2[VO(O_2)(OH_2)_3]^+ + O_2 \qquad (2) \\ &2[VO(O_2)_2(OH_2)]^- + 4H^+ + 2H_2O \rightarrow 2[VO(O_2)(OH_2)_3]^+ + O_2 \qquad (3) \\ &2[VO(O_2)(OH_2)_3]^+ \rightarrow 2[VO_2]^+ + O_2 + 6H_2O \qquad (4) \\ &[VO_2]^+ \rightarrow gelation \qquad (5) \end{split}$$

The initially aqueous  $V_2O_5$  solution changed color from yellow to orange following the addition of  $H_2O_2$ , which is ascribed to the formation of the diperoxovanadate anion  $[VO(O_2)_2(OH_2)]^-$  (Equation 1). The solution then took on a red color following sonication for several minutes, which suggests that the monperoxovanadate cation  $[VO(O_2)(OH_2)_3]^+$  is the main ionic species in the solution (Equations 2 & 3). The release of oxygen gas was noted by vigorous bubbling that occurred during the mixing of  $V_2O_5$  and  $H_2O_2$ . The solution was then further diluted to 0.06 M and sonicated for 80 minutes, during which the color gradually turned to a brownish red while the solution was notably more viscous. These changes could be attributed to the transformation of the dioxovanadium cation  $[VO_2]^+$  (Equation 4). The increased viscosity and brownish red hue of the gel suggests that  $V_2O_5 \cdot nH_2O$  gelation has occurred (Equation 5). After sonication, the brownish red mixture of  $V_2O_5 \cdot nH_2O$  gel and solution was diluted to 7.5 mM for deposition. During electrochemical deposition, electrons were directed towards the negatively charged Pt counter electrode, and the V<sup>5+</sup> species from the  $V_2O_5$  colloidal particles and  $[VO_2]^+$  dioxovanadate cations were reduced on the surface of the Ni-foil (Equations 6 & 7):

$$V_2O_5 + 4H^+ \rightarrow 2[VO_2]^+ + 2H_2O$$
 (6)  
 $[VO_2]^+ + e^- \rightarrow VO_2$  (7)

 $VO_2$  serves as the nucleation center that initiates and catalyzes the formation of  $V_2O_5 \cdot nH_2O$  through low pH conditions upon deposition.

$$2[VO_2]^+ + nH_2O \rightarrow V_2O_5 \bullet nH_2O + 2H^+$$
(8)

#### Characterization

Nitrogen adsorption-desorption isotherms were collected in order to evaluate the surface area and pore characteristics. The Barrett-Joyner-Halenda (BJH) pore size distributions obtained from the isotherms suggest that the  $180^{\circ}$ C/vac and  $450^{\circ}$ C/air annealed samples contain broadly distributed pores, the majority of which are smaller than 15 nm, with a respective average pore size of 3.22 and 3.19 nm; the overall pore volumes were nearly identical as well. The Brunauer-Emmett-Teller (BET) derived specific surface areas were 38.7 and 32.6 m<sup>2</sup> g<sup>-1</sup>, respectively, confirming that the varying thermal treatments had little change on morphology outside of slight coarsening and surface roughening effects.



Fig. S1. (a) BJH desorption pore size distributions, (b) nitrogen adsorption-desorption isotherms, and (c) TGA analysis of the various V<sub>2</sub>O<sub>5</sub> samples

The amount of water in the samples was examined using thermogravimetric analysis (TGA) and was quantified at approximately 12% and 0.4% for the vacuum and air annealed materials, respectively.

TEM was carried out in order to qualitatively compare the extent of crystallinity inherent to each sample. Fig. S2(a-c) displays the TEM images collected for the as-processed, 180°C/vac, and 450°C/air samples, respectively. The inset in each figure corresponds to its respective FFT which can also be used to, more objectively, interpret the degree of crystallinity. The amorphous nature of the as-processed and 180°C/vac samples is noted, as revealed in Fig. S2a and S2b. Moreover, the as-processed and 180°C/vac annealed samples have near similar trace amounts of crystallographic order as seen in the micrographs and their corresponding diffuse FFT spots. These findings, when paired with TGA, indicate that the low-temperature vacuum annealing process effectively maintains the non-crystalline, amorphous quality of the  $V_2O_5$  material while removing surface absorbed water. The single crystallinity of the 450°C/air sample is evident, as noted by the atomic columns of the crystallographic lattice; the FFT pattern (Fig. S2c inset) shows clean  $V_2O_5$  diffraction, attesting to the highly crystalline nature of the material. This characterization is also supported by the measured lattice interspacing of 3.34 Å that corresponds to the  $d_{(001)}$  spacing and the distance between two (001) crystallographic planes of the orthorhombic  $V_2O_5$  structure.



