

Feasibility and Limitations of High-Voltage Lithium-Iron-Manganese Spinels

Supporting information

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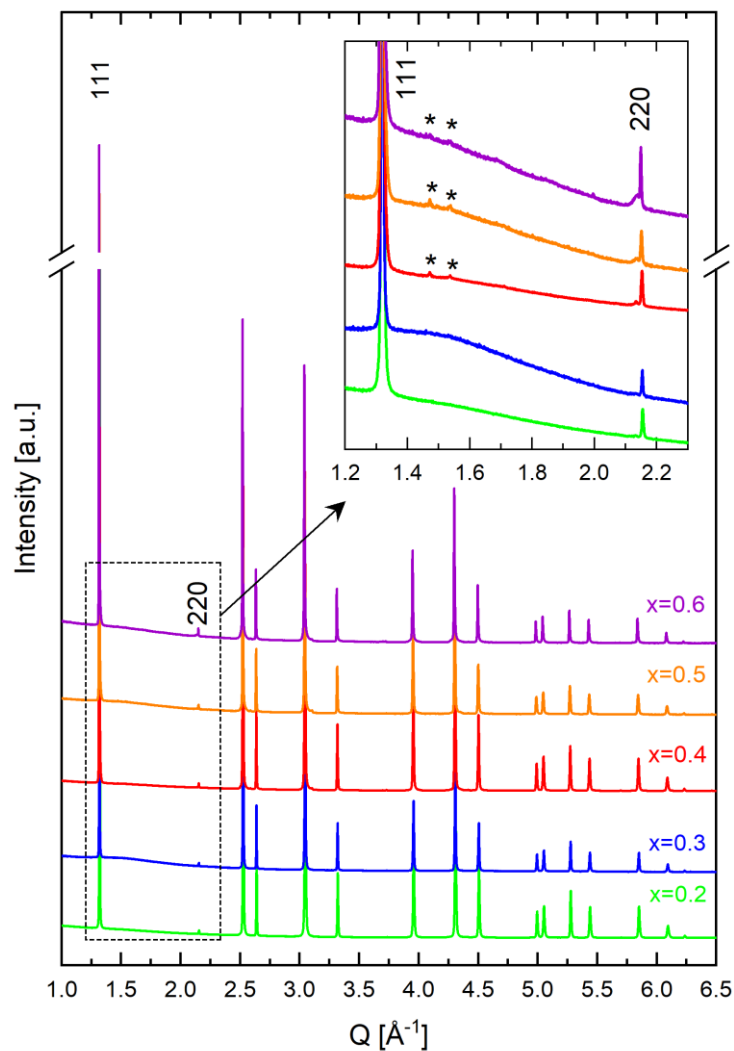


Figure S1: Synchrotron powder diffraction patterns for $\text{LiFe}_x\text{Mn}_{2-x}\text{O}_4$ ($0.2 \leq x \leq 0.6$). Secondary phase reflections are highlighted with the symbol * for Li_2MnO_3

Table S1: Calculated weight fractions of phases identified from SRPD data. Considering Li_2MnO_3 fractions is critical for the refinement of the spinel parameters, as main reflections of Li_2MnO_3 overlap with the spinel main reflections. Given the small amount of free standing and low intense Li_2MnO_3 reflections the listed statistical errors might be underestimated.

x in $\text{LiFe}_x\text{Mn}_{2-x}\text{O}_4$	LiFe_5O_8 wt.-%	Li_2MnO_3 wt.-%	Spinel wt.-%
0.4	< 1	1.0 ± 0.1	98.2 ± 0.2
0.5	< 1	2.0 ± 0.1	97.5 ± 0.2

