Supporting Information

Lithium intercalation mechanisms and critical role of multi-doping in $LiFe_xMn_{2-x-y}Ti_yO_4$ as high-capacity cathode material for Lithium-ion batteries

D. Callegari[1], M. Coduri[1], M. Fracchia[1], P. Ghigna[1], L. Braglia[2], U. Anselmi Tamburini[1] and E. Quartarone[1,*]

[1]*Department of Chemistry and INSTM-GISEL, University of Pavia, Via Taramelli 16 27100 Pavia, Italy*

[2]*CNR - Istituto Officina dei Materiali, TASC, I-34149 Trieste, Italy*

**Corresponding author:* *eliana.quartarone@unipv.it*

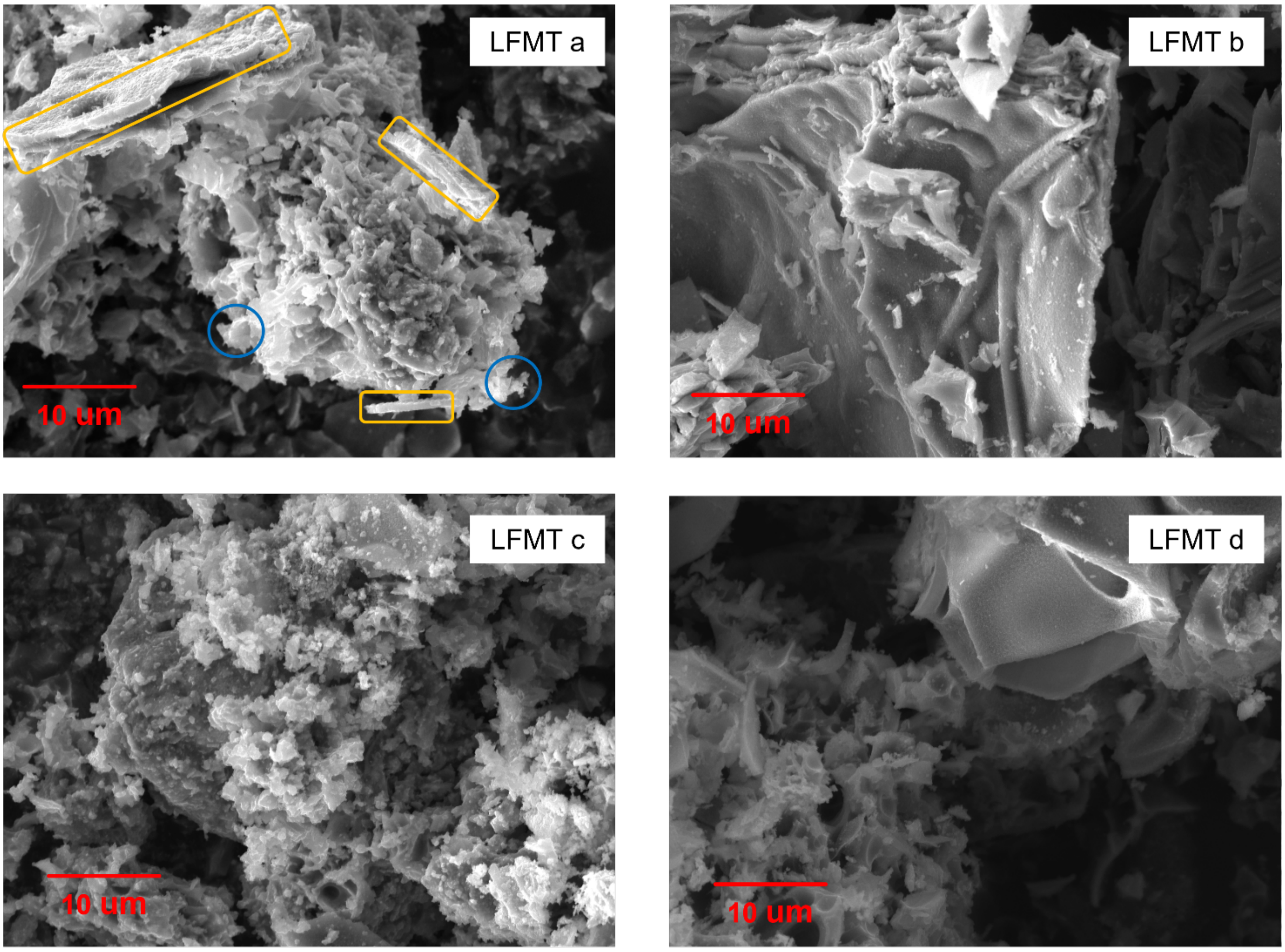


Figure S1: SEM image of the pristine LFMT sample prepared via sol−gel route and calcination at low temperature

