

AQUEOUS SYNTHESIS OF THREE SODIUM VANADIUM OXIDES AS CATHODE MATERIALS FOR ZINC-ION BATTERIES

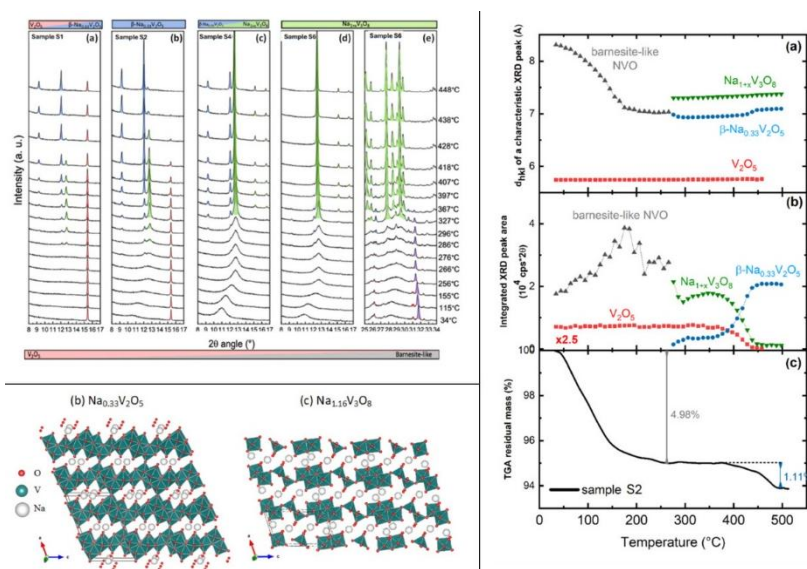
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ABSTRACT

Aqueous zinc-ion batteries (ZIBs) are gaining attention due to their high safety, low cost, and abundant materials though finding a suitable cathode material remains challenging. Vanadium pentoxide (V_2O_5) stands out for its high capacity but is prone to structural collapse due to the insertion and extraction of voluminous hydrated zinc ions and water molecules during cycling. Introduction of Na^+ ions into V_2O_5 is known to improve structural stability. In this work, we report the synthesis of $\beta\text{-Na}_{0.33}V_2O_5$ and $Na_{1.16}V_3O_8$ via an aqueous route involving stirring V_2O_5 powder in an aqueous NaCl solution, followed by heat treatment. The formation of the $\beta\text{-Na}_{0.33}V_2O_5$ tunnel phase and the $Na_{1.16}V_3O_8$ layered phase were followed by high-temperature X-ray diffraction. Samples of nanocrystalline barnesite, pure $\beta\text{-Na}_{0.33}V_2O_5$, and pure $Na_{1.16}V_3O_8$ were then compared in terms of morphology, specific surface area, and electrochemical performance as cathode materials in zinc-ion batteries. The tunnel structure of $\beta\text{-Na}_{0.33}V_2O_5$ ensured good stability, with a consistent discharge capacity of about 300 mAh g^{-1} at 0.1 A g^{-1} but did not allow easy insertion of zinc ions at high current density. Conversely, the layered structure of the nanocrystalline barnesite and $Na_{1.16}V_3O_8$ phases led to easier zinc ion insertion into the structure. Among the three materials, nanocrystalline barnesite exhibited the highest specific capacity (initially 319 mAh g^{-1} at 0.1 A g^{-1}) and displayed superior stability over 2000 cycles, attributed to sodium ions and water serving as stabilizing pillars for the structure.



1. Introduction

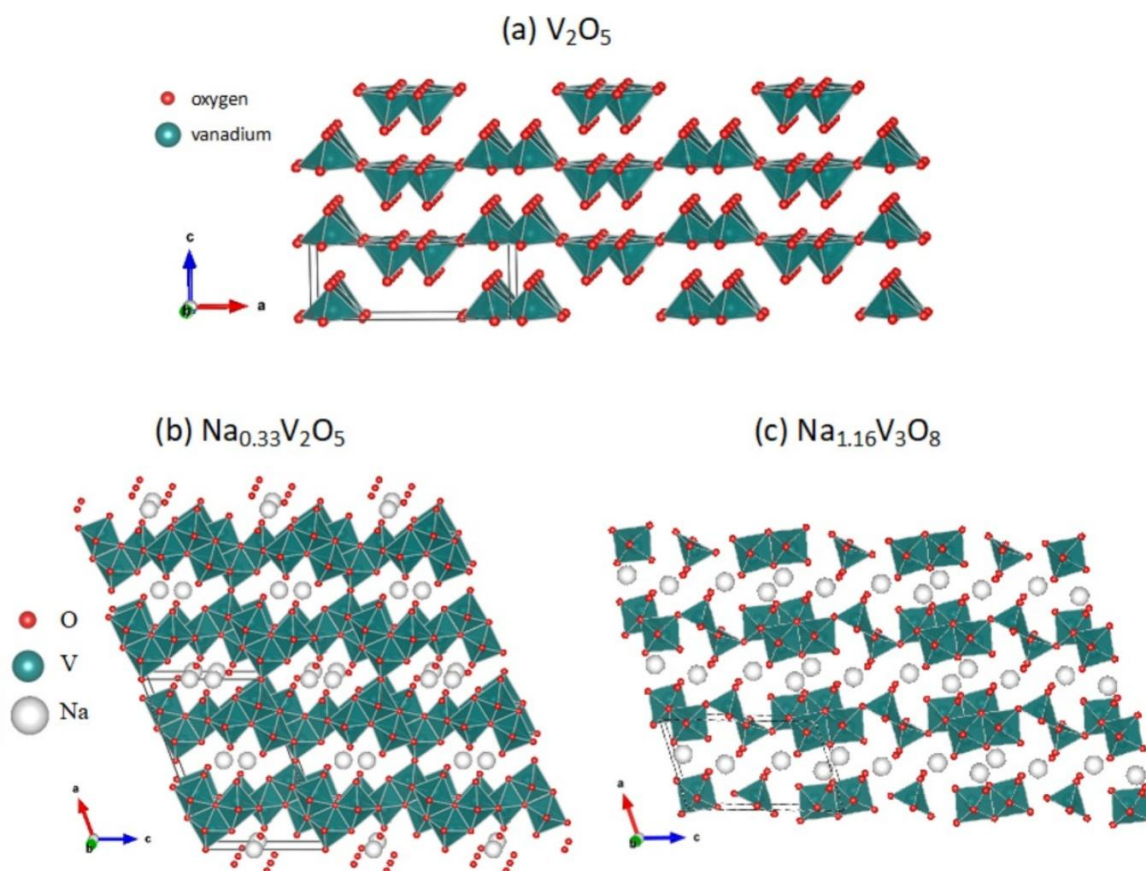
Rechargeable aqueous zinc-ion batteries (ZIBs) have recently received increasing attention due to their high safety, low cost, and material abundance. Nevertheless, finding a suitable cathode material with a high capacity and good stability remains a challenge. The most promising cathode materials for ZIBs reported in the literature are vanadium and manganese oxides. Among these materials, vanadium pentoxide (V_2O_5) yields the most convincing capacities, in the range of 410 mAh g^{-1} [1]. However, V_2O_5 requires an activation phase before reaching stable capacities. Furthermore, vanadium oxide cathodes sometimes experience stability problems during the electrochemical cycling, especially at high current density. This is often explained in literature by a collapse of the layered crystallographic structure of V_2O_5 (Figure 1a) due to the voluminous zinc ions that are inserted into and extracted from the dense cathode material during cycling [2].

