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Supporting information for

Fast microwave treatments of single source alkoxides for nanostructured Li-ion battery electrodes

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Experimental procedure

Synthesis of $[Fe(O^tBu)_2(THF)]_2$

NaO^tBu (5.766 g, 60 mmol, Sigma Aldrich) and $FeBr_2$ (6.470 g, 30 mmol, Sigma Aldrich) were weighed in an Ar-filled glovebox and transferred to a Schlenk flask. Dry THF (90 mL) was added and the mixture was stirred at room temperature for 24 hr. After that, a grey precipitate of NaBr was formed and the liquid phase was transferred into a separate flask using a glass syringe. Finally, the solvent was evaporated under vacuum to yield extremely air sensitive grey-greenish crystals of $[Fe(O^tBu)_2(THF)]_2$. All the manipulations were performed under Ar using a Schlenk line.

Synthesis of "$[Mn(O^tBu)_2(THF)]_2$"

The same preparation method was followed using NaO^tBu (5.766 g, 60 mmol, Sigma Aldrich) and $MnBr_2$ (6.443 g, 30 mmol, Sigma Aldrich) in 90 mL of dry THF in order to synthesise the equivalent Mn-containing alkoxide "$[Mn(O^tBu)_2(THF)]_2$".

Synthesis of "$[Fe_{0.5}Mn_{0.5}(O^tBu)_2(THF)]_2$"

Similar salt elimination reactions were conducted to prepare the bimetallic alkoxide "$[Fe_{0.5}Mn_{0.5}(O^tBu)_2(THF)]_2$". $FeBr_2$ (3.235 g, 15 mmol), $MnBr_2$ (3.221 g, 15 mmol) and NaO^tBu (5.766 g, 60 mmol) in 90 mL of dry THF were used in the preparation of "$[Fe_{0.5}Mn_{0.5}(O^tBu)_2(THF)]_2$".

Microwave synthesis of $LiFe_{1-x}Mn_xPO_4$ (x=0, 0.5 and 1) nanostructures from "$[M(O^tBu)_2(THF)]_2$" (M=Fe or Mn) and "$[Fe_{0.5}Mn_{0.5}(O^tBu)_2(THF)]_2$" alkoxide precursors

In order to access the olivine $LiFe_{1-x}Mn_xPO_4$ phases, the metal alkoxide precursors $[Fe(O^tBu)_2(THF)]_2$, "$[Mn(O^tBu)_2(THF)]_2$" and "$[Fe_{0.5}Mn_{0.5}(O^tBu)_2(THF)]_2$" (0.030 g, 0.050 mmol) were individually mixed with $LiOH.H_2O$ (0.007 g, 0.150 mmol, Sigma Aldrich) and crystalline H_3PO_4 (0.015 g, 0.150 mmol, Sigma Aldrich) in 4 mL of benzyl alcohol (Sigma Aldrich) and then irradiated with microwaves for 15 min at 80 °C and 10 min at 240 °C using a CEM Discover SP microwave synthesizer (2.45 GHz). The resulting products were washed thoroughly with ethanol (2 x 30 mL) and acetone (2 x 30 mL) to obtain the Li*M*PO$_4$ (*M*=Fe and Mn) powders. Finally, the materials were carbon coated with sucrose by mixing the obtained powders with sucrose (Sigma Aldrich) to obtain a final mixture of 15% carbon content and heating in a tube furnace for 1 hr at 700 °C under Ar flow.

Ultrasonic-assisted synthesis of Mn_3O_4 hausmannite from "$[Mn(O^tBu)_2(THF)]_2$" alkoxide precursor

As previously reported by Gun´ko *et al.*, the careful hydrolysis and ultrasonic treatment of $[Fe(O^tBu)_2(THF)]_2$ affords nanoparticles of magnetite (Fe_3O_4). In this work, the remaining "$[Mn(O^tBu)_2(THF)]_2$" and NaBr precipitate obtained after syringing out the "$[Mn(O^tBu)_2(THF)]_2$" liquid phase was hydrolysed with 60 mL of degassed H_2O and kept in the ultrasonic bath for 1 hr to yield nanostructured Mn_3O_4 hausmannite. The addition of degassed H_2O and the ultrasonic treatment were repeated 6 times. After that, the obtained precipitate was washed again 4 times with 30 mL of distilled H_2O to completely remove the remaining NaBr. Mn_3O_4 nanoparticles were carbon coated with sucrose by mixing the obtained powders with sucrose to obtain a final mixture of 15% carbon content. Heat treatment of the mixture at 700 °C under Ar atmosphere leaded to the formation of the reduced oxide MnO due to the sucrose acting as a reducing agent. C/Mn_3O_4 powders were obtained simply by heating for 1 hr at 500 °C under air (heat treatment for 1 hr at 700 °C under air produced the oxidation of Mn_3O_4 to Mn_2O_3).

