Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information:

Lithium manganese oxyfluoride as a new cathode material exhibiting oxygen redox

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Experimental

LMOF was synthesised using a mechanochemical ball-milling method. LiF (Sigma Aldrich, 99.995%), Li_2O (Alfa Aesar, 99.5%) and Mn_2O_3 (Sigma Aldrich, 99.9%) were mixed by mortar and pestle in a 2:1:1 molar ratio and then sealed in air-tight zirconia jars in an argon-filled MBraun glovebox with H_2O and O_2 less than 1 ppm. The mixture was then ball-milled for 18 hours at 750rpm in a Fritsch Pulverisette 7 planetary ball-mill. Milling was carried out in 5 minute intervals separated by 10 minute rests to avoid excessive heat generation.

Free-standing electrodes were prepared by mixing 80 wt% active material, 10 wt% Carbon Super P conductive additive and 10 wt % polytetrafluoroethylene (PTFE) binder in a mortar and pestle and then calendared between rollers to a thickness of ~0.25mm and cut into squares approximately 25-50 mm^2 in area. Sample loadings were typically 5-10 mg cm^{-2}. **Electrochemical testing** was performed in 2032 coin cells using a Li-metal disk as a negative electrode and glass microfibre separators (Whatman) soaked in LP30 electrolyte (BASF Selectilyte, 1M $LiPF_6$ in 1:1 of EC:DMC). All electrode processing was carried out under inert Ar atmosphere.

Powder X-ray Diffraction (PXRD) was performed using a Rigaku Smartlab diffractometer using Cu Kα1 radiation (λ = 1.54051 Å). The PXRD data were analysed using the Rietveld method of refinement and FullProf Suite software.

Solid-state nuclear magnetic resonance (NMR) experiments were performed in a 3.2 mm probe-head on a 400 MHz Bruker Avance III spectrometer at the ^{19}F Larmor frequency of 376.6 MHz and ^{7}Li of 155.5 MHz. Magic angle spinning (MAS) of 20 kHz was applied. The spectra were recorded with rotor-synchronised Hahn-echo pulse sequence; the applied π/2 pulse length and the delay between π/2 and π pulses were 2.5 µs and 46.3 µs, respectively for both ^{7}Li and ^{19}F. All samples were ground and packed in an Ar-filled glovebox; The ^{19}F and ^{7}Li spectra were externally referenced with $CFCl_3$ and 1 M LiCl aqueous solution at 0.0 ppm.

For **Inductively Coupled Plasma – Optical Emission Spectroscopy** (**ICP-OES)** of the precursor mixture and ball-milled material, 5mg of each powder were dissolved in concentrated aqua-regia and diluted to 1:100 and 1:200 each. For ICP-OES on cathodes (see Table S1.) free-standing electrodes prepared as discussed above were dissolved in concentrate aqua-regia, filtered using glass fiber membrane syringe filters followed by dilution to 1:100 and 1:200. For ICP-OES on the residue collected after cycling, the coin cells were disassembled in an Ar-filled glovebox, the cathode extracted and all the remaining parts were washed with 1mL concentrated aqua-regia and 14mL 2% nitric acid. The Li anode and black precipitate were completely dissolved. The entire liquid solution was mixed thoroughly and a filtered sample diluted 1:30 with 2% nitric acid. This diluted sample was subjected to ICP-OES analysis.

Operando electrochemical mass spectrometry (OEMS) analysis was carried out to study the different gases generated during cell cycling. The set up consisted of a quadrupole mass spectrometer (Thermo Fischer) equipped with turbomolecular pump (Pfeiffer Vacuum) and mass-flow controllers (Bronkhorst). Two electrode type cells (ECC-Std from EL-CELL) with gas inlet and outlet ports were used for the *operando* measurements. The cell consisted of Li anode, 1M $LiPF_6$ in PC electrolyte and the same cathode as described above.

Scanning Electron Microscopy (SEM) image was taken using a Zeiss Gemini SEM-500 at an operating voltage of 3 keV. Pristine LMOF powder was loaded onto a stub topped with Copper tape.

