

Experimental details:

Samples of $\text{Sr}_2\text{MnO}_2\text{Cu}_{2m-0.5}\text{S}_{m+1}$ were prepared as described in reference 3. Chemical lithiation using *n*-BuLi at room temperature was carried out as described in reference 6.

Electrochemical lithium insertion/extrusion tests were performed in two-electrode Swagelok cells using lithium foil as counter electrode. The working electrode consisted of a powder mixture of the sample of interest with 20% acetylene black. Two sheets of Whatman GF/D borosilicate glass fiber soaked with 1M LiPF_6 in ethylene carbonate/dimethyl carbonate (EC:DMC) (1:1 ratio) were used as a separator. The cells were tested using an Arbin potentiostat in galvanostatic mode at C/20 rate (i.e. complete Cu-Li exchange within 20 hours).

The ^7Li and ^6Li MAS NMR measurements were performed by using a Chemagnetics CMX 200 MHz spectrometer in combination with an Oxford 4.7 T cryomagnet at Larmor frequencies of 77.8 and 29.4 MHz, respectively. Spinning of the samples was performed in 2 mm rotors at 35 kHz.

A rotor-synchronized spin-echo pulse sequence ($\pi/2$ - τ - π - τ -acq) was used to avoid dead time effects during data acquisition. $\pi/2$ times of 2.3 μs were used for ^7Li (^6Li : 4.2 μs). Typically 5000 scans were acquired for ^7Li spectra (^6Li : 300000 scans) with a repetition time of 0.5 s. The spectra were referenced to 1M LiCl at 0 ppm.

Figure S1: ^7Li MAS NMR spectra of a) $\text{Sr}_2\text{MnO}_2\text{Li}_2\text{S}_2$, b) $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$ ($x = 1.2$), c) $\text{Sr}_2\text{MnO}_2\text{Li}_4\text{S}_3$, d) $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$ ($x = 3.3$), e) $\text{Sr}_2\text{MnO}_2\text{Li}_6\text{S}_4$, and f) $\text{Sr}_2\text{MnO}_2\text{Cu}_{5.5}\text{S}_4$ ($x = 6.1$). x denotes the amount of Li inserted electrochemically per formula unit. Spectra a, c, and e represent chemically intercalated samples and spectra b, d, and f represent electrochemically intercalated samples. The asterisks and crosses denote the spinning sidebands. The chemical shifts are referenced to 1M LiCl. One can see that for all three samples the spectra after chemical and electrochemical intercalation are very similar.

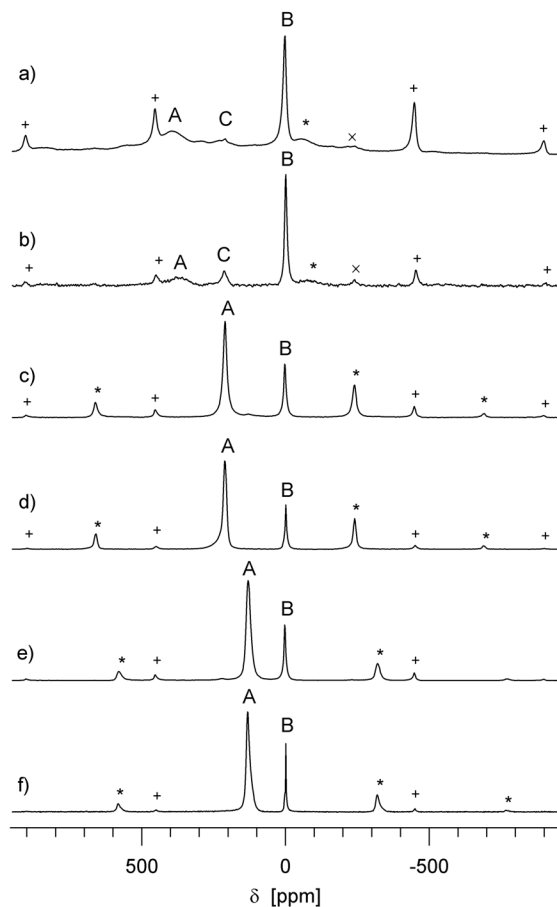


Figure S2: ^7Li MAS NMR spectra of $\text{Sr}_2\text{MnO}_2\text{Li}_{2.5}\text{S}_{2.5}$ ($m=1/m=2$ intergrowth) for temperatures between 30°C and 180°C . Comparison with the spectra of the $m = 1$ and the $m = 2$ sample (Figs. 3 and S3) shows that this spectrum is simply a superposition of both the $m = 1$ and $m = 2$ spectra. Peak A(1) corresponds to the Li ions in the single layers of sulphur tetrahedra (with 4 Mn ions in the 1st cation coordination shell, as in the $m = 1$ sample) and peak A(2) corresponds to lithium ions in the double layers of sulphur tetrahedra (with 2 Mn ions in the 1st cation coordination shell, as in the $m = 2$ sample).

