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Electronic Supplementary Information

Structural characterization of an amorphous VS_4 and its lithiation/delithiation behavior studied by solid-state NMR spectroscopy

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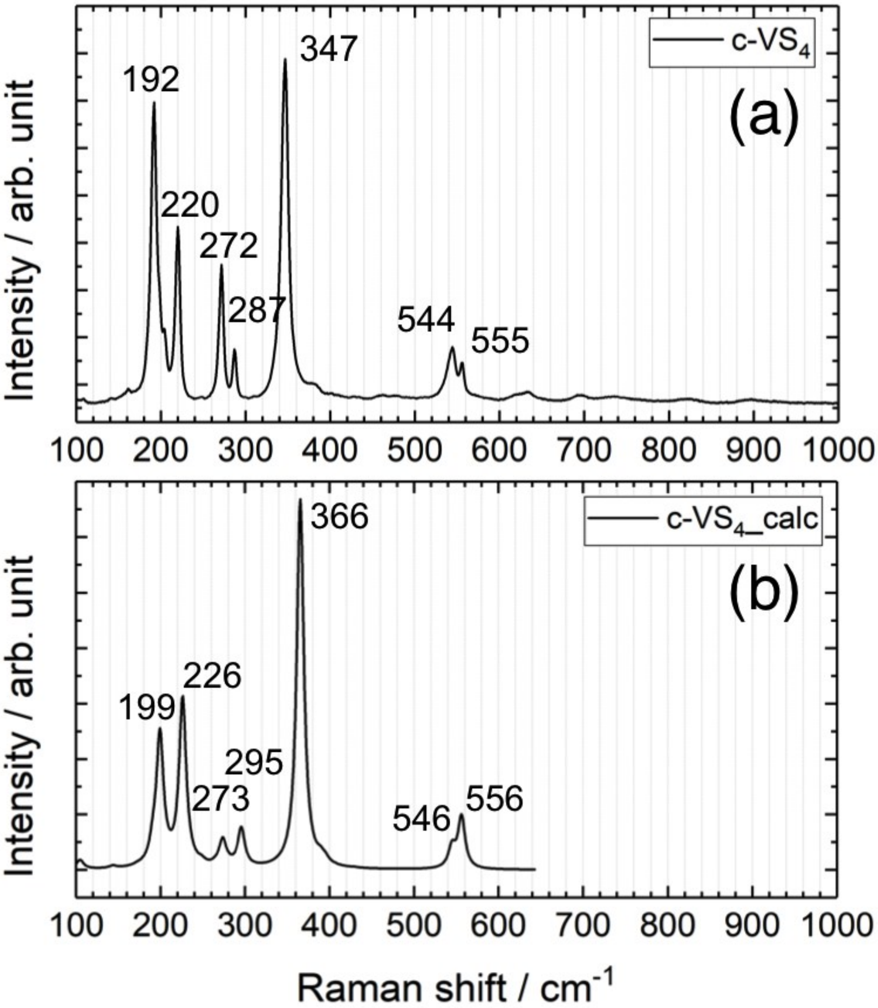

Fig. S1. (a) Experimental and (b) calculated Raman spectra of c-VS$_4$. The calculated spectrum was simulated with a 632.8 nm excitation wavelength at 300 K, adopting a Lorentzian smearing of 10 cm^{-1}. The Raman frequency and intensity calculations were performed after full geometry optimization of the c-VS$_4$ structure using a CASTEP module implemented in Materials Studio 2018 (BIOVIA).[S1,2]

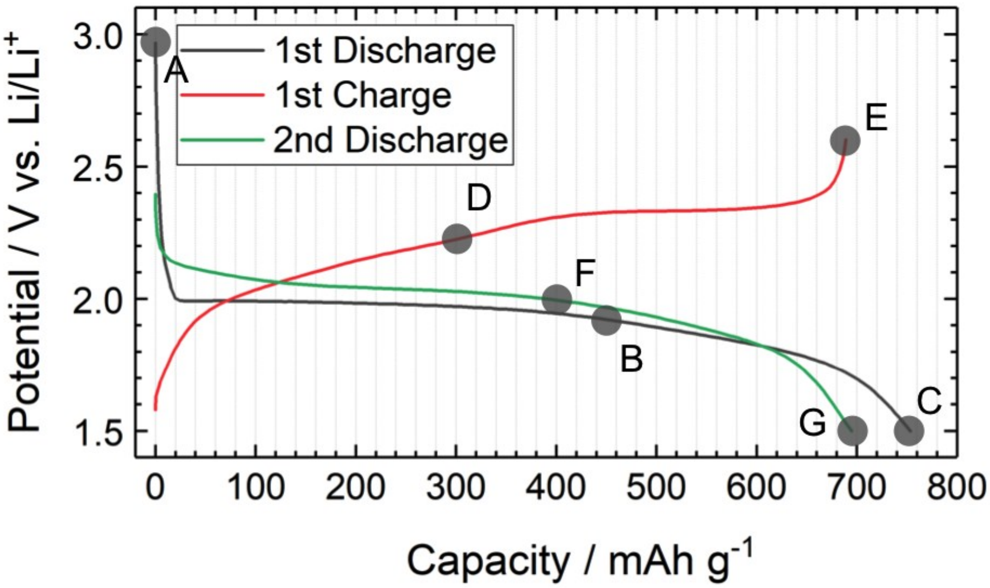

Fig. S2. Charge–discharge profile of the Li//a-VS_4 cell. Sampling points are marked on the figure.