Structural characterization of $LiFe_{1-x}Mn_xPO_4$ (x=0, 0.5 and 1) and Mn_3O_4 hausmannite nanostructures

High resolution powder x-ray diffraction (XRD) analysis of the $LiFe_{1-x}Mn_xPO_4$ (x=0, 0.5 and 1) nanostructures prepared using the "$[M(O^tBu)_2(THF)]_2$" (*M*=Fe or Mn) and "$[Fe_{0.5}Mn_{0.5}(O^tBu)_2(THF)]_2$" alkoxide precursors were conducted at the I11 beamline at Diamond Light Source using 0.5 mm diameter glass capillaries. These high intensity X-rays (λ=0.825704 Å) can probe more deeply into the sample than conventional laboratory XRD diffractometers and allow to perform a more detailed structural analysis of our materials.

Powder x-ray diffraction (XRD) characterization of the brownish Mn_3O_4 hausmannite powders was carried out with a PANalytical X' Pert powder diffractometer using Cu Kα radiation operated at 40 kV and 40 mA. The diffraction data were collected in the 2θ range between 10 and 80° in steps size of 0.017 (2θ) and an integration time of 2 s per step.

Electron microscopy of $LiFe_{1-x}Mn_xPO_4$ (x=0, 0.5 and 1) and Mn_3O_4 hausmannite nanostructures

Scanning electron microscopy (SEM) analysis were conducted using a Carl Zeiss Sigma variable pressure analytical SEM. SEM samples were prepared on carbon adhesive stubs and coated with 99:1 Au:Pt using a plasma sputter coater to avoid charging feedback. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a FEI Tecnai TF20 microscope fitted with a field emission gun, operated at 200 keV. TEM samples were dispersed in ethanol and the resulting solution was then dropped onto an amorphous holey carbon coated grid.

Electrochemical performance of $LiFe_{1-x}Mn_xPO_4$ (x=0 and 0.5) and Mn_3O_4 hausmannite nanostructures

Galvanostatic cycling with potential limitation of the electrode materials were conducted in a BioLogic VSP potentiostat using Swagelok type cells. The working electrode consisted of a mixture of C/$LiFePO_4$ (C/$LiFe_{0.5}Mn_{0.5}PO_4$ or C/Mn_3O_4):carbon black KET JENBACK EC-600JD (AkzoNobel):PTFE (polytetrafluoroethylene) (Fischer Scientific) in a 60:30:10 weight ratio pressed into a pellet. A thin plate of lithium metal (Sigma Aldrich, ribbon, thickness x W 0.75 mm x 45 mm 99.9% trace metal basis) was used as a counter electrode and the electrolyte solution employed was 1 M $LiPF_6$ dissolved in EC (ethylene carbonate):DEC (dymethyl carbonate) 1:1 molar ratio (Solvionic). (De)Assembly of the electrochemical cells were performed in an Ar-filled glovebox (0.5 ppm O_2; 0.5 ppm H_2O). The electrodes were thoroughly washed with THF and dried prior to XRD analysis of the cycled material.

