

Supplementary information

for

Influence of the Mn/Fe ratio on the electrochemical and structural properties of P2-Na_xMn_{1-y}Fe_yO₂ phases as positive electrode material for Na-ion batteries.

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| P2-Na_{0.66}Mn_{2/3}Fe_{1/3}O₂ | | | | | | |
|--|---------------|---------------|-----|----------|-----------|-----------------------|
| Space group: P6₃/mmc | | | | | | |
| a _{hex.} = 2.9400(1) Å, c _{hex.} = 11.1812(6) Å | | | | | | |
| Atom | Wyckoff | Coordinates | | | Occupancy | ADP (Å ²) |
| Na _f | 2d | 0 | 0 | 1/4 | 0.20(2) | 2.9(5) |
| Na _e | 2b | 2/3 | 1/3 | 1/4 | 0.46(2) | |
| Mn | 2a | 0 | 0 | 0 | 0.67 | 0.65(4) |
| Fe | 2a | 0 | 0 | 0 | 0.33 | |
| O | 4f | 1/3 | 2/3 | 0.093(1) | 1 | 1.1(1) |
| Distances: | M-O | Na-O | | | | |
| | 6 x 1.99(1) Å | 6 x 2.44(1) Å | | | | |
| R _{wp} = 13.29%; R _B = 5.73% | | | | | | |

| P2-Na_{0.62}Mn_{1/2}Fe_{1/2}O₂ | | | | | | |
|--|---------------|---------------|-----|----------|-----------|-----------------------|
| Space group: P6₃/mmc | | | | | | |
| a _{hex.} = 2.9405(1) Å, c _{hex.} = 11.1957(2) Å | | | | | | |
| Atom | Wyckoff | Coordinates | | | Occupancy | ADP (Å ²) |
| Na _f | 2d | 0 | 0 | 1/4 | 0.18(1) | 1.8(7) |
| Na _e | 2b | 2/3 | 1/3 | 1/4 | 0.44(2) | 1.9(4) |
| Mn | 2a | 0 | 0 | 0 | 0.5 | 0.29(3) |
| Fe | 2a | 0 | 0 | 0 | 0.5 | |
| O | 4f | 1/3 | 2/3 | 0.093(1) | 1 | 0.7(1) |
| Distances: | M-O | Na-O | | | | |
| | 6 x 1.99(1) Å | 6 x 2.44(1) Å | | | | |
| R _{wp} = 15.33%; R _B = 8.93% | | | | | | |

Table S1: Structural parameters and reliability factors calculated from the synchrotron XRPD pattern of the P2-Na_{0.66}Mn_{2/3}Fe_{1/3}O₂ and P2-Na_{0.62}Mn_{1/2}Fe_{1/2}O₂ pristine materials.

