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**Sodium insertion in high pressure β -V₂O₅: a new high capacity
cathode material for sodium ion batteries**

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ABSTRACT

β -V₂O₅, obtained by a high-temperature high-pressure method, exhibits a layered structure that favours the insertion of Na⁺. In this work, we report the electrochemical insertion of sodium in high pressure β -V₂O₅ and its performance as cathode material for sodium-ion batteries. The material shows a first discharge capacity of 132 mAh g⁻¹ in the 3.6-2.0 V range at a C/20 current density and a maximum capacity of 147 mAh g⁻¹ under equilibrium conditions, corresponding to the insertion of 1 Na⁺ ion per formula unit. The β -V₂O₅//Na cell delivers a specific energy as high as 370-410 Wh kg⁻¹. The amount of inserted sodium points to the reduction of 50% of the available V⁵⁺ ions. After 20 cycles, the discharge capacity retains 86% of the initial capacity. Concerning the reaction mechanism of high pressure β -V₂O₅ upon sodium insertion/de-insertion, several phase transitions are inferred from the voltage-composition profile. Ex situ XRD reveals the appearance of several Na_xV₂O₅ phases in the 0 ≤ x ≤ 1 compositional range, which are closely related with the non-sodiated high pressure β -V₂O₅ structure. An irreversible structural transformation occurs during the very first inserted sodium, at the beginning of the first discharge, and the original high pressure β -V₂O₅ structure is not recovered upon full Na⁺ extraction. Electrochemical performances are outstanding though.

Keywords: vanadium oxide; sodium insertion; battery material; cathode; ex situ XRD;

1. Introduction

The success of lithium-ion batteries in the electronic market has triggered their use in electrical vehicles and even large-scale energy storage. To alleviate the scarcity of lithium resources, this latter application may be better addressed by using sodium batteries. These batteries, though developing less specific capacity with present available sodium insertion hosts[1], have the advantage of lower cost due to the high abundance of sodium. Thus, a great effort is now being made to unveil new materials able to intercalate large amount of sodium at either high or low potential. Taking into account the available materials for the cathode, capacity seems to be limited to 150 mAh g^{-1} (NaFePO_4 , $\text{Na}_2\text{FePO}_4\text{F}$, etc.[2]) and, as in the case of lithium-ion battery materials, the investigation of possible two-electron systems is relevant. Among V-compounds able to provide two electron transfer upon lithium insertion, $\text{Li}_2\text{VO}_2\text{F}$ with a disordered cubic rock-salt structure (space group Fm-3m)[3] has a theoretical capacity of 462 mAh g^{-1} , which significantly exceeds that of the conventional LiCoO_2 and LiFePO_4 cathode materials. VO_2F with a rhombohedral R-3c structure, obtained using a high-temperature high-pressure solid-state reaction delivers 250 mAh g^{-1} above 2.15 V. A higher capacity can be even reached at the expense of a lower voltage output though [4]. Motivated by the high capacity exhibited by this oxyfluoride a more easily scalable preparation method based on high-energy ball-milling was developed shortly after[5]. Thus, even though high-pressure materials seem to be far from large-scale application, unveiling their properties may trigger new advances in synthesis to make them easily available.

The high capacity and cycling stability[6] of ambient pressure α -V₂O₅ makes it an interesting candidate as cathode for lithium-ion batteries. It should be noted that its high pressure form β -V₂O₅ (HP- β -V₂O₅ hereafter) [7] has also been proposed as host for Li-ion batteries[8], and 2 Li⁺/formula unit are reversibly intercalated upon discharge to 1 V vs. Li⁺/Li. A remarkable capacity of 250 mAh g⁻¹ is observed after 80 cycles.[8] The lithium insertion mechanism, however, seems to be very intriguing, since at least six different Li_xV₂O₅ phases were detected.

Even though most of the high pressure polymorphs present a significant decrease of cell volume (denser structures) and higher coordination numbers[9, 10] than the corresponding ambient pressure forms, in some of them, such as HP- β -V₂O₅, volume reduction is not very high[7, 11] and are therefore interesting as cathode materials for batteries. In contrast, the high-pressure form[11] of olivine LiFePO₄ is electrochemically inactive. In HP- β -V₂O₅ each vanadium atom is coordinated to six oxygen atoms, making up distorted [V-O₆] octahedra[7]. Specifically, the structure consists of quadruple units of [V-O₆] octahedra, which share edges; and these units are arranged in layers (Fig. S1 of Supporting Information).

