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Ag₂V₄O₁₁: from primary to secondary battery^z

^z Dedicated to Prof. Doron Aurbach, a researcher who genuinely investigated so many battery chemistries, providing major findings to our community.

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8 **Keywords**

9 Silver vanadate, sacrificial lithium salt, energy storage device, rechargeable Li-ion battery.

10 **Abstract**

11 $\text{Ag}_2\text{V}_4\text{O}_{11}$ (Silver Vanadium Oxide, SVO) is the positive electrode in primary Lithium/SVO batteries
12 that had known an extraordinary success as a power source in implantable cardiac defibrillators (ICD).
13 However, its use in rechargeable batteries is questioned due to the need of the negative lithium metal
14 electrode that acts as the lithium source and that cannot be safely recharged in standard liquid
15 electrolytes. In this study, a proof of concept of rechargeable graphite/SVO battery is demonstrated.
16 The introduction of 3,4-dihydroxybenzointrile dilithium salt (Li_2DHBN) as a sacrificial lithium source
17 in the positive electrode allows *in situ* lithiation of the graphite electrode. The cell can further be
18 cycled as a secondary battery. Different parameters have been investigated such as the particle size of
19 $\text{Ag}_2\text{V}_4\text{O}_{11}$ synthesized by solid state and hydrothermal processes, especially with regards to peak
20 power delivery. *In situ* XRD was used to investigate the link between irreversible silver reduction,
21 which allows high electronic conductivity, and amorphization of the SVO structure.

22 **Statements and Declarations**

23 The authors disclose no financial interests that are directly or indirectly related to the work submitted
24 for publication.

25 All authors contributed to the study conception and design. Conceptualization and Methodology were
26 managed by T. Brousse and O. Crosnier. Material preparation, data collection and analyses were
27 performed by E. Le Calvez and O. Crosnier. The first draft of the manuscript was written by E. Le
28 Calvez and all authors commented on previous versions of the manuscript. All authors read and
29 approved the final manuscript.

30 **Introduction**

31 Lithium/silver vanadium oxide ($\text{Ag}_2\text{V}_4\text{O}_{11}$, SVO) primary batteries have been developed from
32 1979.[1] Since then, they have met an outstanding commercial success mainly due to their ability to
33 power implantable cardiac defibrillator (ICD) while meeting all the requirements of such peculiar
34 application.[2] To summarize the major requirements expected for such batteries, it can be emphasized
35 that an ICD continuously monitors heart function and on demand delivers a high-energy shock to the
36 heart to treat arrhythmias. Practically, this means that apart from the continuous delivered current (10
37 to 50 μA) required to power the monitoring circuitry, there is a need to sustain high power pulses, in
38 the range of 1 to 4 A, to rapidly charge the high voltage capacitors whose discharge to the heart
39 interrupts the ventricular fibrillation. The Li/SVO battery is also able to be operated at 37°C (human
40 body temperature) with less than 2% self-discharge per year on open-circuit storage or under low
41 current drain. Long shelf life is also depicted.[2] Moreover, a practical energy density close to 1000
42 Wh/L makes the Li/SVO system attractive for applications where battery size is of concern.

43

44 $\text{Ag}_2\text{V}_4\text{O}_{11}$ cathode of this primary battery and more largely the Li/SVO battery itself has been
45 extensively studied by the team of Prof. Esther Takeuchi in numerous papers tackling all aspects of
46 this energy storage device.[2–7] SVO cathode belongs to the class of vanadium bronzes and possesses
47 semiconducting properties. Its electrochemical reduction is depicted as a multistep process taking
48 place between 3.2 and 1.5 V vs Li^+/Li , leading to the overall reaction:

49



51

52 This results in a theoretical capacity of 315 mAh.g^{-1} within this potential window. The irreversible
53 reduction of silver occurring at the highest potential of the electrochemical window, provides
54 electronic conductivity to the surface of the SVO particles, which further enhances the high rate
55 capability of this electrode. The growth of silver nanoparticles or nanowires upon the first stage of
56 reduction has been evidenced by different teams.[8–10]

57

58 Although, Li/SVO batteries have been practically cycled over tenth of charge/discharge cycles, the use
59 of the metallic lithium anode is detrimental to the safety of a practical use as rechargeable power
60 source for ICD. This is indeed mainly related to the growth of lithium dendrites upon cycling at such
61 temperatures, which can shortly lead to internal short-circuiting the battery.[11] However, with the
62 growing interest in inductively rechargeable batteries, it can be great to design a SVO-based battery
63 which keeps the advantages of this interesting cathode material. This supposes that a lithium source
64 can be implemented in the battery and that this lithium reservoir is not supplied by a metallic lithium
65 foil.

66

67 It can be noted that such a problematic is quite similar to that encountered by lithium-ion capacitors
68 that are using a graphite-based negative electrode and an activated carbon positive electrode.[12–14]
69 The lack of a lithium source is detrimental to the operation of such devices and practical solutions
70 have been proposed to prelithiate the graphite anode during a preliminary charging step. These
71 solutions are of three kinds: the use of a metallic lithium sacrificial electrode,[12] the use of the
72 electrolyte as a lithium ions provider (at the expense of a decrease in ionic conductivity)[15] and the
73 use of a lithium-rich sacrificial compound that can irreversibly provide lithium cations before
74 becoming a dead weight in the battery.[16–18] This later solution has found some practical interest
75 especially when molecules with high capacities are targeted.[19–23]

