W. Deriouche[a,b], E. Anger[a], N. Amdouni[b], V. Pralong[a,*]

[a] Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, 14000 Caen, France
[b] Unite de Recherche Physico-chimique des Materiaux Condenses, Universite Tunis
El Manar, Faculte des Sciences de Tunis, Campus Universitaire, 2092 El Manar
Tunis, Tunisia
e-mail: valerie.pralong@ensicaen.fr

Sodium intercalation into α- and β-VOSO₄

Na-ion battery is one of the best alternatives to Li-ion battery. Abundance of sodium on earth is three orders of magnitude higher than lithium, which should make Na-ion battery technology cheaper. But alkaline-ion battery prices, which tend to increase because of the massive world demand, also depend on the choice of electrode materials. Therefore, cost-effective electrode development remains an important subject of research because this will allow Na-ion battery to be even more competitive. Electrochemical performances of anhydrous $VOSO_4$ as electrode for Na-ion battery are reported in this letter. Two anhydrous phases of vanadyl sulfate have been studied. The first one, α-$VOSO_4$, shows that up to 0.8 sodium per formula unit (Na/f.u.) can be intercalated in this phase, and a reversible intercalation of 0.4 Na/f.u. has been observed with a strong polarization. The second one, β-$VOSO_4$, can intercalate up to 0.9 Na/f.u. with a reversible intercalation of 0.4 Na/f.u. leading to a reversible capacity of 64 mAh/g.

Introduction

The search for new materials that could be used as electrode material for the Na-ion batteries is one of today's most challenging issues. Many families of transition metal oxides as well as transition metal polyanionic frameworks have been proposed these last five years. Among them, Na-Super-Ionic-Conductors (NaSICON) are one the most popular materials due to their good cycling ability and Na⁺ mobility. However, sulfates represent an interesting and low-cost class with only few reported members. Therefore, few sodiated iron sulfates [1–4] can be found in the literature and only

one example of sodiated vanadate sulfate has been reported up to date ($Na_2VO(SO_4)_2$) as an electrode material for Na-ion battery [5]. This material delivers a reversible capacity of 60 mAh/g at 4.5 V vs Na⁺/Na.

In this work, we report the use of anhydrous vanadyl sulfate as an electrode material for Na-ion battery. Anhydrous $VOSO_4$ exists in two forms at room temperature: α-$VOSO_4$ is tetragonal and is formed by dehydration of its hydrate below 280 °C [6], β-$VOSO_4$ is orthorhombic and may be prepared either from the reaction of H_2SO_4 and V_2O_5 [7] or by dehydration

above 280 °C, although decomposition occurs when using this last method [8]. The charge-discharge profile of both known phases, α- and β-VOSO$_4$, will be discussed.

Experimental

The alpha form, α-VOSO$_4$, was prepared by a simple dehydration of VOSO$_4$·xH$_2$O (5 g, Sigma Aldrich) at 260 °C for 2 days, then stored in a glove-box to prevent rehydration from air moisture. On the other hand, β-VOSO$_4$ was prepared by a precipitation reaction starting from stoichiometric amounts of hydrated vanadium oxysulfide VOSO$_4$·xH$_2$O (1.8 g) heated at 140 °C in 100 mL of sulphuric acid solution (0.1M H$_2$SO$_4$) for 2 hours. The resulted green mixture was then filtered and washed with water. The obtained powder is then left overnight at 160 °C in an oven before being stored in argon-filled glove-box. The compounds were characterized by X-ray powder diffraction (XRD) using a Philips X'Pert 2 diffractometer with Bragg-Brentano geometry (Cu Kα radiation). Note that due to their instability in air, the reduced phases' XRD patterns were registered under vacuum using a chamber attached to the XRD instrument. The electrochemical characterization was performed in cells build in Swagelok compression tube fitting with a solution 1M NaClO$_4$ in propylene carbonate (PC) as electrolyte and metallic sodium as counter electrode. The working electrode was prepared from a mixture of active material with acetylene black in a weight ratio of 50:50. The electrochemical cells were cycled at constant current between 1.0–3.0 V at different galvanostatic rates on a VMP III potentiostat/galvanostat (Biologic SA, Claix, France) at room temperature.

Results and discussion

First report on preparation of the phase alpha of anhydrous vanadyl sulfate was published in 1965 by J. Tudo [6]. Its crystal structure was optimized and its magnetic properties studied by R. J. Arnott and J. M. Longo in 1970 [9]. They suggest that trace of water was present in Tudo's sample. This phase crystallizes within a tetragonal structure (space group: P4/n) with a = 6.258 Å, c = 4.122 Å and a volume of V = 161.42(3) Å^3. Along the c-axis, we can observe continuous chains of corner-shared VO$_6$ octahedra, as shown in Fig. 1. All these chains are corner-shared with SO$_4$ tetrahedra forming a three-dimensional network.