In this work, we investigate the suitability of HP- β -V₂O₅ for Na⁺ ion insertion reaction in the high voltage range (above 2 V) in view of its use as the cathode in Na-ion batteries. HP- β -V₂O₅ with a layered structure is obtained by a high-temperature high-pressure method[7]. Although at a first thought, a compound obtained by high-pressure synthesis may not seem to be viable for being used as a battery electrode (due to the predicted lack of vacancies or channels for cation

diffusion), the truth is that the layered structure of HP- β -V₂O₅ has been shown to favour the insertion of Li⁺ [8]. In this report we show that up to 1 Na⁺ ion/formula unit can be intercalated, developing a significant capacity of 147 mAh g⁻¹. Furthermore, the structural changes upon sodium insertion in HP- β -V₂O₅ have been monitored with ex situ XRD. Interestingly, ambient pressure α -V₂O₅ is known to be electrochemically susceptible to Na⁺ insertion, but only through special morphologies, like nanoparticles [12, 13], nanocomposites [14] or xerogels [15]. It is worth saying that commercial (ambient pressure) vanadium pentoxide exhibits rather poor electrochemical Na⁺ insertion properties, as will be shown in the Results and Discussion section. Interestingly, ab initio studies have shown that calculated ion diffusion barriers of sodium in α -V₂O₅ is much higher than the one calculated for sodium in HP- β -V₂O₅ [16]. Thus, performances of HP- β -V₂O₅ as cathode material for sodium batteries are expected to be much better.

It is important to note that there is some contradiction in the literature regarding the proper nomenclature of β -V₂O₅. Concerning crystal chemistry, Volkov *et al.* [17] initially indexed the X-ray diffraction pattern of β -V₂O₅ (ICDD PDF 4591074) with a very large tetragonal cell with $a = 14.259$ Å, $c = 12.576$ Å ($V=2557$ Å³). Later, Filonenko *et al.* [7] solved the crystal structure of β -V₂O₅ by X-ray and neutron powder diffraction. It crystallizes monoclinic, space group P2₁/m, with $a = 7.1140(2)$ Å, $b = 3.5718(1)$ Å, $c = 6.2846(2)$ Å and $\beta = 90.069(3)^\circ$ ($V=160$ Å³). Other authors [18-21] claim to have prepared “ β -V₂O₅” under different synthesis conditions. However, the quality of crystallographic data reported in these papers is rather poor, and the indexation of the X-ray

patterns, based on a few diffraction maxima, likely due to preferred orientation effect, does not match either with the initial (wrong) unit cell reported by Volkov et al. [17] Therefore, the V_2O_5 samples reported by these authors are much likely different forms of vanadium pentoxide.

We must note that upon sodium intercalation in HP- β - V_2O_5 the phases formed have the nominal composition $Na_xV_2O_5$, and their structures obtained through topotactic reaction, relate to HP- β - V_2O_5 (S.G: P $2_1/m$, layered)[22] . However, the sodium bronze β - $Na_{0.33}V_2O_5$ (S.G: C2/m, tunnel structure) which exhibit a quite different structure and is also able to intercalate additional sodium [13], produces β - $Na_{0.33+x}V_2O_5$ phases which are related to the bronze structure. Therefore, both sodiated compounds would have different structures.

2. Experimental

Synthesis of HP- β - V_2O_5 was carried out by treating previously dried α - V_2O_5 (Aldrich, 99.9%) in a belt-type press at 40 kbar and 800 °C for 30 minutes[7].

X-ray diffraction measurements were performed by means of a Bruker D8 high-resolution diffractometer equipped with a solid-state position sensitive rapid LynxEye® detector (PSD), using dichromatic $CuK\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$, $1.54439 \text{ \AA}$).

Morphological characterization of pristine HP- β - V_2O_5 , a pristine electrode and an electrode after cycling was carried out by means of Scanning Electron Microscopy (SEM) using a JEOL JSM-6400 microscope.

