Supplementary Information for:

Reversible densification in nano-Li $_2$ MnO $_3$ Cation Disordered Rock-salt Li-ion Battery Cathode

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Supplementary Figures



Figure S1. Combined Rietveld refinements of (top) NPD and (bottom) SXRPD data for nano- Li_2MnO_3 using a layered rock-salt model of micro-structured Li_2MnO_3 (left) and cation disordered MnO-type rock-salt (right) structures.



Figure S2. Evidence of the high degree of local disorder in nano- Li_2MnO_3 . The fit of the short r-range neutron and X-ray PDFs using the proposed averaged models from Figure 1 produced a large mismatch to the data.



Figure S3. Top and bottom figures show the Rietveld fits of the nano- Li_2MnO_3 samples studied by operando total scattering at t = 0 and 72h. Middle: Evolution of all the parameters obtained by sequential Rietveld refinement.



Figure S4. Calculated XPDF data from a disordered rock-salt model where cation-cation and Li-O distances have been fixed, and oxygen position within MnO_6 have been moved varied from a regular octahedral to form O-O dimers 2.3 (b) and 1.4 Å (c) apart while keeping a constant Mn-O distance at 1.9 Å, as suggested in previous work. Note also that the changes in centrosymmetricity of the Mn centers in c are not compatible with the observed pre-edges in the XANES spectra.



Figure S5. Peak fitting of the short r-range of in-situ PDFs using five Gaussian functions and a sloped background.



Figure S6. Ex-situ data collections. The extended region of the ex situ spectra in this Figure were fitted to quantitatively evaluate short-range order structural parameters



Figure S7. Experimental $\chi(k)$ (top) and FT (bottom) EXAFS spectra for pristine and charged to 4.5 V compositions.



Figure 8. Normalized main k β transition of the Mn_2O_3 and MnO_2 standards and nano-Li₂MnO₃ cathode material at the start and end of charge/discharge cycles. The grey translucent rectangle indicates the magnified energy range in the right figure, where curve-fitted $k\beta_{1,3}$ transitions are denoted by dashed vertical lines.



Figure S9. . XES (main k8 and V2C) of Mn standards in different oxidation states compared with the in-situ data collections for pristine, charged and discharged compositions. The red dashed vertical line serves as an estimation of the OS of Mn in pristine nano- Li_2MnO_3 , charged to 4.5 V and discharged to 1.2 V samples based on the comparison with well-known manganese oxides.



Figure S10. Curve fitted XES energy transitions and integrated intensities. The dashed vertical line indicates the end of charge of the battery and the black squares the absence of data due to beam loss.



Figure S11. Quadrupole and dipole transitions simulations for nano-Li₂MnO₃ using a 2x2x2 supercell of the cation disordered rock-salt $Fm\overline{3}m$ model with composition Li₂₁Mn₁₁O₃₂.



Figure S12. Simulated V2C spectra for pristine (top) and charged nano- Li_2MnO_3 . The 'undensified' model shows a shift of the $k\beta''$ and $k\beta_{2,5}$ transitions to higher energy values consistent with a higher expected oxidation state of Mn, and a lower intensity of the $k\beta''$ transition that could be correlated to the lower coordination number of oxygen. Note this trend is opposite to the experimentally observed evolution of the $k\beta''$ integrated intensity that increases by 5 %.



Figure S13. V2C simulations for unphysical $Li_5Mn_{11}O_{32}$ and $H_{15}Li_5Mn_{11}O_{32}$ models with identical Mn-O and Mn-OH distances. The proposed protonated model is based on the structural model proposed for manganese dioxide spinel^[1], where protons are incorporated into the crystal bonding the lattice oxygen as –OH without major changes to the structure. Note Li, Mn and O atomic positions are identical in the unprotonated model. The simulations confirm that even in the hypothetical case where oxygen protonation did not change Mn-O distance, ligand protonation entails significant changes of the V2C spectra, which are not experimentally observed.



Figure S14. V2C simulations for tunnelled α -MnO₂ structure with empty channels (violet) and occupied by H₃O⁺ molecules (blue). The changes in the spectra are compatible with the 5% intensity increase of the k β'' transition experimentally observed for charged nano-L₂MnO₃.



Figure S15. V2C simulations for Li₆Mn₁₃O₃₂ containing dimerized and regular MnO₆ from Figure S3.



Figure 16. Operando S(Q) of $Li_4Mn_2O_5$: C composites at selected potential values. The asterisks indicate the growing diffuse scattering intensity during cycling.



Figure S17. Experimental (left) and simulated (right) V2C spectra for well-known Mn standards in oxidation states 2, 3, 4 and 5. The comparison between curve fitted peak position and intensities is given in Table S3.