An approach to prevent this structural degradation consists in stabilizing the crystallographic structure of the material by inserting elements acting as pillars to expand the interlayer spacing and facilitate the insertion/extraction of Zn^{2+} [2]. In the case of V_2O_5 , the spacing of the crystallographic framework could be achieved by inserting ions between the vanadium oxide layers, forming a metallic vanadate of the form $M_xV_{2+m}O_{5+n}$. Since Nazar's group developed $Zn_{0.25}V_2O_5 \cdot nH_2O$ as a cathode material with a relatively high energy density and good cycling stability [4], a series of compounds have been tested by insertion of water molecules [5] and/or metal ions such as Na^+ [6,7], Ca^{2+} [8], K^+ [9], or Mg^{2+} [10], into the structure of V_2O_5 . Tunnel structures (Figure 1b) or more spaced layered structures (Figure 1c) can be obtained by this process. Because of the promising electrochemical results of vanadates and the convincing availability of sodium, more focus was put on the use of sodium vanadium oxides as cathode material in ZIBs. The sodium vanadate family spans a broad range of compositions, including anhydrous or hydrated crystalline phases (such as $Na_{0.33}V_2O_5$ [6], $Na_{0.56}V_2O_5$ [11], $Na_{1.1}V_3O_{7.9}$ [12], $Na_2V_6O_{16} \cdot 1.63H_2O$ [13], and $Na_2V_6O_{16} \cdot 2H_2O$ [14]), as well as nanocrystalline or amorphous hydrated materials (e.g. $NaV_3O_8 \cdot 1.5H_2O$ [15], and $NaV_3O_8 \cdot 1.35H_2O$ [9]). Due to ecological reasons, aqueous solution routes are frequently used for the synthesis of these compounds, using a hydrothermal treatment or a heat treatment to promote crystallization. One of the simplest routes relies on stirring a V_2O_5 powder in an aqueous solution of a sodium salt ($NaCl$, $NaOH$, ...). The range of products resulting from such an aqueous synthesis that are reported in literature is broad. For example, different authors used V_2O_5 and $NaCl$ as precursors for their aqueous route and obtained the following phases: V_2O_5 [16-18], $NaV_3O_8 \cdot 1.35H_2O$ [9], $NaV_3O_8 \cdot 1.5H_2O$ [19], $NaV_3O_8 \cdot 1.69H_2O$ [20]. Some of these results suggested that achieving reproducibility might be an issue and there were gaps in the understanding of the formation mechanisms of some phases.

For these reasons, we present in this work further results on the aqueous synthesis and structural evolution of sodium vanadium oxides to contribute to the resolution of the existing literature inconsistencies. We prepare precursors of different compositions which crystallize into pure phases or mixtures of V_2O_5 , β - $Na_{0.33}V_2O_5$ and $Na_{1.16}V_3O_8$ during heat treatment. The crystallization process was studied by high-temperature X-ray diffraction (HTXRD), especially to investigate the formation of pure β - $Na_{0.33}V_2O_5$ phase without a hydrothermal step. The characterization of nanocrystalline

barnesite, $\text{Na}_{0.33}\text{V}_2\text{O}_5$ and $\text{Na}_{1.16}\text{V}_3\text{O}_8$ through XRD, Scanning Electron Microscope (SEM) and Brunauer-Emmett-Teller specific surface area determination (BET) gave an insight into their crystallographic structure, microstructure, specific surface area. Finally, the electrochemical performance of nanocrystalline barnesite, $\text{Na}_{0.33}\text{V}_2\text{O}_5$ and $\text{Na}_{1.16}\text{V}_3\text{O}_8$ was evaluated as positive electrode materials in Zn-ion batteries.

Figure 1. (a) Layered structure of V_2O_5 ; (b) tunnel structure of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ and (c) layered structure of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ plotted with Vesta [3] using lattice parameters and atomic positions from PDF 00-041-1426, PDF 01-084-8341 and PDF 04-025-2006 respectively.



2. Experimental part

2.1. MATERIALS AND CHEMICALS

V_2O_5 (98%), NaCl (99%), and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (98%) were purchased from Sigma Aldrich. Carbon black (99.9% purity) and polyvinylidene fluoride (PVDF) were purchased from Alfa Aesar. A 0.1 mm thick zinc foil was purchased from Goodfellow.

2.2. AQUEOUS SYNTHESIS OF $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$, $\text{Na}_{1.16}\text{V}_3\text{O}_8$ AND NANOCRYSTALLINE BARNESITE

Precursor powders with Na/V ratios ranging between 0.07 and 0.30 (approximate values based on EDX) were obtained by stirring V_2O_5 powder in aqueous NaCl solutions, followed by a heat treatment of the precursors according to the protocol described by Wan et al. [15]. In each experiment (see Table SI-1 for details), NaCl was dissolved in 30 mL of deionized water before adding 2 g V_2O_5 and stirring the suspension with a magnetic bar for 2 days at room temperature. The red precipitates were separated by centrifugation, washed with deionized water (3 dispersion/centrifugation cycles), and freeze-dried for 24 h with an Alpha 2–4 LSC basic freeze-dryer from Martin Christ GmbH. Samples from the precursor powder batches were heated in air at 500 °C either in a muffle furnace with a 150 °C/h heating ramp or in the HTK1200N Anton Paar chamber of the X-ray diffractometer with a 120 °C/h heating ramp.

2.3. STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION

Room temperature X-ray diffractograms were collected with a Bruker D8 Twin-twin diffractometer (Bragg-Brentano geometry, Cu K α radiation, Lynxeye XET 1D detector, $2\theta = 5\text{--}80^\circ$, 0.02° step size and 0.1 s/channel step time). In situ high-temperature diffractograms were collected on powder samples packed in 0.4-mm deep alumina holders placed in the HTK1200N Anton Paar chamber. 5-min scans ($2\theta = 8\text{--}17^\circ$ or $2\theta = 25\text{--}34^\circ$, 0.02° step size) were collected continuously during the heating ramp and the beginning of the dwell times. 20-min scans ($2\theta = 6\text{--}70^\circ$, 0.02° step size) were collected before the experiment, at the end of the dwell time, and after the experiment. The Bruker Topas software was used to extract peak positions and intensities by peak fitting or to refine the cell parameters and phase percentages by Rietveld refinement, using atomic positions taken from the PDF4+ database of the International Center for Diffraction Data (PDF 01-084-8341 for $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$; PDF 04-025-2006 for $\text{Na}_{1.16}\text{V}_3\text{O}_8$ and PDF 00-041-1426 for V_2O_5). The room temperature cell parameters were refined on the ex-situ datasets to minimize the sample displacement error, while the phase percentages were estimated from in situ datasets because they were less affected by preferential orientation effects. In all cases, the fundamental parameters approach was used to model the instrumental contribution [21].

Thermogravimetric analysis was performed in air at 2°C min^{-1} with a LABSYS evo TGA 1150 instrument. Scanning electron micrographs were obtained on gold-coated powders under high vacuum and 15 kV using a Clara FEG-SEM from TESCAN coupled to energy dispersive X-ray analysis (EDX). The specific surface area was determined by the BET technique using a Micromeritics Asap 2020 Plus instrument. Degassing was applied for 48 h at 60 °C with a heating ramp of $10^\circ\text{C min}^{-1}$. The adsorption measurement was performed by the Rouquerol method under N_2 from 0 to 0.3 with a 0.03 step.

2.4. ELECTROCHEMICAL CHARACTERIZATION

Electrochemical measurements were performed using Swagelok cells assembled in an ambient atmosphere. Zinc foil, Whatman®-type glass fiber filter, and 3 M zinc triflate solution were used as the counter-electrode, separator, and electrolyte, respectively. The working electrode was prepared by manually grinding the sodium vanadium oxide (NVO) active material with carbon black and polyvinylidene fluoride in 70:20:10 ratio, followed by pressing 1.5 mg of this mixture onto a stainless-steel grid under a load of 6 tons. Galvanostatic charge and discharge cycling tests were performed at different constant current densities in a range of 0.1 A g⁻¹–5 A g⁻¹ at room temperature using a LAND battery test system (Wuhan, China). Cyclic voltammetry was carried out at room temperature with a Bio-Logic VMP3 galvanostat within the range of 0.2 V–1.6 V versus Zn/Zn²⁺ with a scanning rate of 0.5 mV s⁻¹.