76

77 In this study, we propose to couple both approaches and provide a proof of concept of a graphite/
78 $\text{Ag}_2\text{V}_4\text{O}_{11}$ secondary battery. This will be achieved by mixing a lithiated organic material, namely 3,4-
79 dihydroxybenzointrile dilithium salt (Li_2DHBN) to $\text{Ag}_2\text{V}_4\text{O}_{11}$ positive electrode. This molecule will
80 irreversibly provide lithium cations to a graphite electrode during an initial *in situ* charging step, while
81 the graphite/ $\text{Ag}_2\text{V}_4\text{O}_{11}$ cell can be further cycled. Indeed, Li_2DHBN salt exhibits very interesting
82 characteristics as a sacrificial lithium salt source in a Li-ion capacitor, with a high irreversible capacity
83 (365 mAh.g^{-1}) which is delivered at a too high potential ($<4.5\text{V}$ vs Li^+/Li) which prevents electrolyte
84 decomposition. After delithiation, it dissolves in the electrolyte without gas formation, thus not
85 altering the pressure in the cell. Moreover, the delithiated form of Li_2DHBN seems to be
86 electrochemically inactive within a large potential window as demonstrated in our previous study.[23]

87

88 1. Experimental section

89 a. Synthesis of $\text{Ag}_2\text{V}_4\text{O}_{11}$ and Li_2DHBN

90 $\text{Ag}_2\text{V}_4\text{O}_{11}$ powders have been prepared by two distinct procedures. A solid-state synthesis
91 method was used to synthesize $\text{Ag}_2\text{V}_4\text{O}_{11}$, further depicted as $\text{Ag}_2\text{V}_4\text{O}_{11}$ SS. Stoichiometric amounts of
92 V_2O_5 (Alfa Aesar, 99.9% metal basis) and Ag_2O (ACROS Organics 99%) were thoroughly mixed
93 using an agate mortar and pestle. The powdered mixture was heated at 550°C for 12 h in air using an
94 alumina crucible. A hydrothermal method was also used to synthesize $\text{Ag}_2\text{V}_4\text{O}_{11}$ H. Stoichiometric
95 amounts of V_2O_5 (Alfa Aesar, 99.9% metal basis) and AgNO_3 (ACROS Organics 99%) were
96 introduced into a Teflon-lined vessel containing 15 mL of water. Then, 200 μL of ethylenediamine
97 (Alfa Aesar) were added dropwise under stirring. After two hours, the vessels were introduced into
98 their autoclaves and put in an oven at 180°C for 48h.

99 3,4-dihydroxybenzointrile dilithium salt (Li_2DHBN) has been synthesized in a similar way to
100 our previous report.[23] Briefly, 3,4-dihydroxybenzointrile (Sigma-Aldrich) was introduced in a
101 beaker which contained 14 mL of tetrahydrofuran in an oxygen free glove box. Then, LiH (Sigma-

102 Aldrich) was also introduced in order to start the ionic exchange between protons and lithium. After
103 15h of stirring, Li₂DHBN had totally precipitated and the powder was recovered by filtration and then
104 dried under vacuum at 150°C.

105 **b. Characterization**

106 **i. Powder X-ray diffraction**

107 Powder XRD data were collected using a PANalytical X'Pert Pro diffractometer with a Cu
108 source ($K_{\alpha 1}=1.5406\text{\AA}$, $K_{\alpha 2}=1.5444\text{\AA}$) and K_{α} filter (Nickel) in the Bragg-Brentano reflection
109 geometry. Data were collected from 10 to 90° 2 θ . *In situ* electrochemical cycling XRD patterns were
110 obtained using a lab-produced cell, close to “Lerliche cell” using a Beryllium window and by cycling
111 the cell at 0.02 A.g⁻¹ with 30 min at open circuit voltage for XRD pattern acquisition.[24] All XRD
112 were collected with ~0.008° 2 θ steps.

113 **ii. SEM**

114 SEM micrographs were obtained using a Zeiss MERLIN Instrument operated at 20 kV using
115 in-Lens annular detector. Samples were prepared by dispersing a small fraction of the powder on a
116 piece of conducting carbon tape. EDX spectra were collected at 8.0 mm working distance using an X-
117 Max 50 mm² OXFORD Instruments detector.

118 **iii. Electrochemistry**

119 To balance the mass ratio between Ag₂V₄O₁₁, Li₂DHBN and graphite, the electrode composition
120 has been determined considering both the irreversible capacity of Li₂DHBN (365 mAh.g⁻¹) as well as
121 the reversible capacity of graphite (around 370 mAh.g⁻¹) and Ag₂V₄O₁₁ (150 mAh.g⁻¹ which represents
122 the capacity of Ag₂V₄O₁₁-H at 0.02 A.g⁻¹ as shown later). Then, mass ratio between Li₂DHBN and
123 graphite was calculated to be 1.01. Mass ratio between Ag₂V₄O₁₁ and graphite was chosen as 2.46 in
124 order to get the same capacity on the positive and negative electrode once the first lithiation has been
125 performed. For these reasons, Li₂DHBN/Ag₂V₄O₁₁ electrode was fabricated with the ratio 1 Li₂DHBN:
126 2.50 Ag₂V₄O₁₁. The different freestanding electrodes are prepared following these compositions:

127 1) Li₂DHBN based electrode consisted of 45% of Li₂DHBN, 45% of conductive carbon and 10%
128 of PTFE.

129 2) Positive electrode (Li₂DHBN with Ag₂V₄O₁₁ composite electrode) was fabricated following
130 these proportions: 62.50% of Ag₂V₄O₁₁, 25.00% of Li₂DHBN, 6.25% of conducting carbon and 6.25%
131 of polyvinylidene fluoride (PTFE) binder.