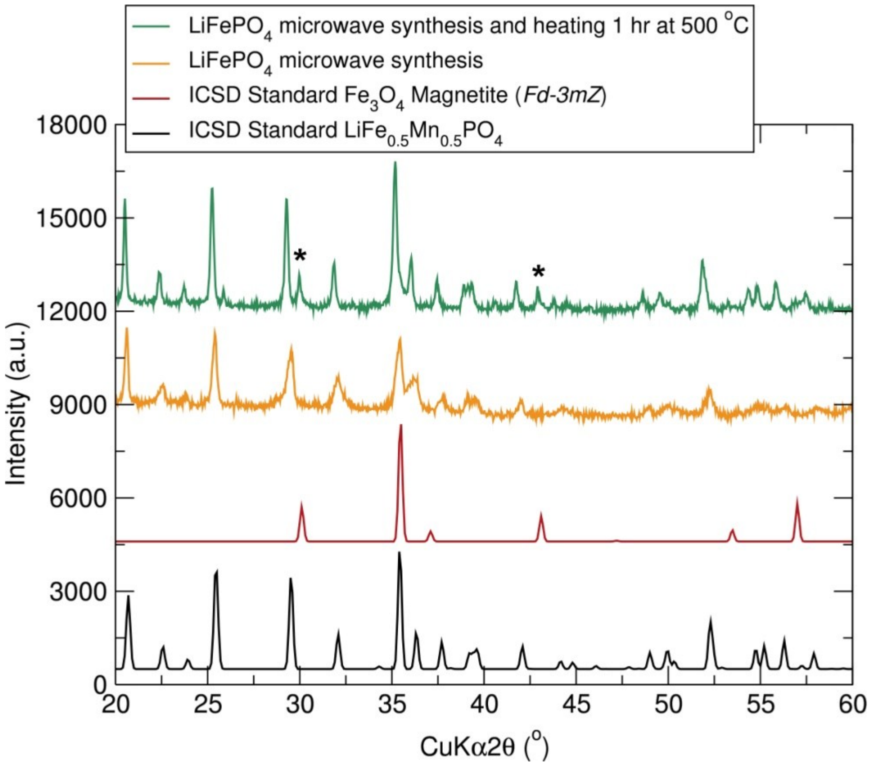

Fig S1. Powder XRD pattern of $LiFe_{0.5}Mn_{0.5}PO_4$ prepared from stoichiometric mixture of $[Fe(O^tBu)_2(THF)]_2$ and "$[Mn(O^tBu)_2(THF)]_2$" alkoxide precursors. * indicates Fe_3O_4 impurities.

High resolution powder XRD data of $LiFe_{1-x}Mn_xPO_4$ (x=0, 0.5 and 1) nanostructures were fit by Rietveld analysis to the orthorhombic *Pnma* space group using Fullprof programme. The structural and profile parameters were refined according to a Thompson-Cox-Hastings pseudo-Voigt profile function and the refinement process order was the following: (i) scale factor (ii) the background was carefully modelled using a 6-coefficient polynomial function (iii) zero point and sample displacement correction, (iv) cell parameters, (v) profile parameters, (vi) atomic positions and finally (vii) atomic thermal displacement parameters (B_{iso})

Table S1. Calculated lattice parameters from Rietveld refinements for the $LiFe_{1-x}Mn_xPO_4$ (x=0, 0.5 and 1) nanostructures prepared from metal alkoxide precursors.

Sample	$LiFePO_4$	$LiFe_{0.5}Mn_{0.5}PO_4$	$LiMnPO_4$
Space group	*Pnma*	*Pnma*	*Pnma*
a (Å)	10.3267	10.3662	10.4492
b (Å)	6.0056	6.0348	6.1016
c (Å)	4.6925	4.7093	4.7459
V ($Å^{-3}$)	291.017	294.609	302.589
R_{wp}	19.0 %	20.5 %	25.0 %
R_{exp}	10.8 %	13.5 %	16.9 %
X^2	3.107	2.320	2.187