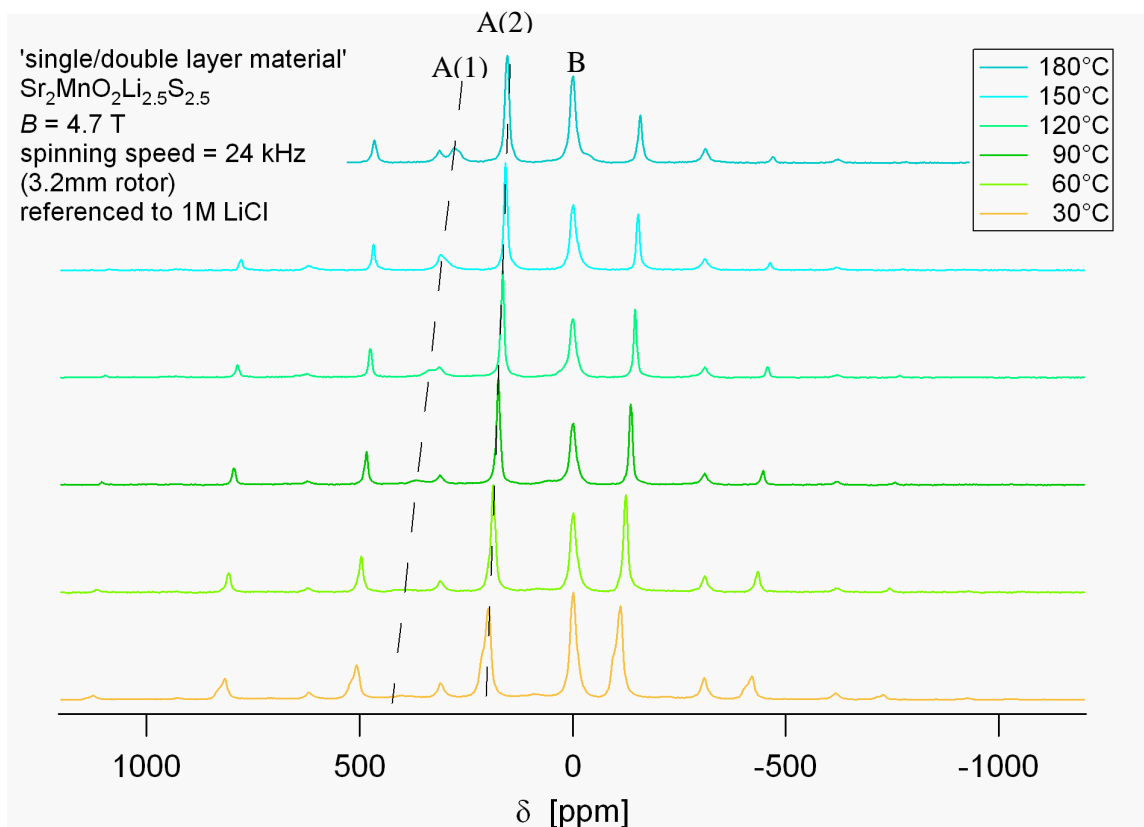


Figure S3: ^7Li MAS NMR spectra of $\text{Sr}_2\text{MnO}_2\text{Li}_6\text{S}_4$ for temperatures between -30 and 90°C . Broadening of peak A at low temperatures is seen.

