Supplementary Information for: Sidorenkite: A new intercalation cathode material for Na-ion batteries

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	Sidorenkite mineral	Synthetic sidorenkite
a (Å)	8.986	9.014
b (Å)	6.736	6.644
c (Å)	5.160	5.189
α()	90	90
β()	90.12	89.7
γ()	90	90
Volume (Å ³)	312.318	310.741
Space group	P21/m	P21/m

Table S1 Cell parameters of the natural mineral¹ and synthetic sidorenkite

Atomic positions and refined parameters are included in the attached CIF file.

Proposed Stoichiometry	Shift Na(1) site site	(ppm) Na(2)	Charge/ discharge potential vs. Na/Na ⁺ (V)	^a % Total Na(1) site area/Na(1) at -180 ppm area
Na ₂ (1)Na(2)Mn ²⁺ XY	-180	493 (or 370 ^b)	Pristine (OCV 2.4 V)	100/100
$\frac{Na_{2}(1)Na_{0.5}(2)Mn_{0.5}{}^{2+}Mn_{0.5}{}^{3+}}{XY}$	-180, -13	na	3.5	100/50.4
Na ₂ (1)Mn ³⁺ XY	-180, -13, broad resonance spreading to 400	na	3.83	69/13
$Na_{1.75}(1)Mn_{0.75}^{3+}Mn_{0.25}^{4+}XY$	92, -13, weak - 180	na	4.09	45.7/2.2
$Na_{1.5}(1)M{n_{0.5}}^{3+}M{n_{0.5}}^{4+}\ XY$	92, -13 shoulder	na	4.17	56.5/na
Na(1)Mn ⁴⁺ XY	194 (v. broad), -13 (weak)	na	4.5	45.9/na
Na _{1.25} (1)Mn _{0.25} ³⁺ Mn _{0.75} ⁴⁺ XY	-4/-14 main -180 weak broad resonance to 260	na	3.85	60/10.7
$\frac{Na_{1.25}(1)Na_{0.1}(2)Mn_{0.3}{}^{3+}Mn_{0.7}{}^{4+}}{XY}$	-13, weak broad resonance 0-300 -180 weak	na	3.7	19/2.6
$\frac{Na_{1.25}(1)Na_{0.4}(2)Mn_{0.4}{}^{3+}Mn_{0.6}{}^{4+}}{XY}$	-180, -13	~493, (or 370) weak and broad	3.3	28/11
$\frac{Na_{1.25}(1)Na(2)Mn_{0.25}{}^{2+}Mn_{0.75}{}^{3+}}{XY}$	-180, -13	~493 (or 370)	2	62.5/41.1

Table S2. Summary of the ²³Na NMR shifts observed in sidorenkite at various stages of charge and discharge with suggested stoichiometry based on the value of the shifts.

^{a)} Areas are calculated with respect to the pristine material based on the NMR spectra in Figure 8. Total Na(1) area corresponds to the Na(1) site; it is centered at -180 ppm in pristine material, but in cycled material it has multiple shifts, or a range of shifts that depend on the oxidation state of the nearby Mn ions. "Na(1) at -180 ppm area" corresponds to the intensity (and thus occupancy) of the site that gives rise to the -180 ppm resonance. ^{b)} The center of mass of the Na(2) resonance is ~ 493 and 370 ppm at 7.05 and 4.7 T.



Figure S1. A schematic illustration of the set up of the *in situ* XRD experiment on Na-ion cells.



Figure S2. In situ XRD patterns ($\lambda = 0.7745$ Å) of sidorenkite cell 1, cycled at a C/20 rate. The most significant changes are highlighted by light blue shading.

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Figure S3. *In situ* XRD patterns of sidorenkite cell 2, with large particle size sidorenkite. The wavelength used is 0.7745 Å. (a) The full XRD pattern. Diffraction peaks from the stainless steel current collector are noted with arrows. (b) Zoomed view around (-101), (201), (-121) and (002) reflections of sidorenkite.

Projection MATPASS method

Acquiring ²³Na NMR of paramagnetic materials can be very challenging due to a wide range of shifts and broadening of NMR peaks resulting from paramagnetic effects and large quadrupolar couplings. High magnetic fields are helpful to enhance signal sensitivity and minimize quadrupolar effects, but lead to a wider spread of the shifts and larger shift anisotropies due to paramagnetic interaction, while lower fields yield a narrower distribution of shifts and smaller shift anisotropies, but poorer resolution due to quadrupolar broadening. Thus, a compromise needs to be made when choosing an appropriate magnetic field depending on the properties of the materials of interest. Fast magic angle spinning (MAS) is desirable to achieve good spectral resolution and broadband radio frequency (r.f.) pulse excitation is required to observe quantitatively all the unique local environments. However, due to structural disorder and large anisotropic NMR interactions involved, fast MAS alone is not sufficient to resolve all the chemical sites, thus advanced NMR methods utilizing r.f. pulses to separate isotropic peaks from their anisotropic counterparts have been employed in this study, such as the recently developed projection magic angle turning phase adjusted sideband separation (projection-MATPASS) technique.^{2,3} The projection-MATPASS method is often used in fast MAS experiments of half integer nuclei to separate different orders of spinning side bands and reconstruct isotropic spectra.⁴ The pulse width used in projection-MATPASS experiment was 1 μ s and 8 t₁ increments were used to completely separate the spinning sidebands of different orders. The pure isotropic spectra were obtained by adding all the F₁ (indirect dimension of the spectra) slices after Fourier transformation and aligning all the peaks from different rows in F_1 dimension at their isotropic positions by performing spectral shear.



Figure S4. ²³Na MAS NMR spectrum of pristine sidorenkite acquired on a 11.75 T magnet at a 50 kHz spinning speed using the projection-MATPASS pulse sequence.



Figure S5. ²³Na MAS NMR spectrum of sidorenkite discharged to 3.3 V acquired on a 11.75 T magnet at a spinning speed of 50 kHz using the projection-MATPASS pulse sequence.



Figure S6. ²³Na MAS NMR spin-echo spectrum of sidorenkite discharged to 3.7 V after charged to 4.5 V. The spectrum was acquired on a 4.7 T magnet at a spinning speed of 38 kHz.



Figure S7. 23 Na MAS NMR spin-echo spectrum of sidorenkite discharged to 2 V after charged to 4.5 V. The spectrum was acquired on a 4.7 T magnet at a spinning speed of 38 kHz.



Figure S8. Mn XANES edge position (defined as the first inflexion point on the absorption edge) as a function of Mn valence for various oxides (black circles) and polyanion compounds (red triangles). Dotted line shows the calibration curve for manganese oxides standards (black circles) using a linear function ($R^2 = 1$). Note the deviation of polyanion compounds from this calibration line derived from simple oxides. Therefore for Mn compounds with more complex structure than simple oxides, it is not straightforward to derive the Mn valence state from XANES edge position, and vice versa.



Figure S9. Mn XANES zoomed in around the pre-edge.

References:

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