Soft X-ray Absorption Spectra (SXAS) and **Resonant Inelastic X-Ray Scattering (RIXS)** spectra were recorded at beamline BL27SU of the RIKEN/JASRI Spring8 synchrotron in Japan. *Ex situ* cathode samples were loaded onto adhesive copper tape and measured under 10^{-6} Pa high-vacuum conditions.

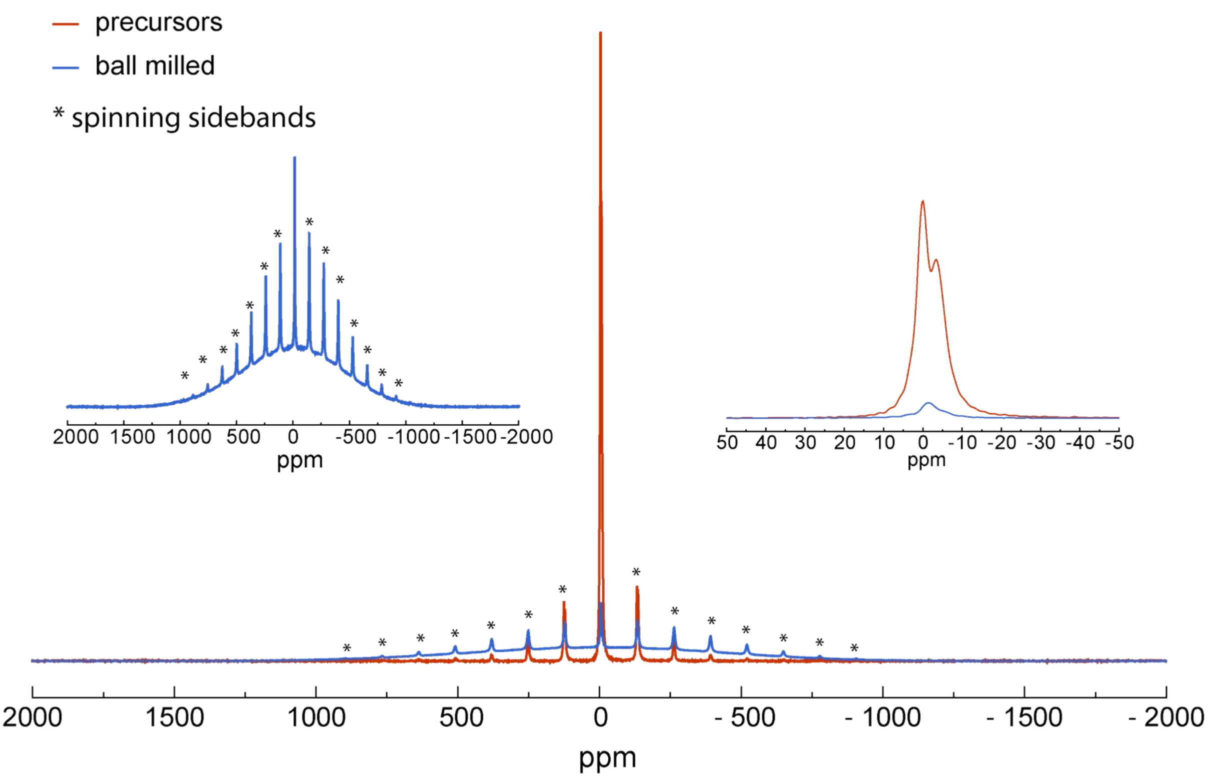
Iodometric Titration was carried out to determine Mn valence. A known mass of LMOF (approximately 5 mg) was completely dissolved in 25 mL of 1 M hydrochloric acid in deionised water that had been degassed with Argon. A few drops of starch indicator and an excess of potassium iodide was added. The mixture was constantly purged with Ar and stirred vigorously whilst titrating with 0.03 M sodium thiosulphate in deionised water until the mixture was colourless. The concentration of the sodium thiosulphate solution was standardised using potassium iodide.

Supplementary Figures and Tables

Table S1 Crystal structure data for the pristine LMOF sample. Site occupancies were fixed to the targeted composition, Li_2MnO_2F, and the cell parameter and peak width allowed to vary. The resulting refinement gave cell parameter, a = 4.1176(5) with $\chi^2 = 1.535$.