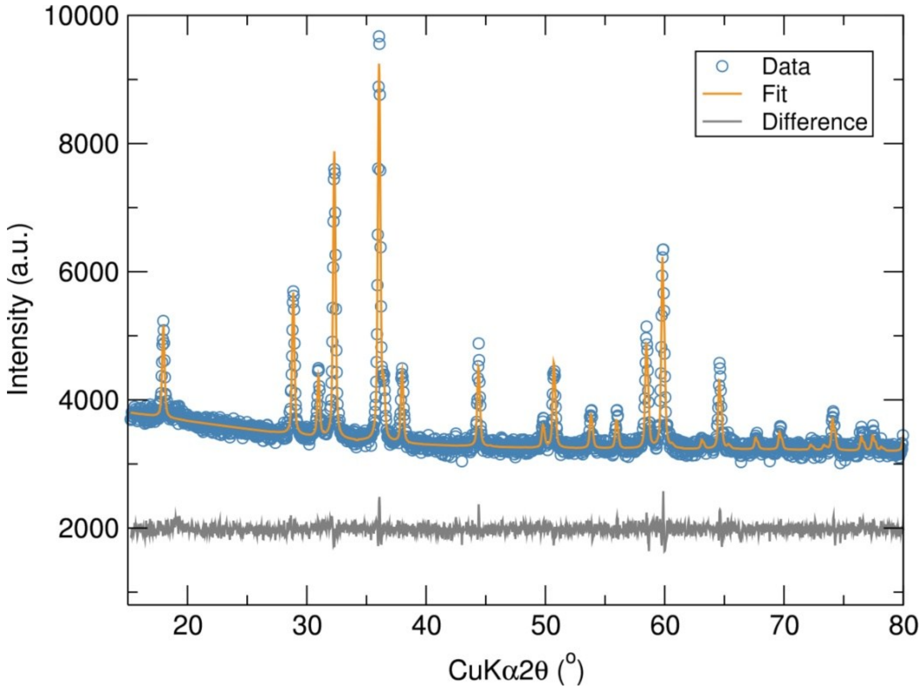

Fig S2. Rietveld analysis of powder XRD data from hausmannite Mn_3O_4 nanoparticles [R_{wp}=19.5%, R_{exp}=15.87%, a=5.765502 Å, b=5.765502 Å and c=9.463403 Å].

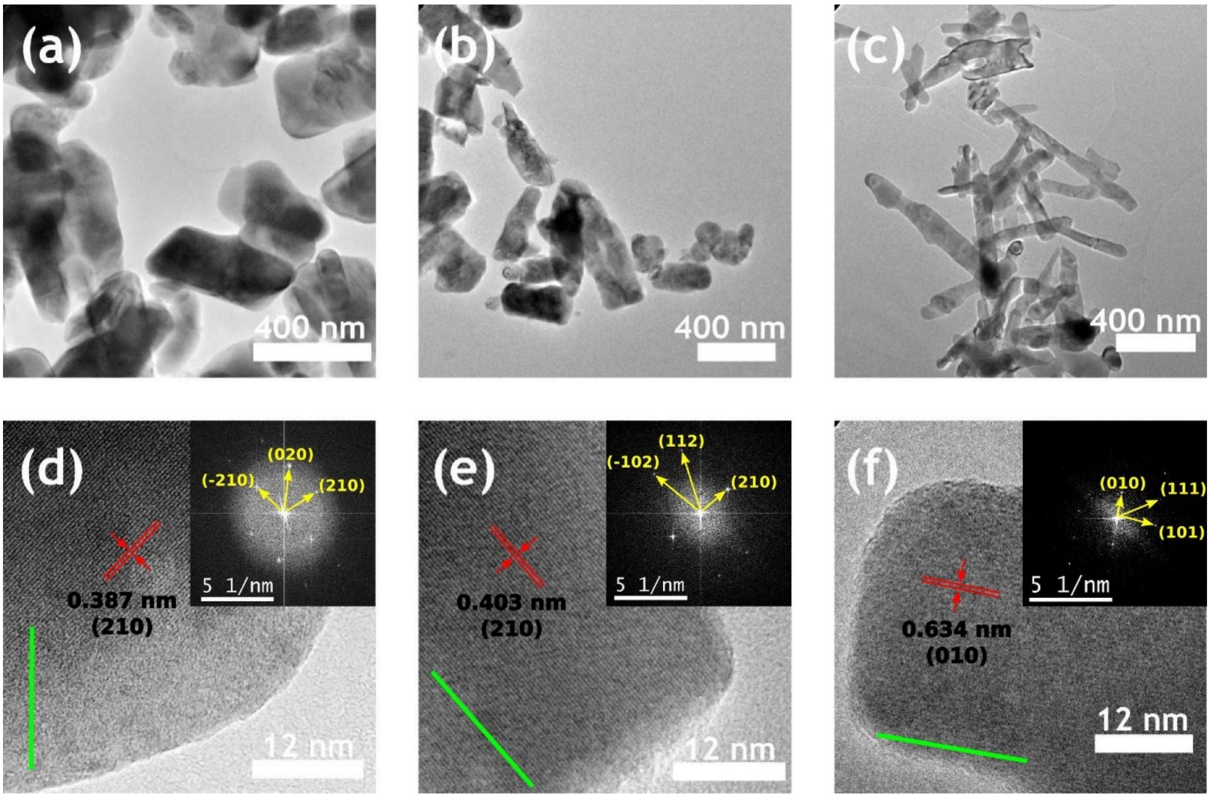

Fig S3. High resolution TEM images of **(a)** and **(d)** $LiFePO_4$, **(b)** and **(e)** $LiFe_{0.5}Mn_{0.5}PO_4$ and **(c)** and **(f)** $LiMnPO_4$ nanostructures prepared from metal alkoxide precursors.