132 3) 89.00% of graphite, 1.00% of conducting carbon and 10.00% of PTFE were used for the
133 fabrication of the freestanding negative electrode.

134

135 First, electrodes were prepared by thoroughly grinding the active material, conducting carbon
136 (Superior graphite) and polyvinylidene fluoride (PTFE) binder (Sigma-Aldrich, 60 wt.% dispersion in
137 H₂O) in a 75:15:10 wt. ratio, with about 2 mL of ethanol, until a homogeneous paste was obtained.
138 Then, the paste was dried at 70°C overnight before introducing in glove box for incorporation of
139 Li₂DHBN, as reported in our previous paper.[23] The latter was rolled out to a thickness of ~150 μm
140 using a glass cylinder. Then, electrodes were cut into 12 mm diameter disks using a manual electrode
141 puncher.

142
143 All the resulting electrode weights ranged between 5-10 mg·cm⁻², consistent with reasonable mass
144 loading.[25] Electrochemical experiments were performed using Swagelok®-type cells in a 2-
145 electrode configuration. Cells were mounted inside an Argon-filled glovebox (<0.1 ppm O₂, H₂O)
146 using a single Lithium (Li) foil as both the reference and counter electrode (99.9%, Sigma Aldrich). A
147 glass fiber separator (Whatman) and 200 μL of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate
148 (EC/DMC) 1:1 v/v (Solvionic, 99.9% purity, electrochemistry grade) were used as the separator and
149 electrolyte, respectively. All electrochemical studies were performed using a MPG2 BioLogic
150 Potentiostat/Galvanostat controlled by EC-Lab Software. Galvanostatic cycling with potential
151 limitation (GCPL) was performed in a series of 5 cycles at 0.02, 0.05, 0.10, 0.20, 0.50, 1.00 and 2.00
152 A·g⁻¹ (considering mass of active materials) between 1.5V and 3.2V vs Li⁺/Li. The charge-discharge
153 plots shown in the related figures always correspond to the third charge/discharge cycle.

154

155 2. Results & Discussion

156 In this work, we revisited the electrochemistry of Ag₂V₄O₁₁ not only as primary lithium-ion
157 battery cathode materials but also as active materials in positive electrodes for rechargeable batteries.
158 For these reasons, two different syntheses have been performed to compare the influence of particle
159 size on lithium ions intercalation.

160 Ag₂V₄O₁₁ has a monoclinic structure (space group C2/m) with cell parameters close to a=
161 15.48 Å, b= 3.58 Å, c= 9.58 Å and β= 128.74 Å.[26] The layered structure of this oxide is formed by
162 2x2 edge-sharing highly distorted octahedra that are linked together by corner-sharing, as presented in
163 Figure 1. These layers are formed along the *a* axis. Between these (V₄O₁₂)_n layers, silver cations (Ag⁺)
164 are coordinated with 7 oxygen atoms. In fact, the stability of these layers seems to be possible thanks
165 to the sharing of some octahedral by their edges.[27] The structure is very close to Cu_{1.8}V₄O₁₁ as
166 pointed out by Rozier *et al.* [9] Ag₂V₄O₁₁ has been considered in the past as a possible electrode
167 material for high power primary lithium ions batteries due to its layered structure as well as the
168 possible reduction of both silver and vanadium cations during the discharge as previously explained.
169 Indeed, silver nanoparticles help to increase the electronic conductivity of the electrode.

170 As presented in Figure 2.A, XRD patterns show that a pure phase is obtained with both
 171 syntheses. All the main reflections peaks of the phase are visible between 20 and 60°. Furthermore, a
 172 large difference in terms of crystallite size is observed, as it can be seen with the much broader peaks
 173 observed in the case of Ag₂V₄O₁₁ H. In fact, the average crystallite size is found to be > 1 μm in the
 174 case of solid-state synthesis and ~250 nm in the case of hydrothermal synthesis. These results are
 175 found by applying the Scherrer equation on (110) and (003) peaks.

176 SEM images at different magnifications are presented in Figure 2.(B-E). Both types of
 177 particles presented preferential growth along [30 $\bar{2}$] with rods like shape. [28-29] Nevertheless,
 178 particles size is found to be much smaller in the case of Ag₂V₄O₁₁ - H as expected from XRD patterns:
 179 particles synthesized using solid-state synthesis exhibit a size of a few tens of micrometers, while
 180 hydrothermal particles are nanorods of about 500 nm long with a diameter of 50 nm. Moreover, these
 181 nanorods are agglomerated and form micrometer size secondary particles.

182 Thanks to the large difference in terms of crystallite and particle size between hydrothermal
 183 and solid-state reactions, it is of interest to compare the respective electrochemical responses of both
 184 materials vs a lithium metal electrode. For this reason, charge-discharge cycles at different current
 185 densities have been performed. The results are presented in Figure 3.(A-B). To avoid the re-oxidation
 186 of Ag⁰ to Ag⁺ the potential should not exceed 3.2V upon oxidation sweep.^{6,7} Thus, the selected
 187 potential range of the experiment has been set up between 1.5V and 3.2V vs Li⁺/Li. During the first
 188 reduction, capacities are 277 mAh.g⁻¹ and 292 mAh.g⁻¹ for respectively solid-state and hydrothermal
 189 Ag₂V₄O₁₁ electrodes. These values correspond to the insertion of respectively 6.1 and 6.5 Li⁺/
 190 Ag₂V₄O₁₁. This large capacity during the first reduction is assigned to both silver reduction which
 191 allows Ag⁺/Li⁺ displacement reaction (Equation 2) and V⁵⁺/V⁴⁺ reduction followed by the partial
 192 reduction of V⁴⁺ into V³⁺ (Equation 3). The charge storage mechanism of this first reduction will be
 193 discussed later. The low coulombic efficiency of the first cycle is also explained by the irreversible
 194 reduction of Ag⁺ to metallic silver and then part of the Li⁺ needs to remain in the interlayer to prevent
 195 the collapsing of the pristine layered structure.