Electrochemical experiments were performed in CR2032 coin cells assembled in argon atmosphere. Sodium metal was used as the negative electrode and stacked with a glass fibre paper separator and a positive electrode all immersed in a 1 M NaClO₄ 1:1 solution of ethylene carbonate (EC) and propylene carbonate (PC) as the electrolyte. Preliminary electrochemical characterization was carried out on 8 mm diameter pellets pressed from a HP-β-V₂O₅, Super P Timcal carbon and PVDF composite in an 85:10:5 weight ratio, respectively. For longer cycling studies and C-rate performances, a slurry containing HP-β-V₂O₅, Super P Timcal carbon and PVDF in an 80:10:10 weight ratio was cast onto aluminium foil from which electrode disks with 12 mm diameter were cut. For ex situ XRD studies, positive electrodes with 10 mm diameter were discharged in Swagelok™ type cells against sodium metal until the desired Na compositions were reached. Galvanostatic discharge-charge experiments were carried out at C/20 rate, i.e. a current to provide insertion of 1 Na in 20 hours. The voltage at which processes take place were determined by cyclic voltammetry measurements which were run at 10 mV/10 min rate in the 3.6-2.0 V potential range. Near equilibrium experiments were performed in the 3.6-1.7 V voltage range using the galvanostatic intermittent titration technique (GITT) to estimate the composition of phases between x=0 and x=1. A current of 82.5 μA was applied for 30 min to reach a 0.025 incremental change of sodium content. The cell was allowed to relax afterwards for 4 h. Potentiostatic intermittent titration technique (PITT) experiments were run to analyse the nature of the insertion reactions. A cell was discharged at 10 mV steps every 8 h in the 3.5-2.0 V voltage range.

Impedance spectroscopy was used to analyse the change in the charge transfer process upon cycling. Typical experiments were performed at open circuit voltage condition in a two-electrode cell before and after cycling. The measurements were carried out at room temperature using a VMP3 battery tester with an Electrochemical Impedance Spectroscopy channel. A sinusoidal potential perturbation of 10 mV was applied while measuring impedance variation in the frequency range from 3×10^5 Hz to 0.1 Hz.

3. Results and discussion

The high-pressure synthesis produced a reddish-brown powder that was determined to be HP- β -V₂O₅ according to the X-ray powder diffraction pattern (Fig. S2 of *Supporting Information*). Refined lattice parameters fully agree with those previously reported [7]. Experimental conditions and refined lattice parameters are given in Table S1 of *Supporting Information*, whereas main structural parameters of the Rietveld refinement are listed in Table S2 of *Supporting Information*.

Fig. 1 shows three consecutive voltammograms obtained at a 10 mV/10 min scan rate in the 3.6-2.0 V range vs Na⁺/Na. The first reduction wave shows two processes, labelled with A and B and centred at 3.1 and 2.5 V, corresponding to a two-step reduction of V⁵⁺ to V⁴⁺. However, the peak A seems to involve at least two different processes and a shoulder on the low voltage side is inferred from the pronounced asymmetry of the peak. Two intense peaks, labelled with C and D, appear at 3.15 and 3.4 V in the oxidation wave. Their profiles and peak separation, however, do not point to a full correspondence with the peaks A and

B observed in the first reductive wave. Furthermore, the second reduction wave reveals significant differences with respect to the first reduction wave. This may point to a (structural) change in HP- β -V₂O₅ during the first reduction, but after which reversible oxidation and reduction continues, as it can be deduced from the similarities of second and third reduction-oxidation waves.

Fig. 1. Voltammograms at a 10mV/10min step rate in the 3.6-2.0 V range corresponding to reduction-oxidation cycles of HP- β -V₂O₅

Fig. 2a shows the galvanostatic discharge-charge cycles at C/20 current rate of HP- β -V₂O₅ obtained from a slurry cast onto aluminium foil. Ca. 0.9 Na⁺/f.u. (132 mAh g⁻¹) are intercalated in the first discharge which are fully deintercalated upon charge (Fig. 2a). The second and third discharge cycles show a quite similar profile, however the loss of capacity is evident. Capacity slightly decreases in the first few cycles (Fig. 2b), as usually found for composite electrodes. For instance the same effect has been observed for nanowires of the bronze β -Na_{0.33}V₂O₅

[13]. Further cycling of HP- β -V₂O₅ at C/20 and C/10 is accompanied by an increase of capacity to stable 120 mAh g⁻¹ and 80 mAh g⁻¹, respectively (Fig. 2b). We ascribe this phenomenon to electrochemical milling that may reduce kinetic limitations and polarization therefore. However, this effect is not clearly observed at higher current rates (C/5) for which decrease of polarization due to electrochemical milling may be negligible compared to polarization due to high current.