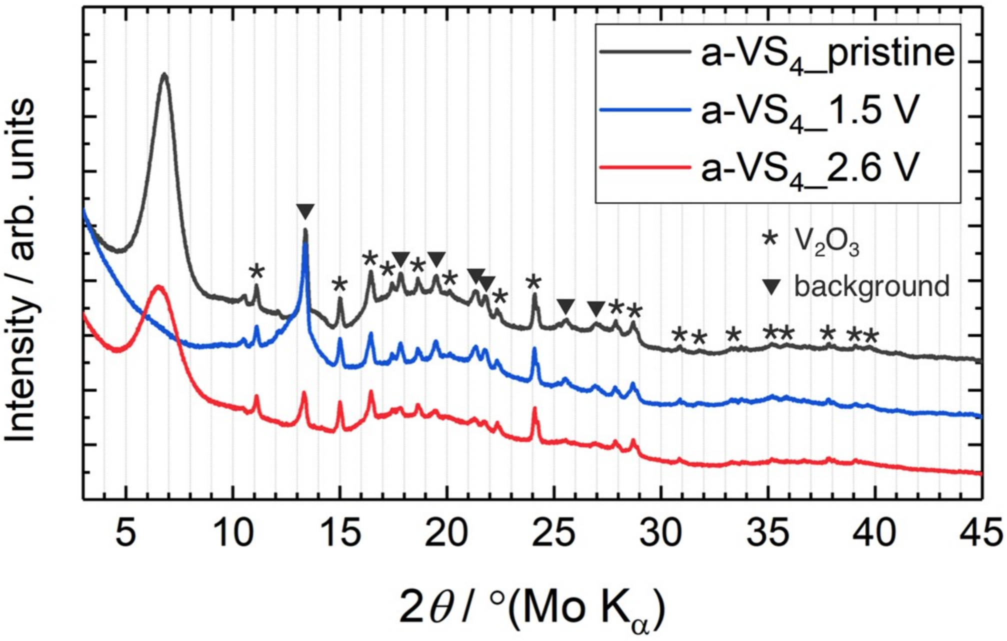

Fig. S3. XRD profiles of a-VS$_4$ electrode samples (**A**, **C**, and **E**). The measurements were carried out on a SmartLab X-ray diffractometer (Rigaku) with a Mo K$_\alpha$ source. Powdered samples were sealed in borosilicate glass capillaries in an Ar-filled glove box. V$_2$O$_3$ is a minor impurity phase in a starting material V$_2$S$_3$. Background peaks come from the outside of the samples.