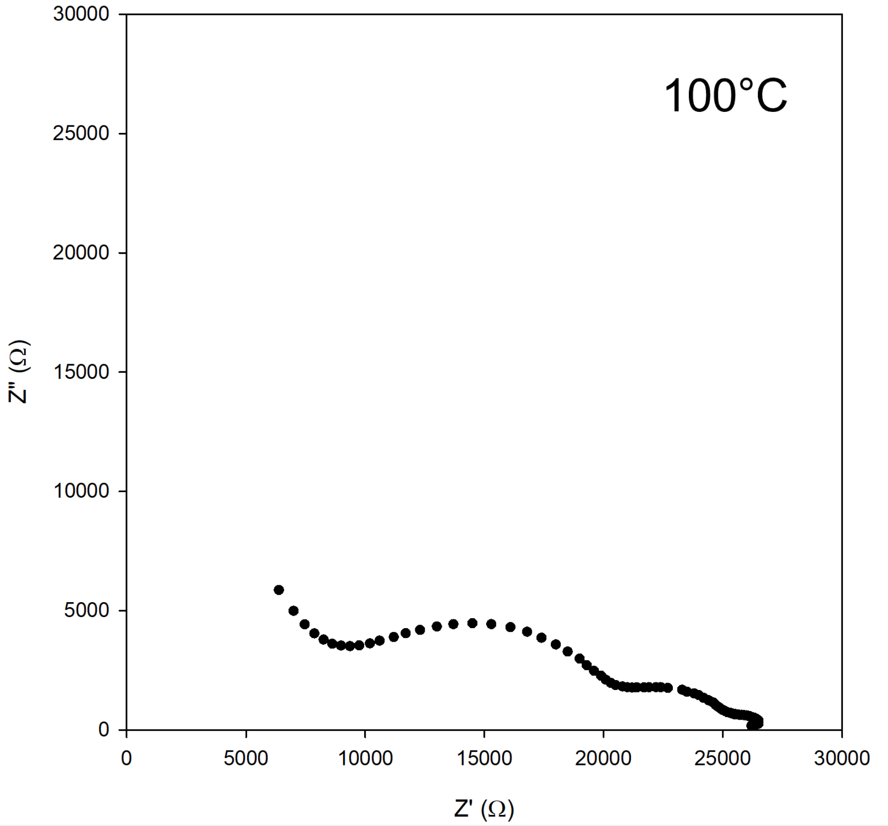


Figure S2(I): Impedance spectrum of a LFMT c pellet, recorded/obtained at 100°C

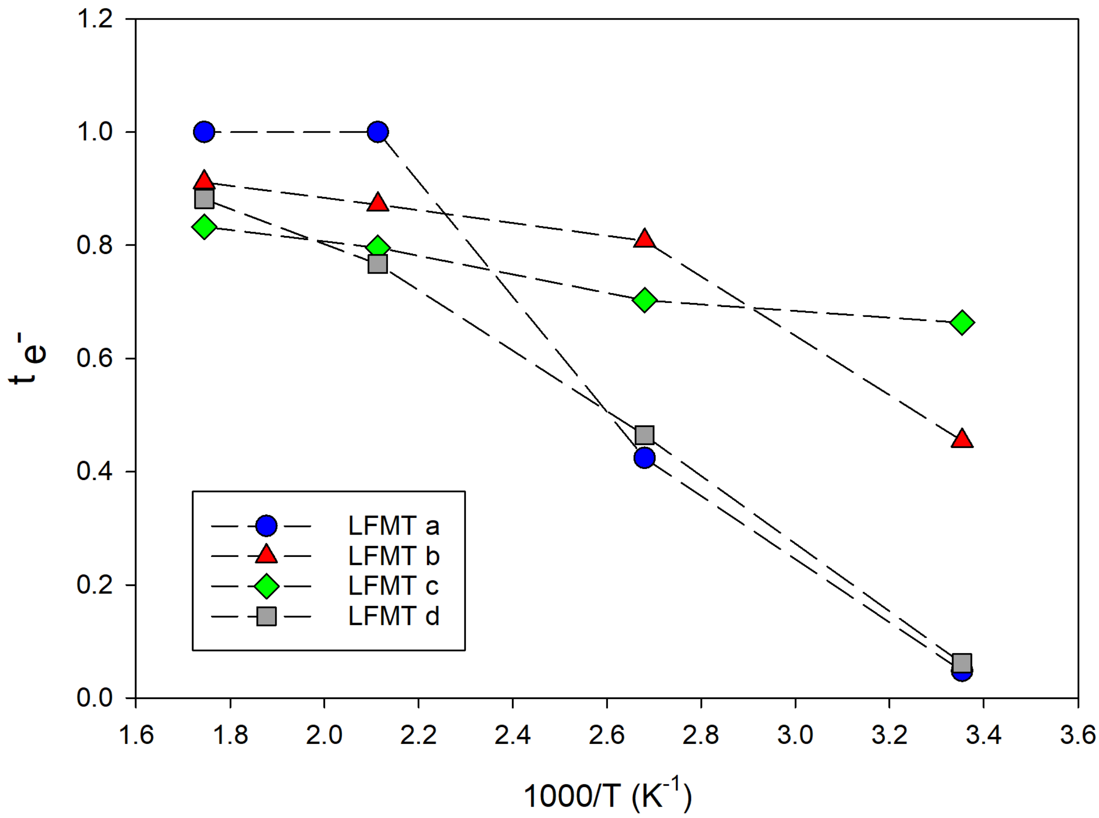


Figure S2(II): Electron transference numbers, t_{e}^{-}, vs T, as calculated by the respective Nyquist plots