3. Results and discussion

3.1. PRECURSOR POWDERS OBTAINED AFTER STIRRING V₂O₅ IN NaCl SOLUTIONS

This study was based on experiments where V₂O₅ powder was dispersed in NaCl solutions of various concentrations and stirred for 2 days at room temperature (for experimental conditions, see Table SI-1). In agreement with other authors [18,19,22–24], we systematically observed (i) a change in the suspension color from orange yellow to dark orange to red (Figure SI-1), (ii) a decrease in pH (typically from 3.5 to 2) and (iii) an increase in viscosity. The rate of progress could be significantly different from batch to batch. For example, the XRD patterns of samples S4, S5, and S6 (Figure 2a), prepared in nominally identical conditions, differ by the amounts of residual V₂O₅ and the position of some of the peaks of the nanocrystalline NVO phase (see later). The most likely explanation for the difference from batch to batch is the practical difficulty of reproducing the same stirring conditions for a reactional medium whose viscosity increases very significantly. Furthermore, residual NaCl was also found in some samples (e.g., samples S4 and S6), despite the systematic procedure used for washing. Again, the viscous nature of the produced medium after reaction could be the main reason.

A set of 6 precursor powders (samples S1 to S6 in Table 1) with Na/V ratio ranging from 0.07 to 0.30 (approximate values based on EDX) were selected for further discussion. As shown in Figure 2a, the diffraction peaks observed in the diffractograms of these uncalcined precursor powders can be indexed using the reference patterns for a barnesite-like phase, V₂O₅, and NaCl. The barnesite-like phase is nanocrystalline, with crystallite sizes in the 5–15 nm range. In Table 1, this phase is abbreviated as “NVO”, because small shifts in peak positions indicate that the stoichiometry of the nanocrystalline phase is more variable than the composition reported for the Na₂V₆O₁₆·3H₂O barnesite mineral [25].

Figure 2. (a) XRD patterns before heat treatment for comparison with database reference patterns for V_2O_5 (PDF 00-041-1426) and $Na_2V_6O_{16} \cdot 3H_2O$ (PDF 00-016-0601). The asterisks correspond to NaCl reflections. (b) XRD patterns after heat treatment at 500 °C (samples S1-500 to S6-500 corresponding to the samples S1 to S6 after calcination), for comparison with database reference patterns for $Na_{1.16}V_3O_8$ (PDF 04-025-2006) and β - $Na_{0.33}V_2O_5$ (PDF 01-084-8341). The ■ symbols correspond to V_2O_5 reflections.

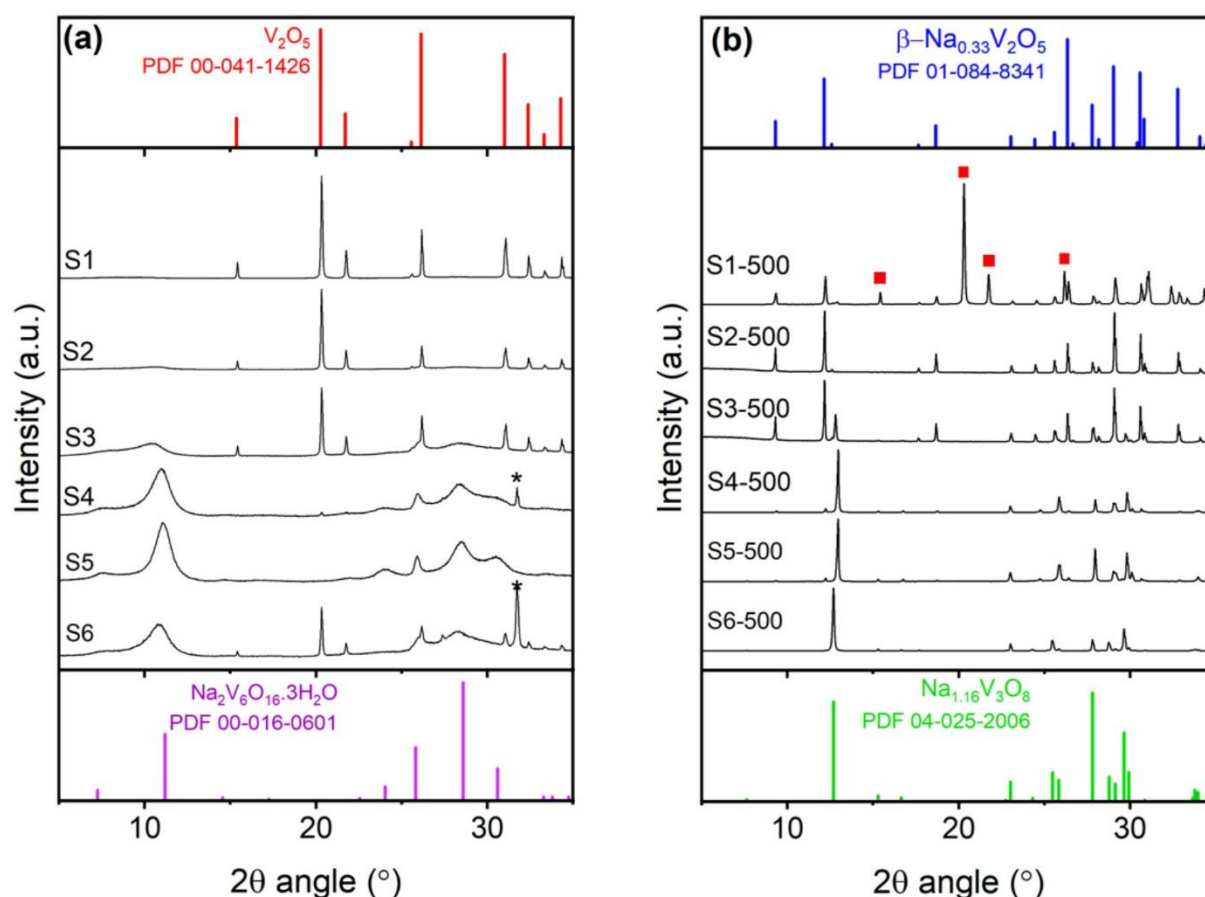


Table 1. Sample labels, approximate Na/V and Cl/Na ratios obtained by EDX, crystalline phases observed in X-ray diffractograms for uncalcined and calcined powders (see Figure 2). ■ V_2O_5 ; ■ β - $Na_{0.33}V_2O_5$; ◆ $Na_{1.16}V_3O_8$; ◆ $Na_{1+x}V_3O_8$.

Label	Na/V ratio (EDX)	Cl/Na ratio (EDX)	Phases in uncalcined powder	Phases in calcined powder
S1	0.07	/	V_2O_5 , (NVO)	■ ■
S2	0.14	/	V_2O_5 , NVO	■
S3	0.18	/	V_2O_5 , NVO	■ ◆ ◆
S4	0.25	0.042	NVO, (V_2O_5), NaCl	◆ ◆ ■
S5	0.26	/	NVO	◆ ◆ (■)
S6	0.30	0.087	NVO, V_2O_5 , NaCl	◆

3.2. PHASES OBSERVED AFTER CALCINATION

The XRD diffractograms after calcination in air at 500 °C are shown in Figure 2b (samples S1–500 to S6–500 corresponding to the samples S1 to S6 after calcination); the observed crystalline phases are summarized in Table 1. The samples S2 and S6 transformed into single phases with peak positions matching reference patterns for β -Na_{0.33}V₂O₅ (PDF 01-084-8341) and Na_{1.16}V₃O₈ (PDF 04-025-2006), respectively. The other calcined samples contain mixtures of two crystalline phases: S1-500 is composed of V₂O₅ and β -Na_{0.33}V₂O₅ while S3-500, S4-500, and S5-500 contain β -Na_{0.33}V₂O₅ and a phase (best seen in the diffractogram of sample S5-500) where the peaks of Na_{1.16}V₃O₈ are shifted to larger 2 θ angles (smaller interplanar distances). This phase will be called Na_{1+x}V₃O₈ in the following and appears with the symbol "◆" (instead of "●" for Na_{1.16}V₃O₈) in Table 1. The lattice parameters obtained for sample S5-500 and those collected by Onoda et al. [26] for a Na_{1.16}V₃O₈ single crystal in the $P2_1/m$ space group are reported in Table 2: the difference is largest for the a cell parameter but does not exceed 1%. Based on a comparison of the cell parameters of the S5-500 sample with the composition dependence of the lattice constants reported in Onoda et al. [26], the x value in Na_{1+x}V₃O₈ is likely to be ≤ 0.1 for this "◆" phase.