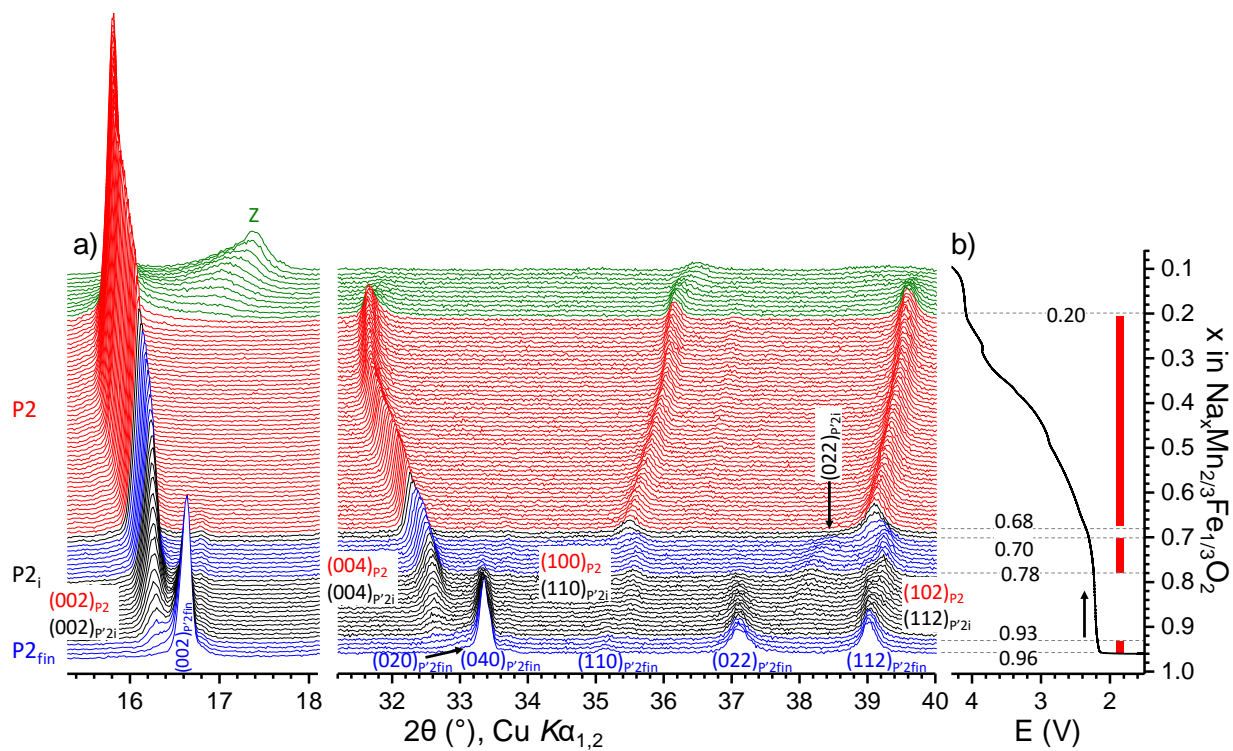


Figure S1: Inversed representation of the *operando in situ* XRPD experiment carried out on the $\text{Na}_x\text{Mn}_{2/3}\text{Fe}_{1/3}\text{O}_2$ system: (a) XRPD patterns and (b) corresponding cycling curve. The various structural domains are indicated by different colors. The various structural domains are indicated by different colors. The P2 solid solution domains is indicated by the red lines.

