

New insights in the characterization of the electrode/electrolyte  
interfaces within  $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  cells, by X-ray Photoelectron  
Spectroscopy, Scanning Auger Microscopy and Time-of-Flight  
Secondary Ions Mass Spectrometry

## **Electronic Supplementary Information**

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## Evolution after ten cycles

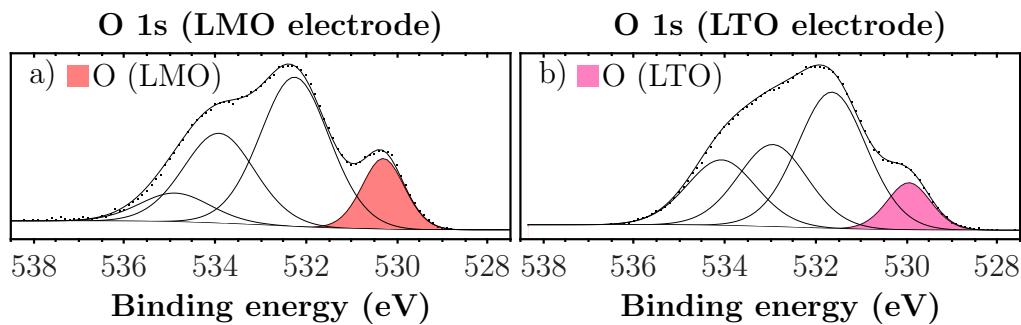


Figure 1: O 1s XPS spectra of a) the positive electrode and b) the negative electrode after the tenth charge

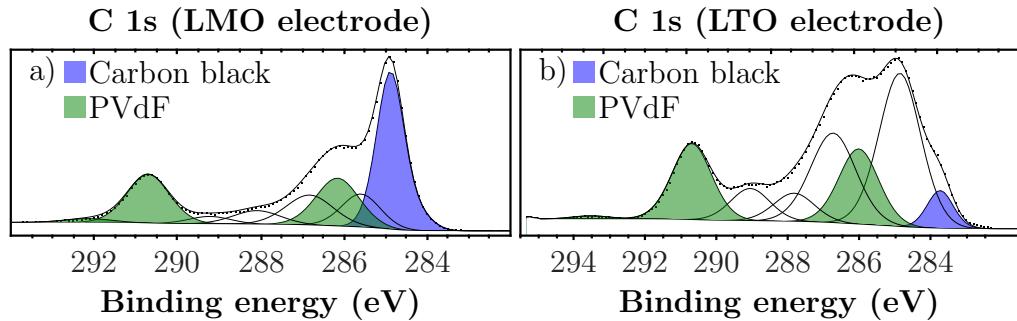


Figure 2: C 1s XPS spectra of a) the positive electrode and b) the negative electrode after the tenth charge

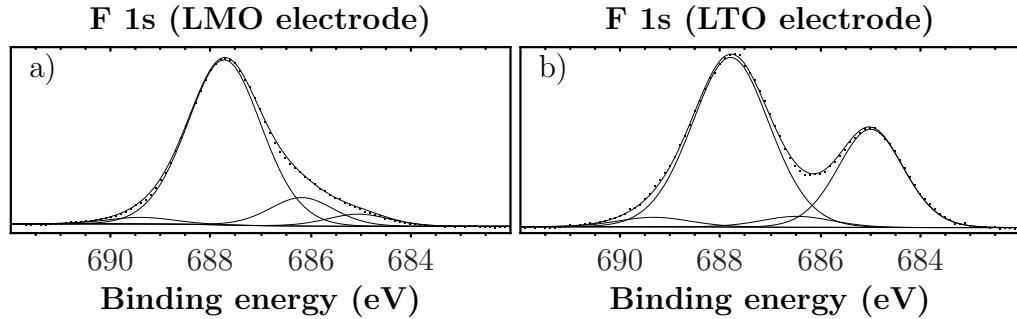


Figure 3: F 1s XPS spectra of a) the positive electrode and b) the negative electrode after the tenth charge

