Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

FeV_2S_4 as high capacity electrode material for sodium-ion batteries

Markus Krengel,[a] Philipp Adelhelm,[b] Franziska Klein,[c] and Wolfgang Bensch[a]*

[a] Christian-Albrechts-Universität zu Kiel, Institute of Inorganic Chemistry
Max-Eyth-Straße 2, 24118 Kiel, Germany
[b] Friedrich-Schiller-University Jena
Institute for Technical Chemistry and Environmental Chemistry
Center for Energy and Environmental Chemistry (CEEC)
Lessingstraße 12, 07743 Jena, Germany
[c] Justus-Liebig-University Giessen, Institute of Physical Chemistry
Heinrich-Buff-Ring 58, 35392 Giessen

* Corresponding author. Fax: (+49) 481-880-1520
E-mail address: wbensch@ac.uni-kiel.de

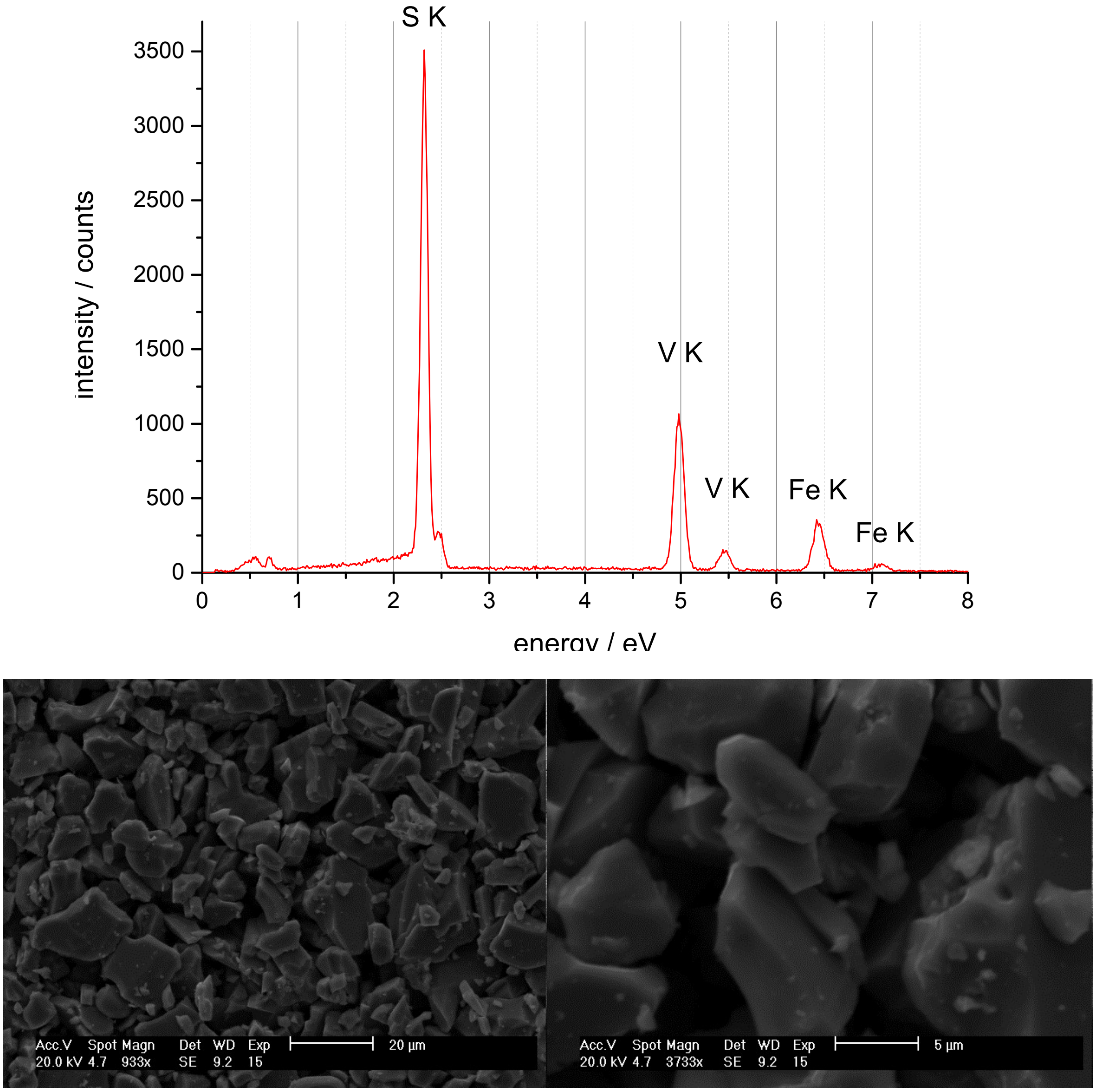


Fig. S1 EDX spectra and SEM images of the synthesized material.

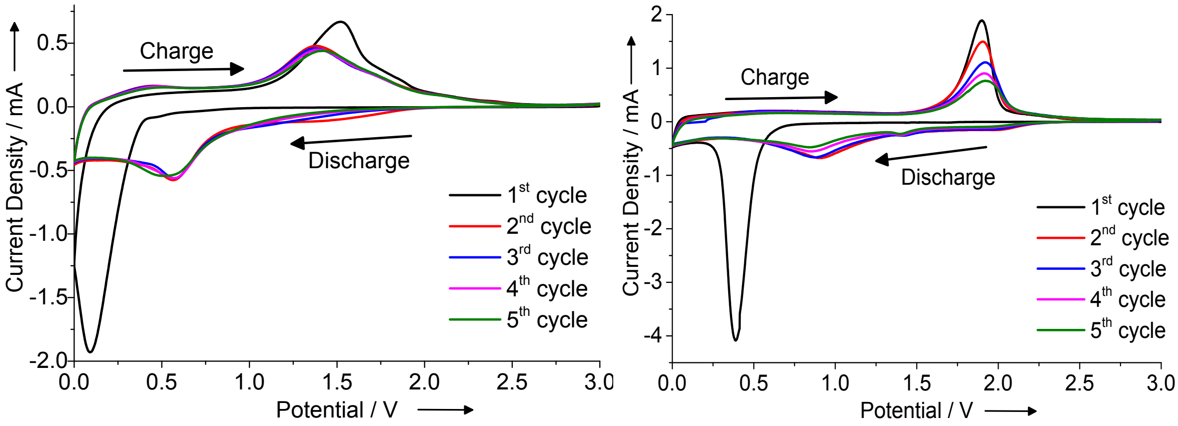


Fig. S2 Cyclic voltammetry curves of Na- (left) and Li-FeV_2S_4 cell (right).

The CV curves of FeV_2S_4 against lithium and sodium metal are displayed in Fig. 4. Cycling was performed in a range from 0 to 3 V in a sweep rate of 0.1 mVs^{-1}. In the first cycle of the Na-FeV_2S_4 cell one strong reduction peak at 0.1 V and one broad oxidation peak at 1.5 V are observed in accordance with the plateau of the galvanostatic measurement. The shift of the reduction peak in the CV cycle can be explained by the larger overpotential within the cell due to the higher current density. The second cycle is completely different with a very flat reduction peak at 1.5 V and a stronger pronounced one at 0.6 V. The oxidation peak is visible at 1.4 V suggesting the formation of a new phase after the first cycle. In the third cycle, the reduction peak at 1.5 V vanished but the rest of the profile is very similar to the previous cycle. For the first cycle of the Li-FeV_2S_4 cell one strong reduction and oxidation peak can be observed at 0.4 V and 1.9 V, respectively. The difference of the CV peaks and the plateaus of the galvanostatic measurements can again be explained by the higher current density. The second cycle shows 3 reduction peaks, 2 very flat ones at 2 V and 1.4 V and a stronger one at 0.9 V. The oxidation peak occurs at 1.9 V. In the following cycles identical profiles appear being accompanied by a continuous decrease of peak intensity and a small shift of the peaks can be detected.