Table 2. Comparison of the lattice parameters reported by Onoda et al. [26] for a Na_{1.16}V₃O₈ single crystal and the lattice parameters obtained for the S5-500 Na_{1+x}V₃O₈ sample in the present work.

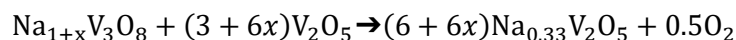
	a (Å)	b (Å)	c (Å)	β (°)
PDF 04-025-2006 Na_{1.16}V₃O₈	7.318	3.610	12.165	107.75
Sample S5-500 Na_{1+x}V₃O₈	7.258	3.607	12.185	107.79

3.3. PHASE TRANSFORMATION DURING CALCINATION

The sequence of crystalline phase transformation was investigated by in situ high-temperature X-ray diffraction for samples S1, S2, S4 and S6. After heating to 500°C in the high-temperature chamber of the diffractometer, these samples form respectively (i) β -Na_{0.33}V₂O₅ with approx. 40 wt% V₂O₅ (sample S1), (ii) pure β -Na_{0.33}V₂O₅ (sample S2), (iii) β -Na_{0.33}V₂O₅ with approx. 12 wt% Na_{1+x}V₃O₈ (sample S4), and (iv) Na_{1.16}V₃O₈ (sample S6).

Figure 3 shows a selection of the diffractograms collected in a narrow 2 θ window while the temperature was increased continuously at a rate of 2° min⁻¹, i.e., the temperature increased by 10 °C during the recording of each 5-min scan. Figure 4 focuses on sample S2 (which transforms into pure β -Na_{0.33}V₂O₅) and shows the temperature dependence of (a) the interplanar d values corresponding to the maxima of the deconvoluted peaks, (b) the peak intensities (= areas of the deconvoluted peaks), and (c) the mass loss measured by thermogravimetric analysis.

Up to ~ 250 °C, the broad peak of the nanocrystalline barnesite-like NVO phase progressively shifted from $10.5^\circ 2\theta$ towards higher 2θ angles. This was observed for all samples and is particularly visible in the datasets for samples S4 and S6 (Figure 3 c and d). The 5% mass loss below 200 °C observed in the TGA of sample S2 (Figure 4c) supports the assumption that this shift to smaller interplanar distances corresponds to a dehydration of the barnesite-like phase [27]. Starting at ~ 275 °C, the broad peak progressively narrowed down into two characteristic peaks of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ and $\text{Na}_{1+x}\text{V}_3\text{O}_8$ phases. It is interesting to note that the formation of distinct $\text{Na}_{0.33}\text{V}_2\text{O}_5$ and $\text{Na}_{1+x}\text{V}_3\text{O}_8$ phases occurred only once the dehydration was complete. This is in general agreement with ex-situ diffractograms reported by Fan et al. [24] for a sodium vanadate material prepared by stirring V_2O_5 in a Na_2SO_4 solution. The two peaks then grew side by side up to a temperature of about 350 °C. Beyond this temperature, samples S1 and S2 entered a second stage of transformation, where the intensity of the peaks of V_2O_5 and $\text{Na}_{1+x}\text{V}_3\text{O}_8$ decreased while the intensity of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ peaks increased concomitantly. This evolution proceeded until the complete disappearance of the peak of either $\text{Na}_{1+x}\text{V}_3\text{O}_8$ (sample S1) or V_2O_5 (sample S2). The second, smaller mass loss above ~ 380 °C in the TGA of sample S2 (Figure 4c) happened in the same temperature range as the transformation of V_2O_5 and $\text{Na}_{1+x}\text{V}_3\text{O}_8$ into $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$. The equation



suggests that this mass loss could be explained by a release of oxygen due to the partial reduction of V^{5+} into V^{4+} .

The second stage did not exist in sample S4 since it did not contain any V_2O_5 .

In sample S6, the small amount of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ phase formed beyond 275 °C was rapidly transformed into the sodium-rich phase $\text{Na}_{1.16}\text{V}_3\text{O}_8$. NaCl, having survived the washing step, is assumed to have provided an extra source of sodium (see Figure 3e). The EDX spectra of sample S6 before and after calcination (see Figure SI-2) reveals the disappearance of the Cl peak after calcination.

Figure 3. (a-e) High-temperature X-ray diffraction study of samples S1, S2, S4, and S6: selection of 5-min diffractograms collected during the heating at $2\text{ }^{\circ}\text{C min}^{-1}$. A second 2θ range was collected for sample S6 to follow the NaCl peak. The end temperature of each scan is shown at the figure. The peaks highlighted in red, purple, blue, and green correspond to V_2O_5 , NaCl, $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$, and $\text{Na}_{1+x}\text{V}_3\text{O}_8$, respectively. The broad peak moving to higher 2θ angles in the low-temperature range corresponds to the barnesite-like NVO nanocrystalline phase.