Table 1: Binding energies (BE) and atomic concentrations (at.%) of the different chemical environments identified by XPS at the surface of LMO electrodes cycled in full cell, at the end of the 10<sup>th</sup> charge and at the end of the 10<sup>th</sup> discharge (only P 2p<sub>3/2</sub> and maxima of Mn 2p envelopes binding energies are specified)

	10 <sup>th</sup> charge		
orbital	BE (eV)	%at.	assignment
<b>Li 1s</b>	54.4	1.1	Li (LMO)
	56.0	1.4	lithiated species
<b>P 2p</b>		2.5	
	134.1	0.2	phosph.
	135.3	0.5	fluorophosph.
	136.8	0.4	$\text{LiPF}_6$
		1.1	
<b>C 1s</b>	284.9	22.3	CB
	285.6	7.9	C-C/C-H
	286.2	10.0	$\text{CH}_2$ PVdF
	286.9	5.8	C-O
	288.1	3.2	C=O
	289.2	1.6	O-C=O
	290.7	10.0	$\text{CF}_2$ PVdF
	292.1	0.9	$\text{CF}_3$ PVdF
		61.7	
<b>O 1s</b>	530.3	1.3	O (LMO)
	532.2	4.0	$\text{O}=\text{C}/\text{C}-\text{O}-\text{Li}$
	533.7	1.9	C-O-C
	534.7	1.5	$\text{O}-\text{P}/\text{C}-\text{O}-\text{C}$
		8.6	
<b>Mn 2p</b>	642.2	0.6	$\text{Mn}^{3+}$
	643.0	0.3	$\text{Mn}^{4+}$
		0.9	
<b>F 1s</b>	685.0	1.3	LiF
	686.2	3.0	fluorophosph.
	687.7	20.3	$\text{CF}_2$ PVdF
	689.4	0.7	$\text{CF}_3$ PVdF
		25.2	
<b>Mn 3s</b>	$\Delta\text{Mn 3s}$		
	5.1 eV		

Table 2: Binding energies (BE) and atomic concentrations (at.%) of the different chemical environments identified by XPS at the surface of LTO electrodes cycled in full cell, at the end of the 10<sup>th</sup> charge and at the end of the 10<sup>th</sup> discharge (only P 2p<sub>3/2</sub>, Ti 2p<sub>3/2</sub> and maxima of Mn 2p envelopes binding energies are specified)

	10 <sup>th</sup> charge		
orbital	BE (eV)	%at.	assignment
<b>Li 1s</b>	54.6	2.4	Li (LTO)
	55.7	6.6	
		9.1	
<b>P 2p</b>	133.5	0.7	phosphates
	134.4	0.6	fluorophosph.
	136.0	0.1	LiPF <sub>6</sub>
		1.4	
<b>C 1s</b>	283.7	2.2	CB
	284.9	14.1	C-C/C-H
	286.0	6.6	CH <sub>2</sub> PVdF
	286.7	9.0	C-O
	287.8	2.6	C=O
	289.1	2.8	O-C=O
	290.7	6.6	CF <sub>2</sub> PVdF
	293.5	0.3	CF <sub>3</sub> PVdF
		44.2	
<b>Ti 2p</b>	458.7	1.0	Ti <sup>4+</sup>
<b>O 1s</b>	530.0	2.0	O (LTO)
	531.6	9.2	C-O-Li
	532.9	5.6	C-O/P-O
	534.1	4.4	C-O
		21.3	
<b>Mn 2p</b>	641.5	1.0	MnF <sub>2</sub>
	$\Delta \text{Mn 3s} = 6.1 \text{ eV}$		
<b>F 1s</b>	685.0	6.8	LiF/MnF <sub>2</sub>
	686.5	0.8	fluorophosph.
	687.8	13.8	CF <sub>2</sub> PVdF
	689.3	0.7	CF <sub>3</sub> PVdF
		22.1	