First report on the phase beta of anhydrous vanadyl sulfate was published in 1927 by A. Sieverts and E. L. Müller [7]. In 1970, its crystal structure and its magnetic properties have been studied in the same paper than α-VOSO$_4$ [9]. This phase crystallizes within an orthorhombic structure (space group: Pnma) with a = 7.384 Å, b = 6.275 Å, c = 7.078 Å and a volume of V = 327.92(3) Å^3. β-VOSO$_4$ is described by Gaubicher et al. as chains of corner-sharing distorted vanadium oxygen octahedra along the a-axis. Those chains are linked to sulphate groups which alternately point in opposite directions along the c-axis [10].

Interestingly, Gaubicher et al. published the reversible intercalation of 0.6 lithium ions into β-VOSO$_4$ at 2.84 V vs Li$^+$/Li. After a first intercalation of 0.9 lithium through a biphasic process at 1.75 V, a solid solution reaction takes place. The structure of the reduced phase Li$_{0.9}$VOSO$_4$ has not been solved [10].

We investigated the charge-discharge profile of α-VOSO$_4$ carried out at C/20

between 1.0 and 3.0 V (Fig. 2a). The slope of the curve suggests that a solid solution process occurs during both charge and discharge. The theoretical capacity for the intercalation of 1 sodium per $VOSO_4$ is 160 mAh/g. The first discharge allows the intercalation of 0.8 Na/f.u. at an average voltage of 1.58 V with an average of 0.6 Na/f.u. reversibly deintercalated after 4 cycles. This corresponds to a reversible capacity of 96 mAh/g. The intercalation and deintercalation of sodium occur in two distinct processes centered respectively at 1.45 then 1.15 V for the intercalation and 2.42 then 2.68 V for the deintercalation, as observed on Fig. 2b.

The charge-discharge profile of β-$VOSO_4$ carried out at C/20 between 1.0 and 3.0 V is depicted in Fig. 2c. The slope of the curve suggests also that a solid solution process occurs during both charge and discharge. The first discharge allows the intercalation of 0.9 Na/f.u. at an average voltage of 1.58 V, but only 0.4 Na/f.u. were reversibly deintercalated, corresponding to a reversible capacity of 64 mAh/g. This potential characterizes the V^{4+}/V^{3+} redox potential. The capacity remains almost unchanged after 4 cycles. The intercalation

a

b
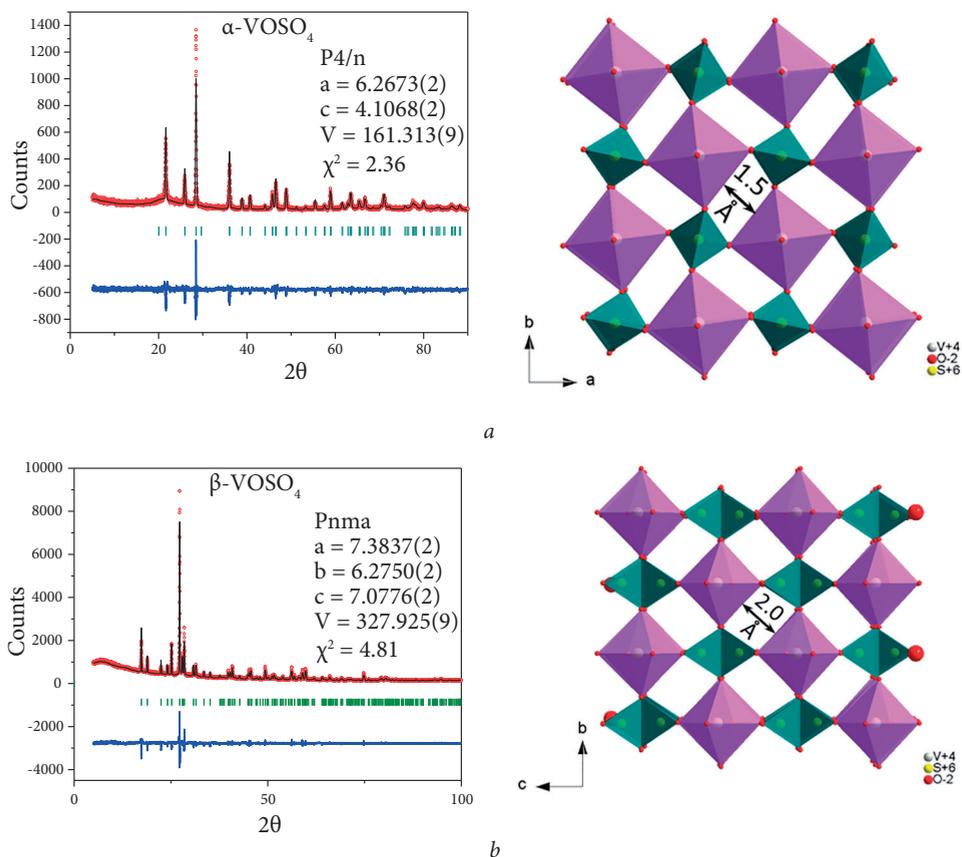
Fig. 1. (a) Rietveld refinement of the XRD pattern for α-$VOSO_4$ and its structure along the *c*-axis; (b) Rietveld refinement of the XRD pattern for β-$VOSO_4$ and its structure along the *a*-axis

