Supporting Information

Operando electrochemical fluorination to achieve Mn^{4+}/ Mn^{2+} double redox in Li_2MnO_3-like

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Experimental

Material synthesis. The Li_2MnO_3-like cathode materials were synthesized by the solid-state reaction by using $LiOH·H_2O$ (Adamas,99%) and $MnCO_3$ (Aladdin,99.95%) as precursors, in which the molar ratio of $LiOH·H_2O$: $MnCO_3$ was 2:1. The precursors were mixed in ethanol and mechanical ball milled for 12 hours. The drying mixture was calcined at 500°C for 12 hours to obtain the final materials.

Material Characterization. X-ray diffraction (XRD) patterns were collected on a powder diffractometer(Rigaku Ultima IV) equipped with Cu-K_α radiation in the 2-theta range from 10° to 80°. The morphologies of materials were characterized by Quanta 200 filed emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) spectra were acquired from a JEM-2100F microscope.

Electrochemical tests. The synthesized Li_2MnO_3-like material was mixed with carbon black and polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP) with a weight ratio of 8:1:1 to obtain a slurry. The slurry was then cast on an aluminum foil current collector, then it was dried under vacuum at 100°C overnight to obtain a cathode film. The loading of positive active material is 2.21~2.47 mg/cm^2. To assemble a cell for electrochemical tests, Coin cells (CR2025) were assembled in an Ar atmosphere glove box using Li metal foil as the counter electrode. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate (EC/DMC=1:1) solution. The tests were carried out on a battery test system (Neware, Shenzhen, China). Electrochemical impedance spectroscope (EIS) data was performed on a CHI600A Electrochemical workstation (Chinster, Shanghai, China), with 5 mV ac excitation over a frequency range of 1 mHz to 100 kHz. Cyclic voltammogram (CV) test was performed at a scan rate of 0.1 mV/s among voltage range of 1.5 V to 4.8 V (vs. Li^+/Li) by a CHI600A Electrochemical workstation (Chinster, Shanghai, China). DEMS analysis was used to detect and analyze the gas during cycling, and DEMS analyses in half cells were tested with a constant current density of 10 mA/g with the loading of 16 mg/cm^2 when charging to 4.8 V in the first cycle.

Soft X-ray absorption spectroscopy (sXAS) measurements. Soft X-ray absorption spectroscopy (sXAS) measurements of Mn edge and O K-edge in partial fluorescence yield (PFY) mode were carried out at the IOS (23-ID-2) beamline of National Synchrotron Light Source II at Brookhaven National Laboratory. We followed the same normalization methodology as in the literature.[1, 2] For each sample, the PFY-sXAS were collected from four local areas and the average intensity is firstly normalized by an individual photodiode scan. A linear sloping background is next removed by linear fitting of the flat low-temperature region from 520.0 to 523.0 eV before the absorption peaks. Lastly,

the spectrum is normalized by setting the low-energy region to zero intensity and the main peak to unity intensity. For Mn L_3 edge, the curves of TEY and FY models are normalized by setting the low-energy region at 638.0 eV to zero intensity and the main peak region at ~643.7 eV to unity intensity. For O K-edge, the curves of TEY and FY models are normalized by setting the low-energy region at 526.0 eV to zero intensity and the main peak region at ~529.5 eV to unity intensity.

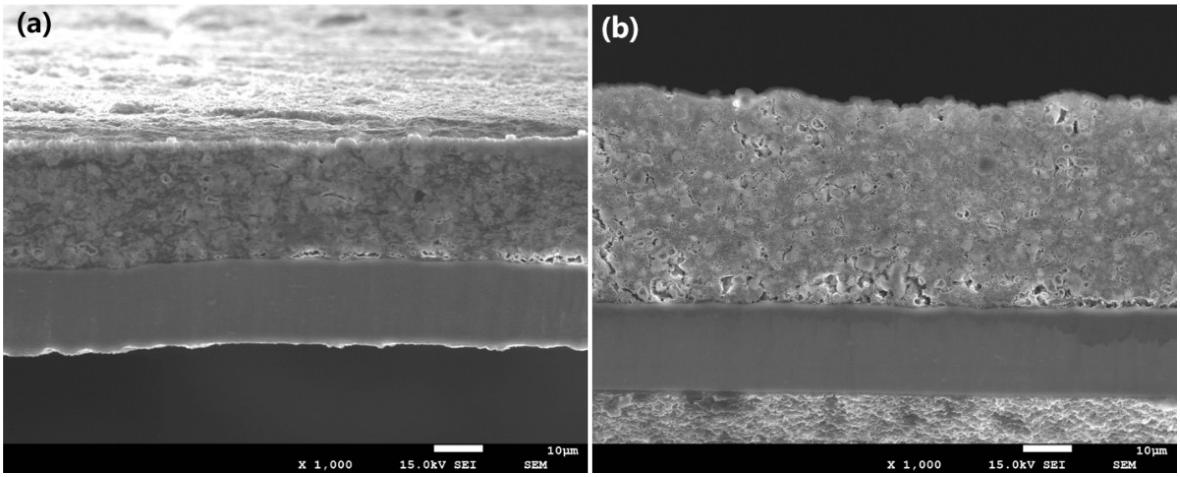

Fig. S1 SEM of the positive plates prepared by the FIB lift-out technique: (**a**) the pristine state, (**b**) the initial discharged to 1.5V