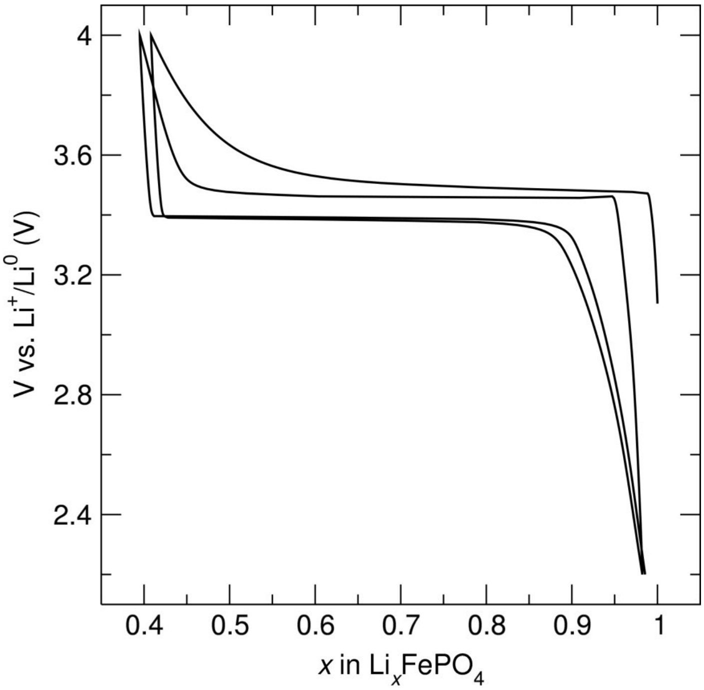

Fig S4. Voltage-composition profile between 2.2 and 4.0 V of C/$LiFePO_4$ (15% C sucrose), C black and PTFE in a 60:30:10 weight ratio cycled at C/20.

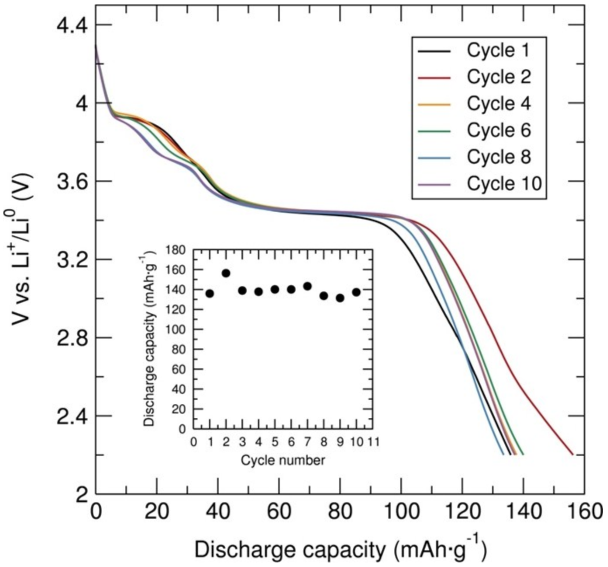

Fig S5. Cycling performance of C/$LiFe_{0.5}Mn_{0.5}PO_4$ (60% active material, 30% carbon black, 10% PTFE binder) cycled between 2.2 V and 4.0 V at C/20 rate.

