Unravelling redox processes of Li$_7$MnN$_4$ upon electrochemical Li extraction-insertion using *operando* XAS

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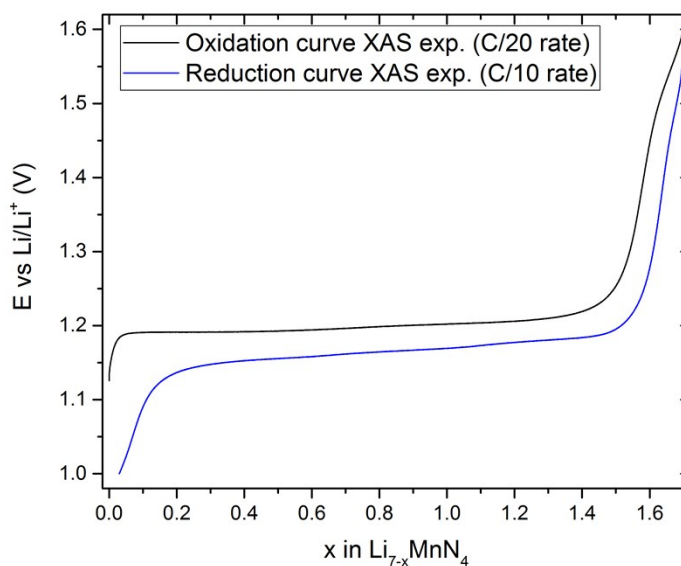c. IMN, UMR6502 La Chantrerie, rue Christian Pauc, 44306 Nantes, France

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ESI 1

Electrochemical curve of the full oxidation/reduction cycle studied here

ESI 2

Constraints and initial guess introduced in the MCR-ALS model:

i) Concentration constraints

- <u>non-negativity</u>: the concentration profile cannot be negative
- <u>closure</u>: the total concentration of manganese is kept to 100%
- <u>known-concentrations</u> : environment 3 is absent at the beginning of the reaction, and environment 1 at the end.
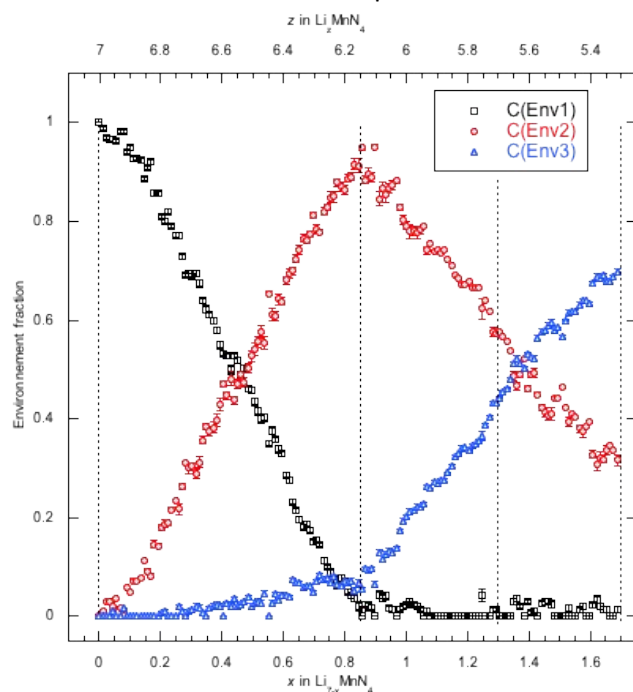
ii) Spectra initial guess: the three "pure" environments (Env1, Env2 and Env3) are calculated from the following initial assumption:

- We know the nature of the initial material: Env1=Li_7MnN_4
- We assume that the maximum concentration of the intermediate specie corresponds to x=0.9 *i.e*. Env2=$Li_{6.1}MnN_4$
- At the end of the oxidation, the average manganese oxidation state should be $Mn^{6.7+}$. We assume that it is the result of a 30% Mn^{6+} + 70% Mn^{7+} mixture. Therefore, the initial guess for the third environment is Env3=($Li_{5.3}MnN_4$-0.3 $Li_{6.1}MnN_4$)/0.7.

During the MCR-ALS iterations the three environments are allowed to vary under the concentration and normalization constraints

ESI 3
Selected recomposition of various spectra using pure environment spectra Env.1, Env. 2 and Env. 3 determined from the MCR-ALS procedure.

x in $Li_{7-x}MnN_4$	C(Env1) %	C(Env2) %	C(Env3) %
0	100	0	0
0.85	0	95	5
1.3	1	57	43
1.7	0	31	69