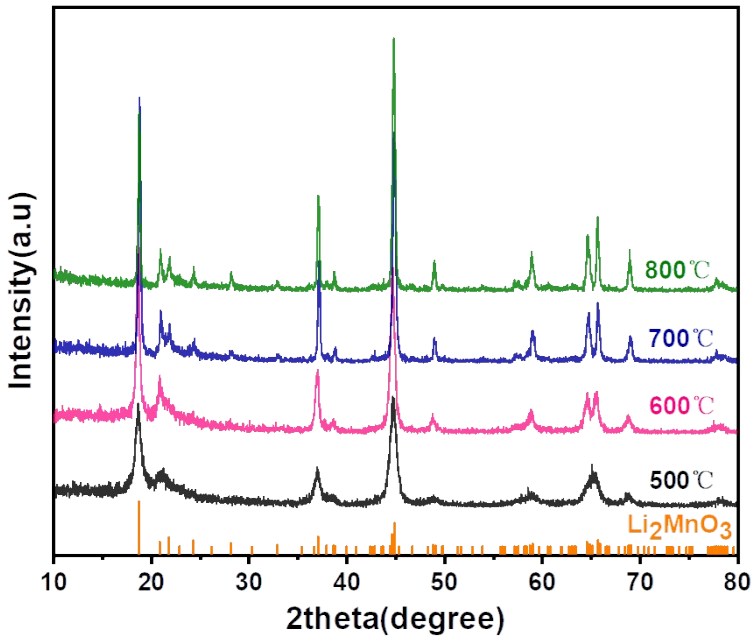

Fig. S2 XRD patterns of the Li_2MnO_3 powders calcinated at different temperatures.

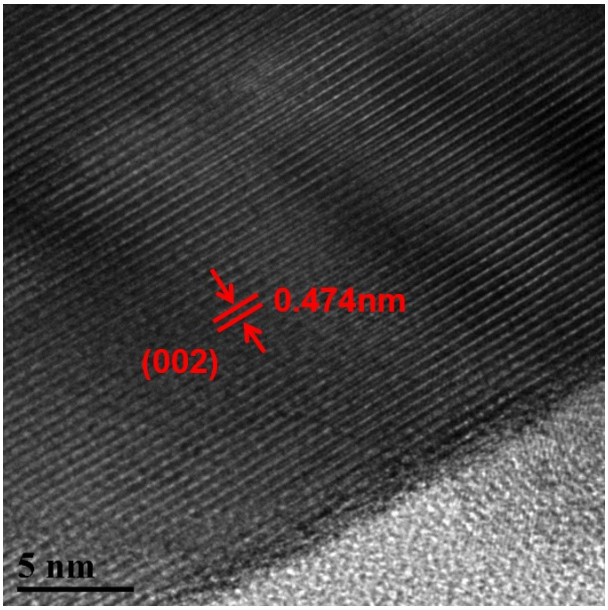

Fig. S3 The TEM image of Li_2MnO_3 calcined at 600℃.

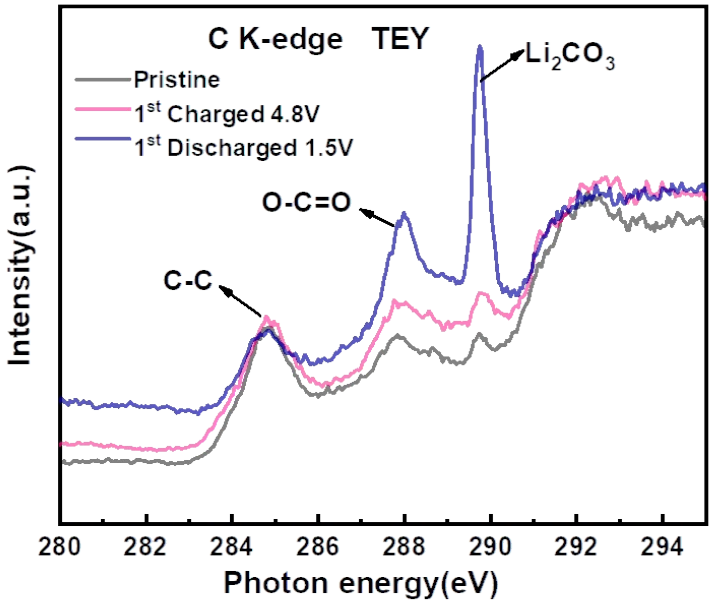

Fig. S4 Changes in C K-edge XAS spectra in different states.