Atom	Wyckoff position	x	y	z	Occupancy
Li1	4a	0	0	0	0.667
Mn1	4a	0	0	0	0.333
O1	4b	0.5	0.5	0.5	0.667
F1	4b	0.5	0.5	0.5	0.333

Space group: $Fm\bar{3}m$ a = b = c = 4.1176(5) Å α = β = γ = 90°



<u>**Figure S1**</u> ^{7}Li MAS NMR spectra for a precursor mixture of LiF, Li_2O and Mn_2O_3 ground together in a mortar and pestle in a 2:1:1 ratio compared with that for the pristine LMOF. The left inset gives a zoomed-in view of the spectrum of the ball-milled sample and the right inset gives a zoomed in view of the isotropic shifts for the sharp peaks of both spectra. Spectra are normalised to account for sample mass. The MAS rate was 20 kHz. The two intense chemical shifts from Li_2O and LiF appear to almost completely diminish to give a single shift near 0 ppm in the ball-milled material which we attribute to Li in locally diamagnetic regions of the Rocksalt material which experience virtually no net paramagnetic interactions from Mn. The much broader Gaussian peak of the ball-milled sample is attributed to multiple overlapped Li sites, which are coupled with paramagnetic Mn.

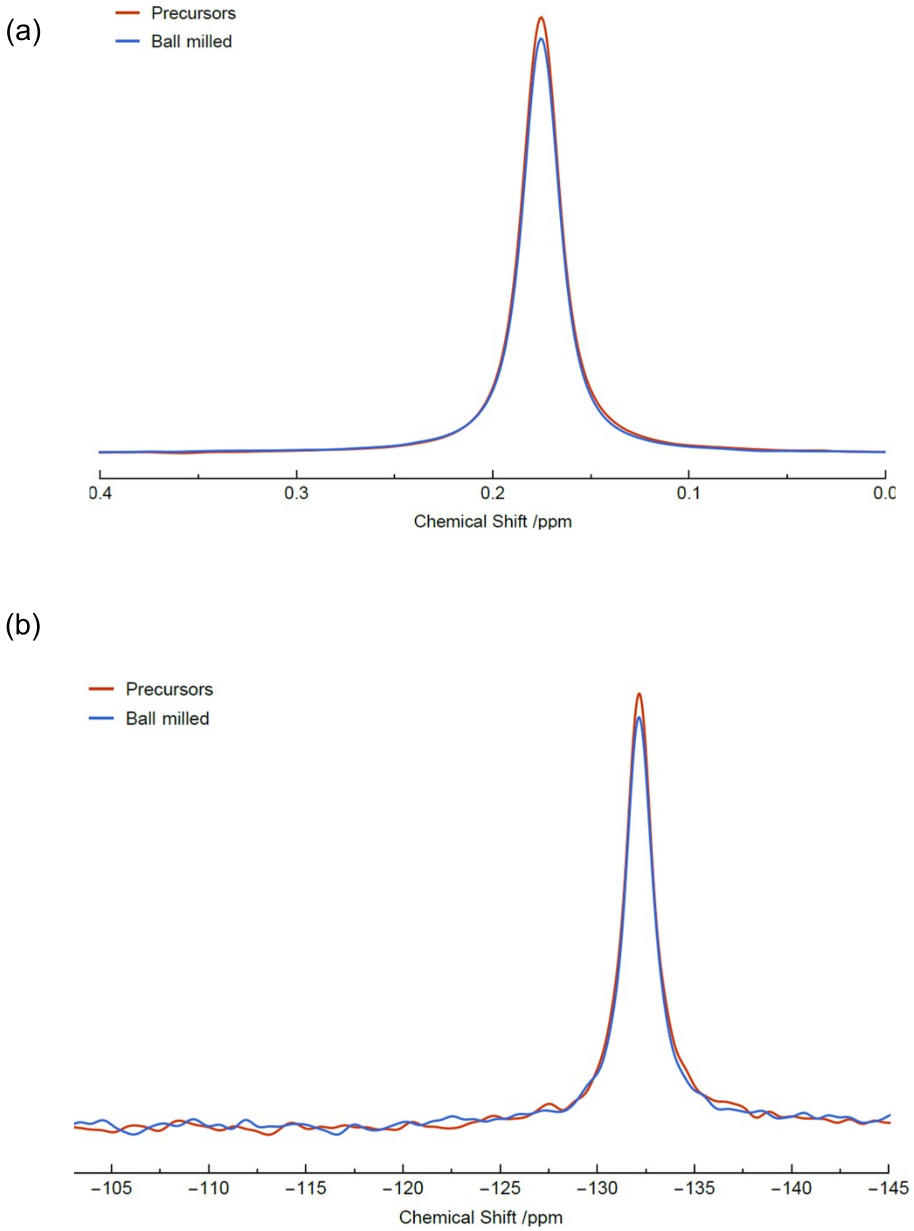


Figure S2 (a) ^{7}Li and (b) ^{19}F NMR spectra for solutions of the precursor mixture of LiF, Li_2O and Mn_2O_3 ground together in a mortar and pestle in a 2:1:1 ratio compared with that for the pristine LMOF. Both samples were completely dissolved in 12 M hydrochloric acid at concentrations of 0.644 and 0.636 mg ml^{-1} respectively (= 0.988). From NMR peak intensities, scale factor of Precursors : Ball-milled = 0.952 in both Li and F.

Table S2 Oxidation states for Mn measured using Iodometric Titration

Precursor Mixture	**Ball-milled**
3.001	3.257
3.015	3.286
3.003	3.268
3.006	3.266
2.990	3.282
3.003(8)	**3.272(11)**
$LiF + Li_2O + Mn_2O_3$	**$Li_2MnO_{2.14}F$**

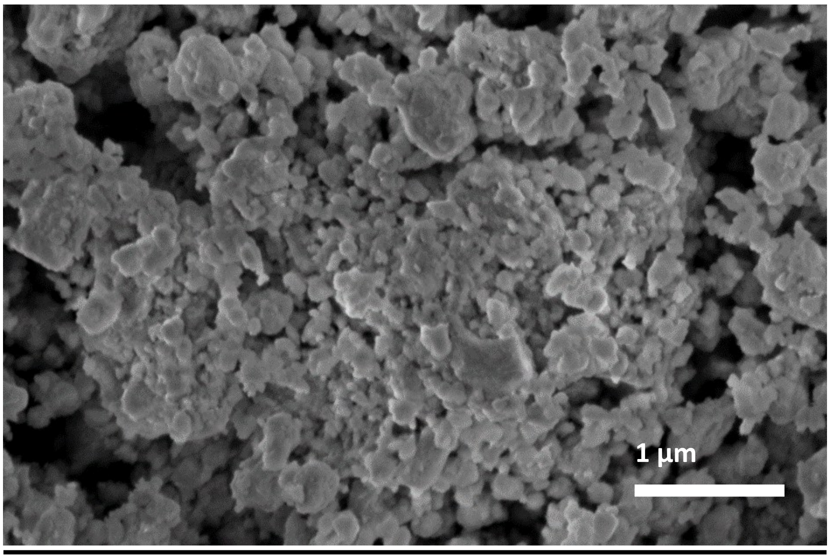


Figure S3 Scanning Electron Microscopy (SEM) images of pristine LMOF. Image was taken at an operating voltage of 3 keV using a Zeiss Gemini SEM-500.