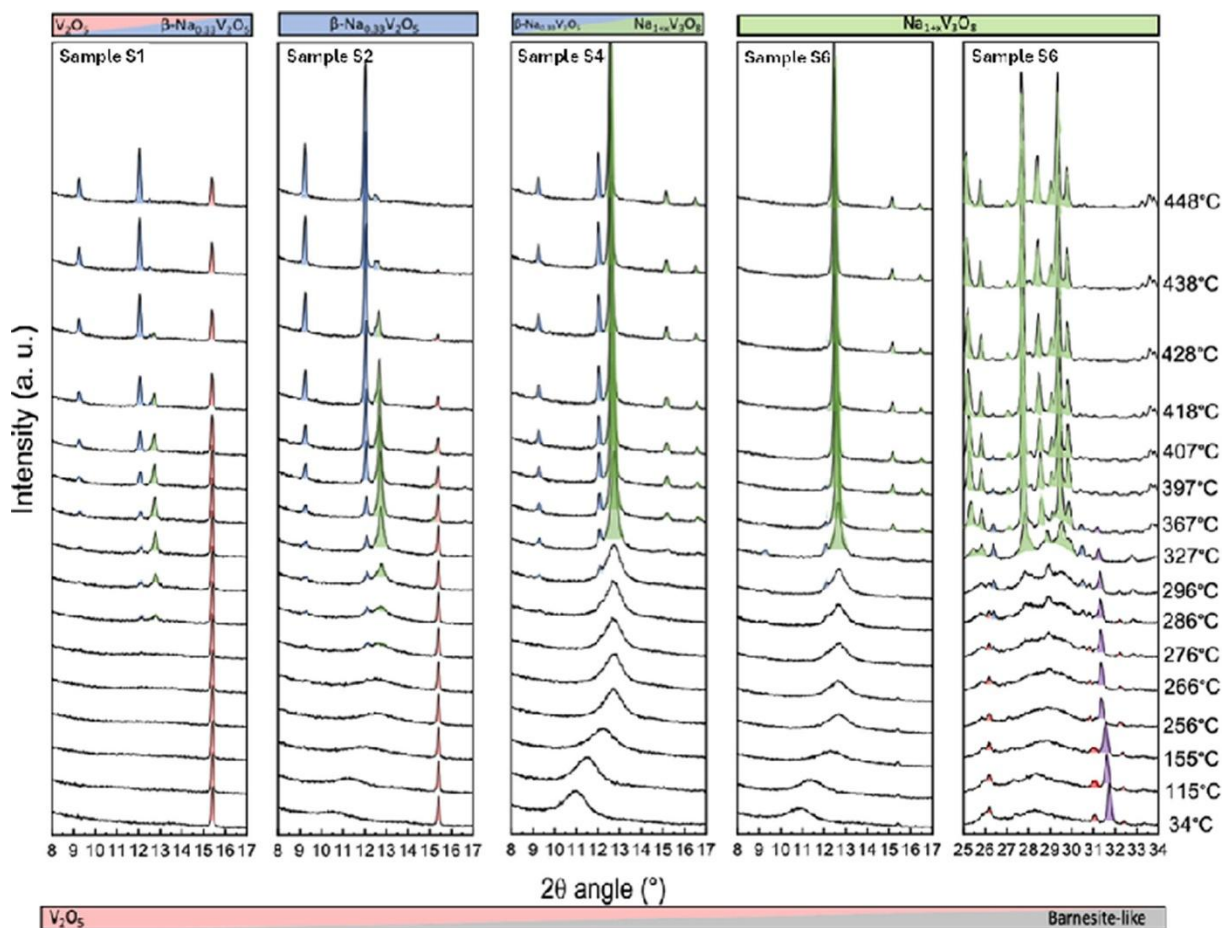
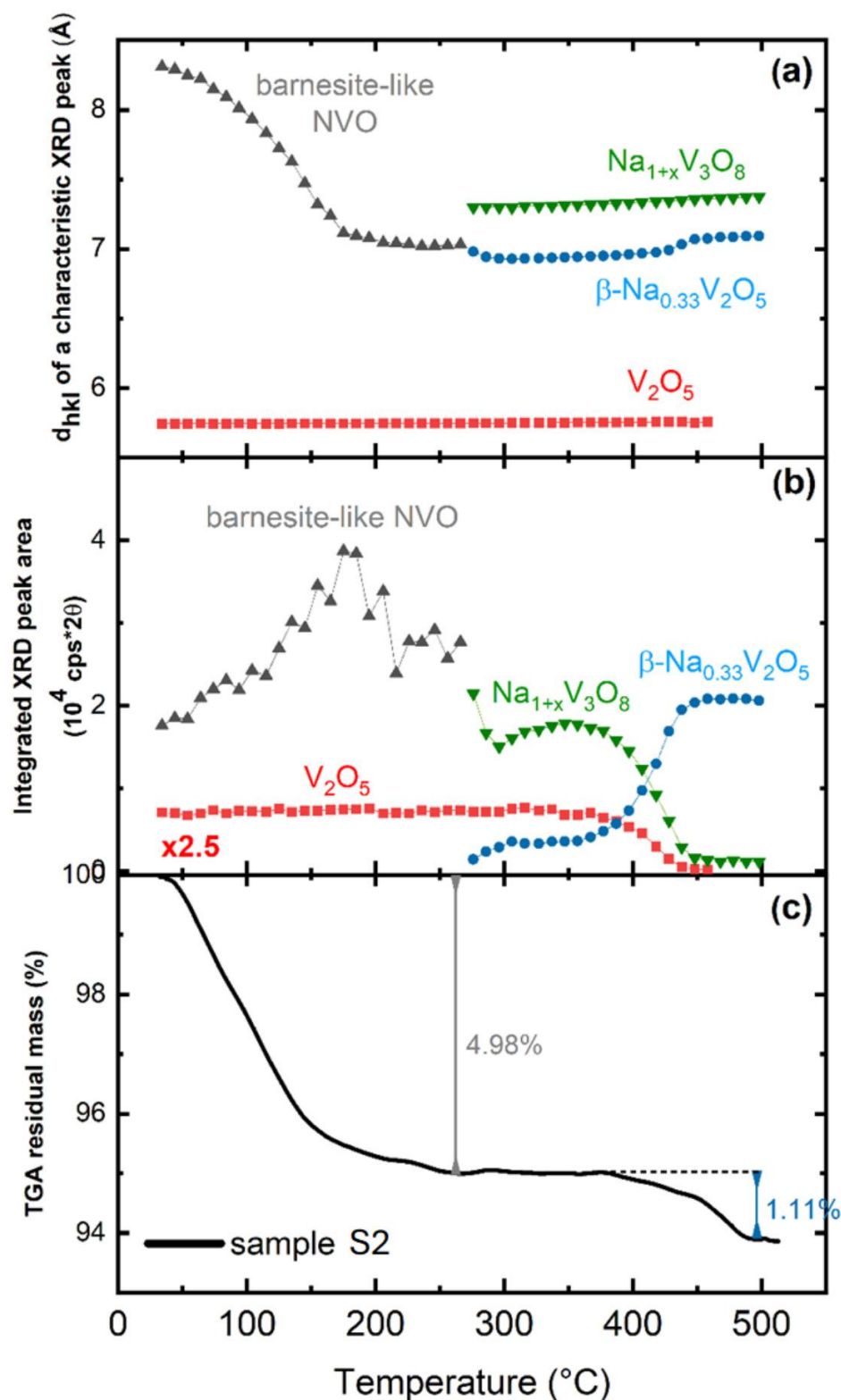


Figure 4. (a,b) Temperature dependence of the interplanar spacing d_{hkl} (in Å) and the integrated intensity of one characteristic peak for each crystalline phase detected during the high-temperature X-ray diffraction experiment on sample S2; (c) thermogravimetric curve of sample S2 performed at the same heating rate as the HTXRD experiment.



3.4. MORPHOLOGICAL AND ELECTROCHEMICAL CHARACTERIZATIONS OF NANOCRYSTALLINE BARNESITE (SYNTHESIZED AS SAMPLE S5), β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ (SYNTHESIZED AS SAMPLE S2-500) AND $\text{Na}_{1.16}\text{V}_3\text{O}_8$ (SYNTHESIZED AS SAMPLE S6-500)

The SEM micrographs of the pure phase nanocrystalline barnesite (synthesized as sample S5), β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ (synthesized as sample S2-500), and $\text{Na}_{1.16}\text{V}_3\text{O}_8$ (synthesized as sample S6-500) are shown in Figure 5. The nanocrystalline barnesite presents long and thin nanobelts (Figure 5a), a shape that is frequently reported and largely characterized for sodium vanadium oxides in literature [15,27]. The particles in the β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ and $\text{Na}_{1.16}\text{V}_3\text{O}_8$ samples were formed during the calcination and consist of thicker and shorter nanobelts. In the case of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ the particles are becoming more isotropic. The BET specific surface areas are in agreement with these observations: $18.75 \text{ m}^2 \text{ g}^{-1}$ for the uncalcined nanocrystalline barnesite, against $6.84 \text{ m}^2 \text{ g}^{-1}$ and $4.24 \text{ m}^2 \text{ g}^{-1}$ for the two calcined phases of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ and $\text{Na}_{1.16}\text{V}_3\text{O}_8$ respectively. Transmission Electron Microscope (TEM) images of the calcined phase of β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ can be found in Figure SI-3 giving more insights into the crystal orientation, the observable lattice fringes and the thickness of the nanobelts. The latter revealed an orientation of the lattice fringes along the length of the nanobelts with a d-spacing between 0.65 nm and 0.9 nm, and a nanobelt-thickness between 200 nm and 300 nm.

Finally, we report data of the electrochemical characterization of nanocrystalline barnesite, $\text{Na}_{0.33}\text{V}_2\text{O}_5$ and $\text{Na}_{1.16}\text{V}_3\text{O}_8$ as cathode active materials in *Swagelok* cells against Zn counter-electrode, using $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ 3 M as an electrolyte solution. Figure 6 shows the cyclic voltammograms at 0.5 mV s^{-1} in the voltage range of 0.2–1.6 V. Nanocrystalline barnesite presents two pairs of discharging/charging peaks at 0.77/1.06 V and 0.48/0.73 V suggesting a multistep intercalation/deintercalation of Zn^{2+} into the structure. The cathodic peaks of nanocrystalline barnesite are shifted for the first cycle but the CV curves present a similar shape for the following cycles suggesting good reversibility. The CV curves of $\text{Na}_{1.16}\text{V}_3\text{O}_8$ are quite similar to nanocrystalline barnesite in terms of shape and potential differences. Thus, it can be hypothesized that the cathode material is not considerably altered during the insertion and extraction of the zinc ions, which confirms once more the stability and steadiness of sodium vanadate materials [27]. In $\text{Na}_{0.33}\text{V}_2\text{O}_5$, there are initially two pairs of cathodic/anodic peaks, but they are in a different domain, at 1.10/1.40 V and 0.45/0.86 V suggesting a different mechanism than nanocrystalline barnesite or $\text{Na}_{1.16}\text{V}_3\text{O}_8$. The discrepancy between the working potential differences obtained for $\text{Na}_{1.16}\text{V}_3\text{O}_8$ / nanocrystalline barnesite and $\text{Na}_{0.33}\text{V}_2\text{O}_5$ can be explained by crystallographic structures that induce different electrochemical behaviors [28]. During cycling, a third peak is detected at 0.8 V and 1 V in discharge and charge respectively. After that, the CV curves of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ show a similar shape, which indicates a high reversibility of the charge/discharge process.