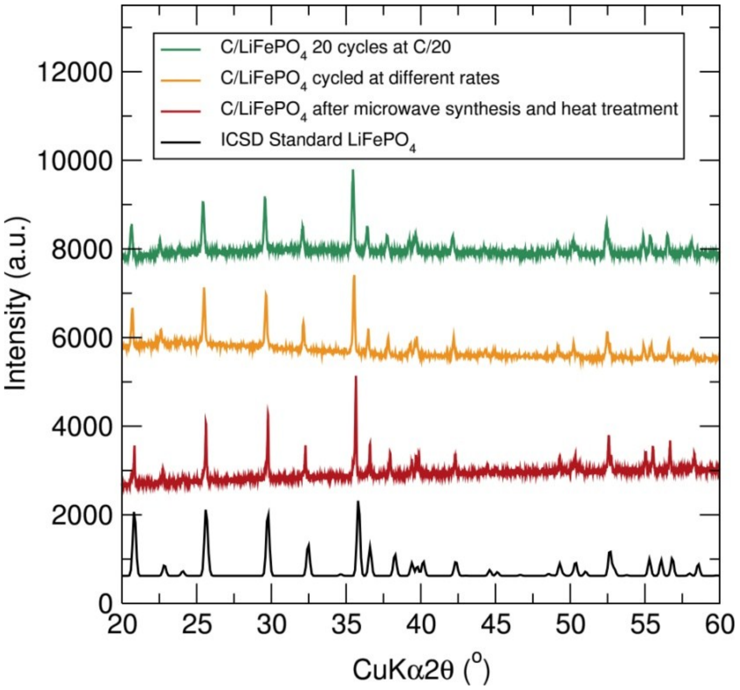

Fig S6. Powder XRD of cycled C/$LiFePO_4$ between 2.2 and 4.0 V at different rates and for 20 cycles at C/20 in the discharge state.

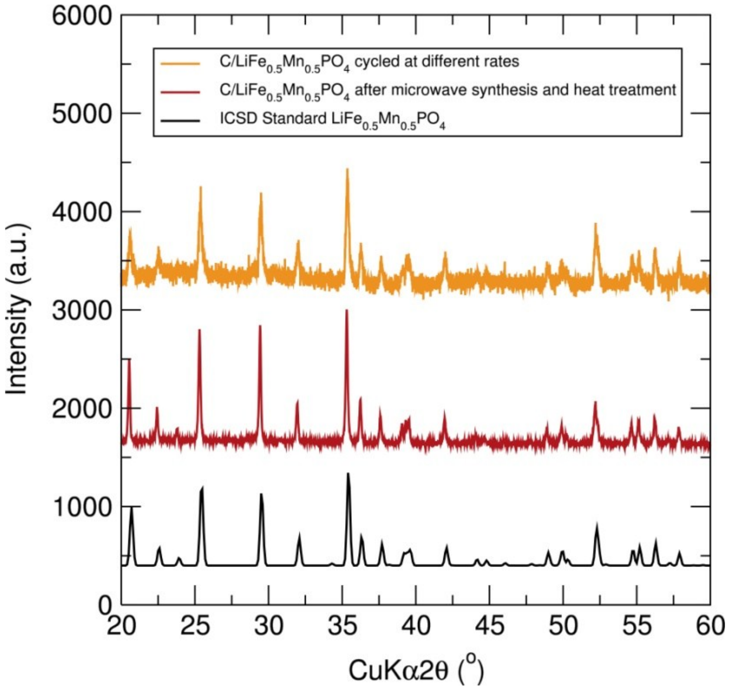

Fig S7. Powder XRD of cycled $C/LiFe_{0.5}Mn_{0.5}PO_4$ between 2.2 and 4.3 V at different rates in the discharge state.