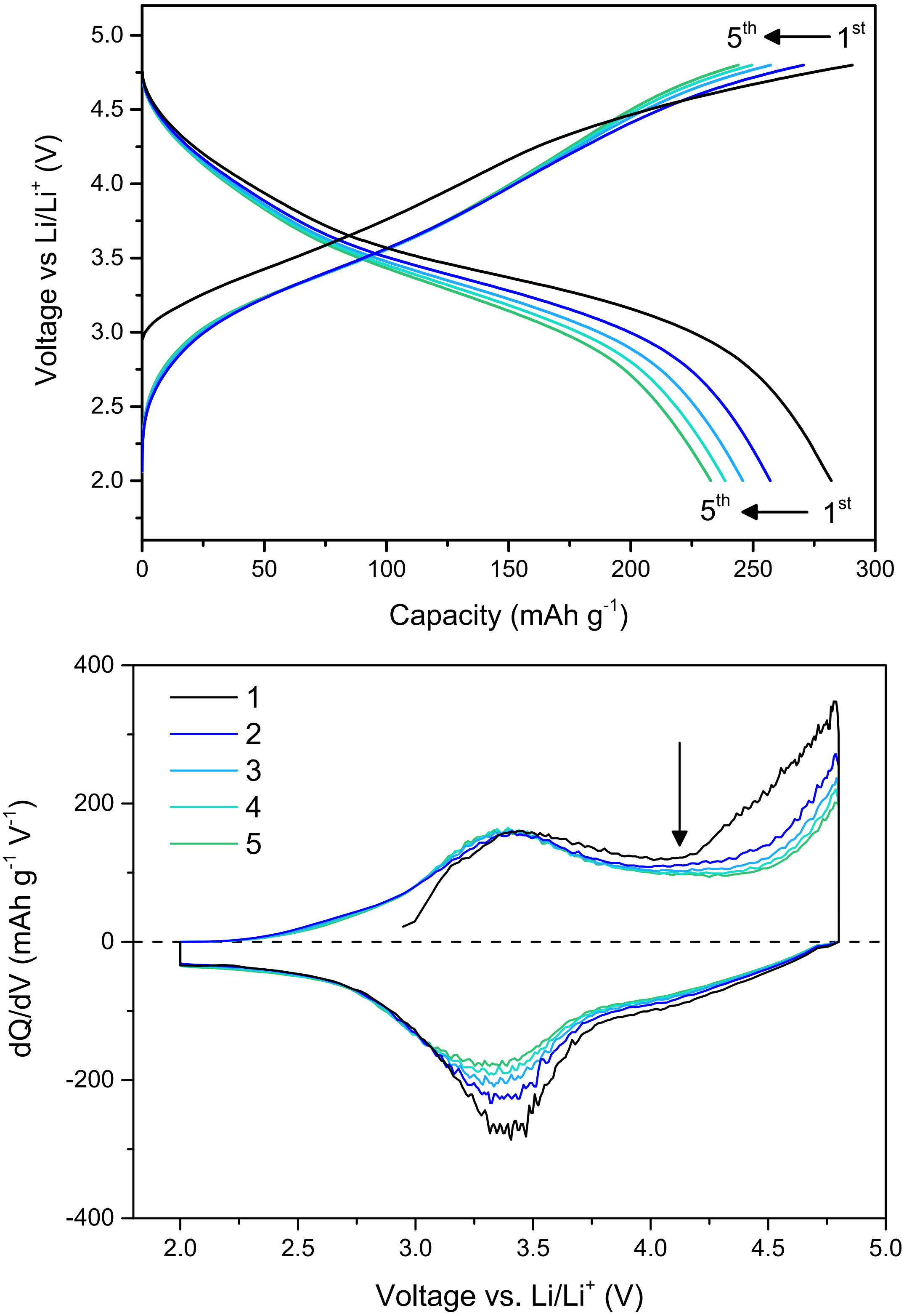


Figure S4 Load curve (above) and dQ/dV plotted versus Voltage (below) for a LMOF electrode cycled between 2 V and 4.8 V at a rate of C/10 (22.4 mA g^{-1}). The arrow marks the point at which processes occurring at higher voltages can no longer be attributed to $Mn^{3+/4+}$.

Table S3 ICP-OES measurements yielding Li:Mn ratio for cathodes at different states of charge and capacities calculated using Li:Mn ratio as obtained from ICP-OES. Electrode materials were charged at a current rate of C/10 (22.4 mA g^{-1})

	Before cycling	**Charged to 4.8V**	**Discharged to 2V**
Li : Mn ratio from ICP-OES (error)	1.95(5)	0.67(5)	1.99(5)
Li content, x, in $Li_xMn_{0.95}O_{2.05}F_{0.95}$ from ICP-OES (error)	1.85(5)	0.64(5)	1.89(5)
Li content, x, in $Li_xMn_{0.95}O_{2.05}F_{0.95}$ from electrochemistry	1.90	0.65	1.85