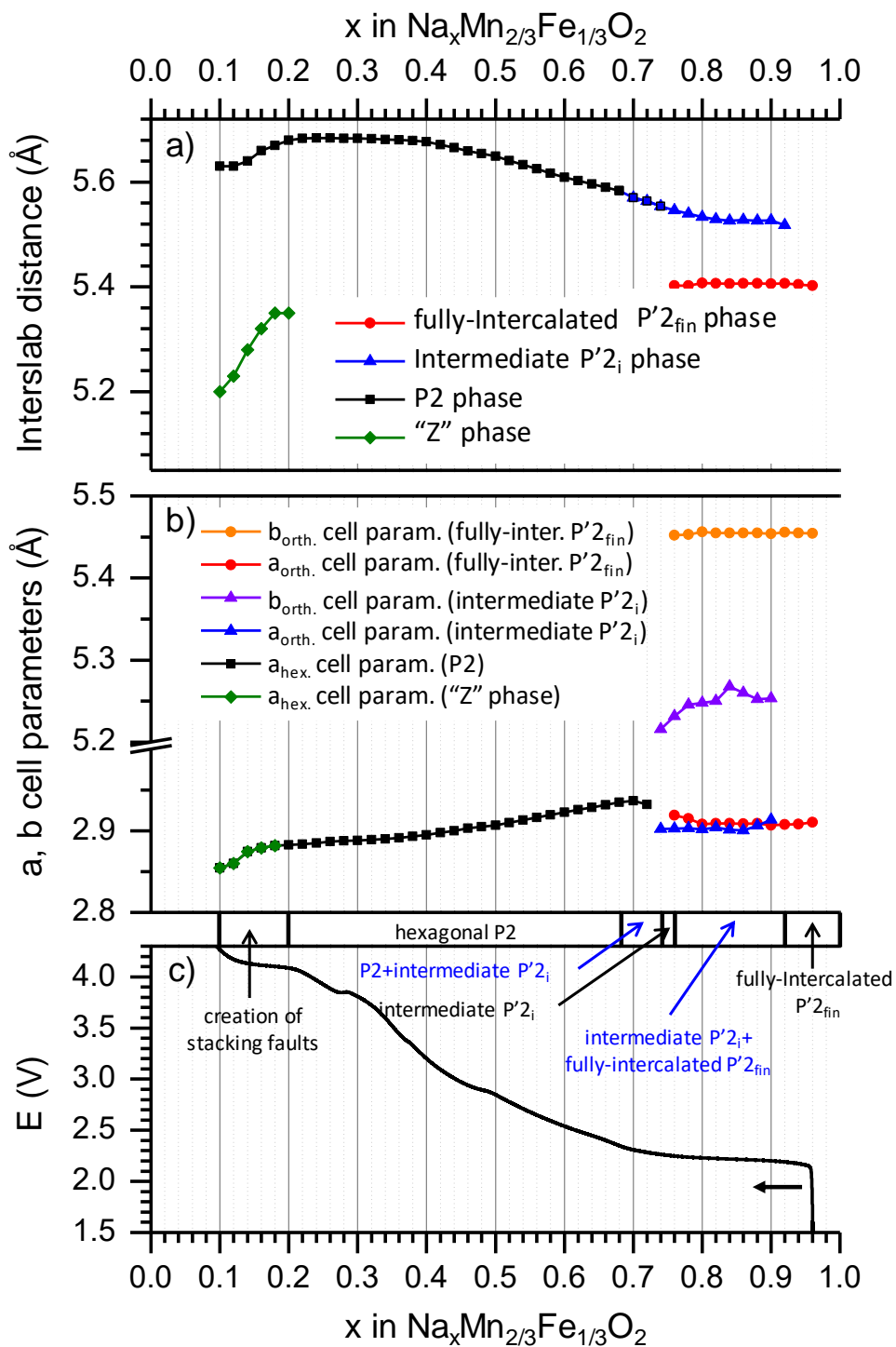


Figure S2: Evolution of the (a) interslab distance and (b) a and b cell parameters of the different $\text{Na}_x\text{Mn}_{2/3}\text{Fe}_{1/3}\text{O}_2$ phases upon sodium deintercalation. The galvanostatic curve versus x is also shown as a guide in (c).