198 After this first cycle, both materials presented a relatively high reversible capacity between
 199 1.5V-3.2V vs Li⁺/Li. At a current density of 0.02 A.g⁻¹, a capacity of around 150 mAh.g⁻¹ is observed
 200 for the electrodes prepared using both Ag₂V₄O₁₁ powders. This capacity represented 3.3 Li⁺/
 201 Ag₂V₄O₁₁. However, when the current density increases, a faster decrease in the capacity retention is
 202 observed for Ag₂V₄O₁₁ – SS sample compared to Ag₂V₄O₁₁ - H. For example, at 0.10 A.g⁻¹ and 0.50
 203 A.g⁻¹, Ag₂V₄O₁₁ – SS exhibits respectively 78 and 14 mAh.g⁻¹ while Ag₂V₄O₁₁ - H shows 109 and 73
 204 mAh.g⁻¹. A smaller lithium diffusion pathway that limits the intrinsic kinetic limitations of this phase

205 can explain this better capacity retention. In fact, Fick's first law concerning diffusion explained that
206 diffusion length has a strong impact on diffusion time. ($L \propto \sqrt{D \cdot t}$ where L is the diffusion length, D,
207 is the diffusion coefficient and t, is the diffusion time).

208 Figure 3.D shows the cyclability of both powders at 0.2 A.g⁻¹ upon cycling. After 250 cycles
209 and considering the second cycle as the reference, capacity retentions of about 75% and 110% are
210 observed for solid-state and hydrothermal Ag₂V₄O₁₁, respectively. It can be noticed that the capacity
211 increases after few cycles in the case of Ag₂V₄O₁₁-H, which can be due to a continuous change of the
212 structure during these first cycles allowing a greater insertion of the lithium ions. From our
213 understanding, nanomaterials undergo lower stress which leads to a better capacity retention upon
214 cycling.

215 To understand more in-depth the charge storage mechanism occurring in Ag₂V₄O₁₁-H, *in situ*
216 XRD experiments were performed at 0.02 A.g⁻¹ between 1.5 and 3.2V vs Li⁺/Li during the first
217 reduction. In 2010, Sauvage *et al.* carried out in-depth *in situ* XRD characterizations on micrometric
218 Ag₂V₄O₁₁. [32] They found that at the early stage of the lithiation, Li⁺ insertion occurs without Ag⁺
219 displacement and/or reduction. For this reason, no amorphization takes place. However, after the
220 insertion of around one lithium per chemical formula, a progressive loss of crystallinity occurs in
221 parallel to silver reduction until full amorphization at 2.2 Li⁺ per chemical formula. Then, steady
222 reduction of silver continues until reaching a fully metallic silver state. *In situ* XRD experiment of
223 Ag₂V₄O₁₁ - H is represented in Figure 4(A-B-C). It is found that both amorphization and silver
224 reduction take place at the beginning of the lithiation. In the case of Ag₂V₄O₁₁-H, Li⁺/Ag⁺
225 displacement reaction occurs at the first stage of the reduction process and not V⁵⁺/V⁴⁺ reduction. The
226 reaction is in this sense dependent of particle size, which is in agreement with literature data. [31] The
227 collapse of the structure can be explained by the bigger ionic radii of silver cations (1.22 Å) compared
228 to Li⁺ ions (0.76 Å) which does not allow the layer architecture to be stable.^{9, 10} Furthermore, the
229 reduction of silver creates nanoparticles of metallic silver at the surface of Li_xAg_{2-y}V₄O₁₁ (x < y)
230 particles. This "coating" has been reported to increase the electronic conductivity and then allows its
231 use as high power primary cathode material. [33-35]

232 Then, after the characterization of Ag₂V₄O₁₁ with two different morphologies, the next step was to
233 show that this lithium-free oxide could be used in association with a sacrificial lithium source in a
234 secondary lithium-ion battery setup. In other words, the idea of the present paper is summarized in
235 Figure 5.A. Here, Ag₂V₄O₁₁ - H will be used as efficient negative electrode materials. Moreover,
236 Li₂DHBN was considered as a source of lithium as it shows a relevant behavior in Li-ion
237 capacitor. [23]

238 First, two different electrodes have been prepared, one serving as the reference with only 3,4-
239 dihydroxybenzotrile dilithium salt (Li₂DHBN) and a second one which is a composite of Ag₂V₄O₁₁

240 and Li₂DHBN. Details on the mass ratio between Ag₂V₄O₁₁ and Li₂DHBN can be found in the
241 experimental section. To provide lithium to the system, the irreversible delithiation of Li₂DHBN
242 occurs between 3.0V and 4.0V vs Li⁺/Li. This delithiation has been performed using a charging rate of
243 C/10 considering the mass of Li₂DHBN. As shown in Figure 5.B, the delithiation behavior of the
244 pristine Li₂DHBN and the composite positive electrodes is similar with a capacity of about 300
245 mAh.g⁻¹ (per g of Li₂DHBN). This capacity translates in a release of 1.7 Li⁺/Li₂DHBN. The difference
246 in terms of delithiation potential is due to the larger open circuit potential of the composite electrode
247 containing Ag₂V₄O₁₁ - H and Li₂DHBN. We can then conclude that delithiation of Li₂DHBN occurs in
248 a similar manner with or without the presence of Ag₂V₄O₁₁ - H.

