

## Electronic Supplementary Information: Short-range ordering in battery electrode, the 'cation-disordered' rocksalt $\text{Li}_{1.25}\text{Nb}_{0.25}\text{Mn}_{0.5}\text{O}_2$

### 1 Experimental

$\text{Li}_{1.25}\text{Nb}_{0.25}\text{Mn}_{0.5}\text{O}_2$  powder was prepared by a standard solid state reaction from stoichiometric amounts of  $\text{Li}_2\text{CO}_3$  (99.9%, Aldrich),  $\text{Mn}_2\text{O}_3$  (98%, Alfa Aesar) and  $\text{Nb}_2\text{O}_5$  (99.5%, Aldrich). A 5% excess of  $\text{Li}_2\text{CO}_3$  was typically used to account for Li loss at the reaction temperature. The precursors were mixed in a Retsch PM100 planetary ball mill for 5 h. Pellets of approximately 1 g were pressed and heated to 1000°C in an alumina crucible inside a tube furnace under flowing Ar (with a flow rate of approximately  $0.5 \text{ cm}^3\text{min}^{-1}$ ) for 12 h. Reactions were performed inside both alumina and quartz tubes—quartz being more favourable for the 'quenching' step due to the smaller expansion/contraction upon heating/cooling. Ordered and disordered phases could be obtained inside both types of tube. The phase purity and crystal structures of synthesised materials were examined using powder X-ray diffraction (XRD) on a Panalytical Empyrean diffractometer using  $\text{CuK}\alpha$  radiation (1.540598 and 1.544426 Å). Structure solution was achieved with Rietveld refinement using TOPAS Academic v6.<sup>1,2</sup>

Neutron powder diffraction (NPD) experiments were performed using the POLARIS time-of-flight instrument at the ISIS pulsed neutron and muon spallation source in the Rutherford Appleton Laboratory.  $^7\text{Li}$ -enriched samples were synthesised due to the large neutron absorption cross-section of  $^6\text{Li}$ . Samples were measured inside 6 mm diameter vanadium cans. Pair distribution function (PDF) analysis was performed on the obtained neutron total scattering data using GudrunN and TOPAS Academic v6. Fourier transforms were performed with a  $Q_{\text{max}}$  of  $40 \text{ \AA}^{-1}$ .

Magnetic susceptibility measurements were carried out on a Quantum Design Magnetic Properties Measurement System (MPMS) with a Superconducting Quantum Interference Device (SQUID) magnetometer. The zero-field cooled (ZFC) susceptibility was measured in a field of 100 Oe in the temperature range 2 – 400 K. The magnetisation,  $M$ , varies linearly with magnetic field,  $H$ , in a field of 100 Oe and so the approximation for molar susceptibility,  $\chi(T) \sim M/H$  is valid. For both datasets the reciprocal susceptibilities  $\chi^{-1}$  are linear above 150 K and were used to fit to the Curie-Weiss law.

$^7\text{Li}$  NMR experiments were performed on a 4.70 T Bruker Avance III 200 MHz spectrometer using a 1.3 mm Bruker HX MAS probe. Spectra were recorded using rotor synchronised Hahn echo ( $\frac{\pi}{2} - \tau - \pi - \tau -$  acquire) with a delay  $\tau$  of a single rotor period, with typical pulse widths ( $\pi/2$ ) of approximately 1.05  $\mu\text{s}$  and recycle delays of 40 ms. To obtain spectra without sidebands, the

projection magic angle turning phase-adjusted spinning sidebands (pjMATPASS) pulse sequence was used. This two-dimensional pulse programme is designed to separate the isotropic resonance from its sidebands by distributing them across the second dimension, and has been demonstrated by Hu *et al.* to obtain “infinite”-MAS spectra in the case of large ( $> 1$  MHz) shift anisotropy.<sup>3</sup> The intensity originally lost to the sidebands can then be summed back into the isotropic resonance by ‘tilting’ the 2D data and summing the intensities of the rows together, thereby enhancing the signal-to-noise ratio. All experiments were performed at room temperature, with spinning speeds of 60 kHz, corresponding to approximately 45°C due to frictional heating. <sup>7</sup>Li experiments were referenced relative to Li<sub>2</sub>CO<sub>3</sub> at 0 ppm.