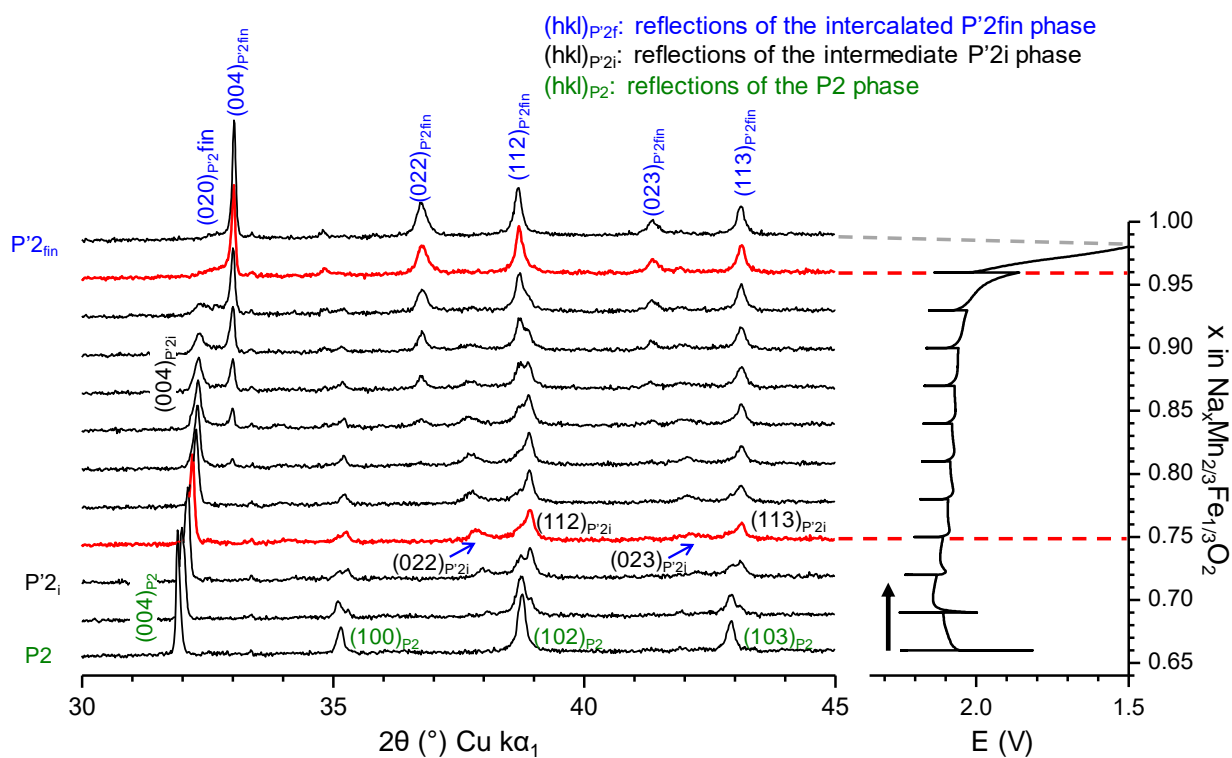


Figure S3: XRD pattern of the $\text{Na}_x\text{Mn}_{1/2}\text{Fe}_{1/2}\text{O}_2$ phases upon sodium deintercalation during a GITT cell charge. The diffraction lines of the intermediate P2'₁ phase $x = 0.75$ phase is indicated in red.

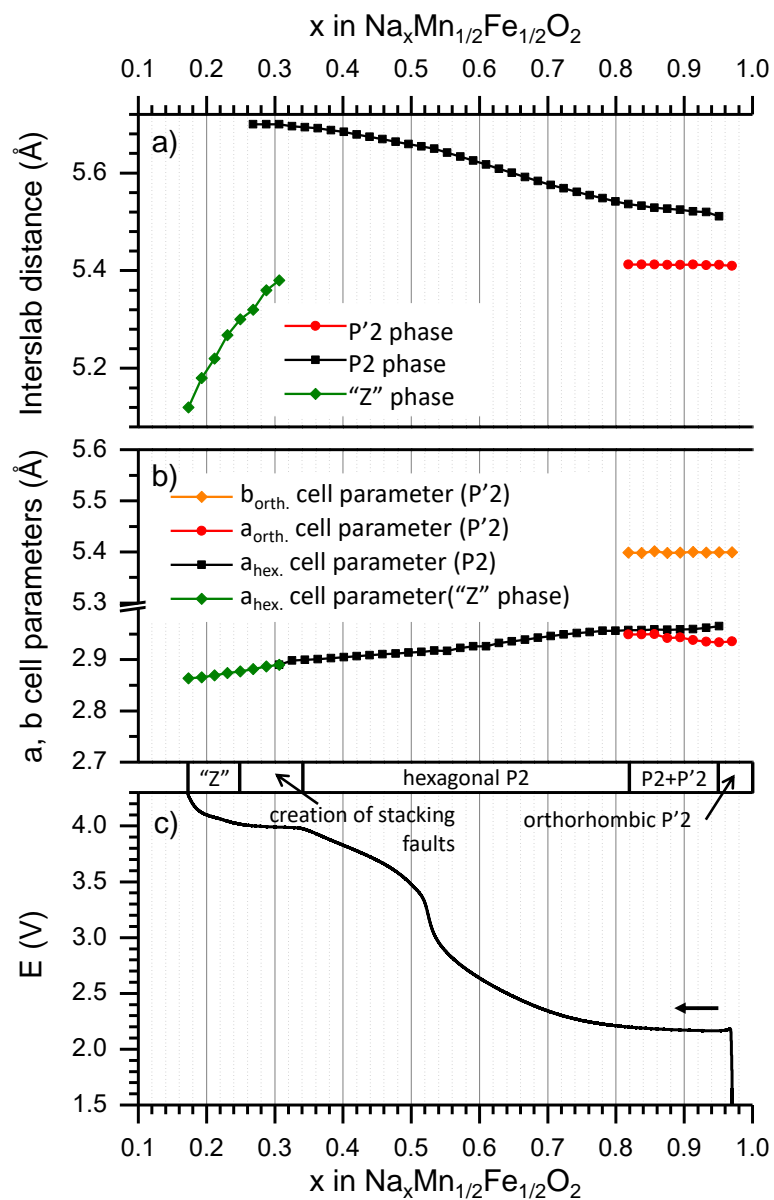
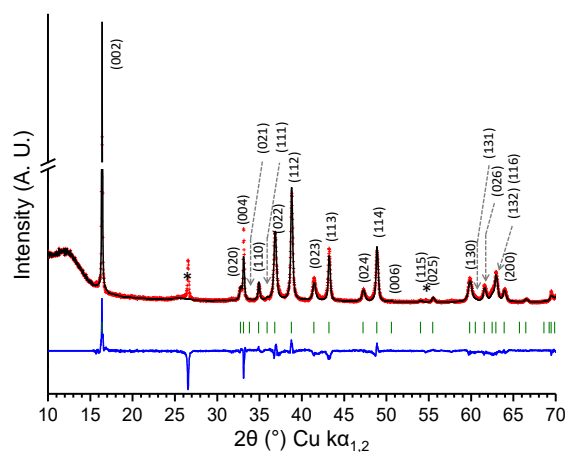