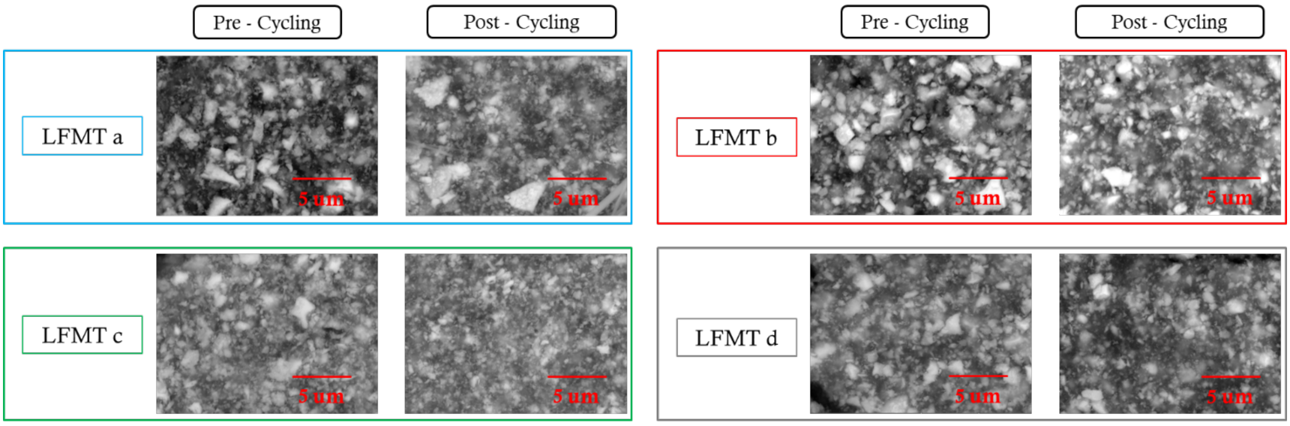


Figure S3(I): (Back-scattered) SEM images of the LFMT electrodes pre- and post-cycling

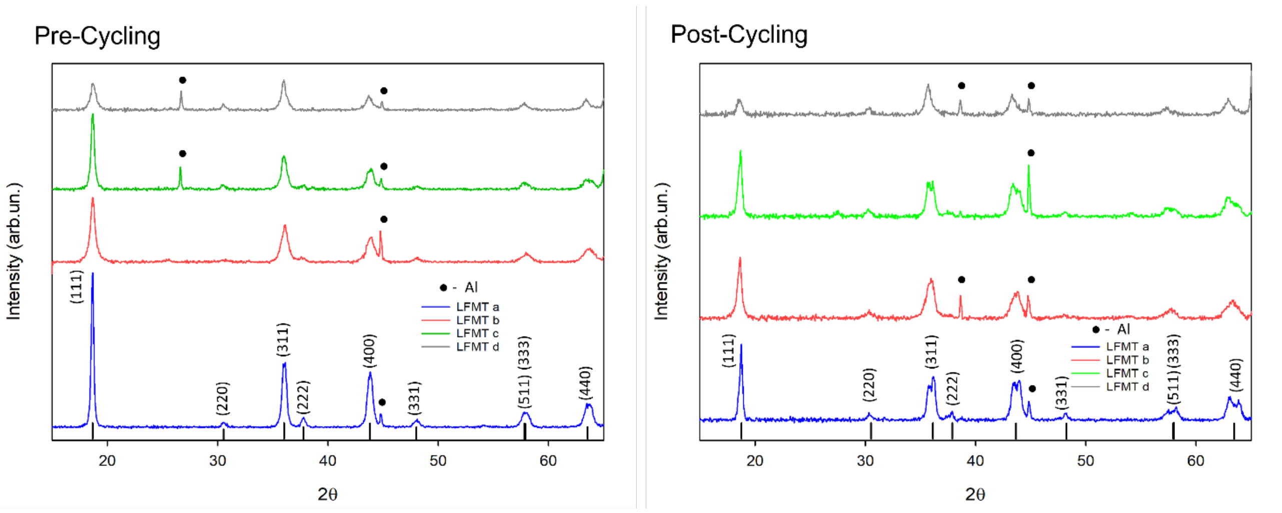


Figure S3(II): XRD patterns of the pre-cycled (left) and post-cycled LFMT electrodes (right). The star ● in plots indicates the Al signal coming from the current collector.