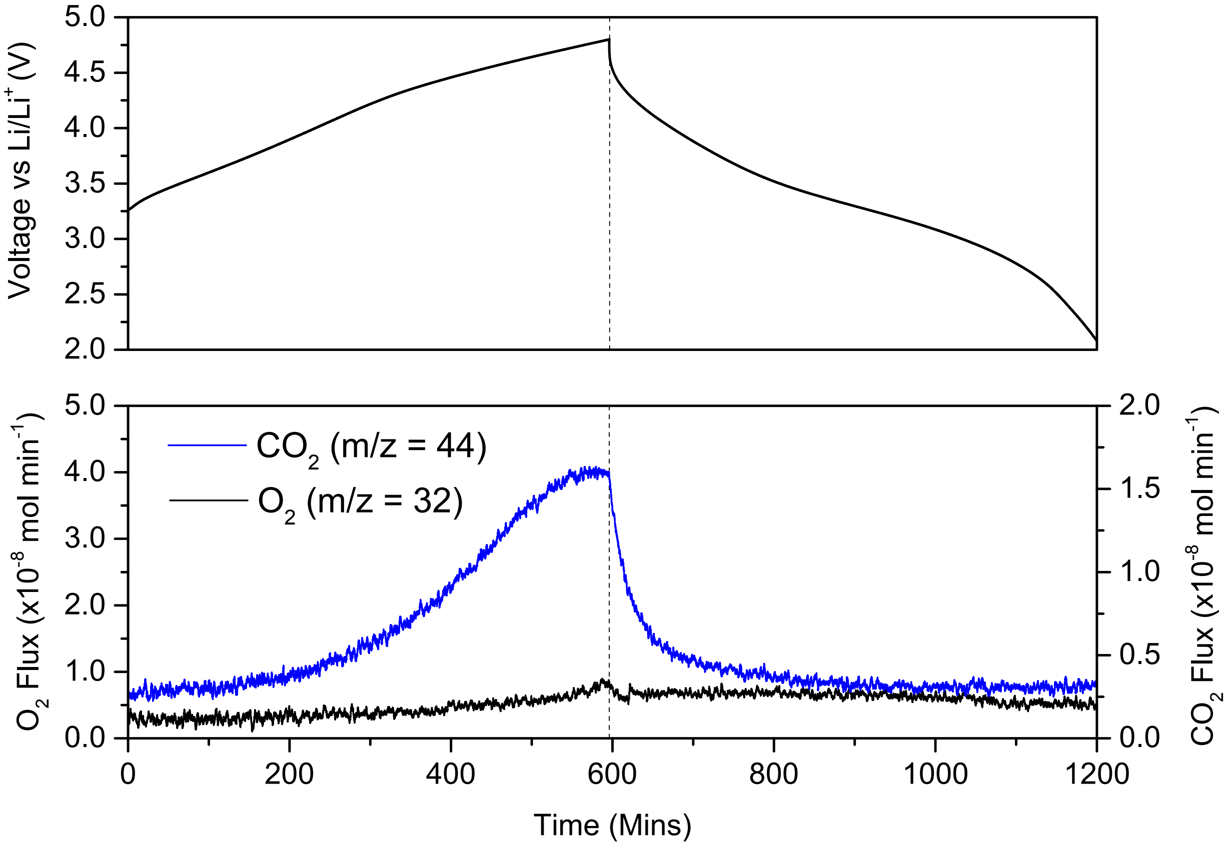


Figure S5 Operando Electrochemical Mass Spectrometry (OEMS) for the first charge and discharge cycle between 2 V and 4.8 V at a current rate of C/10. At high potentials, some carbon dioxide gas evolution was evolved, corresponding to 0.03 moles per mole of LMOF active material. Virtually no oxygen loss was observed.