Supplementary Tables

Path	Pristine/charged						
	Average mod	del	Refined				
	R _{eff} (Å)	N _{degen}	R(Å)	σ (Ų)	N _{degen}		
Mn-01	2.036/	6	1.87(1)/	0.004(1)/	fixed		
	2.029		1.87(1)	0.0024(9)			
Mn-Mn	2.879/	2	2.89(2)	0.0043(42)/	2±1/		
	2.870		/2.89(2)	0.007(4)	5±2		
Mn-O2	3.526/	8	3.51(8)	0.014(11)/	fixed		
	3.515		/3.52(5)	0.007(7)			

Table S1. Description of the paths included in the refinement and best-fit Interatomic bond distances, mean-square atomic displacements and path degeneracy.

Table S2. Curve fitted peak positions and intensities using split pseudo Voigt functions for experimental and simulated V2C spectra in Figure S9-S13.

	kβ'' (eV)	kβ _{2,5}	ΔE (eV)	kβ''/kβ₂,₅ ratio (%)
Experiment			1	
Pristine	6519.0(4)	6533.78(5)	14.78	11.0
Charged to 4.5 V	6518.6(3)	6534.19(6)	15.59	14.7
Discharged to 1.2 V	6518.6(5)	6533.74(5)	15.14	8.29
Simulation				
Pristine (Li ₂₁ Mn ₁₁ O ₃₂)	-17.5(3)	-4.64(4)	13.53	33.02
Undensified (Li₅Mn10O32)	-16.8(6)	-4.18(2)	12.60	36.03
Densified (Li ₆ Mn ₁₃ O ₃₂)	-17.4(5)	-5.06(2)	12.29	37.40
Pronated H₁₅Li₅Mn₁₁O₃₂	-15.9(3)	-1.52(7)	14.38	33.02
Non protonated Li₅Mn ₁₁ O ₃₂	-18.13(6)	-3.57(3)	14.55	32.46
α-MnO₂	-18.1(1)	-3.61(9)	14.48	30.34
H₃O⁺ Mn ₈ O ₁₆	-18.0(2)	-3.5(1)	14.55	29.80
'peroxo'-like (Li₅Mn13O32)	-17.4(1)	-3.15(9)	14.25	38.18

Table S3. Curve fitted peak positions and intensities using split pseudo Voigt functions for experimental (Exp.) and simulated (Sim.) V2C spectra in Figure S9.

	Mn ⁿ⁺	kβ'' (eV)		kβ _{2,5}		ΔE (eV)		kβ''/kβ _{2,5} ratio (%)	
		Exp.	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.
MnO	2	6517.0(7)	-19.3(3)	6530.73(5)	-5.76(6)	13.69	13.52	1.95	17.72
Mn ₂ O ₃	3	6517.2(7)	-18.9(1)	6532.70(3)	-5.12(4)	15.47	13.73	5.11	27.56
MnO ₂	4	6518.3(4)	-19.96(7)	6534.5(1)	-4.31(8)	16.13	14.65	24.78	32.87
Ba ₃ Mn ₂ O ₈	5	6519.7(1)	-18.03(2)	6535.76(3)	-3.78(1)	16.07	14.25	57.16	47.13

Supplementary Methods

Synthesis and sample preparation. The synthetic and sample preparation protocol reported in ^[2] was used in this work.

Ex-situ Neutron and X-ray total scattering data collections. Neutron powder diffraction data^[3] were acquired at the D4c diffractometer^[4] at the Institut Laue-Langevin (ILL) using a monochromatized wavelength of 0.4990 Å. Approximately 1.5 g of nano-Li₂MnO₃ powders were prepared in a cylindrical vanadium can of 6 mm of diameter sealed with Helicoflex in an inert Ar atmosphere. The data were collected at room temperature in the 1.7–135.0° 20° range for 3 h. The data were corrected for background scattering, vanadium can, and self-absorption, and normalized with the Correct software.^[5] The corrected data were Fourier transformed using Qmin = 0.4 Å⁻¹, Qmax =24Å⁻¹.

X-ray total scattering data were acquired at the i15-1 XPDF beamline at the Diamond light source. The sample was prepared in a glass capillary of 1 mm of diameter sealed in an inert Ar atmosphere. The data were collected also under ambient conditions for approximately five minutes. The data were background corrected, normalized and Fourier Transform with the GudrunX software.

Rietveld refinement. Rietveld refinement was performed using the TOPAS software.^[6] The same structural model and microstructural parameters were used to simultaneously fit both neutron and X-ray Bragg diffraction data. The scale factor, lattice parameters, and isotropic thermal parameters (B_{iso}) were refined. The backgrounds were fitted with Chebyshev polynomials and the peak profile shapes were described using a modified Thompson–Cox–Hastings pseudo-Voigt function,^[7] where instrumental profiles were determined by the refinement of standards.

Operando XPDF. Operando XPDF measurements were performed in the I15-1 XPDF beamline at the Diamond light source (UK) using high energy X-rays (76.6 keV) with a wavelength of 0.161669 Å.