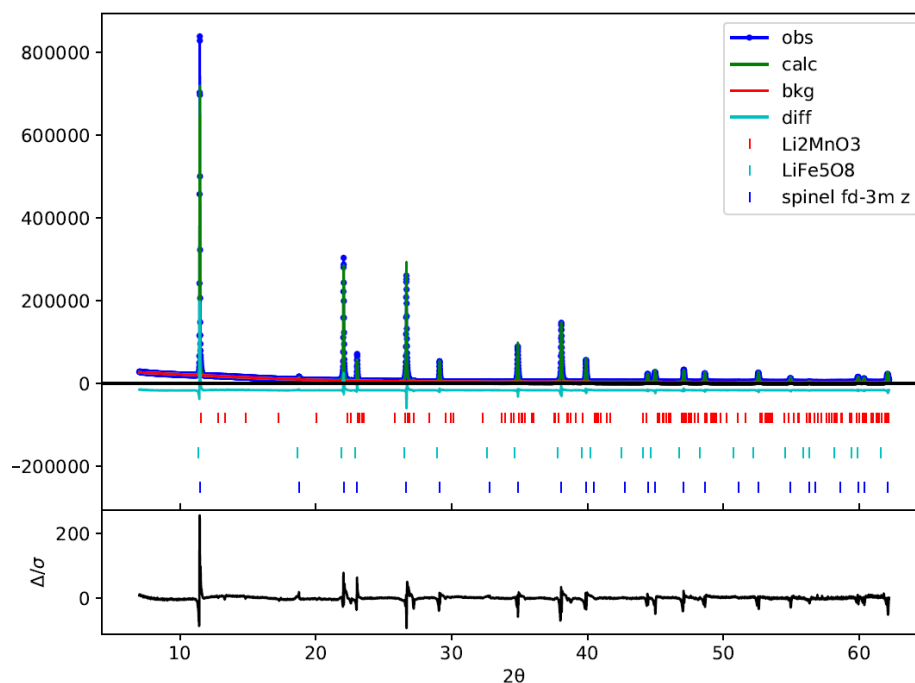


Figure S2: Rietveld analysis from SRPD: Experimental (Iobs) in blue, calculated (Icalc) in green and difference (Iobs – Icalc) in light blue for x = 0.6 to point out intensity residuals in the difference plot for the applied model.

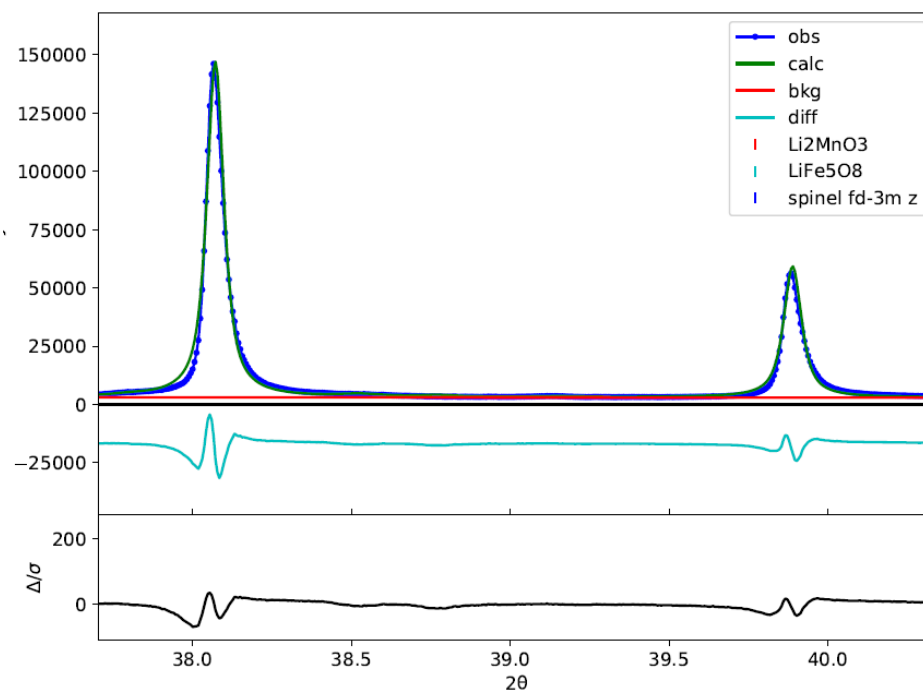


Figure S3: Rietveld analysis from SRPD: Experimental (Iobs) in blue, calculated (Icalc) in green and difference (Iobs – Icalc) in light blue for x = 0.6 for two individual reflections to point out the difficulties in describing the observed asymmetric peak shapes by the applied model.