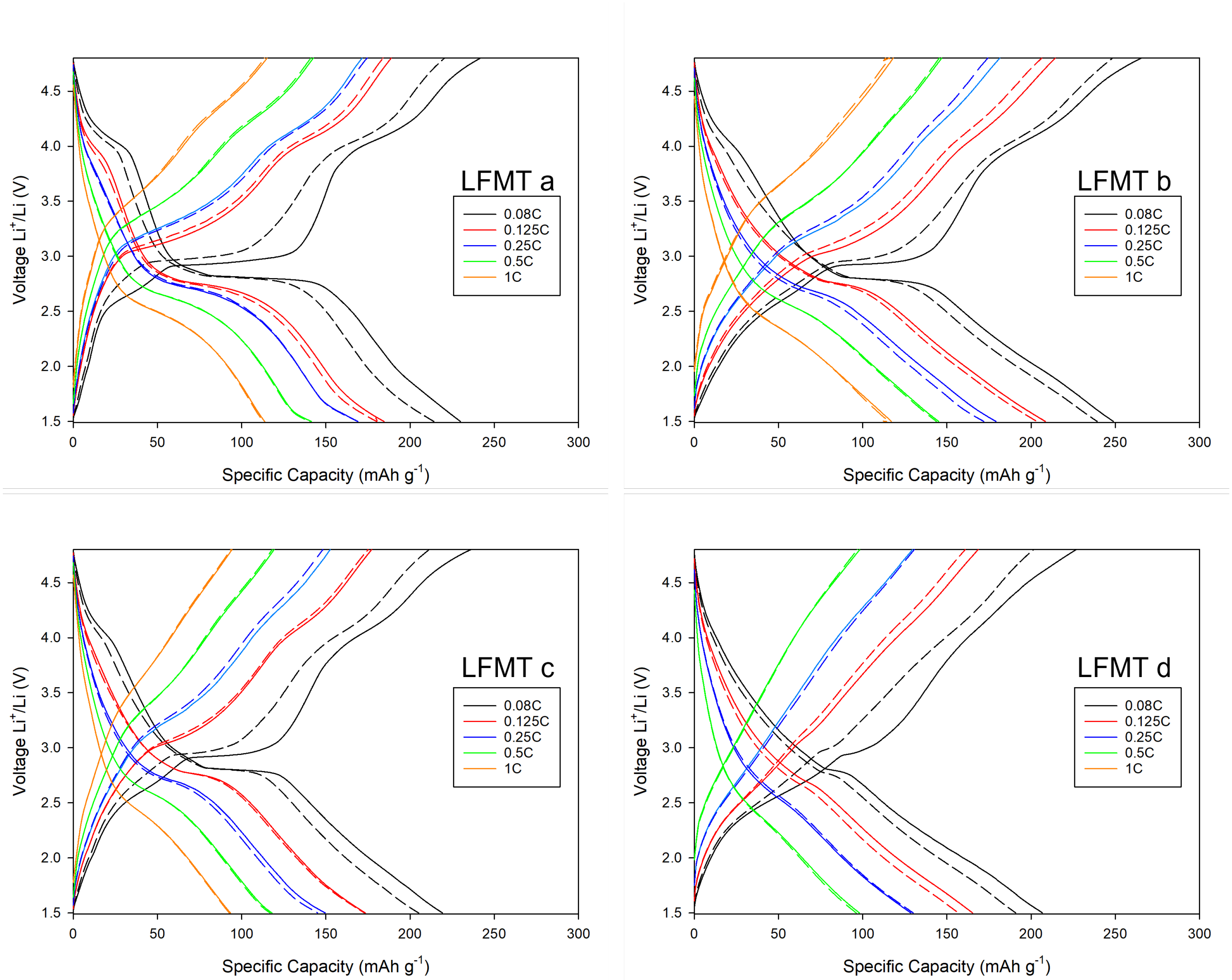


Figure S4: Voltage profiles of the 2nd (solid line) and 5th (dotted line) cycles at each investigated C_{rate}.

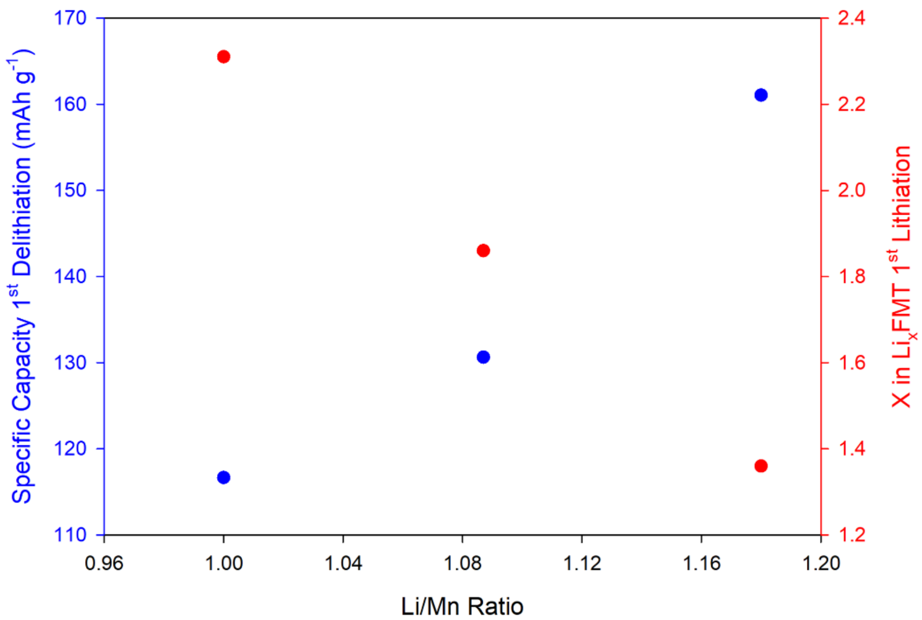


Figure S5(I): 1st Delithiation Capacity (blue) and Lithium stoichiometry, *x*, (red) as a function of the Li/Mn molar ratio in LFMTa-d cathodes.

