

Reactivity of AV_4S_8 (A=Ga,Ge) as a negative electrode for sodium-ion batteriesMichelet C.^{1,2}, Renaud A.^{1,2}, Dupré N.^{1,2}, Crosnier O.^{1,2}, Guyomard D.^{1,2}, Brousse T.^{1,2} and Moreau P.^{1,2}.¹Institut des Matériaux Jean Rouxel (IMN)-UMR 6502, Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France²Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France

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In everyday life, Li-ion batteries have become essential for mobile technologies. The demand for large scale batteries will be increasing even further especially with the generalization of electric vehicles (EVs) and the development of sustainable energy sources, like solar cells or wind turbines, both irregular by nature. Lithium resources do not seem particularly limited but the access to this essential resource is potentially uncertain (Afghanistan, Bolivia). Moreover, the cost of lithium keeps increasing with the prospect of future commercialization of Li-ion batteries for EVs. Thus, other sources of ions, preferentially low cost ones, must be investigated to ensure energy sovereignty.

An increased interest has recently been observed for the use of sodium-ion batteries as an alternative to Li-ion batteries. Different forms of carbon have been tested [1,2] as negative electrodes, as well as other materials including insertion materials [3] and pure metals [4,5]. In our laboratory, we examine the possible use of a class of chalcogenide materials, AV_4S_8 (A=Ga,Ge), as a negative electrode in sodium-ion batteries.

The electrochemical reactivity of AV_4S_8 with Na is large, leading to a specific capacity of 800 mAh/g for the first discharge (figure 1) at a C/20 rate. The irreversibility observed at each cycle depends on the end of discharge cut-off potential; the lower it is, the larger the irreversibility.

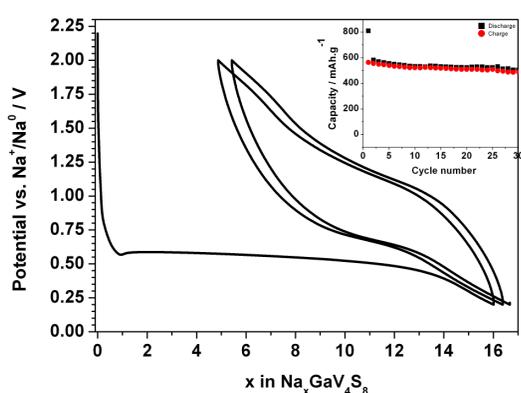


Figure 1. Typical potential-composition curve for a Na/GaV₄S₈ cell discharged and charged between 0.2 and 2.0 V at a C/20 rate (1.2 Na in 1 hour). Capacity in charge and discharge of the same cell is added as an inset.

In order to identify a possible conversion reaction mechanism [6], *in situ* XRD experiments were performed. They demonstrate a progressive amorphization of the material during the first reduction and the appearance of broad features corresponding to a small amount of Na₂S at the end of the discharge. Solid-state ²³Na-NMR was also used to analyze electrodes stopped at different stages of charge and discharge. The formation of Na₂S is proven

but is only sizeable during the last electrochemical step below 0.4 V (Figure 1), precisely when the irreversibility is at its highest.

Coupled EDX and TEM observations of selected electrodes stopped at different stages show an intimate mixture of the elements down to the nm scale. EELS experiments performed at the vanadium L-edge, indicate a reduction of the vanadium oxidation state during the discharge.

Complementary XAS experiments at the vanadium K-edge confirm the reduction of the vanadium. Moreover, germanium K-edge spectra demonstrate that the germanium is reduced with a shift of the edge energy to a lower value. This value is even lower than that corresponding to elemental germanium, indicating that germanium is in close vicinity to sodium. The reduction is followed by an oxidation of the germanium during the subsequent charge but with spectral weights noticeably different from those observed in the initial compound.

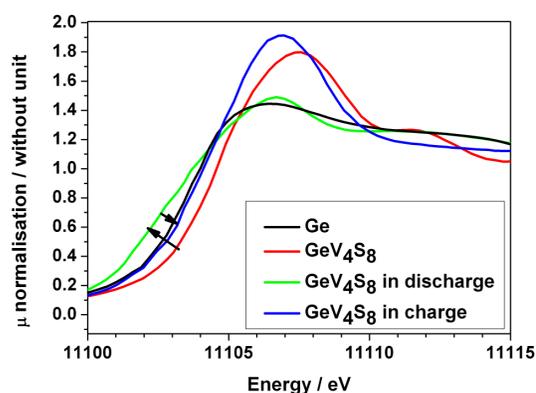


Figure 2. Normalised and absorption corrected XANES spectrum of Ge metal, GeV₄S₈ powder, GeV₄S₈ after discharge and GeV₄S₈ after charge

Synthesis, structural characterization and electrochemical behaviour of AV_4S_8 will be discussed in details in the presentation. Results obtained on the AV_4S_8 phases are very promising and demonstrate that this new class of material is a good candidate as a negative for Na-ion technology. The electrochemical performance of a complete battery, which has been realised with NaFePO₄ as a positive electrode will be presented. Over 50 cycles can be obtained. Further optimization, especially concerning the electrolyte, is however necessary to ensure a low enough irreversibility for a future practical use.

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