Interestingly, α -V₂O₅ shows a very different electrochemical behaviour [12, 23-25]. For comparison, an electrode bearing (commercial) polycrystalline α -V₂O₅ has been elaborated using the same procedure as for HP- β -V₂O₅ and was then cycled at C/20 in the same voltage range as HP- β -V₂O₅.

α -V₂O₅ develops a first discharge capacity of 110 mAh g⁻¹ (Fig. 2b), however severe capacity fading with complete loss of capacity is observed after a few cycles. Lee *et al.* [13] have recently shown that α -V₂O₅ nanowires exhibit better performance, however much lower than HP- β -V₂O₅. This demonstrates impressively the better electrochemical performance of HP- β -V₂O₅ able to deliver a maximum specific capacity of 147 Ah kg⁻¹ and specific energy of 411 Wh kg⁻¹.

Kulish *et al.* have proposed, based on first principles calculations, that HP- β -V₂O₅ may be the most promising vanadium oxide cathode for Na-ion batteries due to a much improved diffusion kinetics and significant lower diffusion barriers when compared with α -V₂O₅ and other vanadium oxides [16].

Fig 2. First three discharge-charge cycles of HP- β - V_2O_5 in the 3.6-2.0 V range at a C/20 rate (a); evolution of specific capacity with number of cycles for HP- β - V_2O_5 at C/20, C/10 and C/5 and commercial polycrystalline α - V_2O_5 at C/20 (b).

The cycling performance of the HP- β - V_2O_5 electrode at different C rates is shown in Fig. 3. At low C rates, good performance of HP- β - V_2O_5 is observed with more than 50% capacity at C/5. However, it cannot stand significant capacity for 1C. Nevertheless, taking into consideration that capacity is greatly recovered when cycling at C/20, this material is worth being further investigated as a promising cathode material for sodium-ion batteries. Electrochemical experiments reveal an important kinetic limitation of this electrode. Note that the material has been used as prepared (large particle size). Fig. 4a shows a SEM image of a pristine electrode with the inset showing the powder used for its fabrication. Well-defined prismatic microcrystals ranging from 1 to 10 μm can be seen in both the powder and the electrode. The “foam” surrounding the crystals in the electrode is the binder used to fabricate the electrode. The morphology of the as prepared HP- β - V_2O_5 is not likely optimum for intercalation reactions, but high-pressure synthesis route does not provide an easy way to obtain crystals having more appropriate morphologies to improve rate performance.

Fig. 4b shows a SEM image of an electrode cycled 150 times at C/5 rate.

As most striking feature this image reveals that though big crystals in the micrometric scale are still present, these were partially cleaved (see regions marked with red arrows). Green circles indicate regions of binder and blue squares, glass fibres from silicon-based separator.

It is likely that a more extended cleavage of V_2O_5 crystals would be a way of improving rate performances of this new cathode material for sodium-ion batteries. On the other hand, new synthetic methods need to be developed to overcome kinetic limitations by tailoring morphology.

Impedance spectroscopy has been carried out to investigate the change of charge transfer resistance upon cycling. Nyquist plots of a fresh cell, after 4 and 188 cycles at C/5 are shown in Fig. S3 of the *Supporting Information*. At high and medium frequencies, depressed semicircles are followed by a straight line, except for the spectrum taken after 4 cycles. Spectra of a fresh electrode and an electrode after 38 cycles have been satisfactorily fitted to the equivalent circuit shown in the insets of Fig. S3 used by Lee et al. [13] for related compounds. R_s corresponds to low resistance of the electrolyte through the connecting pores of separator. A resistor R_f in parallel with a distributed element depending on frequency (CPE_f) describes the impedance of the sodium electrode and thin insulating layer that may be formed due to reaction with the electrolyte at different potential. Finally, a modified Randles-type circuit describes the resistance of the charge-transfer process (R_{ct}), the double layer capacity (C_{dl}) that due to the roughness of the electrode is replaced by a distributed element depending on frequency (CPE_{dl}), and the diffusion of sodium within particles is described with a Warburg element (W_s). For the spectrum taken after 4 cycles the Warburg element has been eliminated during the fitting, because the straight line was not clearly observed at low frequency due to dispersion of data. The value of the charge-transfer resistance (ca. 400 ohm) is very high for the pristine electrode, indicating a limited kinetics. The charge transfer of the electrode cycled four times decreases and results to be quite low (ca. 70 ohm) because of a non-reversible phase transition taking place after the very first sodium atoms inserted during the first discharge (see below). Finally, extended cycling produces an increase of charge transfer resistance (115 ohm) due to

aging of the electrode and increase of surface resistance. However, charge-transfer remains much lower than in the case of fresh β - V_2O_5 .