In terms of electrochemical cycling performance of vanadium-based materials in aqueous ZIBs, Table 3 summarizes the most relevant and recent electrochemical studies on sodium vanadates, specifying the chosen synthesizing process to form the material. This table allows a contextualization of the electrochemical results obtained for the materials synthesized in this work (see last three lines of Table 3).

Figure 7a displays the cyclic performance of the three electrodes at a current density of 0.1 A g^{-1} . The $\text{Na}_{0.33}\text{V}_2\text{O}_5$ material exhibits a very stable discharge capacity of about 300 mAh g^{-1} for 40 cycles thanks to its tunnel structure [28]. The highest initial discharge capacity, 320 mAh g^{-1} is detected for nanocrystalline barnesite and decreases slowly along cycling. The capacity retention is equal to 84% after 40 cycles. In contrast, the $\text{Na}_{1.16}\text{V}_3\text{O}_8$ material delivers initially the lowest capacity of 165 mAh g^{-1} but the capacity increases along cycling meaning that the number of active sites increases at the same time due to the gradual impregnation of electrolytes. As explained in the literature for the case of V_2O_5 , this activation process can also be attributed to the insertion of water molecules into the structure, leading to an increase in the interlayer distance and easier Zn^{2+} insertion [33-36]. Furthermore, Wan et al. have demonstrated that a simultaneous insertion of H^+ and Zn^{2+} ions during the first cycles is also contributing to this activation of the phase [15]. Indeed, $\text{Na}_{1.16}\text{V}_3\text{O}_8$ and V_2O_5 exhibit both layered crystallographic structures prone to undergo such an activation phase by the intercalation of species present in the electrolyte. The coulombic efficiencies of the three different samples are around 100% suggesting the absence of the side reactions which ensures good reversibility during charge/discharge processes of these materials.

The rate performance of the three electrode materials is determined and presented in Figure 7b. The discharge capacities of nanocrystalline barnesite are 270, 230, 205, 159, and 135 mAh g^{-1} at current densities of 0.2, 0.5, 1, 3, and 5 A g^{-1} . The $\text{Na}_{1.16}\text{V}_3\text{O}_8$ electrode delivers 191, 168, 148, 106, and 83 mAh g^{-1} , while the $\text{Na}_{0.33}\text{V}_2\text{O}_5$ delivers 245, 166, 100, 28, and 11 mAh g^{-1} at current densities of 0.2, 0.5, 1, 3 and 5 A g^{-1} . The $\text{Na}_{1.16}\text{V}_3\text{O}_8$ and nanocrystalline barnesite electrodes exhibit good cycling performance at various current densities while the $\text{Na}_{0.33}\text{V}_2\text{O}_5$ electrode suffers from a rapid capacity fading at increased current density. However, the materials did not seem to be significantly degraded during the high current density cycles since the recovery at 0.2 A g^{-1} is correct.

The cycling performance of the three electrodes at a current density of 5 A g^{-1} is further investigated and shown in Figure 7c. The three electrodes exhibit outstanding cycling stability with excellent capacity retention. Not surprisingly, the nanocrystalline barnesite material delivers the highest specific capacity and is the most stable during cycling. The structure of nanocrystalline barnesite is stabilized by sodium ions and water molecules that function as “pillars” [14,28,35-37]. Moreover, the higher specific surface area of this material creates more active sites and leads to fast ion diffusion pathways. $\text{Na}_{0.33}\text{V}_2\text{O}_5$ electrode maintains a discharge capacity lower than 30 mAh g^{-1} which is consistent with the rate capability test. The low electrochemical performance of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ at high current density can be explained by its tunnel-like structure that is less appropriate for the insertion of zinc ions at a high current rate [14,38].

Post-mortem analyses of the two materials yielding the most convincing capacity retentions at high cycling rates (namely $\text{Na}_{1.16}\text{V}_3\text{O}_8$ and nanocrystalline barnesite) have been carried out. SEM images before and after electrochemical cycling of cathodes containing the latter two cathode active materials can be seen in Figure SI-4. The nanobelts formed after the insertion of sodium ions into the crystallographic structure of the vanadium pentoxide are preserved even after 2000 cycles at a high cycling rate (Figure SI-5). This result confirms the excellent morphological stability of these materials during cycling. Furthermore, *post-mortem* XRD analysis have shown that the initial

crystallized $\text{Na}_{1.16}\text{V}_3\text{O}_8$ is amorphized during the electrochemical cycling and is adopting a crystallographic organization like the one of a hydrated zinc vanadium oxide hydroxide ($\text{Zn}_3(\text{OH})_2\text{V}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) (Figure SI-6a). A similar phase transition is observable for the nanocrystalline barnesite that is also transformed with the zinc insertion into a phase resembling the one of hydrated zinc vanadium oxide hydroxide (Figure SI-6b).

Overall, these results can be rated as a fairly good performance based on a powder that was prepared by a straightforward procedure using widely available starting materials. Moreover, these results suggest that the layered structure of nanocrystalline barnesite is superior in terms of capacity and rate performance to non-hydrated $\text{Na}_{1.16}\text{V}_3\text{O}_8$ and $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ with a tunnel-like structure.

Figure 5. SEM images at two magnifications: (a) nanocrystalline barnesite (synthesized as sample S5), (b) $\text{Na}_{0.33}\text{V}_2\text{O}_5$ (synthesized as sample S2 calcined at 500 °C) and (c) $\text{Na}_{1.16}\text{V}_3\text{O}_8$ (synthesized as sample S6 calcined at 500 °C).