249 After this irreversible delithiation of the Li₂DHBN organic molecule, DHBN is dissolved in electrolyte
250 and not present anymore in the positive electrode as explained by P. Jezowski *et al.*[23] Figure 5.C
251 reports on the following cycles at different current densities when metallic lithium is used as the
252 negative electrode. As observed, Ag₂V₄O₁₁ - H presents a discharge capacity on the third cycle of 120
253 mAh.g⁻¹ at 0.02 A.g⁻¹ between 3.2V and 1.5V vs Li⁺/Li. Compared to the Li₂DHBN-free Ag₂V₄O₁₁ - H
254 electrode (Figure 3.B), we observed a decrease of 40 mAh.g⁻¹, which is mainly due to vanadium
255 dissolution during first Li₂DHBN delithiation. [38] In fact, the separator is found to be greenish, which
256 is characteristic of V⁵⁺ species in solution. The following cycles show good capacity retention
257 indicating that Ag₂V₄O₁₁ dissolution only occurs concomitantly with this initial delithiation. At 0.05
258 and 0.1 A.g⁻¹, the values of capacity are equal to 63 and 33 mAh.g⁻¹ respectively (Figure 5.C). These
259 lower capacities compared to the pristine Li₂DHBN-free Ag₂V₄O₁₁ - H electrode (Figure 3.B) can be
260 explained by several reasons. First, the ratio between Ag₂V₄O₁₁ and conductive carbon has not been
261 optimized in Li₂DHBN Ag₂V₄O₁₁ - H electrode with a low amount of conductive carbon (6.25%). In
262 fact, adding more conductive carbon can increase the electronic conductivity of the electrode and then
263 improve the capacity at higher current densities. Furthermore, the electronic percolation can be
264 deteriorated by the dissolution of Li₂DHBN in the electrode. Nevertheless, we note that the electrode
265 works relatively well at moderate current densities. For this reason, the Li₂DHBN Ag₂V₄O₁₁ - H
266 composite electrode has been further associated with a graphite negative electrode in a full device
267 assembly.

268 The two first cycles of the Li₂DHBN Ag₂V₄O₁₁ - H electrode vs a graphite electrode are presented
269 Figure 5.(D-E). A thick lithium wire has been used to monitor the evolution of both electrode
270 potentials. During the first charge, at the positive electrode, Li₂DHBN effectively releases its lithium
271 cations (around 1.8 Li⁺/Li₂DHBN), thus evidencing the effectiveness of *in situ* lithiation of the cell. In
272 the negative electrode, graphite inserts lithium cations until reaching ~0.1V vs Li⁺/Li as typically
273 observed for this negative electrode material that has been deeply investigated by Prof. Doron Aurbach
274 and his team.[36–38] The observed capacity is about 350 mAh.g⁻¹, which is very close to its
275 theoretical capacity of 372 mAh.g⁻¹. Moreover, the plateau observed at ~0.8V vs Li⁺/Li represents the

276 formation of the solid electrolyte interphase (SEI). During the second discharge, the cell shows a
277 relatively poor coulombic efficiency with less than 40%. In fact, the graphite electrode only partially
278 releases the inserted lithium. Several explanations can support this poor coulombic efficiency. First of
279 all, the vanadium which is liberated and dissolved during the Li₂DHBN delithiation can further react
280 during the SEI formation and/or migrate to the anode and simply be deposited on the surface of the
281 graphite electrode as observed by Takeuchi.[39-40] This has been largely commented in literature
282 concerning Mn²⁺ dissolution in LiMn₂O₄ and is responsible for similar issues.[41-43] As well, silver
283 metal and/or silver ions can also be dissolved, and migrate to the graphite electrode giving rise to this
284 poor coulombic efficiency. [40-41] Lastly, it is also possible that the delithiated DHBN molecules are
285 involved in the complexation of vanadium species in solution, thus disturbing the formation of the SEI
286 on the surface of graphite, and then partially preventing the lithium ions from leaving the graphite
287 upon subsequent discharge of the cell. As observed in Figure 5.E, the coulombic efficiency is still poor
288 for the following cycle. Based on the literature data, different solutions can be used to increase the
289 coulombic efficiency. Among them, using high concentrated salt and/or adding additives in the
290 electrolyte can reduce vanadium dissolution.[42,44-45] Carbon-coated Ag₂V₄O₁₁ particles can also
291 allow to cancel this drawback.[48] These solutions are currently under investigation to obtain a better
292 coulombic efficiency. Nevertheless, this first insight of how to turn Ag₂V₄O₁₁/Li primary battery into
293 Ag₂V₄O₁₁/graphite secondary (rechargeable) battery has been demonstrated, thanks to *in situ* lithiation
294 of this system using Li₂DHBN sacrificial molecules. This work provides new guidelines to use non-
295 lithiated positive electrodes in rechargeable lithium ion-batteries.