Fig. 3. Variation of specific capacity of a Na || HP- β - V_2O_5 cell at different C/n rates where n stands for the number of hours needed to insert 1 $\text{Na}^+/\text{V}_2\text{O}_5$.

Fig. 4. SEM images of a composite electrode with HP- β - V_2O_5 as the active material before cycling (a) and after 150 cycles at C/5 rate (b). Green circles: binder; blue squares: glass fibre from separator. The inset shows the pristine powder of HP- β - V_2O_5 used for electrode fabrication.

Fig. 5. Open circuit voltage of a Na|| HP- β -V₂O₅ cell discharged in the galvanostatic intermittent mode in the 3.6-1.7 V range at a current equivalent to a C/20 discharge in continuous mode for 0.5 hours. Cell was kept at open circuit for 4 hours between current intervals.

Fig. 5 shows the open circuit voltage of a Na|| HP- β -V₂O₅ cell discharged in the galvanostatic intermittent mode. The upper open circuit voltage region is characterized by a long plateau centred at 3.3 V that can be assigned to a two phase region. Between 3.2 and 3.1 V a voltage drop occurs in a narrow compositional range (region I) pointing to the existence of a narrow solid solution region. Between 3.1 and 2.9 V a pseudo-plateau is observed pointing to a biphasic region. This finding agrees with the fact that reduction peak A in the voltammogram (Fig. 1) seemed to consist of at least two different processes very close to each other. A third plateau is observed at ca. 2.60 V which separates two other narrow solid solution ranges (II and III) and corresponds to the reduction process labelled as peak B in Fig. 1. Taking into consideration

results from the discharge curve shown in Fig. 5 and reduction wave in Fig. 1, the following compositional ranges can be proposed for HP- β - $\text{Na}_x\text{V}_2\text{O}_5$ single phases formed during the first reduction:

Phase I: $x=0.35-0.45$

Phase II: $x=0.65-0.7$

Phase III: $x=0.9-1.0$

Formation of phase III corresponds to the maximum amount of sodium that can be intercalated in HP- β - V_2O_5 in this voltage range (1 Na ion /f.u.). The charge curve of the open circuit voltage experiment depicted in Fig. 5 also shows the same voltage characteristic as the discharge curve except for a less marked evidence of phase II formation.

In view of the complex voltage-composition profile shown in Fig. 2a and 5, which points to numerous structural phase transformations, potentiostatic intermittent titration technique (PITT; see experimental section) was used to shed more light on the high-voltage region of the Na || HP- β - V_2O_5 system regarding both compositional range of phases formed upon Na^+ insertion and their structures. Fig. 6 shows both the variation of current and voltage with sodium content in $\text{Na}_x\text{V}_2\text{O}_5$. On one hand, current relaxation in the gray shaded regions is far from a $t^{-1/2}$ power law and exhibit non symmetrical behaviour on both sides of $|I|$ maxima as exemplified in Fig. S4 a) and b) of *Supporting Information*. Such behaviour is related to regions where two phases coexist with varying relative ratio as x increases. On the other hand, current relaxes faster towards $I=0$ in the yellow shaded regions, following a power law closer to $t^{-1/2}$ as

exemplified in Fig. S4 c) and d) of *Supporting Information*. This is indicative of the formation of solid solutions.

The assignment of compositional regions made in Fig. 6 agrees with the interpretation of the GITT experiment (Fig. 5), since different current relaxation regimes can be observed. However, results from PITT and time dependence of current suggest the existence of another single phase (I') between phases I and II, separated from I and II by two narrow biphasic regions. An identical situation is found for another single phase, II', detected between phases II and III. Regarding phases I, II and III, we notice that compositional ranges deduced from both PITT and GITT only slightly differ despite their different experimental conditions. To summarize, the combination of PITT and GITT experiments evidences the existence of the following phases and compositional ranges:

Phase I: $x=0.35-0.45$

Phase I': $x=0.55-0.65$

Phase II: $x=0.65-0.7$

Phase II': $x=0.83$

Phase III: $x=0.9-1.0$

Fig. 6. Voltage/current vs. composition curves of a Na || HP- β -V₂O₅ cell run under potentiostatic intermittent conditions (10mV/8h). Solid solutions and two-phase regions are shaded in yellow and gray, respectively.