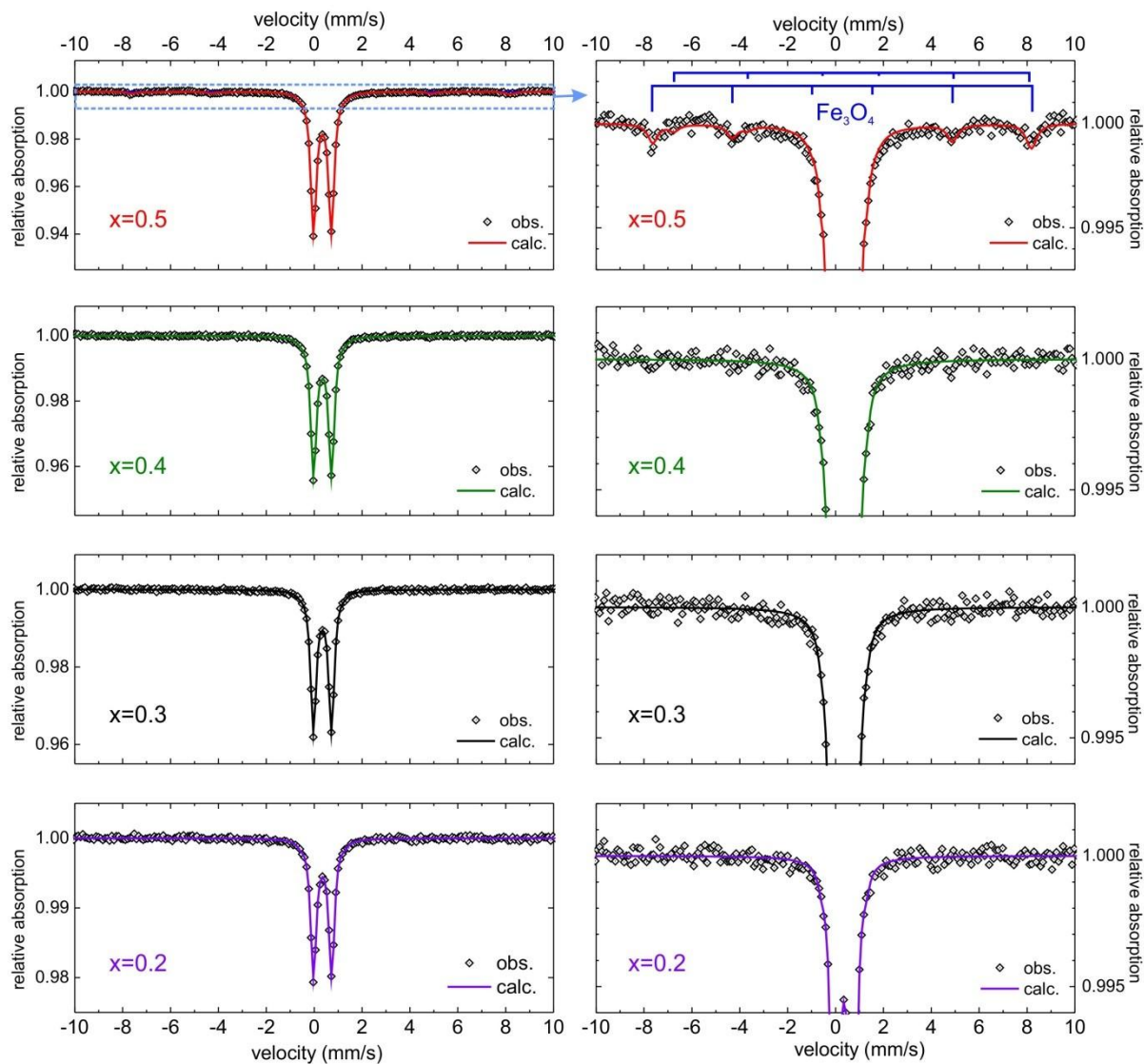


Figure S4: Room temperature ^{57}Fe Mössbauer spectra recorded for the series of $\text{LiFe}_x\text{Mn}_{2-x}\text{O}_4$ spinel materials ($0.2 \leq x \leq 0.5$) with a high-velocity scale. See Table 2 for the refined hyperfine parameters of the different sub-spectra.