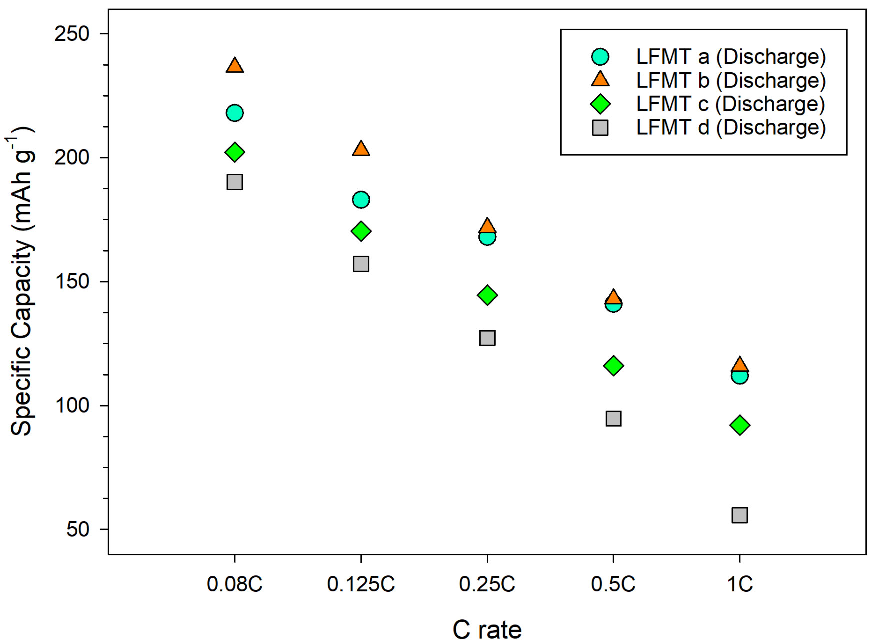


Figure S5(II): Discharge Capacity behavior as a function of C_{rate} in LFMTa-d cathodes.

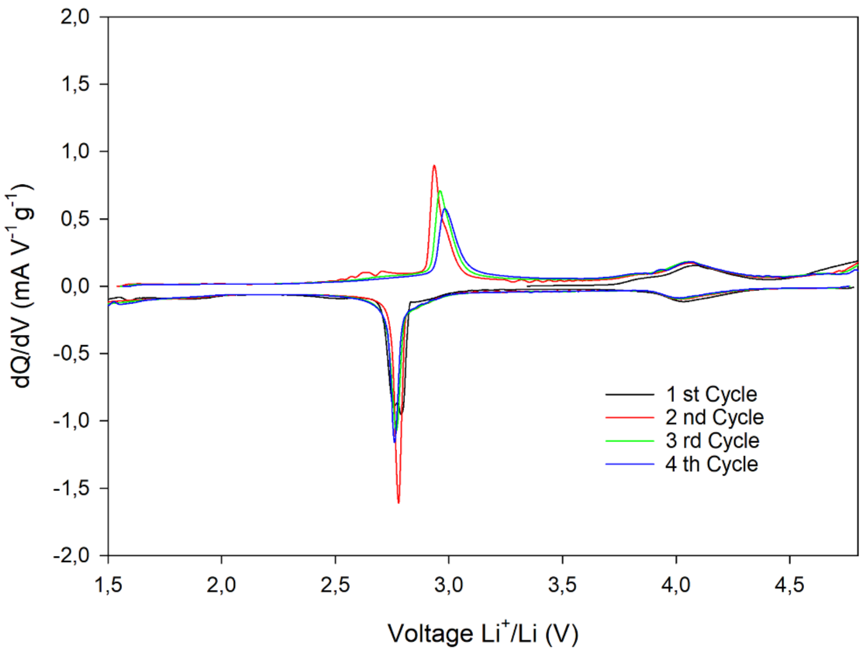


Figure S6(I): *dQ/dV* plots of LFMTa cathode with LP30 + 4% (wt%) of Succinic Anhydride as electrolyte