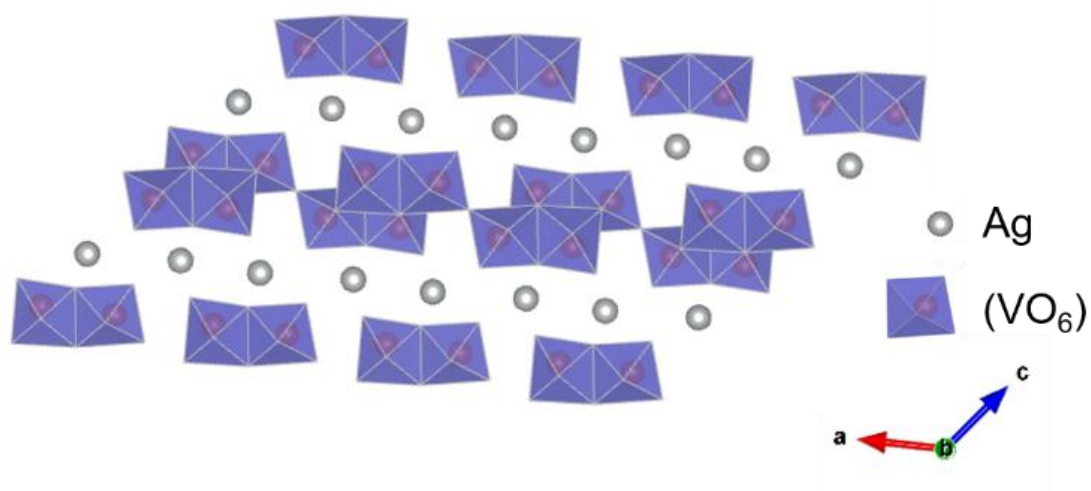
296 **Conclusion**

297 This work presents the characterization of two Ag₂V₄O₁₁ powders synthesized by solid-state and
298 hydrothermal processes. Hydrothermal Ag₂V₄O₁₁ exhibits superior electrochemical behavior with a
299 capacity of 150 mAh.g⁻¹ at a moderate current density (0.02 A.g⁻¹) between 1.5V and 3.0V vs Li⁺/Li
300 after an initial capacity of 300 mAh.g⁻¹. *In situ* XRD has shown the irreversible reduction of silver
301 during the first cycle concomitantly to the amorphization of the structure. Moreover, Ag₂V₄O₁₁ - H
302 was associated to a sacrificial organic lithium salt at the positive electrode and the related composite
303 electrode was tested against graphite as negative electrodes in rechargeable batteries. This is a first
304 report of such a proof of concept of how to turn a performing positive electrode for primary batteries
305 into a rechargeable cathode for a lithium-ion cell. In this study, we highlighted the possibility of using
306 such a device even if coulombic efficiency is still modest for this first insight. Finally, several other
307 possibilities exist for improving the system and potentially achieve better coulombic efficiency,
308 especially with the use of other sacrificial salts (Li₃N, Li₂C₄O₄...).[19-22, 50-51]

309 **Acknowledgements**

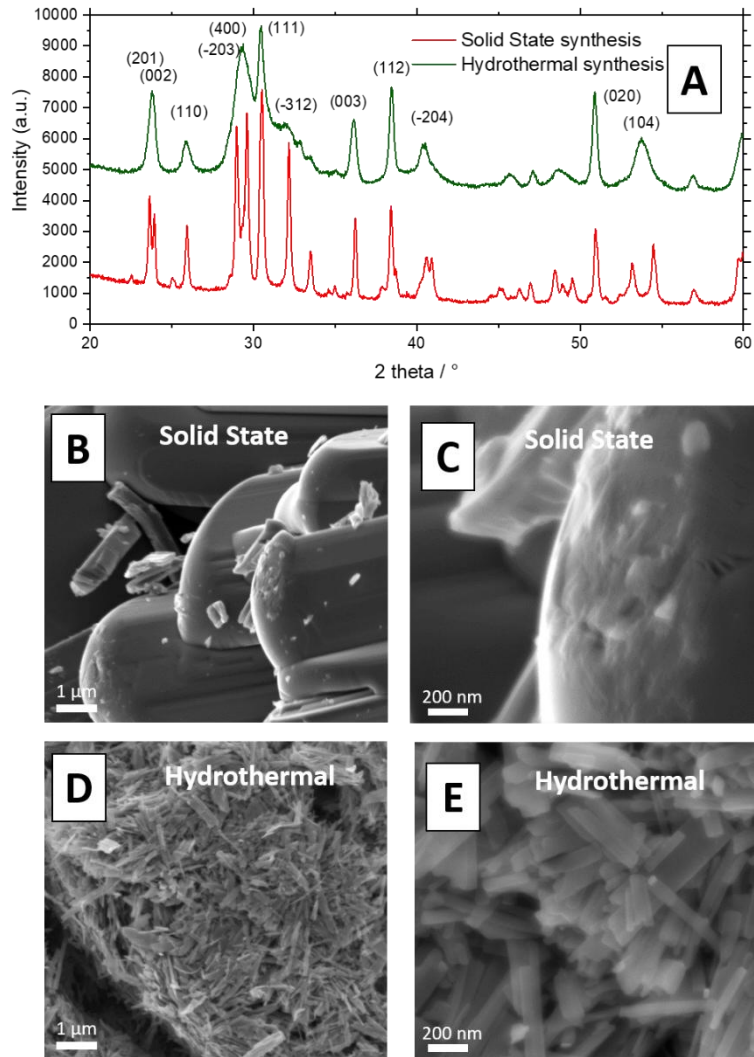
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315 **Figures**