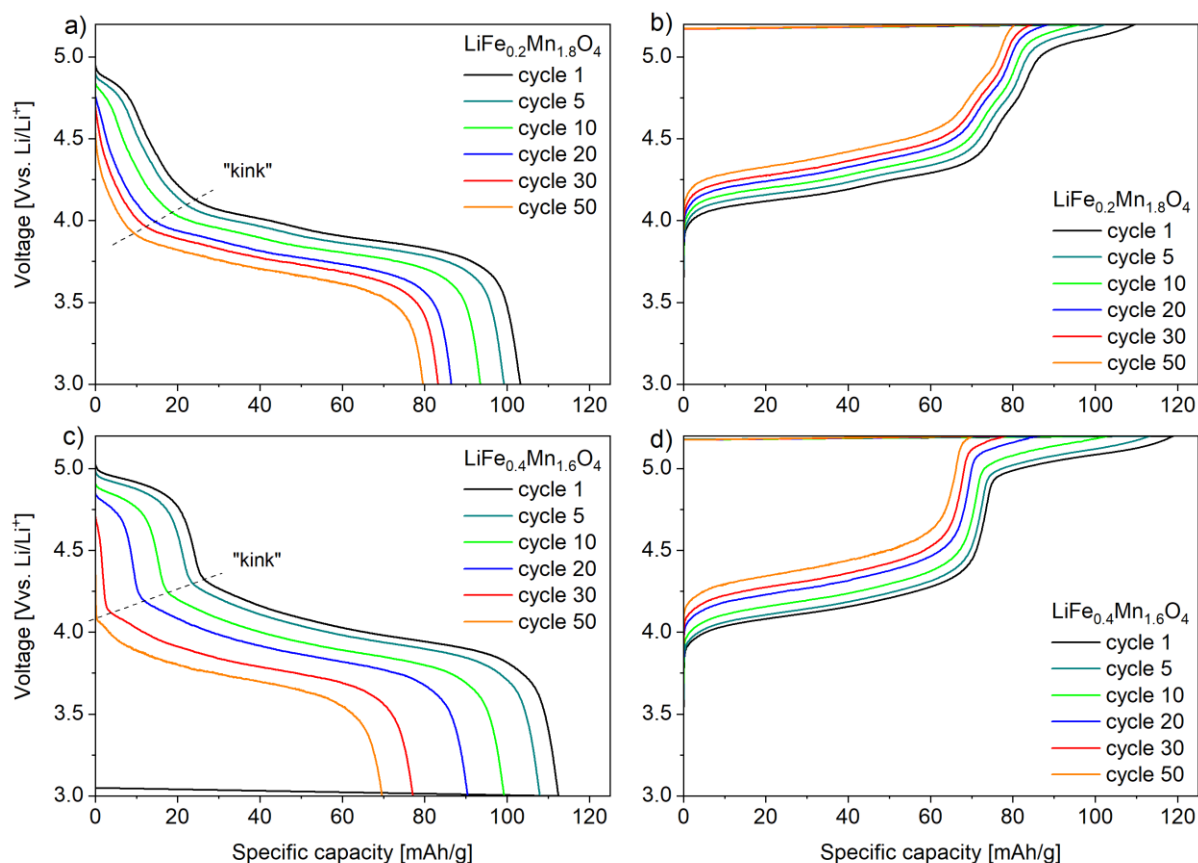


Figure S5: Charge and discharge curves of selected cycles for $\text{LiFe}_x\text{Mn}_{2-x}\text{O}_4$ cycled at a C/5 rate with an upper cut-off voltage at 5.2 V and a lower cut-off voltage at 3.0 V vs. Li^+/Li . a) discharge $\text{LiFe}_{0.2}\text{Mn}_{1.8}\text{O}_4$ b) charge $\text{LiFe}_{0.2}\text{Mn}_{1.8}\text{O}_4$ c) discharge $\text{LiFe}_{0.4}\text{Mn}_{1.6}\text{O}_4$ d) charge $\text{LiFe}_{0.4}\text{Mn}_{1.6}\text{O}_4$. Repeated cycling to 5.2 V vs. Li^+/Li leads to a shift of charge “plateaus” in the high voltage range towards higher voltages and - for the discharge “plateau” - towards lower voltages, from cycle to cycle. Yet, the