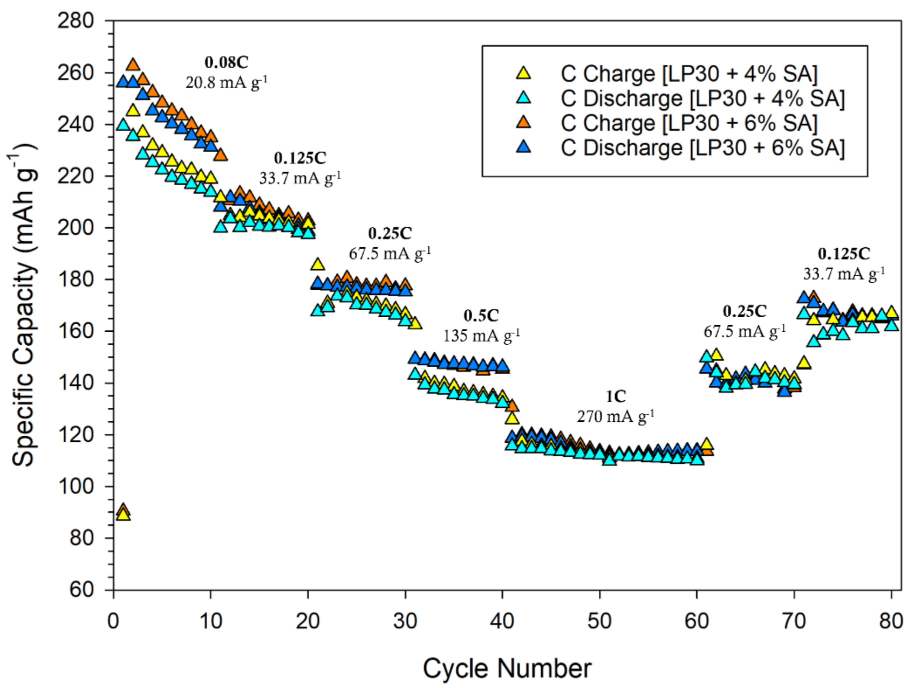
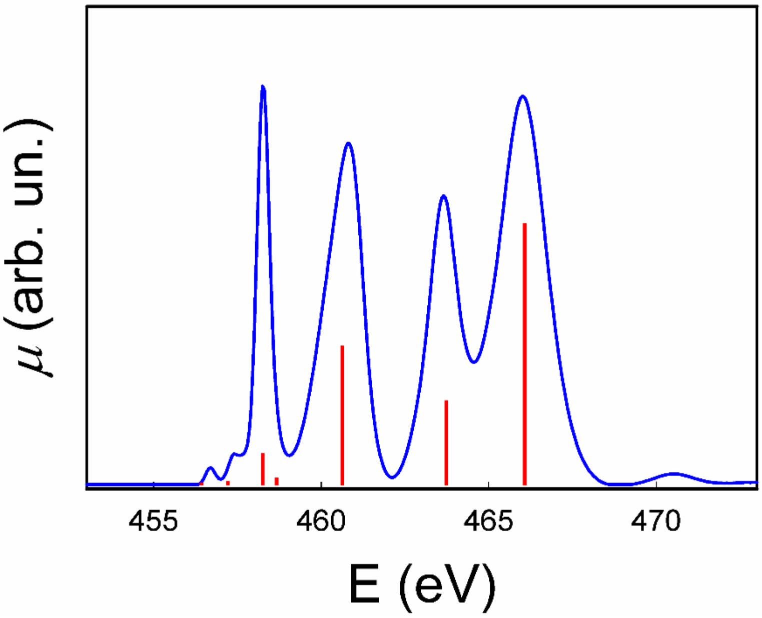
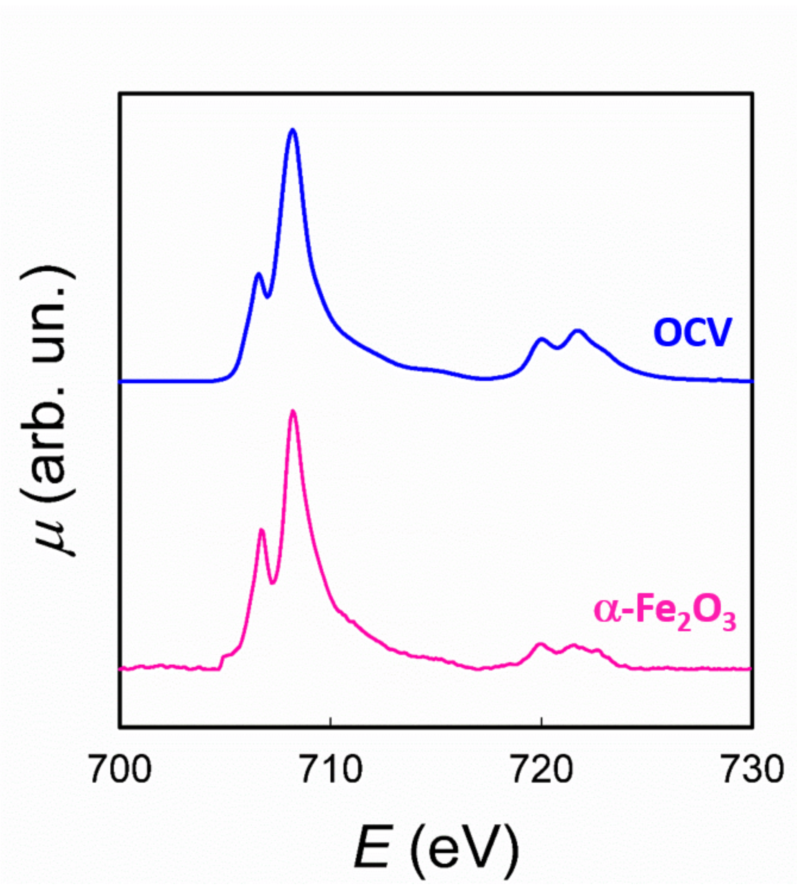


Figure S6(II): Galvanostatic cycling at different C_{Rate} of the cell LFMTa/electrolyte/Li. Electrolyte: $LiPF_6$ 1.0M in EC/DMC (1/1 v/v) + 4% (cyano/yellow) and 6% (wt %) (blue/red) of Succinic Anhydride.