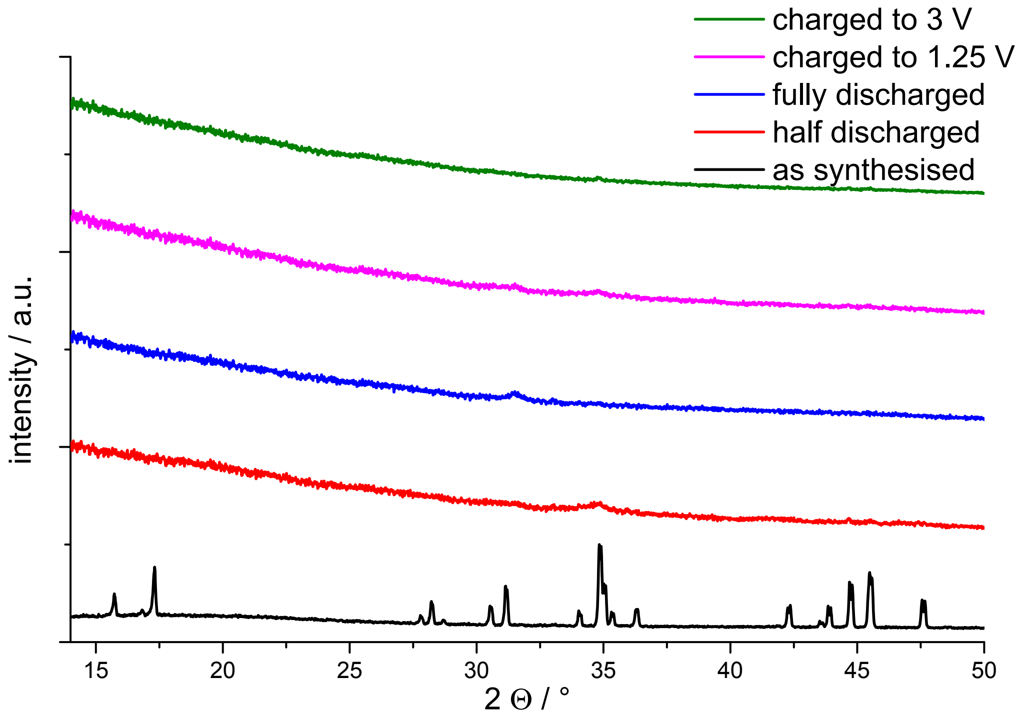
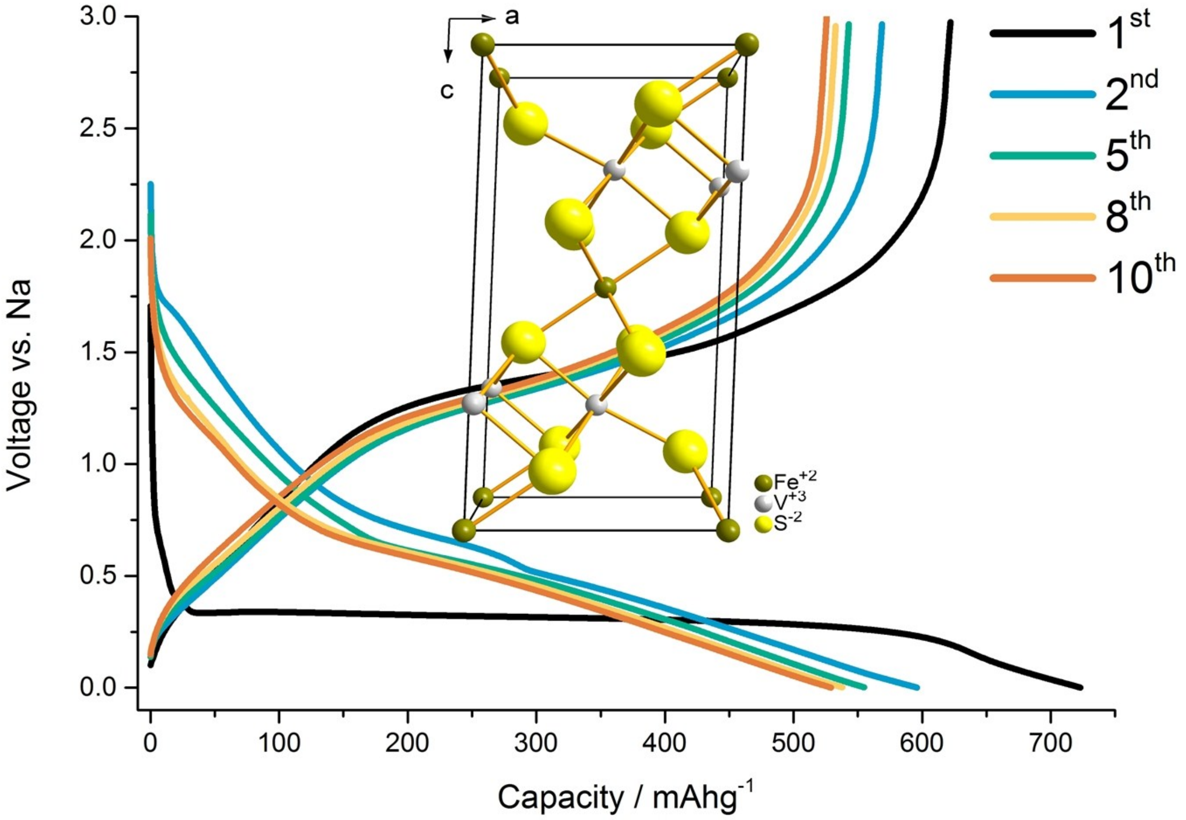