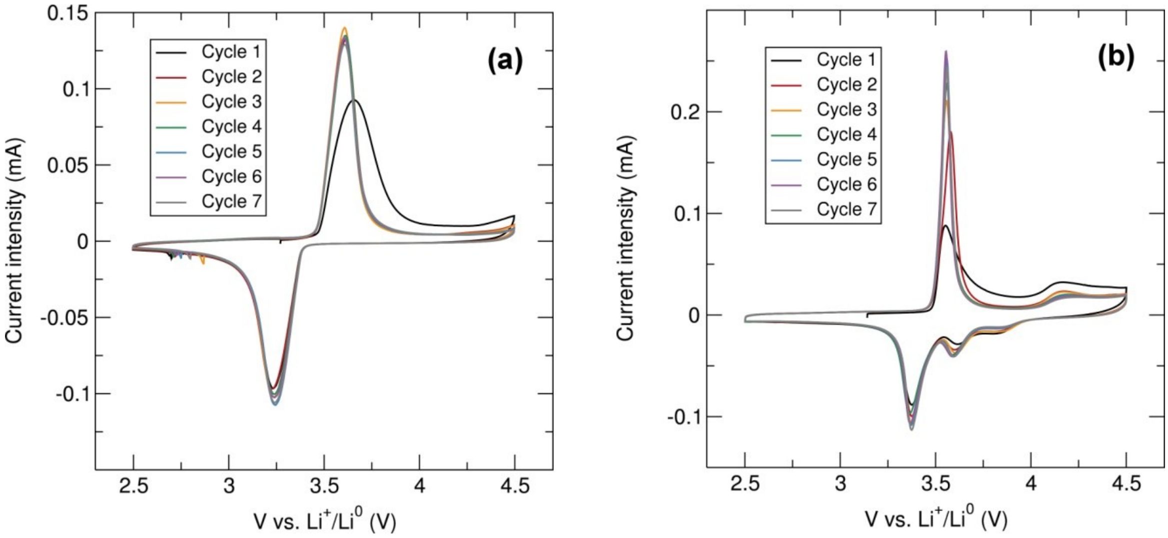

Fig S8. Cyclic voltammogram of (a) $C/LiFePO_4$ and (b) $C/LiFe_{0.5}Mn_{0.5}PO_4$ at 0.1 mV/s scan rate between 2.5 V and 4.5 V.

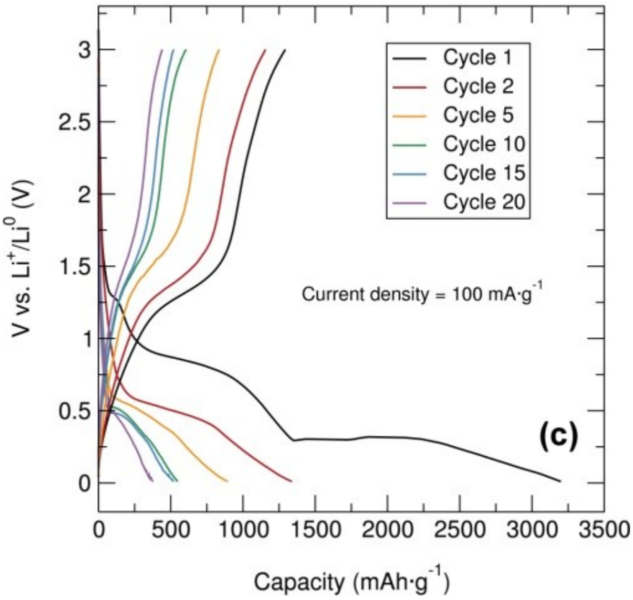

Fig S9 Cycling performance of C/Mn_3O_4, C black, PTFE (60:30:10 weight ratio) over the potential range of 0.01- 3.00 V at 100 mAh·g^{-1}.

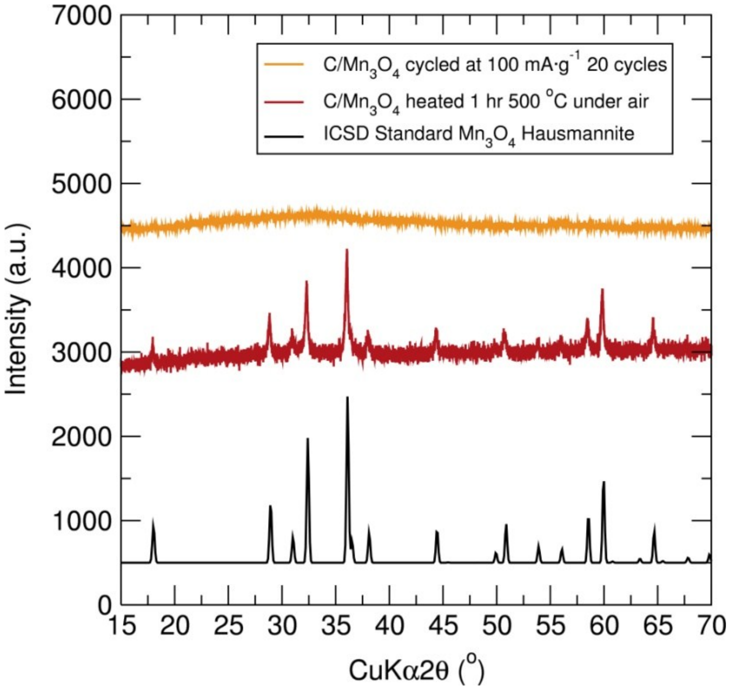

Fig S10. Powder XRD of C/Mn_3O_4 hausmannite after heating for 1 hr at 500 °C and after 20 cycles between 0.01 and 3.00 V at a current density of 100 mA g^{-1}.