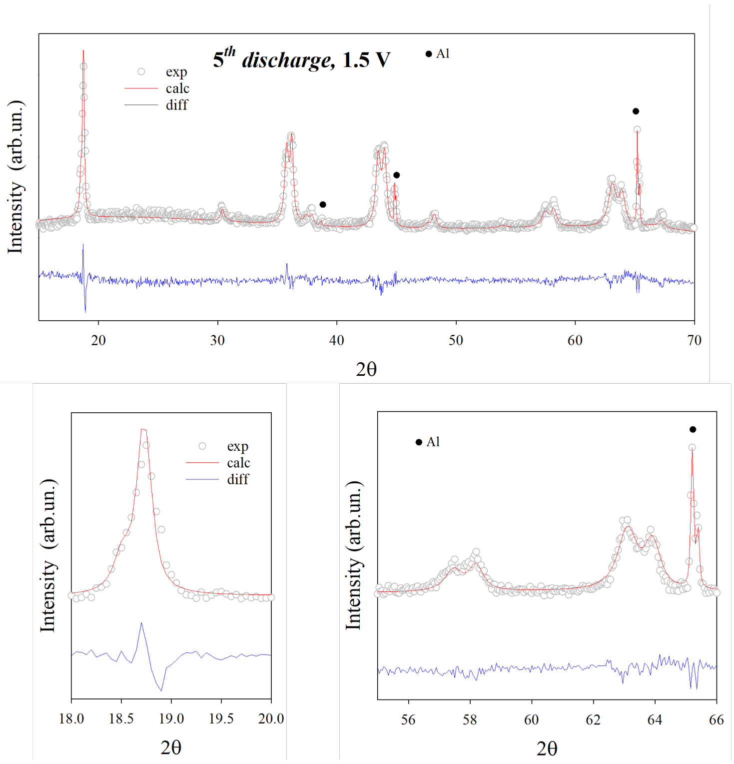


(I)

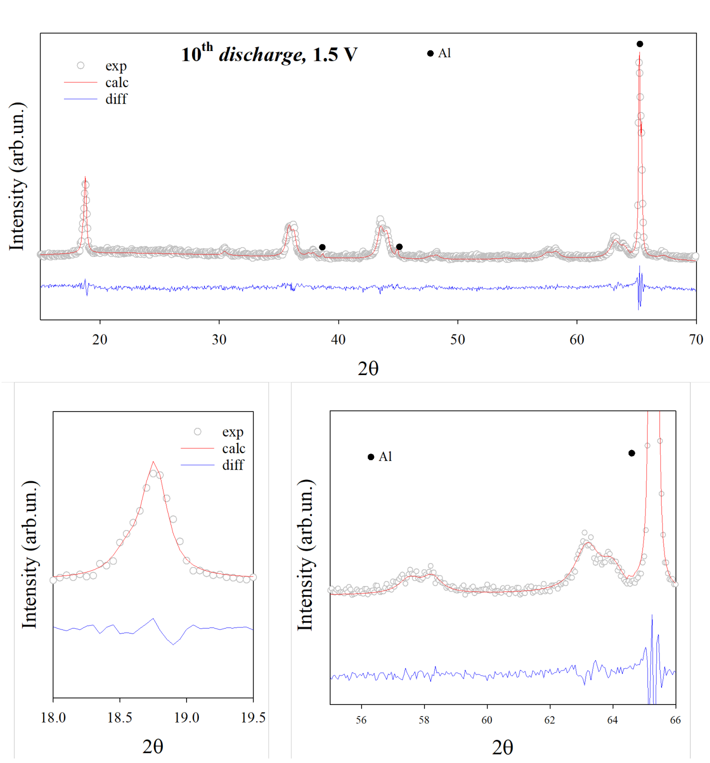


(II)

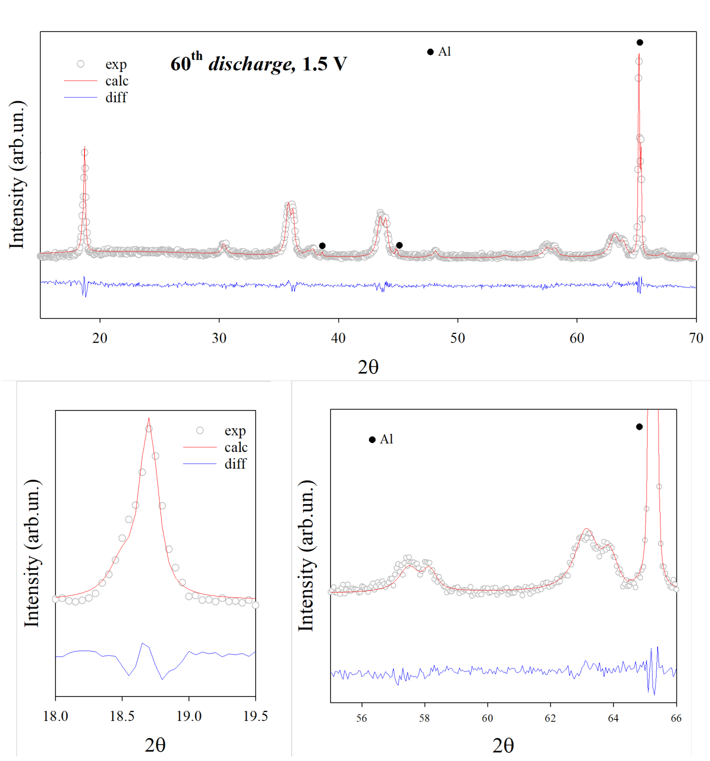
Figure S7: (I) Ti $L_{2,3}$-edges of sample LFMTc at OCV (blue line). The red bars are the multiplets calculated by means of the XTM4XAS program [1], including crystal field, charge transfer, and spin–orbit coupling effects and assuming Ti in Oh environment; (II) XANES spectra at the Fe $L_{2,3}$-edges of LFMTc at OCV (blue line) and Fe_2O_3 (pink line), taken as reference.


