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Operando XAS investigation of manganese redox processes in $\text{Li}_2\text{MnO}_2\text{F}$

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Li-rich disordered rocksalts (DRS) are a promising class of materials for the use as high energy positive electrodes for Li-ion batteries. The structure of these materials deviates from the typical layered oxides structure and can contain abundant transition metals such as manganese or iron. DRS can also reach capacities greater than 250 mAh.g^{-1} making them potential low-cost alternatives for already established cathodes such as LFP or NMC (1). $\text{Li}_2\text{MnO}_2\text{F}$ is a model material that is synthesized through high-energy ball milling and delivers 280 mAh.g^{-1} . Similarly to the Li-rich layered oxides material, a part of this capacity is due to the oxygen redox at high voltage, resulting in voltage and capacity fading over cycles (2)(3). Indeed, the capacity retention of DRS is still low, even when doping or fluorination strategies are employed.

We thus characterized the degradation mechanisms of $\text{Li}_2\text{MnO}_2\text{F}$ to provide new strategies to improve the stability of this material during cycling. K edge X-ray absorption spectra of Mn were measured *operando* in transmission mode, using a custom experimental setup. We analyzed the evolution of the XAS spectra on the two first cycles at C/10 (First charge on Figure 1a) and spectra of electrodes after 10 and 30 cycles. The shift in energy of the XANES edge indicates a reversible behavior of the manganese redox process from $3+$ to $4+$ in cycling and the formation of Mn^{2+} at the end of the discharge.

Moreover, MCR-ALS (Multivariate Curve Resolution - Alternating Least Squares) analysis technique was used to characterize the variation of the XAS spectra to determine the reactional pathway that allow to describe properly the influence of the Mn redox process on the electrochemical curve as shown on Figure 1b. Therefore, these techniques allowed us to deconvolute the oxygen and manganese redox influences on the galvanostatic curve. Moreover, the analysis of the EXAFS data gave us an insight on the local ordering of the pristine material and of its evolution during short and long term cycling. These results provide clues to understand the origin of the electrochemical performances decay of DRS materials and to limit it.

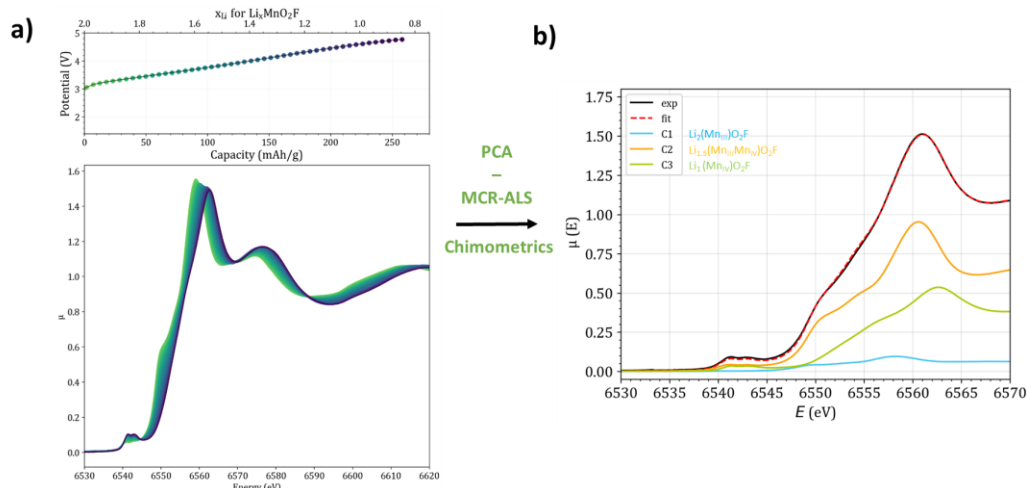


Figure 1 : a) Operando XANES charge data for $\text{Li}_2\text{MnO}_2\text{F}$ b) Example of fitting of a XANES spectrum ($x_{\text{Li}} = 1.8$) using components extracted from MCR-ALS

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