Self-supporting cathode films were manufactured by hand-grinding the active material with Super P carbon (Timcal) for approximately 30 minutes in an agate pestle and mortar, and then adding polytetrafluoroethene (PTFE) binder and further grinding for 5 minutes. By mass, the active material:carbon:binder ratio was typically 75:20:5. The PTFE-containing putty was rolled into a thin film using a glass rod. 12.7 mm diameter discs were punched out of the film, and the weight and thickness of each was recorded. Coin cells were assembled in an Ar filled glove box. Cathodes were placed on steel current collectors and separated from a Li-metal anode by glass fibre soaked with electrolyte. The electrolyte used was 1 M LiPF<sub>6</sub> in a 1:1 ratio solution of ethylene carbonate (EC) and dimethyl carbonate (DMC). All cells were half cells vs Li metal, and so all potentials are with respect to the Li/Li<sup>+</sup> redox couple. Cells were cycled between 1.5 V and 4.8 V, at a constant current with the potential measured as a function of time. The cells were cycled on either a Biologic MPG-2 or an Arbin battery tester in galvanostatic mode at room temperature or 55°C. A current density of 10 mA g<sup>-1</sup> was used unless otherwise specified. In order to perform ex-situ NMR measurements after charge/discharge, cells were disassembled inside an Ar filled glove box and the cathode was removed and washed with 3 x 4 ml DMC (99.9%, Sigma Aldrich) and dried under vacuum for 30 minutes. The cathode material was then cut up into small flakes using a sharp blade and packed into an NMR rotor for analysis.

### **Refinement Information**

A combined refinement was performed on laboratory X-ray, neutron Bragg and neutron PDF data for the same sample of ordered LNbMO. A single structural model was used, which was refined against all data simultaneously—weighted accordingly. The instrumental parameters (such as zero error, *difc* and *difa* for time of flight neutron data) were refined using standards (NIST Si and YAG) and then fixed. No more than 8 background terms were used. The starting model was the unit cell of  $\gamma$ -LiFeO<sub>2</sub>, with the occupancies of the metal lattice positions changed from Li and Fe to Li, Mn and Nb, in their compositional ratios (62.5% Li, 12.5% Nb, 25% Mn). The isotropic thermal displacement parameters

were allowed to refine, but constrained so as to be the same on the same lattice position (regardless

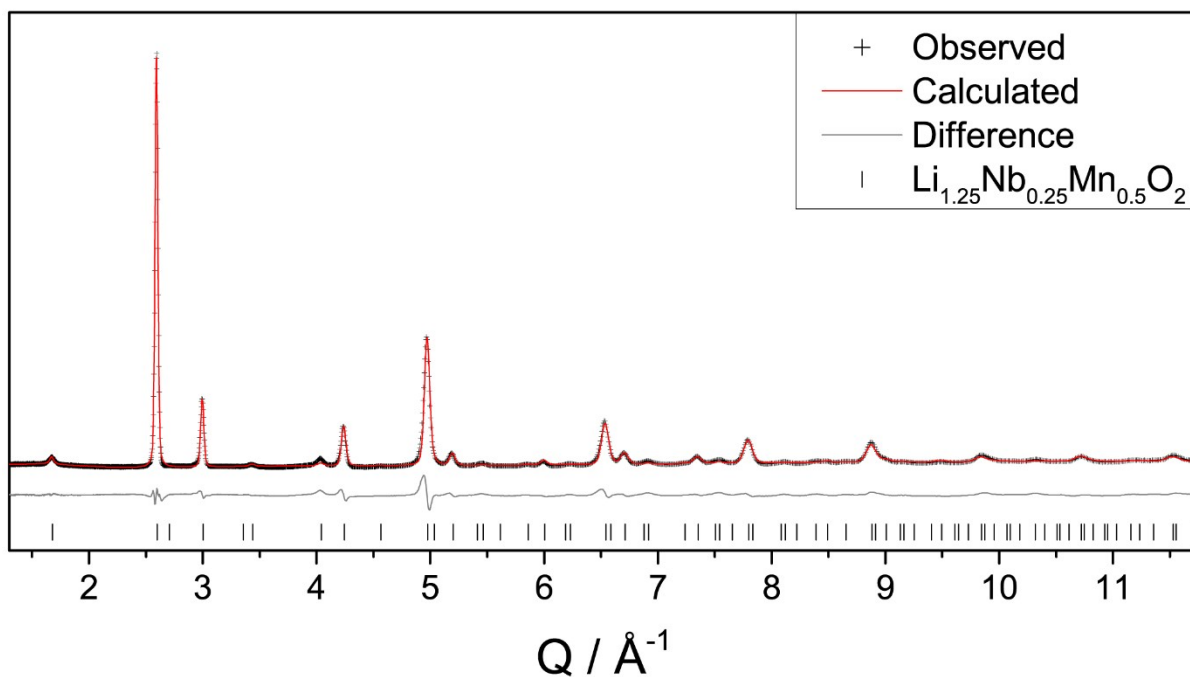


Figure S1. Bank 3 neutron Bragg data for ordered sample of LNbMO. as fit in the combined refinement.  $R_w = 5.259\%$