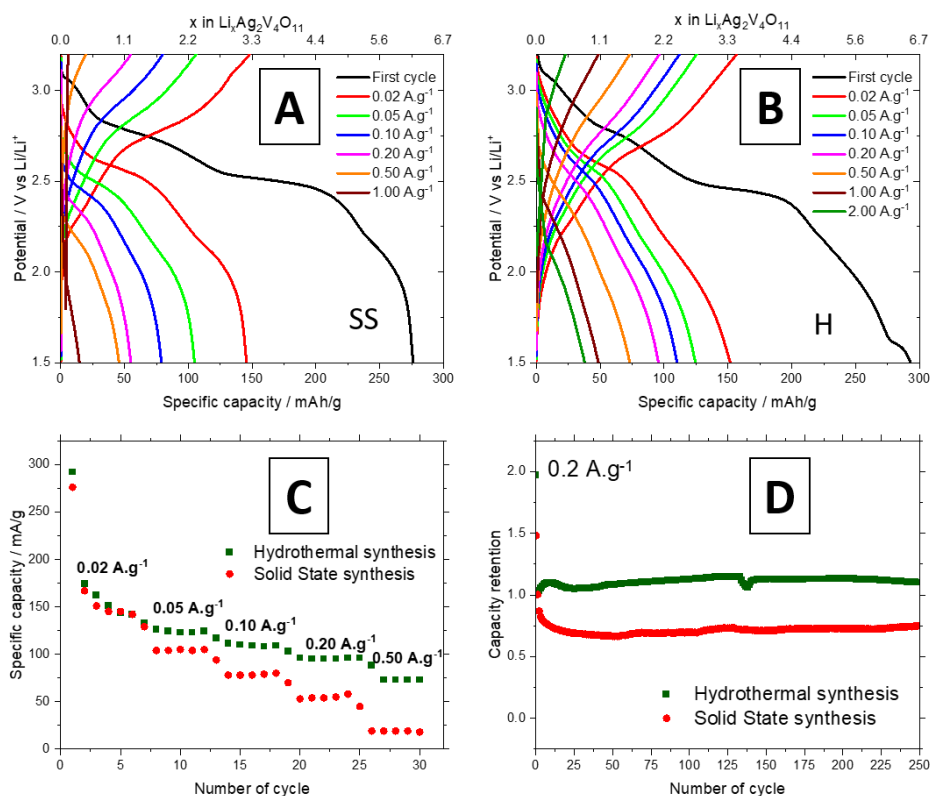
316

317 **Figure 1.** A Crystal structure of $\text{Ag}_2\text{V}_4\text{O}_{11}$



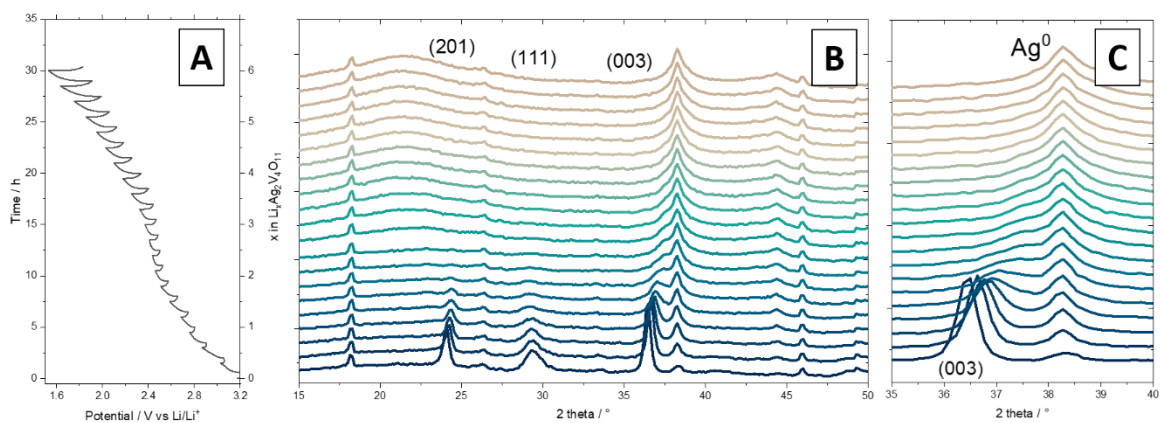
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319 **Figure 2.** (A) Diffractograms of $\text{Ag}_2\text{V}_4\text{O}_{11}$ synthesized by solid state and hydrothermal method (B-C).
 320 SEM images of $\text{Ag}_2\text{V}_4\text{O}_{11}$ synthesized by solid-state method. (D-E). SEM images of $\text{Ag}_2\text{V}_4\text{O}_{11}$
 321 synthesized by hydrothermal method.