5th discharge, 1.5 V
● Al
exp
calc
diff
Intensity (arb.un.)
20
30
40
50
60
70
2θ
18.0
18.5
19.0
19.5
20.0
56
58
60
62
64
66

(I)


10th discharge, 1.5 V
● Al
exp
calc
diff
Intensity (arb.un.)
20
30
40
50
60
70
2θ
18.0
18.5
19.0
19.5
56
58
60
62
64
66

(II)



(III)

Figure S8: Rietveld refinements of specimen LFMTc discharged at 1.5 V after (I) 5, (II) 10 and (III) 60 electrochemical cycles, plotted full range and zoomed into different regions. Empty dots: experimental data, red solid line: calculated profile, blue solid line: difference curve. Full cycles highlight the signal of the Al support of the electrode.

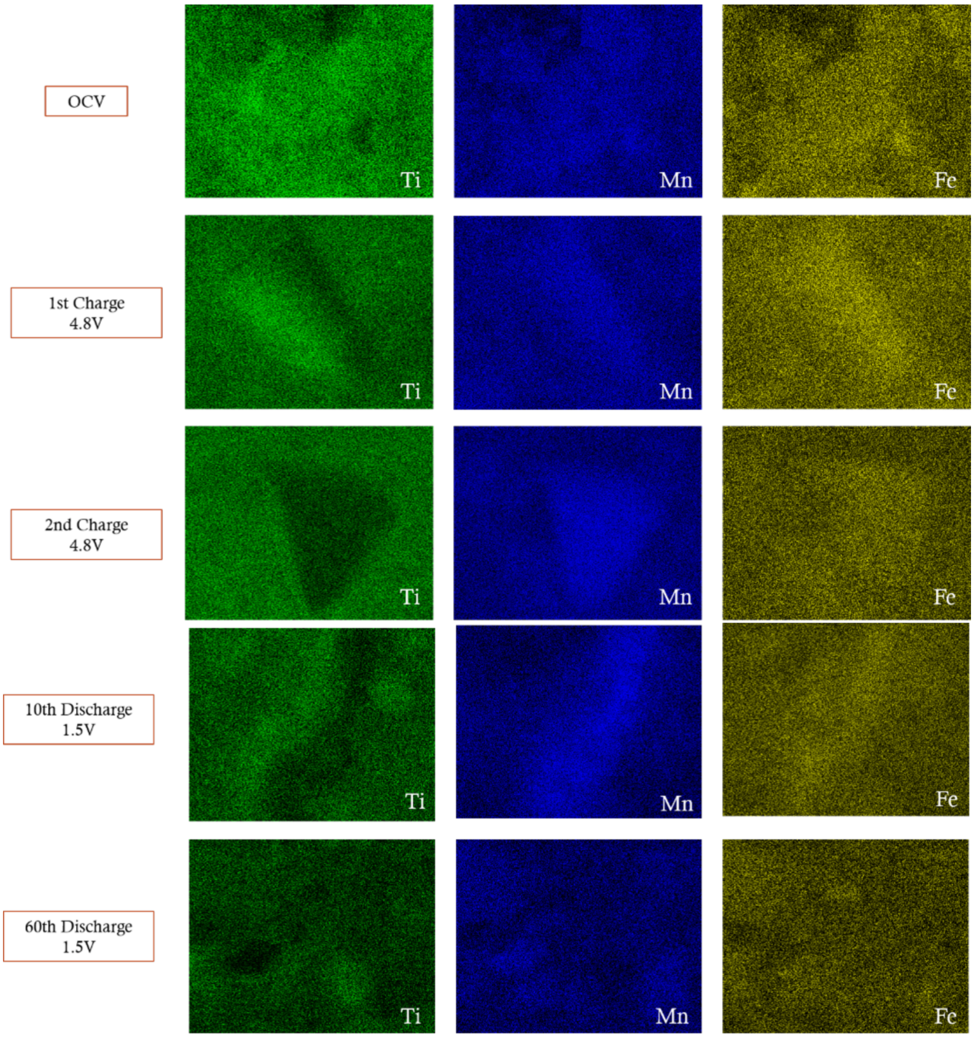


Figure S9: EDX TMs mapping images of the cathodes frozen at OCV, delithiated at 4.8 V and lithiated at 1.5 V at different selected cycles.

	i.r.$_T$ (Å)	***i.r.$_O$ (Å)***
Li^{+}	0.59	0.76
Fe^{3+}	0.49	0.645
Mn^{3+}	-	0.645
Mn^{4+}	0.39	0.53
Ti^{4+}	0.42	0.605
Mn^{2+}	0.66	0.83

Table S1: Ionic radii of the species of interest in tetrahedral (IV) and octahedral (VI) coordination according to Shannon. [2]

References.

1. Stavitski, E.; De Groot, F. M. F. The CTM4XAS Program for EELS and XAS Spectral Shape Analysis of Transition Metal L edges. *Micron*, 2010, 41, 687– 94.
2. R.D. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides", *Acta Cryst.* 1976, A32, 751-767.