Fig. S2. High-resolution TEM images of the (a) as-processed, (b)  $180^{\circ}$ C/vac annealed, and (c)  $450^{\circ}$ C/air annealed V<sub>2</sub>O<sub>5</sub> samples. The inset in each figure is the corresponding FFT pattern for the displayed image. The deposited V<sub>2</sub>O<sub>5</sub> films were exfoliated from their Ni-foil substrate following thermal treatment.

From XPS, the location of the main O1s peak, attributed to lattice oxygen (O-V), is indicative that the material is  $V_2O_5$ , but the measured peak position diminishes with annealing temperature. The as-processed,  $180^{\circ}$ C/vac, and  $450^{\circ}$ C/air annealed specimens recorded O1s peak positions of 530.9, 530.5, and 530.1 eV, respectively, while the equivalent literature standard is typically taken to be 530.0 eV.<sup>[1]</sup> The adjusted  $V2p_{3/2}$  peak binding energy was 518.0, 517.6, and 517.2 eV for the as-processed,  $180^{\circ}$ C/vac, and  $450^{\circ}$ C/air specimens, respectively, which is consistent with literature reports for  $V_2O_5$ . As a whole, the  $V2p_{3/2}$  and O1s peaks for the non-crystalline materials were slightly shifted to higher binding energies than expected, but overall peak-to-peak spacing was maintaind.



Fig. S3. (a-c) High-resolution XPS O1s and V2p peak values and  $\Delta BE[O-V]$  for the as-processed, 180°C/vac annealed, and 450°C/air annealed V<sub>2</sub>O<sub>5</sub> samples compared to literature values for various vanadium oxide compounds; (d) broad survey and XPS spectra of the as-processed, 180°C/vac annealed, and 450°C/air annealed V<sub>2</sub>O<sub>5</sub> samples. Literature values taken from E. Hryha, E. Rutqvist, L. Nyborg, Surface and Interface Analysis, 44 (2012) 1022-1025.<sup>[1]</sup>

Table S1: XPS peak fit values for the as-processed,  $180^{\circ}$ C/vac annealed, and  $450^{\circ}$ C/air annealed V<sub>2</sub>O<sub>5</sub> samples.

Sample	Peak	Peak Location (eV)	$\Delta BE(O-V) (eV)$
as-processed	O 1s	530.9	12.0
	V 2p	518.0	12.9
180°C/vac	O 1s	530.5	12.0
	V 2p	517.6	12.9
450°C/air	O 1s	530.1	12.0
	V 2p	517.2	12.9



Fig. S4. XANES and of the V k-edge EXAFS for the as-processed, 180°C/vac annealed, and 450°C/air annealed V<sub>2</sub>O<sub>5</sub> samples.

The 450°C/air annealed sample was cycled against Li/Li<sup>+</sup> at a discharge rate of 44.7 mA g<sup>-1</sup> (0.1 C) and within the voltage window of 3.8-1.5 V leading to the formation of Li<sub>3</sub>V<sub>2</sub>O<sub>5</sub>. As expected, several discharge plateaus are clearly seen (Fig. S5a). The de/intercalation mechanism in crystalline materials is characteristically distinguished by plateaus in the discharge profile that indicate phase transformation, and ultimately define the limiting values for the stability of each phase that evolves during the process. The plateaus at 3.5, 2.9, and 2.4 V correspond to the  $\epsilon/\delta$ ,  $\delta/\gamma$ , and  $\gamma/\omega$  phase transitions, respectively. While this material exhibits a high initial capacity of approximately 390 mAh g<sup>-1</sup>, the irreversible phase transition associated with the intercalation of a third Li<sup>+</sup> per V<sub>2</sub>O<sub>5</sub> formula unit results in severe capacity degradation upon cycling.



Fig. S5. (a) Initial discharge voltage profile curves for the crystalline ( $450^{\circ}$ C/air annealed)  $V_2O_5$  cycled against Li/Li<sup>+</sup> at 44.7 mA g<sup>-1</sup> current density (0.1 C); cyclic voltammetry profiles at various scan rates for the: (b) amorphous ( $180^{\circ}$ C/vac annealed) and (c) crystalline ( $450^{\circ}$ C/air annealed)  $V_2O_5$ .

#### References

1 E. Hryha, E. Rutqvist, L. Nyborg, Surf. Interface Anal. 2012, 44, 1022.