and deintercalation of sodium occur in two distinct processes centered respectively at 1.90 and 2.40 V for the intercalation and 2.30 and 2.85 V for the deintercalation process, as observed in Fig. 2d.

According to the electrochemical study (lower polarization and almost no shift on capacity after few cycles), β-VOSO$_4$ seems more suitable for the intercalation of Na and therefore should be more deeply investigated. Best performance of β-VOSO$_4$ can be explained by the channels observed in α-VOSO$_4$ structure (1.5 Å) being smaller than in b-VOSO$_4$ structure (2 Å) (see Fig. 1). The difference in channel sizes comes from a difference of configuration of SO$_4$ tetrahedra in these structures. In the α-VOSO$_4$ structure, SO$_4$ tetrahedra are linked to four channels of VO$_6$ octahedra. In contrast, only three channels of VO$_6$ octahedra are connected to the SO$_4$ channels in the β-VOSO$_4$ structure. Consequently, the structure is more constrained with less space between VO$_6$ octahedra chains in a-VOSO$_4$ than in β-VOSO$_4$.

To complete our study, we decreased the size of the particles of α-VOSO$_4$ by using a mechanochemical process (250 rpm/1.5 hrs). Although this ball milling process effectively nanostructured our
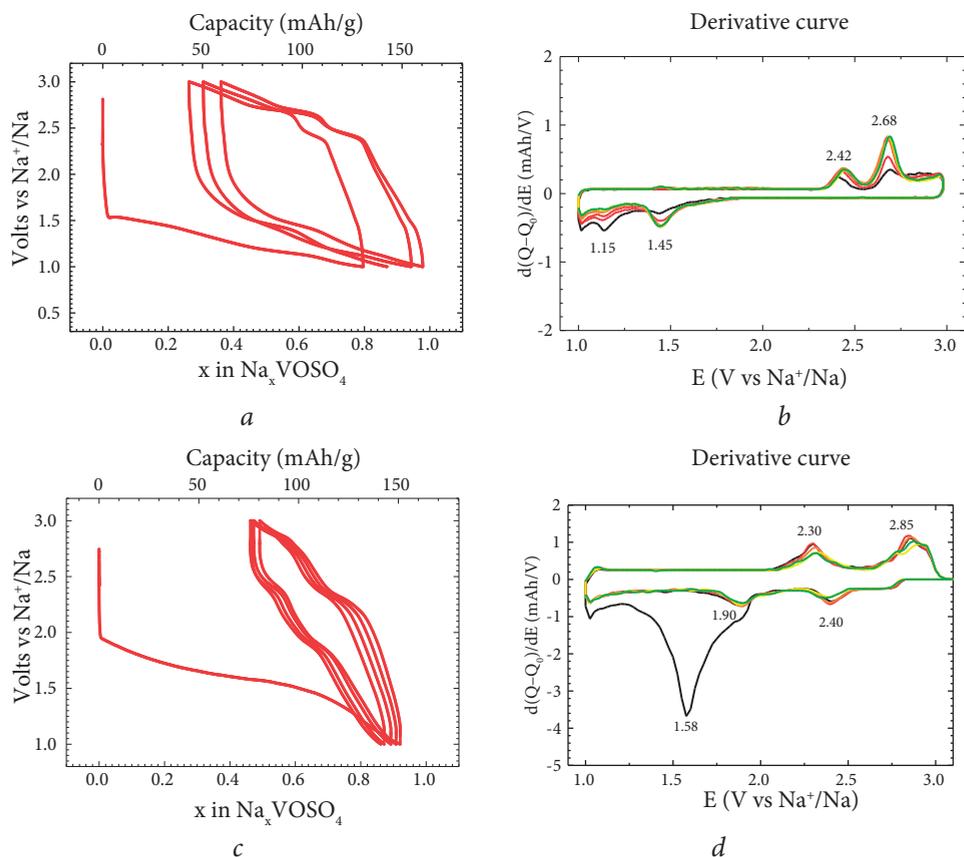

Fig. 2. (a) Potential-capacity curves of α-VOSO$_4$ at the galvanostatic rate of C/20 between 3.0 and 1.0 V; (b) corresponding derivative curves; (c) potential-capacity curves of β-VOSO$_4$ at the galvanostatic rate of C/20 between 3.0 and 1.0 V; (d) corresponding derivative curves

material, as shown on the following X-ray pattern (Fig. 3, middle line), this did not improve the electrochemical properties of our material.