of atom type). The  $a$  lattice parameter was allowed to refine, and the  $c$  parameter was set equal to  $2a$ . Selective broadening of reflections was included for the case that the  $l$  index is odd. The magnitude of this broadening was refined and its reciprocal was used to obtain a 'pseudo-particle size' associated with this ordering—giving an estimate of the ordering correlation length. Banks 1 and 2 of the neutron data (the lower resolution banks) were excluded from the fit, as the lowest angle peak was accounted for in bank 3 and so they contained no new peaks. The diffraction data used in the combined

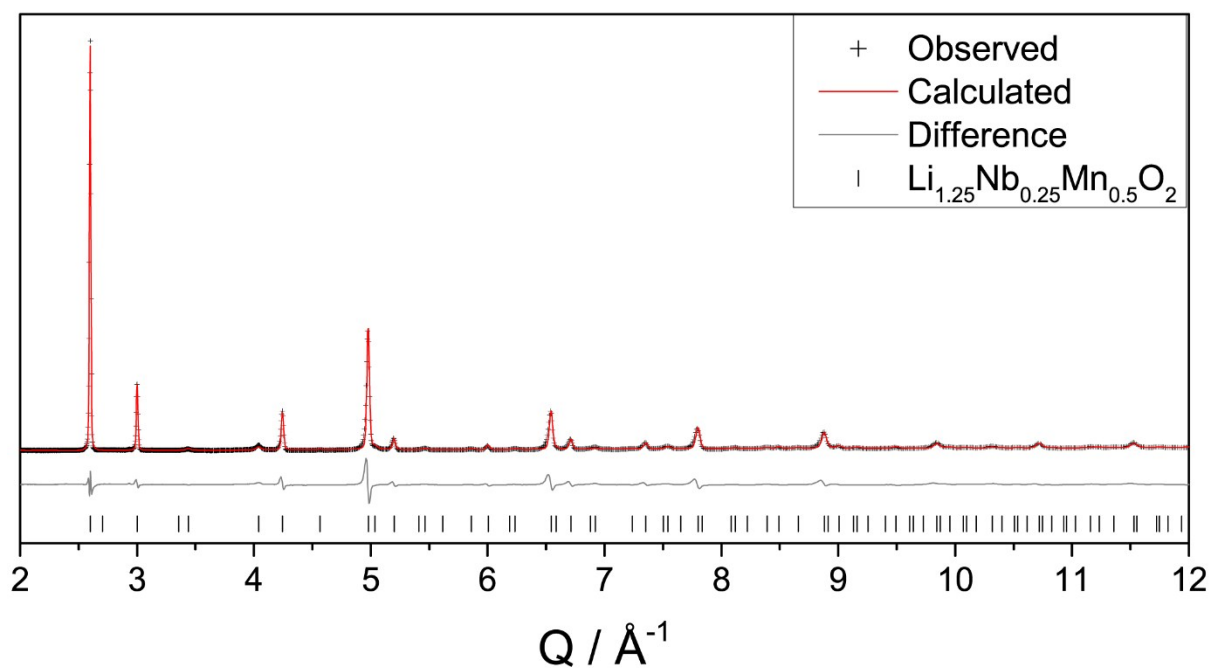


Figure S2. Bank 4 neutron Bragg data for ordered sample of LNbMO. as fit in the combined refinement.  $R_w = 8.204\%$