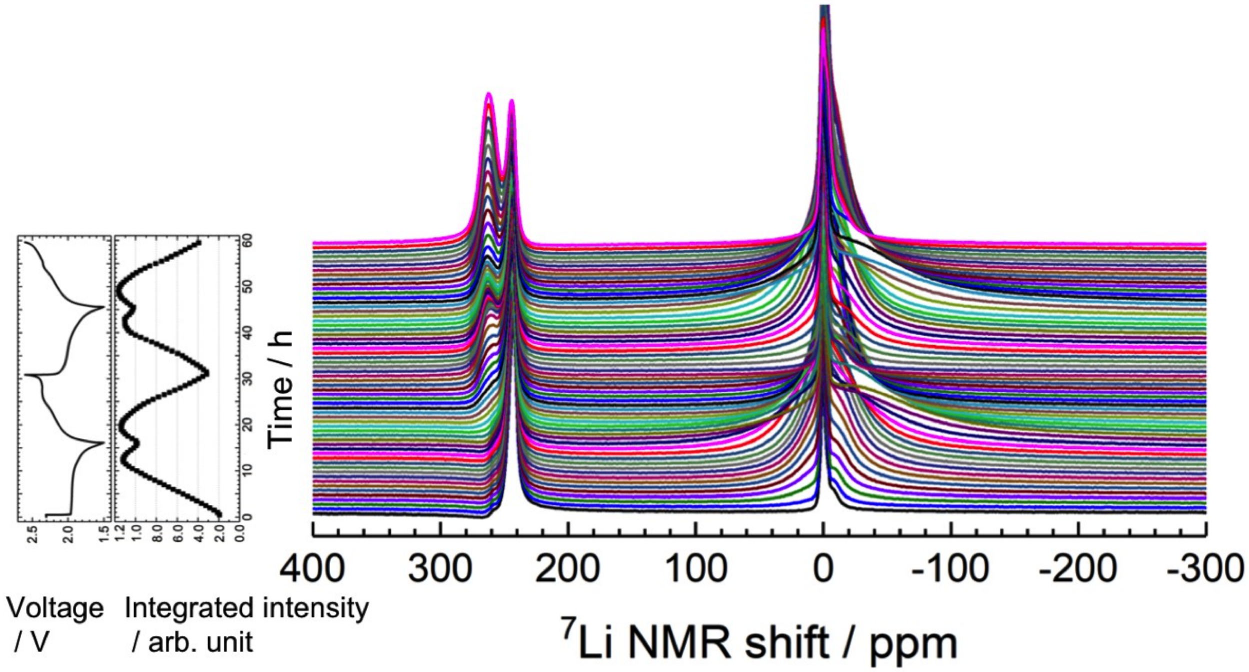

Fig. S4. Time evolution of operando ^{7}Li NMR spectra of the Li//a-VS_4 cell, along with the corresponding charge–discharge profile and integrated intensity plot of the a-Li_xVS_4 signal (including electrolyte signal). The spectra were accumulated for the flat laminate cell placed horizontally in the center of the coil. It is noteworthy that the peak positions of a-Li_xVS_4 and Li metal signals are different from those in Fig. 3 in the main text, due to the bulk magnetic susceptibility (BMS) effect that depends on the bulk shape of the electrode (flat or spherical cell) placed horizontally or vertically with respect to external magnetic field B_0.[S3,4] A new signal from the dendritic/mossy lithium appeared at 262 ppm and increased in intensity during the 1st and 2nd charging processes.[S5]

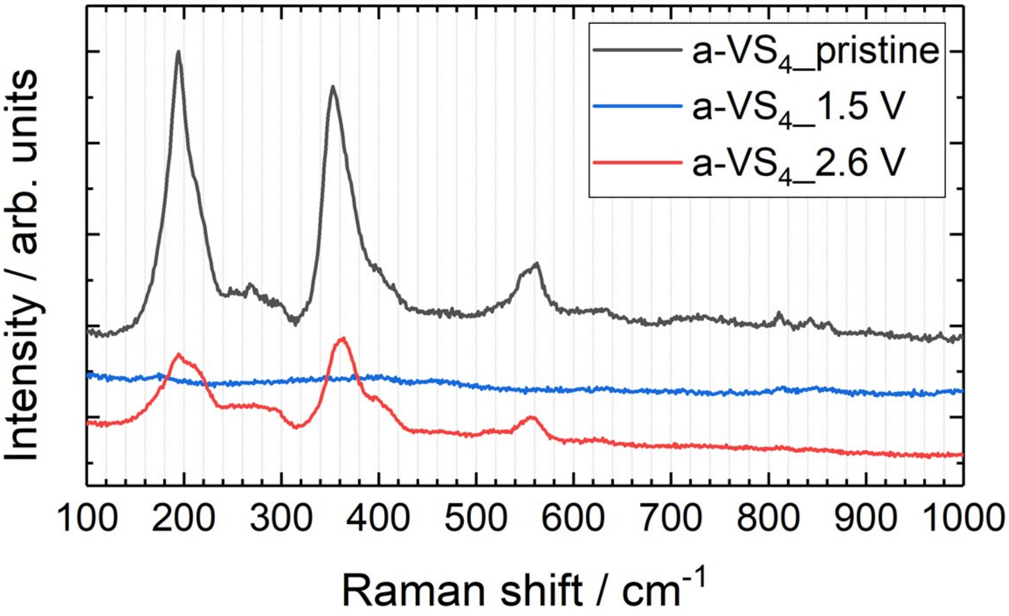

Fig. S5. Raman spectra of a-VS$_4$ electrode samples (**A**, **C**, and **E**).

References

S1 S. J. Clark, M. D. Segall, C. J. Picard, P. J. Hasnip, M. I. J. Probert, K. Refson, M. C. Payne, *Zeit. Kristallogr.*, 2005, **220**, 567–570.

S2 K. Refson, S. J. Clark, P. R. Tulip, *Phys. Rev. B*, 2006, **73**, 155114.

S3 R. Bhattacharyya, B. Key, H. Chen, A. S. Best, A. F. Hollenkamp and C. P. Grey, *Nat. Mater.*, 2010, **9**, 504–510.

S4 N. M. Trease, L. Zhou, H. J. Chang, B. Y. Zhu and C. P. Grey, *Solid State Nucl. Magn. Reson.*, 2012, **42**, 62–70.

S5 K. Shimoda, M. Murakami, D. Takamatsu, H. Arai, Y. Uchimoto and Z. Ogumi, *Electrochim. Acta*, 2013, **108**, 343–349.