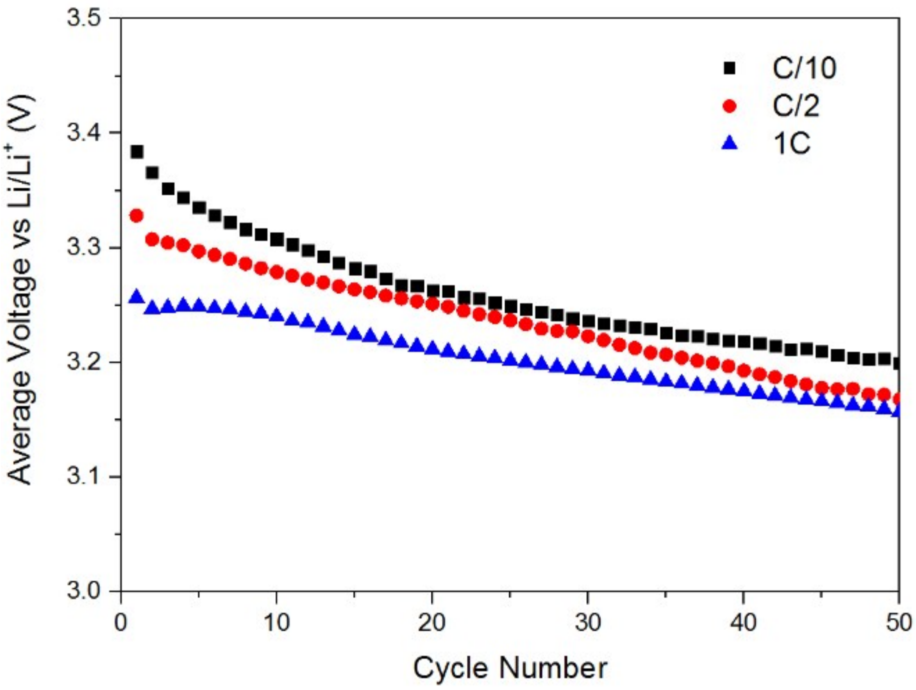
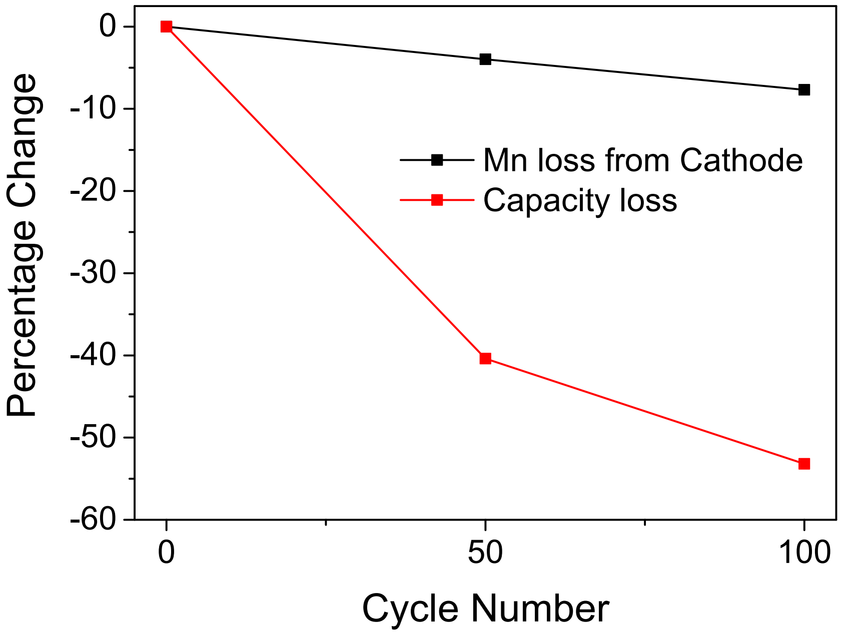


Figure S6 Average discharge voltage as a function of cycle number at progressively faster C-rates C/10, C/2 and 1C (224 mA g^{-1}). Cells were cycled between 2 V and 4.8 V.

Table S4 ICP-OES measurements on residue collected from coin cell components after disassembly yielding the absolute loss of Mn from the cathode material into the electrolyte and deposited on the anode. Cathode materials were cycled vs a Li metal anode between 2 – 4.8V at a current rate of C/2 (112 mA g^{-1}) and extracted before washing the cell parts.

	50 cycles	**100 cycles**
Mass of LMOF in Cathode (mg)	10.88	7.04
Mass of Mn in Cathode (mg)	4.989	3.228
Mn ICP Concentration (mg L^{-1})	0.441	0.552
Mass of Mn lost from Cathode (mg)	0.198	0.248
% loss of Mn from Cathode	3.97	7.68
% capacity loss	40.4	53.2



<u>Figure S7</u> Comparison of Mn lost from Cathode as measured by ICP-OES with capacity loss as a function of cycle number.