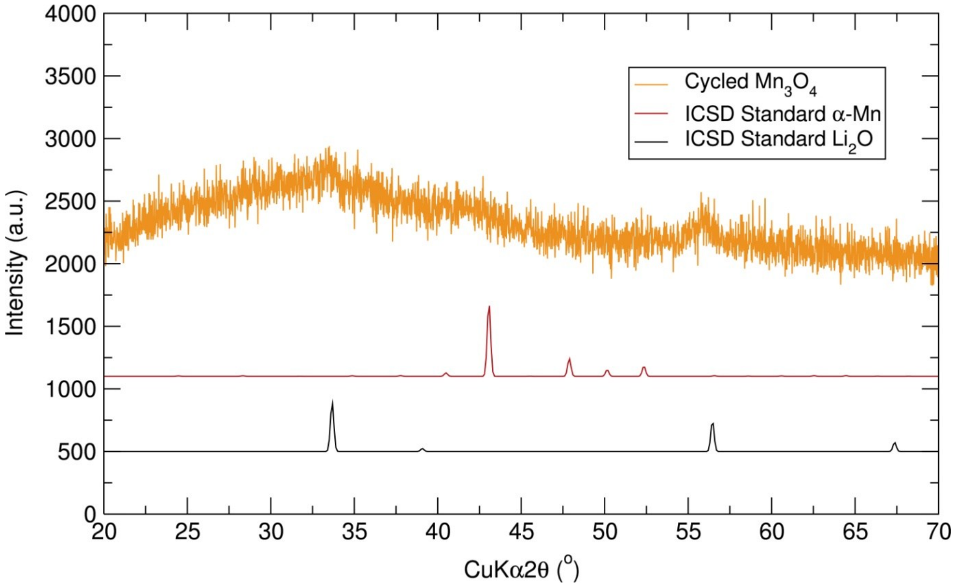

Fig S11. Close up of powder XRD of C/Mn_3O_4 hausmannite after 20 cycles, showing the possible presence of conversion product Li_2O after repeated cycles.

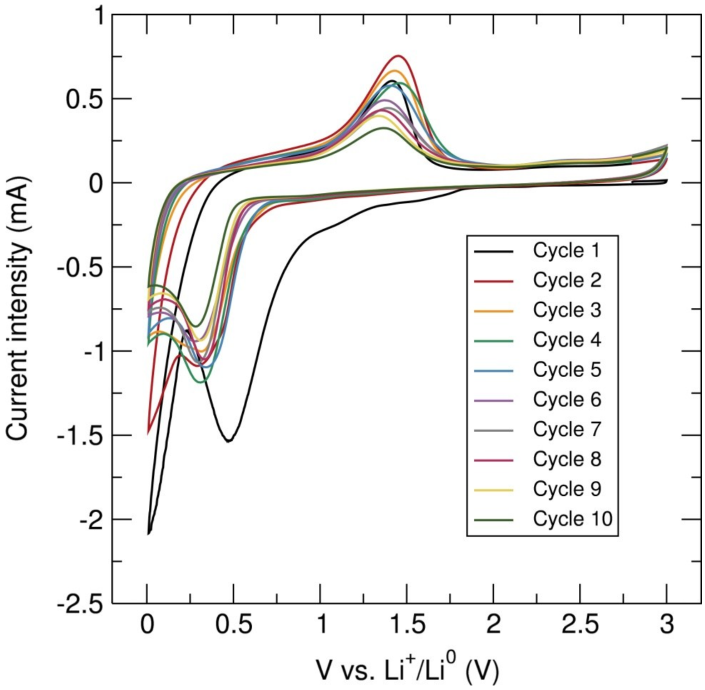

Fig S12. Cyclic voltammogram of C/Mn_3O_4 hausmannite at 0.1 mV/s scan rate between 0.01 and 3.00 V.