In order to reveal the structural features of sodium storage during the electrochemical sodium insertion in HP- β -V₂O₅, ex-situ XRD was carried out. HP- β -V₂O₅ electrodes were discharged under constant current to different x values in the $0 \leq x \leq 1$ compositional range and investigated by X-ray diffraction. Particularly, four points were investigated in the discharge process of the first cycle, which correspond to the single-phase regions deduced from our GITT experiment. These are: before discharge ($x=0$), discharging to 59 mAh g⁻¹ at 3.13 V (corresponding to phase I, 0.4 Na), discharging to 103 mAh g⁻¹ at 2.75 V (corresponding to phase II, 0.7 Na insertion), discharging to 132 mAh g⁻¹ at 2.10 V (corresponding to phase III, 0.95 Na insertion).

Refined cell parameters of all above mentioned $\text{Na}_x\text{V}_2\text{O}_5$ compositions obtained by electrochemical discharge are summarized in Table 1. Selected 2θ angular regions together with the voltage composition curve are plotted in Fig. 7. For phase I ($x=0.4$ Na), a significant shift of characteristic peaks, such as (100) and (-101) towards lower diffraction angles is observed, indicating an elongation of a parameter, and consequently, the separation of the V-O octahedral layers. $\text{Na}_{0.4}\text{V}_2\text{O}_5$ could be successfully indexed in the monoclinic system with $a=10.120(1)$ Å, $b=3.6073(3)$ Å, $c=6.3805(5)$ Å and $\beta=94.405(7)^\circ$. The XRD pattern of phase II ($x=0.7$ Na) is similar to that of phase I exhibiting less pronounced shifts of (100) and (-101) peaks. Refined cell parameters for $\text{Na}_{0.7}\text{V}_2\text{O}_5$ are $a=10.097(1)$ Å, $b=3.6370(5)$ Å, $c=6.4187(4)$ Å and $\beta=92.992(8)^\circ$. For phase III ($x=0.95$ Na), increase of intensity of (200) peak and decrease of intensity of (100) and (-101) become obvious. Indexing yielded the following cell parameters $a=9.576(1)$ Å, $b=3.5840(7)$ Å, $c=6.3171(8)$ Å and $92.91(1)^\circ$. The XRD pattern at the final charge state of the first cycle resembles the sodium intercalated compound rather than pristine non-intercalated HP- β - V_2O_5 . Our interpretation is that, although a reversible Na insertion is inferred from electrochemical discharge-charge cycles, an irreversible transformation of V-O layers is likely produced after insertion of the very first Na^+ ions.

Interestingly, lithium insertion in α - V_2O_5 below 1.9 V has been reported to produce a new phase, ω - $\text{Li}_x\text{V}_2\text{O}_5$ ($x=3$), that can be afterwards deintercalated and which is topotactically related to the α polymorph[26]. For sodium insertion

in HP- β - V_2O_5 the structural transformation is likely to occur at the very beginning of insertion reaction owing to the much bigger size of sodium ions. In any case, a deeper insight into the structural changes and related phase transformations requires the use of high-resolution diffraction techniques such as synchrotron X-ray or neutron powder diffraction, under operando conditions if possible.

Fig. 7. Ex-situ XRD patterns of the $\text{Na}_x\text{V}_2\text{O}_5$ electrode obtained during the first discharge of high pressure β - V_2O_5 for selected compositions $x=0, 0.4, 0.7$ and 0.9 .

In order to prove the origin of the irreversible transformation, HP- β -V₂O₅ || Na cells were subjected to a complete discharge-charge cycle in which the amount of sodium was fixed to x=0.4 (phase I), x=0.7 (phase II) and x=0.95 (phase III). The sodium deintercalated electrodes were then subjected to XRD post-mortem studies. Fig. 8 shows the discharge-charge cycles to x=0.4 (a), 0.7 (b) and 0.95 (c) together with their respective ex situ XRD patterns. Most notably, the desodiated compounds exhibit rather similar XRD pattern, regardless of the amount of previously intercalated sodium, but quite different from that of HP- β -V₂O₅ (Fig. 8d). Accordingly, as it can be seen in Table 1, refined lattice parameters of all desodiated materials (De-Na_xV₂O₅) are similar to each other, but clearly different from those of HP- β -V₂O₅. We conclude from these findings that i) an irreversible structural transformation occurs upon the very first intercalated Na⁺ being completed for x=0.4 Na (phase I); ii) as a logical sequence deduced from X-ray pattern analysis of all desodiated phases, the structural transformations for x>0.4 including the formation of phases II and III proceed reversibly. On the other hand, post-mortem analysis of an electrode cycled 150 times shows that the active material is still crystalline and exhibits the characteristic X-ray diffraction pattern of Phase I (see Fig. S5 of *Supporting Information*). To summarize, insertion of the very first sodium produces the transformation of HP- β -V₂O₅ to Phase I, Na_{0.4}V₂O₅, which further cycles. The good capacity retention upon long cycling (Fig. 2) can be attributed to the small volume change experienced by this material during sodium storage between Phase I and Phase III (NaV₂O₅).