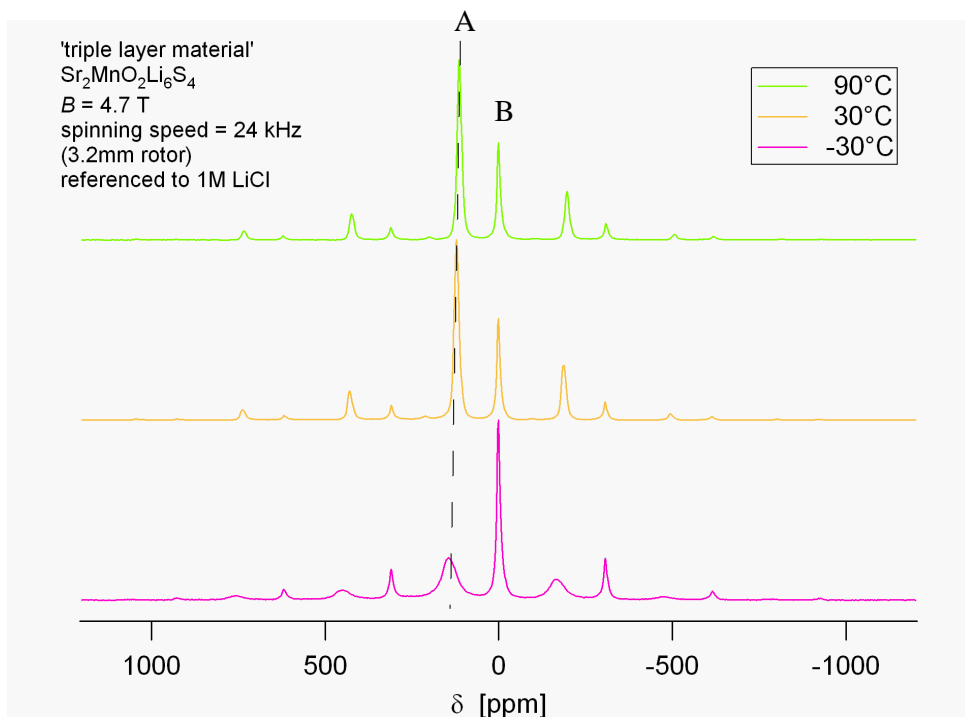


Figure S4: ^7Li MAS NMR spectra of $\text{Sr}_2\text{MnO}_2\text{Li}_2\text{S}_2$ for temperatures between 0 and 120°C . Narrowing of peak A at elevated temperatures is seen.

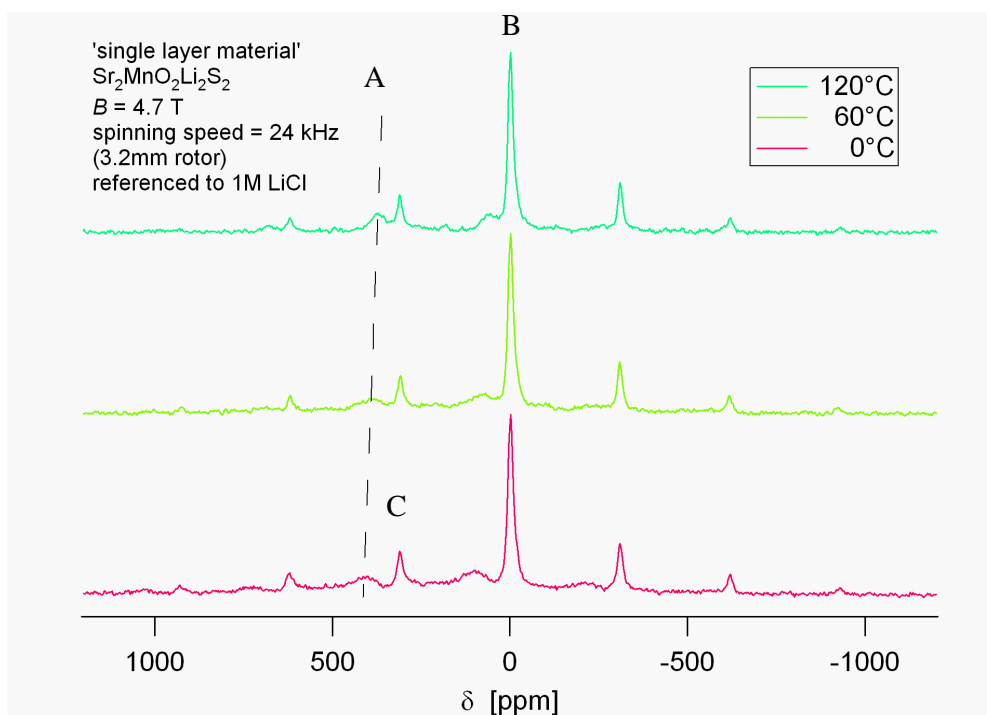


Figure S5: Voltage profiles during the first two cycles for a) $\text{Sr}_2\text{MnO}_2\text{Cu}_{1.5}\text{S}_2$, b) $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$, c) $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_4$, and d) Cu_2S .