Figure S4: Evolution of the (a) interslab distance and (b) a and b cell parameters of the different $\text{Na}_x\text{Mn}_{1/2}\text{Fe}_{1/2}\text{O}_2$ phases upon sodium deintercalation. The galvanostatic curve versus x is also shown as a guide in (c) (from ref 17).



| Space group: Cmcm | | | | | | |
|---|---------|--------------------------|--------------------------|----------|-----------|------------------------|
| $a_{\text{orth.}} = 2.9109(7) \text{ \AA}$, $b_{\text{orth.}} = 5.467(2) \text{ \AA}$, $c_{\text{orth.}} = 10.817(3) \text{ \AA}$ | | | | | | |
| $b_{\text{orth.}}/a_{\text{orth.}} = 1.88$ | | | | | | |
| Atom | Wyckoff | | Coordinates | | Occupancy | ADP (\AA^2) |
| Na _e | 4c | 0 | 0.687(4) | 1/4 | 0.96 | 1.0 |
| Mn | 4a | 0 | 0 | 0 | 1 | 0.5 |
| Fe | 4a | 0 | 0 | 0 | 1 | 0.8 |
| O | 8f | 0 | 0.644(5) | 0.895(2) | 1 | 0.8 |
| Distances : | | M-O | Na-O | | | |
| | | 4 * 2.01(1) \AA | 4 * 2.33(2) \AA | | | |
| | | 2 * 2.25(2) \AA | 2 * 2.40(1) \AA | | | |
| Rwp = 14.36 %; R _b = 9.37 % with excluded regions (graphite) | | | | | | |

Figure S5: Observed and calculated XRPD patterns of the intercalated P'2-Na_{0.96}Mn_{2/3}Fe_{1/3}O₂ phase. Red crosses: experimental, black line: calculated, blue line: difference and green bars: Bragg positions. The * symbol indicates the position of the graphite diffraction lines.

Structural parameters and reliability factors calculated from the XRPD diagram of the P'2-Na_{0.96}Mn_{2/3}Fe_{1/3}O₂ phase.