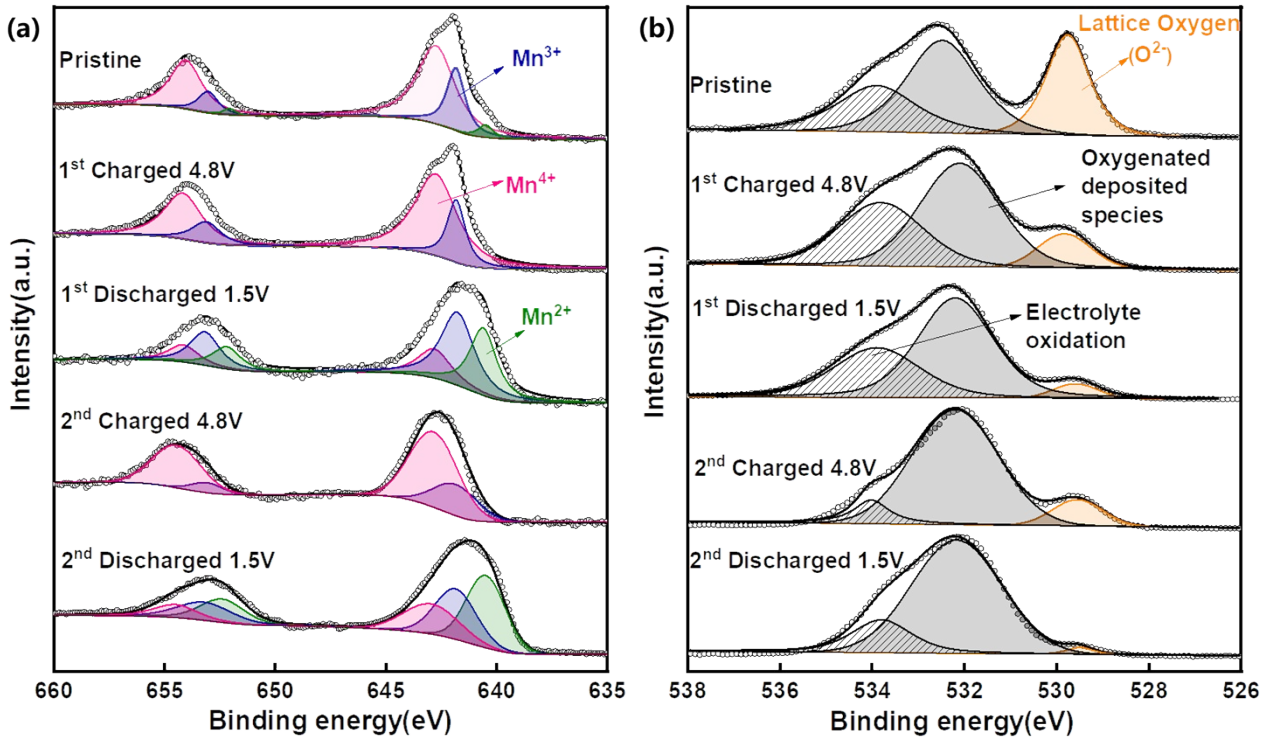

Fig. S5 XPS on the surface of LMOF at various states of electrochemical cycling. (**a**) Mn 2*p* XPS spectra, (**b**) O 1*s* XPS spectra.