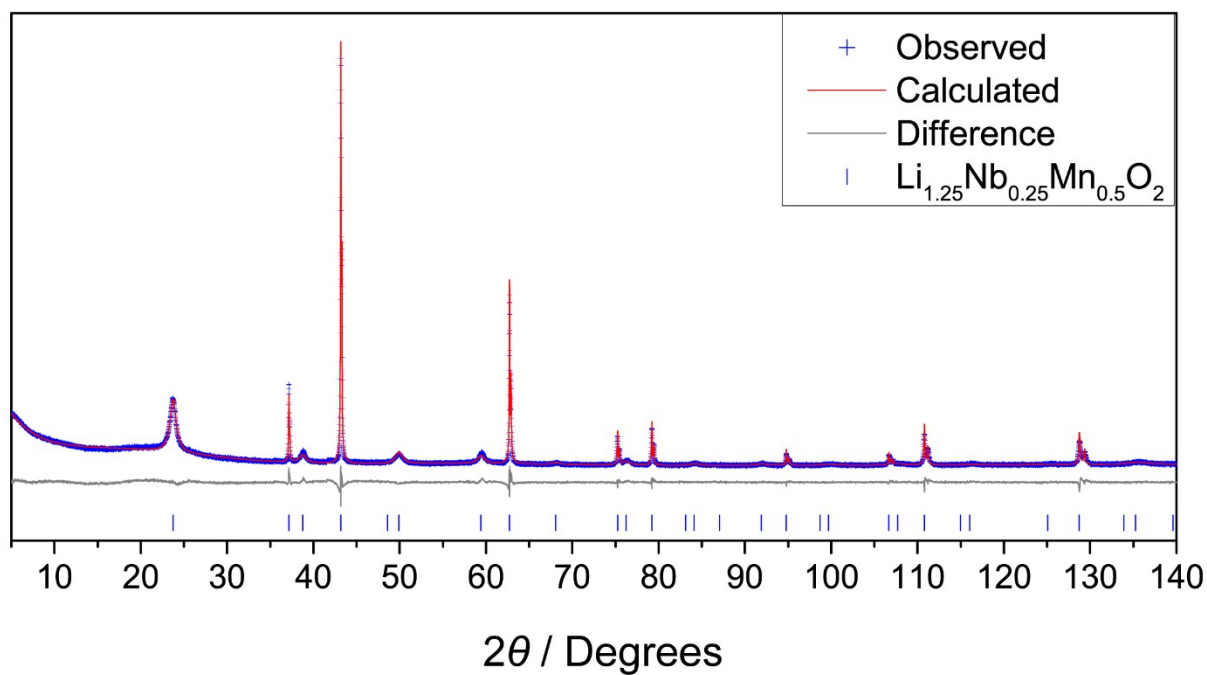


Figure S3. Laboratory XRD data for ordered sample of LNbMO. as fit in the combined refinement.  $R_w = 1.547\%$

refinement but not shown in the main text are shown here. Individual goodness of fit parameters for the individual datasets are given in the figure captions. For Bank 5 of the neutron data,  $R_w = 7.100\%$ . For the neutron PDF data,  $R_w = 14.156\%$ .

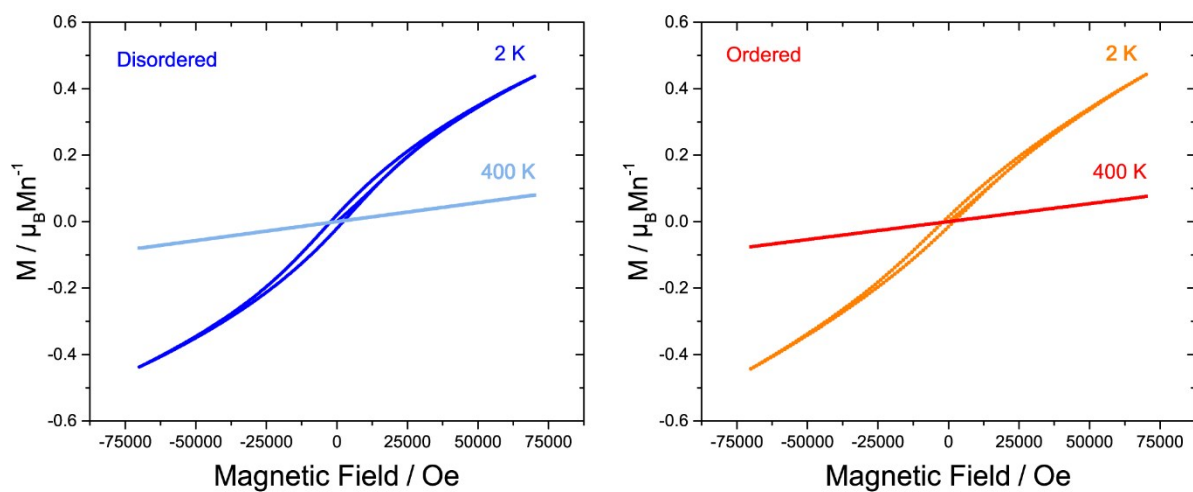


Figure S4.  $M(H)$  plots for disordered and ordered LNbMO at 2 K and 400 K for a magnetic field range of -70000 to +70000 Oe. The hysteresis observed at 2 K is indicative of a spin glass.