same behavior can be observed for the “plateaus” in the 4 V range. This behavior needs to be interpreted as an increase in overvoltages.

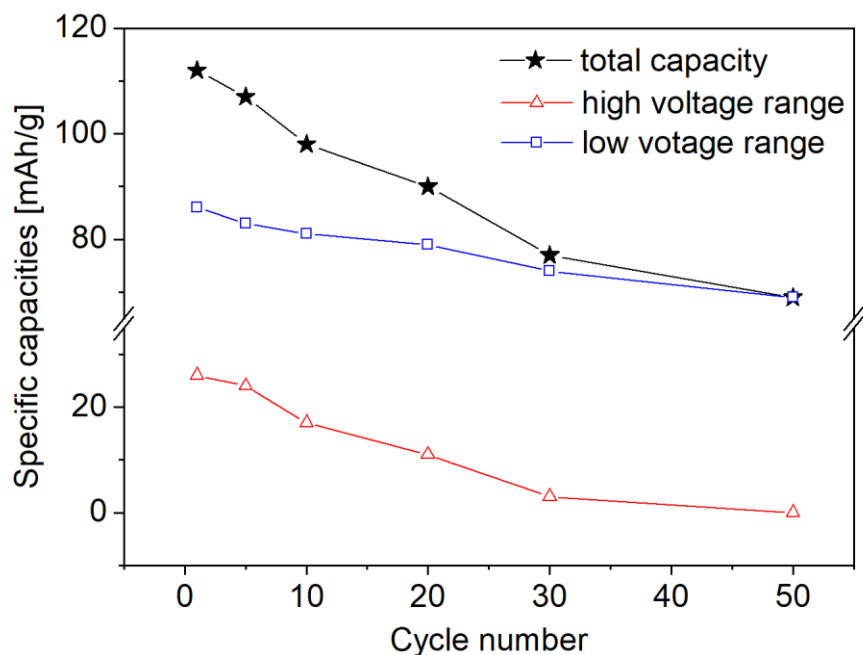


Figure S6: Specific discharge capacities for selected cycles for $\text{LiFe}_{0.4}\text{Mn}_{1.6}\text{O}_4$ cycled at $C/5$ rate with upper cut-off voltage at 5.2 V and lower at 3.0 V vs. Li/Li^+ above and below the “kink” in the discharge curve (Figure S5), which indicates the change from the $\text{Mn}^{4+/3+}$ reaction to the $\text{Fe}^{4+/3+}$ reaction. Lines are drawn to guide the eye. The figure illustrates that most of the total capacity degradation is caused by degradation in the high voltage region.