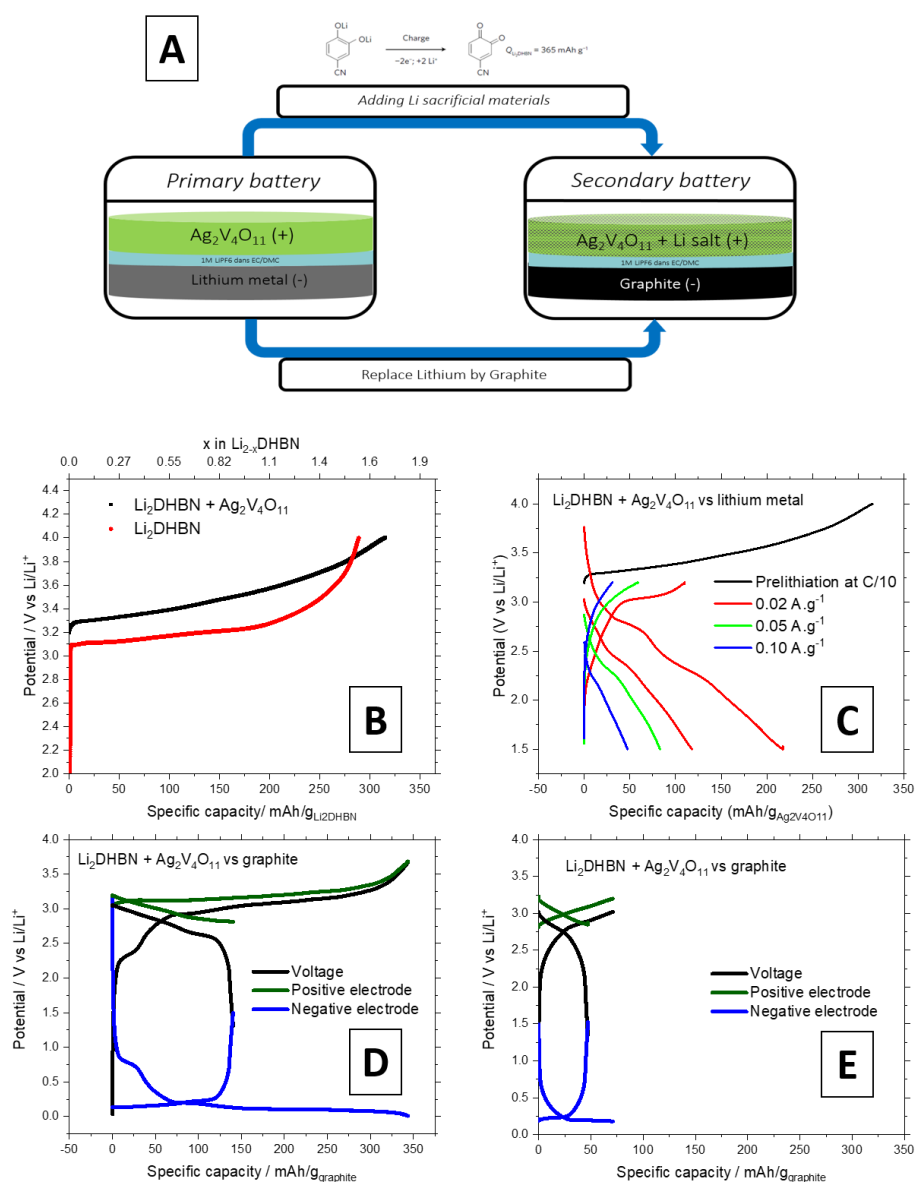
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 323 **Figure 3. (A-B).** Charge-discharge experiments at different current densities for $\text{Ag}_2\text{V}_4\text{O}_{11}$ synthesized
 324 by hydrothermal method. **(C).** Specific capacity vs cycle number at different current densities for both
 325 solid state and hydrothermal powders. **(D).** Cycling stability of both $\text{Ag}_2\text{V}_4\text{O}_{11}$ synthesized by solid
 326 state and hydrothermal methods.

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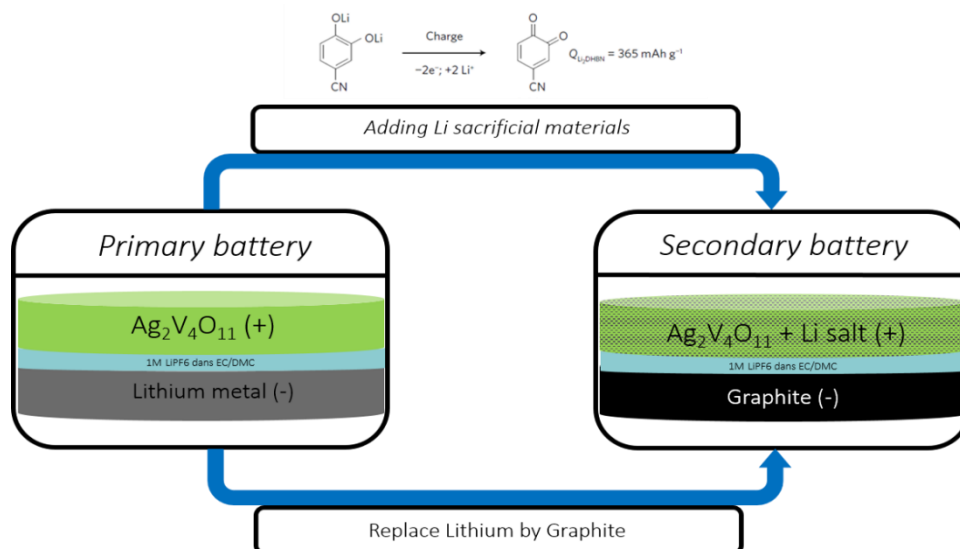
328
 329 **Figure 4.** *In situ* XRD experiment of $\text{Ag}_2\text{V}_4\text{O}_{11}$ synthesized by hydrothermal method. **(A)** First
 330 discharge curve at 0.05 A.g^{-1} **(B-C)** Associated diffractograms of $\text{Ag}_2\text{V}_4\text{O}_{11}$ at different states of
 331 discharge.

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Figure 5. (A) Scheme of the proposed transition from a primary battery to a secondary and therefore rechargeable battery using a sacrificial salt and $\text{Ag}_2\text{V}_4\text{O}_{11}$. (B) Electrochemical delithiation of Li_2DHBN associated or not with $\text{Ag}_2\text{V}_4\text{O}_{11}$ at a charging rate of C/10 (considering the theoretical capacity of Li_2DHBN). (C) Charge and discharge plots of $\text{Ag}_2\text{V}_4\text{O}_{11}$ with Li_2DHBN at different current densities vs metallic lithium. (D) First cycle of $\text{Ag}_2\text{V}_4\text{O}_{11}$ with Li_2DHBN associated with a graphite electrode at C/5 (considering the mass of graphite). (E) Second cycle of $\text{Ag}_2\text{V}_4\text{O}_{11}$ with Li_2DHBN associated with a graphite electrode at C/5 (considering mass of graphite).



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343 **Graphical abstract**

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