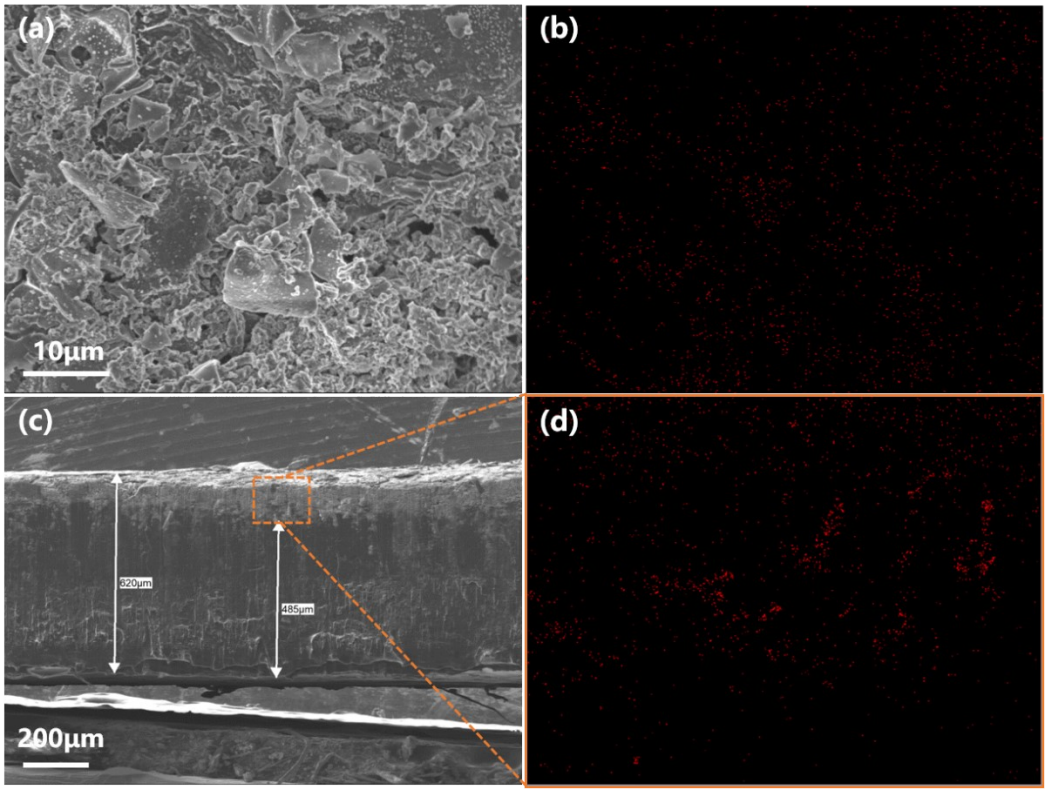

Fig. S6 (**a**) SEM images of Li metal anode surface after the first charge/discharge activation. (**b**) EDS mapping of Mn in (**a**). (**c**) The cross-sectional SEM of Li metal anode. (**d**) EDS mapping of Mn in enclosed in a square in (**c**).

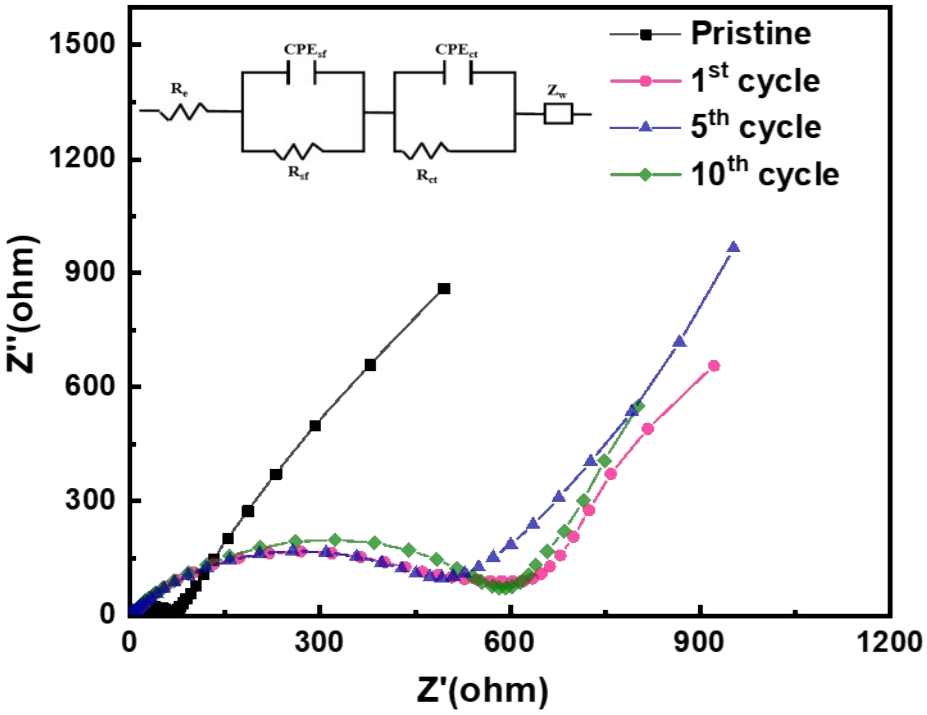

Fig. S7 EIS before cycle and after 1st, 5th,10th cycle at a discharged state of 1.5 V, the equivalent circuit model is shown in the inset.

References

1 K. Luo, M. R. Roberts, R. Hao, N. Guerrini, D. M. Pickup, Y.-S. Liu, K. Edstrom, J. Guo, A. V. Chadwick, L. C. Duda and P. G. Bruce, *Nat. Chem.*, 2016, **8**, 684-691.

2 K. Luo, M. R. Roberts, N. Guerrini, N. Tapia-Ruiz, R. Hao, F. Massel, D. M. Pickup, S. Ramos, Y.-S. Liu, J. Guo, A. V. Chadwick, L. C. Duda and P. G. Bruce, *J. Am.Chem. Soc.*, 2016, **138**, 11211-11218.