The measurements were performed in modified Swagelok cells in radial geometry. The cells were specifically optimized for XPDF and XAS^[8] data collections and nearly replicate the voltage profiles of conventional cells. The measured capacity of 300 mAh g⁻¹ for nano-Li₂MnO₃ was in good agreement with the reported value of 335 mAh g^{-1 [2]} using conventional battery cells. A specially designed holder accommodating up to ten batteries was placed at the sample stage 200 mm away from a Perkin Elmer area detector.

During the experiment, the size of the beam was narrowed to $\sim 8 \ \mu m$ in the vertical direction and each cell position was aligned so that only signal for the active cathode material was detected, thereby avoiding the signals from the separator and lithium metal. Thus, for the processing of the XPDF signal in this work the sole background contributions considered were the empty cell and acetylene black

conductive additive present in the cathode mixture in 30 wt%. ~5 minutes data collections gave excellent data quality for XPDF data analysis and two duplicate of these batteries were measured insitu that gave identical results.

The position of the batteries were calibrated with Si standards and the collected 2D data was processed into 1D diffraction patterns using the DAWN software. Total scattering data was background corrected and normalized with the GudrunX software using a Qmax of 25 Å⁻¹. The sequential Rietveld refinements were performed with the TOPAS v.6 software. ^[6]

Operando Absorption and Emission Spectroscopy. Four commercial standards with Mn in various oxidation states, $Mn^{2+}O$, $Mn_2^{3+}O_3$, $Mn^{4+}O_2$, and $Ba_3Mn_2^{5+}O_8$, were diluted in BN (5 wt %), thoroughly mixed and uniaxially pressed into pellets that were mounted on a sample holder equipped with Kapton windows that allow the entry of X-rays. A C/nano-Li₂MnO₃ cathode mixture was investigated operando and prepared in a commercial Swagelok-type battery^[8] equipped with a 300 µm thick window made of glassy carbon, more details on the preparation of the cell are given in ^[9].

Operando HERFD-XANES and XES experiments were carried out at GALAXIES beamline of the Soleil synchrotron (France) using angle dispersive analysis of the fluorescence X-ray signal emitted from the sample. The spectrometer was equipped with five spherically bent Si(440) crystal analyzers focusing the diffracted beams onto a silicon drift detector for the recording of the Mn K β lines. The energy and experimental setup were calibrated by the recording a Mn foil spectrum. The energy resolution of the spectrometer, including contributions from both the monochromator and the CAS, was estimated by the recorded width of a pseudo-elastic peak.

For operando data acquisitions, the spectrometer was positioned at the maximum of the Mn K β emission line prior to the recording of the XANES spectra. HERFD-XAS spectra were then collected at the selected emission, which allowed discrimination of the detected photons with an energy resolution of 0.8 eV, smaller than the core-hole lifetime of the fluorescence line. This allows obtaining spectra with almost a core-hole lifetime-free broadening, that is, providing optimal energy resolution. XES and V2C data were averaged and background corrected using the PyMCA software.^[10]

EXAFS fitting. The theoretical EXAFS paths were calculated by the program FEFF6.0 embedded in ARTEMIS.^[11] A single parameter E_0 was refined for all paths to align the wavenumber grids of the data with those calculated by FEFF. The number of refined parameters was limited to 8, below the maximum number of 12 variables limited by the Nyquist criterion ($2\Delta k\Delta R/\pi$) with Δk [2:12 Å⁻¹] and ΔR [1.175:3.125 Å]. k weights of 2, and 3 were simultaneously fitted to distribute the sensitivity of the evaluation of χ^2 over the entire k-range and to make better use of the data available. S_0^2 was refined for the MnO standard, and the refined value was constrained in the refinement of the samples.

FDMNES simulations. The HERFD-XANES and V2C spectra were simulated using the FDMNES software. The simulations were done self-consistently using the finite difference method (FDM) for atoms of fixed radius, considering a large cluster of 6 Å around the absorber atoms, as the simulated spectra using a cluster size with a radius greater than 6 Å were identical to the former. Within the chosen radius, the photoelectron interacts with ~90 atoms. $2\times2\times2$ supercell with substitutional disorder composition were built to match the composition Li₂₁Mn₁₁O₃₂ (for pristine nano-Li₂MnO₃), Li₅Mn₁₀O₃₂ (for charged nano-Li₂MnO₃), Li₆Mn₁₃O₃₂ (charged nano-Li₂MnO₃) after densification, H₁₅Li₅Mn₁₁O₃₂ (protonated rock-salt), H₀Li₅Mn₁₁O₃₂ (non-protonated rock-salt). The V2C simulations were verified using the Mn-standards and the simulation parameters from the XANES calculations above; the energy shift between k β " and k $\beta_{2,5}$ transitions and relative integrated intensities for the Mn-standards were adequately reproduced (**Figure S17** and **Table S3**).

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