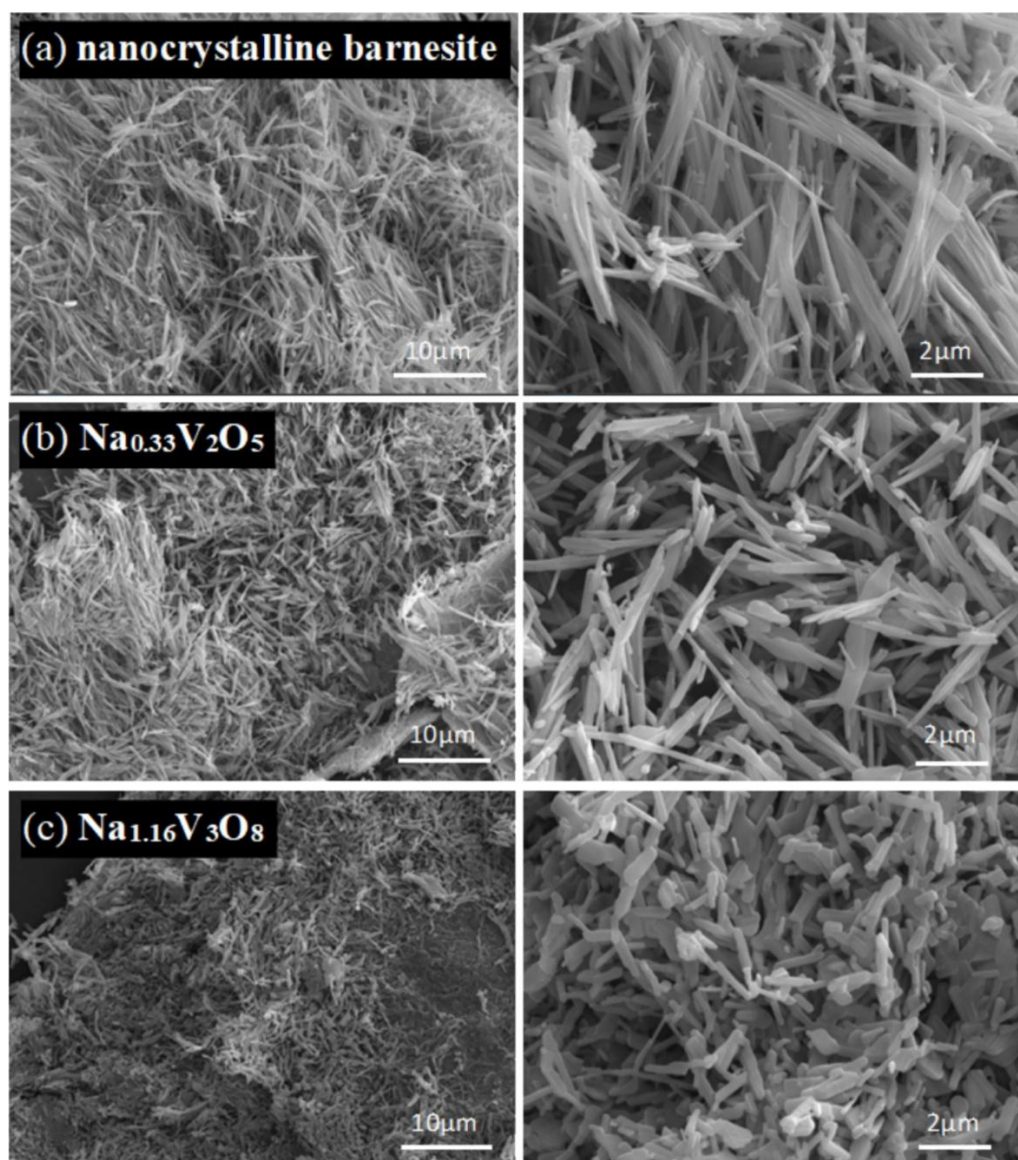


Figure 6. CV curves of (a) nanocrystalline barnesite, (b) $\text{Na}_{0.33}\text{V}_2\text{O}_5$ and (c) $\text{Na}_{1.16}\text{V}_3\text{O}_8$ – for the 1st, 5th and 10th cycle at 0.5 mV s^{-1} in the voltage range of 0.2–1.6 V.

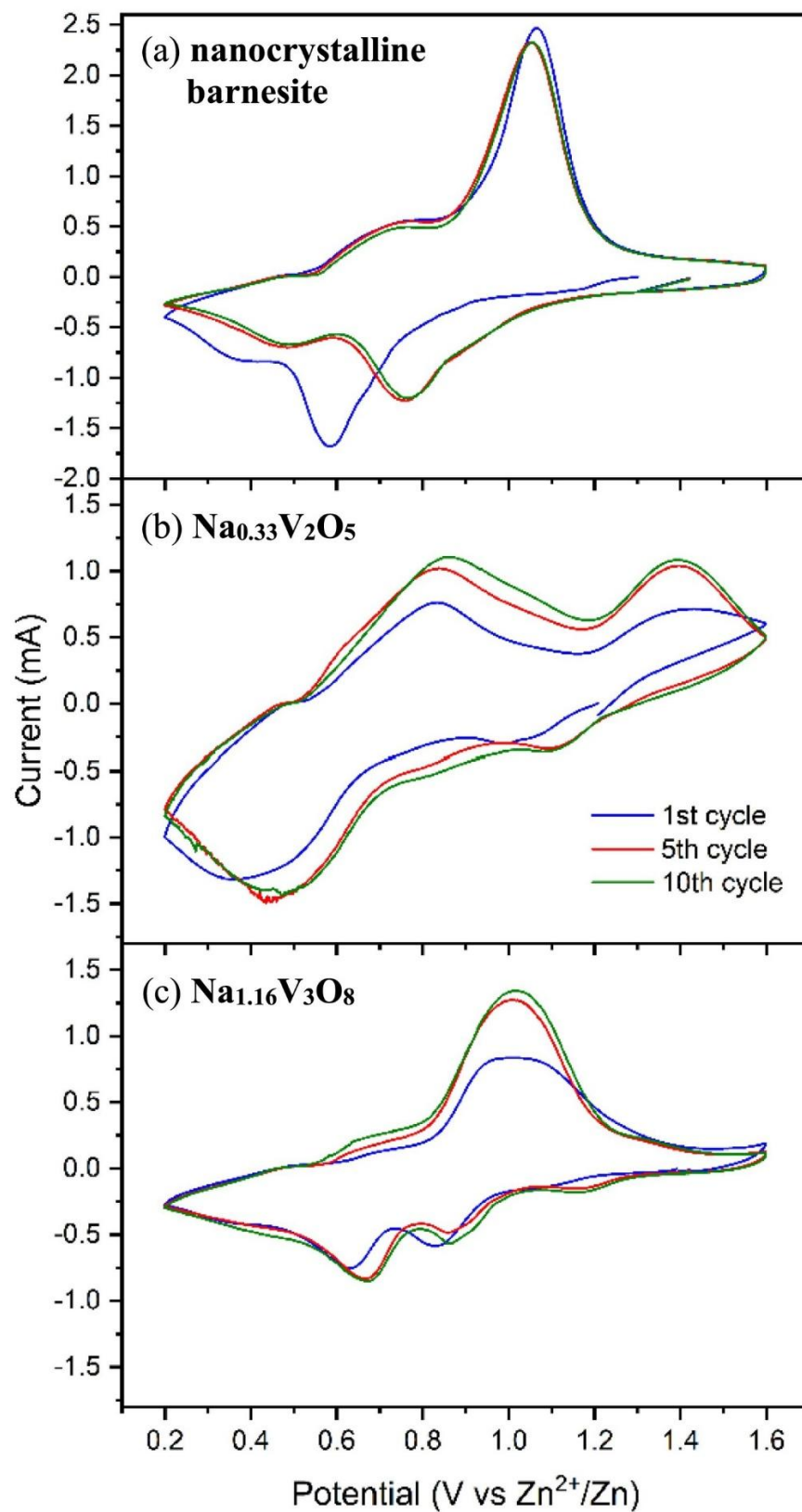
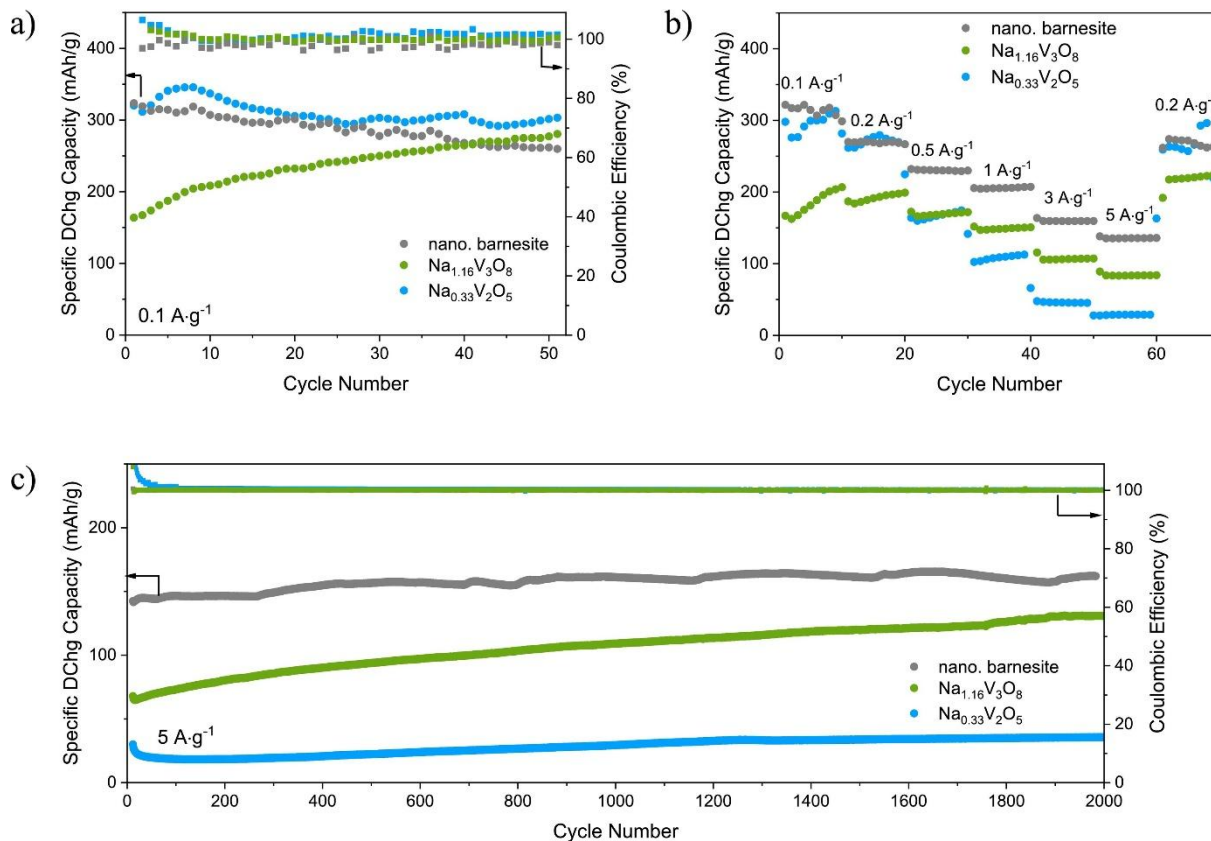


