

Natural Abundance Solid-state ^{33}S NMR Study of NbS_3 : Applications for Battery Conversion Electrodes

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Transition metal sulfides with disulfide linkages, such as vanadium sulfide (VS_4) and niobium sulfide (NbS_3), are technologically important materials with potential applications as electrode materials for lithium ion batteries.¹ The conversion mechanism underlying the electrochemical behaviour of electrode materials based on TM sulfides with disulfide (S_2^{2-}) linkages is attributed to anion redox activity, which comprises reduction of S_2^{2-} to S^{2-} during the discharge process, giving rise to high capacities (~ 1000 mAh/g). In many systems, however, the exact redox mechanism(s) remain poorly understood. Recent ^{33}S NMR studies of Li-S and Mg-S battery systems have reported identification of discharge products (Li_2S and MgS),^{2,3} but to our knowledge the technique has not yet been applied to study sulfide-based conversion electrodes.

In this work, we show that ultra-wideline, natural abundance ^{33}S static spectra of the prospective conversion material NbS_3 can be readily acquired at high field (20 T) in a reasonable time frame (~ 6 h) using the DFS-QCPMG pulse sequence. NbS_3 , which contains both sulfide (S^{2-}) ions and disulfide (S_2^{2-}) groups, adopts a pseudo one-dimensional monoclinic structure (space group $\text{P}\bar{1}$) comprising trigonal prismatic $[\text{NbS}_6]$ units connected into NbS_3 chains extending along the b -axis; these chains are arranged into sheets (along a) which are stacked along c , and held together through weak van der Waals forces.⁴ The NbS_3 chains undergo a linear Peierls distortion wherein adjacent Nb sites pair giving alternating short and long Nb–Nb distances.

To determine the feasibility of acquiring natural abundance ^{33}S NMR spectra, we first performed periodic DFT calculations of Peierls-distorted NbS_3 using the plane-wave CASTEP code. The calculated quadrupolar coupling constants (C_Q) are highly sensitive to the chemical identity of the local ^{33}S sites, with the isolated sulfide ions giving large C_Q values of 4.4 or 6.5 MHz, and the disulfide units exhibiting extremely large C_Q values of ~ 30 MHz. (The largest reported ^{33}S C_Q value to date is 43.3 MHz in elemental sulfur.⁵) Using the DFT-calculated parameters, a ^{33}S spectrum at 20 T was simulated with the QUEST software⁶ (Figure 1, top). The S^{2-} features are relatively narrow whereas the second-order quadrupolar broadened lineshapes arising from S_2^{2-} span an extremely broad frequency range with discontinuities at 10500 ppm and -18500 ppm. The broadband experimental spectrum acquired at 20 T, presented in Figure 1 (bottom), comprises a variable-offset cumulative spectrum (VOCS) of 17 summed sub-spectra; each individual sub-spectrum was acquired in 20 min and the experiment required 6 h in total. Promisingly, the spectrum is in excellent qualitative agreement with the simulation, with a narrower, more intense region centred at 0 ppm corresponding to S^{2-} and a very broad feature corresponding to S_2^{2-} . The latter feature is consistent with a site with $C_Q = 31$ MHz, $\eta_Q = 0.05$ centred at 0 ppm, in good agreement with the calculated parameters of S_2^{2-} .

Finally, the calculated quadrupolar asymmetry parameters of the S_2^{2-} sites reflect the Peierls distortion in that these depend sensitively on whether the disulfide groups lie between short or long Nb–Nb distances. By acquiring ^{33}S spectra for a longer time at the high- and low-frequency discontinuities, we argue that the ^{33}S NMR spectra corroborate this Peierls distortion.

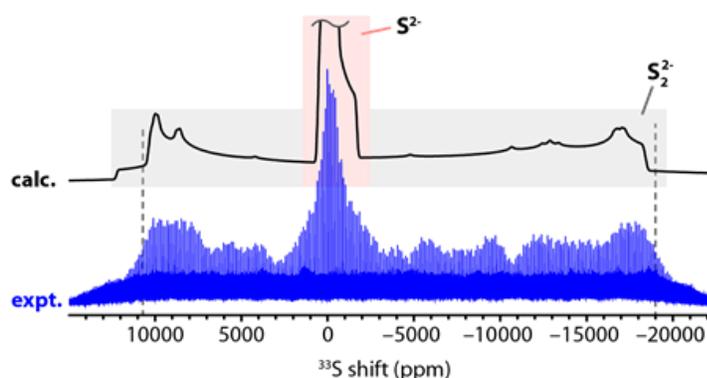


Figure 1: Simulated ^{33}S spectrum at 20 T from DFT-calculated parameters (“calc.”) and experimental ultra-wideline DFS-QCPMG static ^{33}S spectrum of NbS_3 acquired at 20 T using a frequency-stepping approach (“expt.”). Coloured boxes indicate the relevant positions of the second-order quadrupolar broadened S^{2-} and S_2^{2-} features; dotted lines show the discontinuities in the experimental spectrum. Simulated spectra have been performed using the QUEST software of Perras et al.⁶

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