Attempts to chemically reduce either α- or β-VOSO$_4$ using sodium naphthalenide in THF have been unsuccessful due to the dissolution of the material in THF.

Finally, ex situ XRD pattern has been obtained after the first reduction of α-VOSO$_4$. This shows that an amorphization process occurred during the intercalation of sodium into α-VOSO$_4$ phase (Fig. 3, upper line).

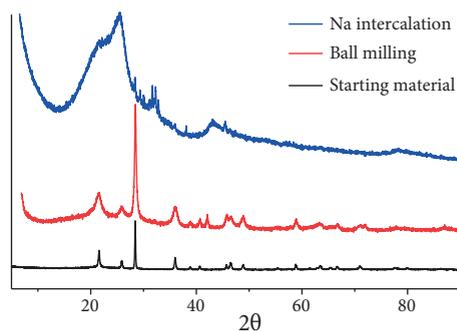Fig. 3. Powder X-ray diffraction pattern of as prepared α-VOSO$_4$ phase (lower curve); powder X-ray diffraction pattern of α-VOSO$_4$ phase after ball milling (middle curve); powder X-ray diffraction pattern of α-VOSO$_4$ phase after Na intercalation (upper curve)

Conclusions

In this work, we demonstrated that α- and β-VOSO$_4$ can be used as an electrode material in Na-ion battery. To the best of our knowledge, this is only the second vanadyl sulfate based material used in Na-ion battery. The β phase exhibits smaller polarization than the α phase. Intercalation and deintercalation of 0.4 Na/f.u. have been observed, which correspond to a capacity of 65 mAh/g. This reversible capacity is quite low, but could be improved by playing with the particle size as well as carbon coating, even though nanosizing has been unsuccessful on the α phase. Then, due to its attractive price and its cycling capability, further investigations on the intercalation of sodium in β-VOSO$_4$ are in progress.

References

1. Singh P, Shiva K, Celio H, Goodenough JB. Eldfellite, NaFe(SO$_4$)$_2$: an intercalation cathode host for low-cost Na-ion batteries. *Energy Environ Sci*. 2015;8:3000–5. DOI:10.1039/C5EE02274F.
2. Mason CW, Gocheva I, Hoster HE, Yu DYW. Iron(III) sulfate: a stable, cost effective electrode material for sodium ion batteries. *Chem Commun*. 2014;50:2249–51. DOI:10.1039/C3CC47557C.
3. Meng Y, Zhang S, Deng C. Superior sodium — lithium intercalation and depressed moisture sensitivity of a hierarchical sandwich-type nanostructure for a graphene — sulfate composite: a case study on Na$_2$Fe(SO$_4$)$_2$·2H$_2$O. *J Mater Chem A*. 2015;3:4484–92. DOI:10.1039/C4TA06711H.

4. Barpanda P, Oyama G, Nishimura S, Chung SC, Yamada A. A 3.8-V earth-abundant sodium battery electrode. *Nat Commun*. 2014;5:4358. DOI:10.1038/ncomms5358.

5. Sun M, Rousse G, Saubanère M, Doublet ML, Dalla Corte D, Tarascon JM. $A_2VO(SO_4)_2$ (A = Li, Na) as Electrodes for Li-Ion and Na-Ion Batteries. *Chem Mater*. 2016;28:6637–43. DOI:10.1021/acs.chemmater.6b02759.

6. Tudo J. Vanadyl sulfate and its reduction by hydrogen sulfide: vanadium sulfides. *Rev Chim Miner*. 1965;2(1):58–177.

7. Sieverts A, Müller EL. Vanadinverbindungen und siedende Schwefelsäure. *Z Für Anorg Allg Chem*. 1928;173(1):313–23. German. DOI:10.1002/zaac.19281730128.

8. Paufler P, Filatov SK, Bubnova RS, Krzhizhanovskaya MG. Synthesis and thermal behaviour of pauflerite, β-$VOSO_4$, and its α-modification. *Z Kristallogr — Cryst Mater*. 2014;229:725–9. DOI:10.1515/zkri-2014–1752.

9. Longo JM, Arnott RJ. Structure and magnetic properties of $VOSO_4$. *J Solid State Chem*. 1970;1(3-4):394–8. DOI:10.1016/0022–4596(70)90121–0.

10. Gaubicher J, Chabre Y, Angenault J, Lautié A, Quarton M. Lithium electrochemical intercalation in β-$VOSO_4$. *J Alloys Compd*. 1997;262–3:34–8. DOI:10.1016/S0925-8388(97)00325–3.