## 2. Magnetic Susceptibility and $M(H)$ plots

### 3. Loss of Order upon Cycling

#### References

- 1 A. Coelho, *TOPAS – Academic: General Profile and Structure Analysis Software for Powder Diffraction Data, Version 6*, Coelho Software, Brisbane, Australia, 2007.
- 2 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65–71.
- 3 Y. Hu, E. M. Levin and K. Schmidt-rohr, *J. Am. Chem. Soc.*, 2009, **131**, 8390–8391.

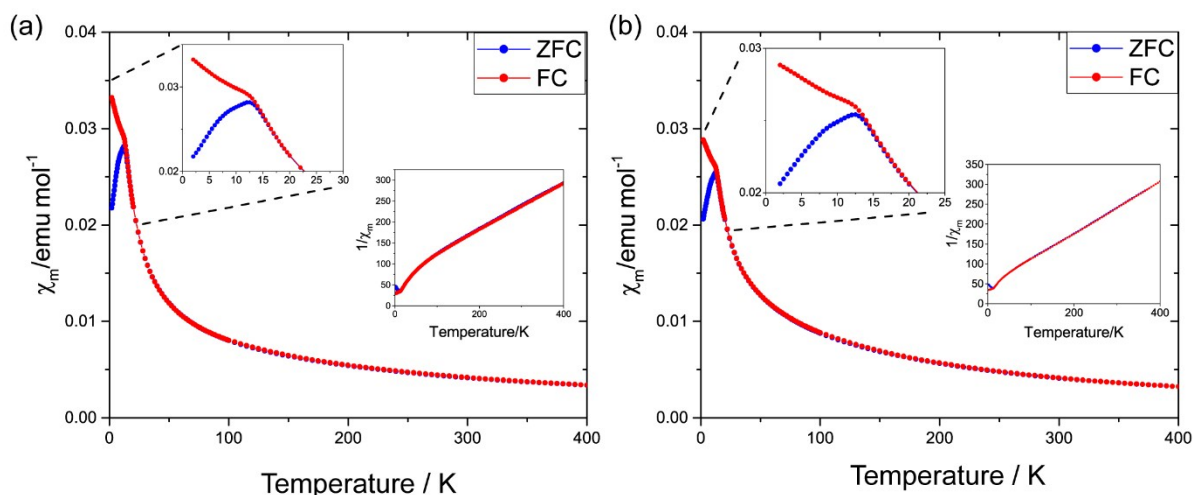


Figure S5. Enlarged magnetic susceptibility data for disordered (blue) and ordered (red & orange) samples of LNbMO. Curie constants of 1.8 (disordered) and 1.53 (ordered) were obtained, giving magnetic moments ( ) of 3.8 and 3.5 respectively, similar to the spin only value of 3.46 expected. Weiss temperatures of -131 K and -70 K were obtained. A transition temperature  $T$  of 13 K was observed for both samples.

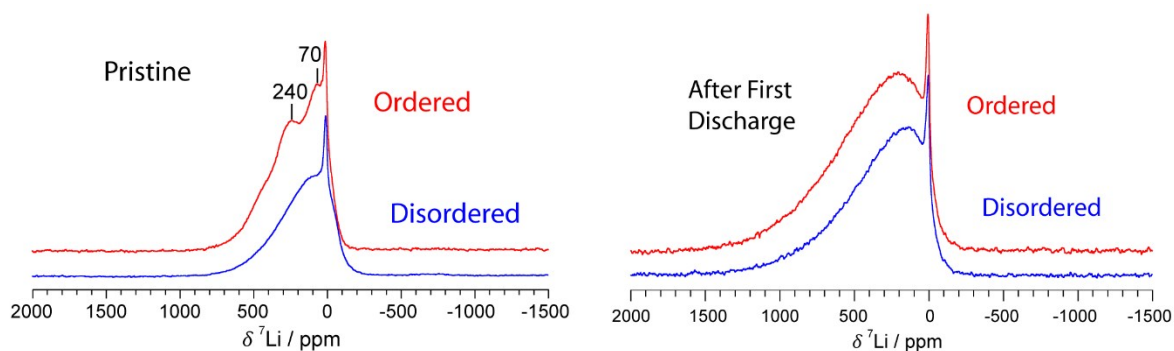


Figure S6. Evolution of NMR spectra for ordered and disordered LNbMO after one charge/discharge cycle. The distinct broad features discernible around 240 and 70 ppm in the pristine ordered material are lost upon cycling, suggesting a more disordered rocksalt structure is formed.