We must recall now that Phase I exhibits less kinetic limitations than HP- β -V₂O₅ as deduced from the lower value of charge-transfer resistance determined by impedance spectroscopy (see above). Thus, the electrochemically driven phase transformation facilitates accommodation of sodium ions in more accessible sites, from which easy sodium extraction and inserted is favoured.

A comprehensive structural determination of the sodiated phases is currently under progress by mean of neutron powder diffraction combined with transmission electron microscopy and in operando synchrotron X-ray diffraction to draw a complete picture of the sodium intercalation path in HP- β -V₂O₅.

Results will be published elsewhere.

Table 1: Crystallographic data for selected compounds of the β -Na_xV₂O₅ system.

Phases	a / Å	b / Å	c / Å	β / °	Vol / Å ³
β -V ₂ O ₅	7.1170(9)	3.5765(6)	6.2989(9)	90.09(1)	160.12(4)
Na _{0.4} V ₂ O ₅	10.120(1)	3.6073(3)	6.3805(5)	94.405(7)	232.24(3)
Na _{0.7} V ₂ O ₅	10.097(1)	3.6370(5)	6.4187(4)	92.992(8)	235.41(5)
Na _{0.9} V ₂ O ₅	9.576(1)	3.5840(7)	6.3171(8)	92.91(1)	216.53(5)
De-Na _{0.4} V ₂ O ₅	10.152(1)	3.6145(5)	6.3925(8)	94.17(1)	233.17(6)
De-Na _{0.7} V ₂ O ₅	10.120(1)	3.6112(6)	6.3848(8)	94.28(1)	232.94(9)
De-Na _{0.95} V ₂ O ₅	10.130(1)	3.5996(5)	6.3294(7)	94.38(1)	230.16(5)

Fig. 8. Full discharge-charge cycles (right) and post mortem X-ray diffraction patterns (left) of HP- β -V₂O₅/Na cells at a C/20 rate. The amount of sodium was fixed to $x=0.4$ in the 3.3-3.13 V range (a), to $x=0.7$ in the 3.30-2.75 V range (b) and to $x=0.95$ in the 3.30-2.10 V range (c).

4. Conclusions

In conclusion, we show for the first time a new sodium insertion material, high pressure β -V₂O₅, enabling up to 1 Na⁺/V₂O₅ with a maximum discharge capacity of 147 mAh g⁻¹ in the 3.6-2.0 V range. HP- β -V₂O₅ delivers a very attractive specific energy of 410 Wh kg⁻¹ for cathode applications in sodium-ion batteries.

We demonstrate that the layered structure of HP- β -V₂O₅ favours the incorporation and mobility of Na⁺ ions. Though high-pressure materials feel to be something away from large-scale application, the appealing electrochemical properties of HP- β -V₂O₅ unveiled in this work may trigger new advances in

synthesis to make it easily available, like in the case of vanadium oxyfluoride VO_2F [4] . The high capacity exhibited by this oxyfluoride boosted the initiative of finding a more easily scalable preparation method based on high-energy ball-milling.

The structural study of sodiated materials confirms that an irreversible phase transformation occurs upon insertion of the very first sodium ions, however the insertion reaction proceeds topotactically in the whole compositional range investigated in this work. Interestingly, the phase transformation improves electrochemical performance since charge-transfer resistance decreases.

Finally, we must notice that the amount of inserted sodium points to the reduction of only half of the available V^{5+} ions. Investigations suggestive of 2e^- transfer for $\beta\text{-V}_2\text{O}_5$, which would lead to a high theoretical capacity of 300 mAh g^{-1} , are now under progress and will be published elsewhere.

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