Table 3. Selection of electrochemical studies done on different sodium vanadate phases summarizing the obtained morphologies, the used treatments, the used electrolytes, the obtained specific discharge capacities, the maximum reported cycle number at high cycling rates and the capacity retention for these high-rate cycling tests (from left to right). The three last lines correspond to the results of this work (T.W.).

Ref.	Material	Morphology	Treatment	Electrolyte	Capacity (mAh·g ⁻¹)	Cycles	Retention (%)
[6]	Na _{0.33} V ₂ O ₅	Nanowires	Na ⁺ pre-intercalation; hydrothermal	3 M Zn(CF ₃ SO ₃) ₂	367 @ 0.1 A·g ⁻¹	1000	93
[29]	β-Na _{0.33} V ₂ O ₅	Microparticles with structural defects	Hydrothermal; calcination	2 M ZnSO ₄	430 @ 0.2 A·g ⁻¹	50	60
[15]	NaV ₃ O ₈ ·1.5H ₂ O	Nanobelts	Aqueous liquid-phase synthesis	1 M ZnSO ₄ + 1 M Na ₂ SO ₄	380 @ 0.05 A·g ⁻¹	1000	82
[12]	Na _{1.1} V ₃ O _{7.9} /rGO	Nanoribbons/graphene	Hydrothermal; calcination; graphene hybridization	1 M Zn(CF ₃ SO ₃) ₂	238 @ 0.05 A·g ⁻¹	100	76.7
[30]	NaV ₆ O ₁₅	Nanosheets	Mechanical activation; calcination	3 M Zn(CF ₃ SO ₃) ₂	325 @ 0.1 A·g ⁻¹	1000	127
[13]	Na ₂ V ₆ O ₁₆ ·1.63H ₂ O	Nanowires	Hydrothermal	3 M Zn(CF ₃ SO ₃) ₂	352 @ 0.05 A·g ⁻¹	6000	90
[31]	Na ⁺ -stabilized NH ₄ V ₄ O ₁₀	Layered nanosheets	Hydrothermal	3 M Zn(CF ₃ SO ₃) ₂	400 @ 0.1 A·g ⁻¹	2000	97.2
[32]	Na ₇ V _{7.6} O ₂₀ ·4H ₂ O	Belt-like shape	Hydrothermal	4 M Zn(CF ₃ SO ₃) ₂	309.4 @ 0.3 A·g ⁻¹	10,000	98.6
[28]	Na ₅ V ₁₂ O ₃₂ (type NaV ₃ O ₈) vs Na _{0.76} V ₆ O ₁₅ (type β-Na _{0.33} V ₂ O ₅)	Layered vs tunneled	Hydrothermal; calcination	1 M ZnSO ₄ + 1 M Na ₂ SO ₄	281 @ 0.5 A·g ⁻¹ vs 135 @ 0.5 A·g ⁻¹	2000 vs 1000	71 vs ~95
T.W.	Nano. barnesite	Nanobelts	Stirring; calcination	3 M Zn(CF ₃ SO ₃) ₂	319 @ 0.1 A·g ⁻¹	2000	114
T.W.	β-Na _{0.33} V ₂ O ₅	Nanobelts	Stirring; calcination	3 M Zn(CF ₃ SO ₃) ₂	346 @ 0.1 A·g ⁻¹	2000	124
T.W.	Na _{1.16} V ₃ O ₈	Nanobelts	Stirring; calcination	3 M Zn(CF ₃ SO ₃) ₂	303 @ 0.1 A·g ⁻¹	2000	194

Figure 7. (a) Cycling performance at 0.1 A g^{-1} , (b) rate capability and (c) long cycling performance at 5 A g^{-1} (after 10 activation cycles at 0.1 A g^{-1}) of nanocrystalline barnesite (synthesized as sample S5), $\text{Na}_{0.33}\text{V}_2\text{O}_5$ (synthesized as sample S2-500) and $\text{Na}_{1.16}\text{V}_3\text{O}_8$ (synthesized as sample S6-500).



4. Conclusions

In this work, a pure $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ phase was obtained by an aqueous route based on stirring V_2O_5 and NaCl. We clarified the crystallization of precursors of different compositions into mixtures or pure phases of V_2O_5 , $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$, and $\text{Na}_{1.16}\text{V}_3\text{O}_8$. We found that pure $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ could be obtained through heat treatment of a precursor powder containing the proper ratio of NVO and residual V_2O_5 . However, the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ phase does not form directly but through the reaction of V_2O_5 with a $\text{Na}_{1+x}\text{V}_3\text{O}_8$ intermediate. Then, we showed that the barnesite-like NVO phase transforms into a $\text{Na}_{1+x}\text{V}_3\text{O}_8$ -rich material, $\text{Na}_{1.16}\text{V}_3\text{O}_8$, if an extra source of sodium, like NaCl, is available.

Three samples composed of pure $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$, $\text{Na}_{1.16}\text{V}_3\text{O}_8$, and nanocrystalline barnesite phases were compared in terms of morphology and electrochemical performance. Nanocrystalline barnesite presents long and thin nanobelts that appear like fibers. After calcination, nanobelts are thicker and shorter evolving towards nanoribbons for the $\text{Na}_{0.33}\text{V}_2\text{O}_5$ sample and to small nanoribbons that seem like microparticles for the $\text{Na}_{1.16}\text{V}_3\text{O}_8$ sample. Then, their electrochemical performance was evaluated as cathode materials in zinc-ion batteries. The tunnel-like structure of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ is very stable but not suitable for the insertion of zinc ions at high current density. The $\text{Na}_{0.33}\text{V}_2\text{O}_5$ material

exhibits a very stable discharge capacity of about 300 mAh g⁻¹ at 0.1 A g⁻¹ but the capacity fades to 30 mAh g⁻¹ when the current density increases to 5 A g⁻¹. As for V₂O₅, the layered structure of nanocrystalline barnesite and Na_{1.16}V₃O₈ phases facilitates the insertion of zinc ions into the structure during electrochemical cycling. These different structures and configurations play a key role in the determination of the electrochemical properties. Sodium ions and water act as pillars to stabilize the structure. Hence, the hydrated material, nanocrystalline barnesite seems to be the most appropriate material for zinc-ion batteries in terms of synthesis, performance, and stability.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Max Larry: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization. **Edith Roex:** Writing – review & editing, Visualization, Validation, Supervision, Investigation, Data curation, Conceptualization. **Audrey Schrijnemakers:** Validation, Investigation. **Abdelfattah Mahmoud:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Conceptualization. **Frederic Boschini:** Validation, Supervision, Resources, Project administration. **Benedicte Vertruyen:** Writing – review & editing, Visualization, Validation, Resources, Methodology, Investigation, Data curation, Conceptualization.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data to this article can be found online at

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