Fig. S3 ***ex situ*** **XRD patterns of the Na-FeV_2S_4 system at different charge states**

For *ex situ* X-ray diffraction studies the different cells were discharged and charged with a current density of 75 mAg^{-1} until they reached the potential mentioned in Fig. S3. For the first discharge, the cells were stopped after 5 h and at 0.01 V, respectively. All cells were disassembled in an argon filled glovebox, the electrodes were washed with pure propylene carbonate and the material was removed from the current collector. The obtained powder was put in a gas-tight sample holder with Kapton windows.

Experimental Section



The FeV_2S_4 sample was synthesized via a solid state reaction method. Stoichiometric amounts of iron (Alfa Aesar, 99.9+ %, <10 µm), vanadium (chempur, 99.5+%, -200 mesh) and sulfur (chempur, 99.999 %) were mixed and grinded in a mortar. The mixture was placed into a quartz tube, sealed under vacuum (< 10^{-4} mbar), and heated with 100 K/h to 873 K in an oven, maintaining this temperature for 24 h and then heated up to 1123 K for 5 days. The quartz tube was cooled to room temperature by switching-off the furnace.

XRD patterns were collected using Mo Kα radiation with a Stoe Stadi-P equipped with a germanium monochromator and a linear PSD detector. Rietveld refinement [1] of the powder pattern was performed with FULLPROF [2] using Pseudo-Voigt function with axial divergence asymmetry. Linear interpolation between a set of selected points was used to model the background. Cell parameters a, b, c and β, as well as all general atom positions were refined. *Ex-situ* XRD measurements were collected using Cu Kα radiation with a Stoe Stadi-P diffractometer equipped with a germanium monochromator and a Mythen 1K detector. SEM images and EDX-spectra were recorded in a Philips ESEM XL 30 with EDAX New XL-30 detecting unit. Acceleration voltage of 20 kV was used to detect the K-Lines.

FeV_2S_4 electrodes were prepared of 80 wt.% FeV_2S_4, 10 wt.% SUPER C65 Carbon (Timcal, Switzerland) and 10 wt.% PVdF (Solvay, Germany) suspended in NMP (N-methyl-2-pyrrolidone). The mixture was spread on an aluminium or copper foil using doctor-blade casting method. Drying of the electrode foils were carried out in a vacuum oven at 100 °C for

24 h. Afterwards 10 mm discs with about 3 mg active material were punched out. Assembly of the swagelock® type cells were carried out in an argon filled glove box with water and oxygen content below 1 ppm using sodium or lithium metal as the anode, glass fiber filter disks (Whatman, United Kingdom) as separator and a solution of 1 M $NaClO_4$ in propylene carbonate or 1 M $LiPF_6$ in ethylene carbonate: dimethyl carbonate (1:1) as electrolyte. All cells (more than 10) were tested galvanostatically in the range of 0.001-3 V with a Materials mated 510 DC and a Zahner XPot at different current rates.

References

1 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65–71.
2 J. Rodríguez-Carvajal, *Phys. B Condens. Matter*, 1993, **192**, 55–69.