Supplemental Data

TABLE SI-I. Structural & metric parameters of the reference LiCo0.5Fe0.5PO4 (*Pnma*) used in the multi-fraction models, *Rbragg* = 2.137%. Determined by pristine ssr-LiCo0.5Fe0.5PO4.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| site | Wyckoff  position | *x* | *y* | *z* | *sof* | *Biso* (Å2) |
| Li1 | 4*a* | 0 | 0 | 0 | 1 | 1.04(3) |
| Co1 | 4*c* | 0.28090(9) | ¼ | 0.9773(3) | 0.5 | 1.04(3) |
| Fe1 | 0.5 | 1.04(3) |
| P1 | 4*c* | 0.0954(2) | ¼ | 0.4140(4) | 1 | 1.15(5) |
| O1 | 4*c* | 0.1008(4) | ¼ | 0.7468(8) | 1 | 1.14(5) |
| O2 | 4*c* | 0.4521(5) | ¼ | 0.2068(8) | 1 | 1.14(5) |
| O3 | 8*d* | 0.1712(4) | 0.0378(5) | 0.2826(5) | 1 | 1.14(5) |
| *a* = 10.26514(7) Å, *b* = 5.96585(4) Å, *c* = 4.69688(3) Å, *V* = 287.638(3) Å3 | | | | | | |

TABLE SI-II. Structural & metric parameters of the reference Li0.5Co0.5Fe0.5PO4 (*Pnma*) used in the multi-fraction models, *Rbragg* = 1.492%. Determined by pristine chemically delithiated ssr-LiCo0.5Fe0.5PO4.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| site | Wyckoff  position | *x* | *y* | *z* | *sof* | *Biso* (Å2) |
| Li1 | 4*a* | 0 | 0 | 0 | 0.5 | 0.93(3) |
| Co1 | 4*c* | 0.27757(9) | ¼ | 0.9707(2) | 0.5 | 0.93(3) |
| Fe1 | 0.5 | 0.93(3) |
| P1 | 4*c* | 0.0957(2) | ¼ | 0.4136(4) | 1 | 0.81(4) |
| O1 | 4*c* | 0.1133(3) | ¼ | 0.7374(8) | 1 | 1.23(5) |
| O2 | 4*c* | 0.4472(4) | ¼ | 0.1750(7) | 1 | 1.23(5) |
| O3 | 8*d* | 0.1711(3) | 0.0433(4) | 0.2743(5) | 1 | 1.23(5) |
| *a* = 10.02637(6) Å, *b* = 5.87359(3) Å, *c* = 4.75578(3) Å, *V* = 280.072(3) Å3 | | | | | | |

TABLE SI-III. Structural & metric parameters of the reference NaCo0.5Fe0.5PO4 (*Pnma*) used in the multi-fraction models, *Rbragg* = 1.716%. No pristine compound NaCo0.5Fe0.5PO4 could be obtained. The data was determined by a multi-fraction compound with a composition as close to NaCo0.5Fe0.5PO4 as possible.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| site | Wyckoff  position | *x* | *y* | *z* | *sof* | *Biso* (Å2) |
| Na1 | 4*a* | 0 | 0 | 0 | 1 | 0.70(6) |
| Co1 | 4*c* | 0.2832(2) | ¼ | 0.9848(9) | 0.5 | 0.70(6) |
| Fe1 | 0.5 | 0.70(6) |
| P1 | 4*c* | 0.1111(4) | ¼ | 0.441(1) | 1 | 0.7(1) |
| O1 | 4*c* | 0.111(1) | ¼ | 0.739(2) | 1 | 3.9(2) |
| O2 | 4*c* | 0.451(2) | ¼ | 0.159(2) | 1 | 3.9 (2) |
| O3 | 8*d* | 0.1757(9) | 0.060(2) | 0.293(2) | 1 | 3.9 (2) |
| *a* = 10.3492(8) Å, *b* = 6.1820(6) Å, *c* = 4.9494(7) Å, *V* = 316.66(6) Å3 | | | | | | |

TABLE SI-IV. Structural & metric parameters of the reference Na0.5Co0.5Fe0.5PO4 (*Pnma*) used in the multi-fraction model, *Rbragg* = 1.324%. No pristine compound Na0.5Co0.5Fe0.5PO4 could be obtained. The data was determined by a multi-fraction compound with a composition as close to Na0.5Co0.5Fe0.5PO4 as possible.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| site | Wyckoff  position | *x* | *y* | *z* | *sof* | *Biso* (Å2) |
| Na1 | 4*a* | 0 | 0 | 0 | 0.5 | 1.40(9) |
| Co1 | 4*c* | 0.2786(2) | ¼ | 0.9842(8) | 0.5 | 1.40(9) |
| Fe1 | 0.5 | 1.40(9) |
| P1 | 4*c* | 0.1000(4) | ¼ | 0.427(1) | 1 | 0.5(1) |
| O1 | 4*c* | 0.1176(9) | ¼ | 0.744(2) | 1 | 1.7(1) |
| O2 | 4*c* | 0.450(1) | ¼ | 0.160(2) | 1 | 1.7(1) |
| O3 | 8*d* | 0.1780(8) | 0.037(1) | 0.294(1) | 1 | 1.7(1) |
| *a* = 10.114(2) Å, *b* = 5.9675(6) Å, *c* = 4.8811(7) Å, *V* = 294.60(7) Å3 | | | | | | |

TABLE SI-V. Structural & metric parameters of the reference LiMn0.5Fe0.5PO4 (*Pnma*) used in the multi-fraction models, *Rbragg* = 1.469%. Determined by pristine ssr-LiMn0.5Fe0.5PO4.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| site | Wyckoff  position | *x* | *y* | *z* | *sof* | *Biso* (Å2) |
| Li1 | 4*a* | 0 | 0 | 0 | 1 | 0.35(2) |
| Mn1 | 4*c* | 0.28215(7) | ¼ | 0.9733(2) | 0.5 | 0.35(2) |
| Fe1 | 0.5 | 0.35(2) |
| P1 | 4*c* | 0.0939(1) | ¼ | 0.4128(3) | 1 | 0.34(3) |
| O1 | 4*c* | 0.0982(3) | ¼ | 0.7384(7) | 1 | 0.56(4) |
| O2 | 4*c* | 0.4547(4) | ¼ | 0.2092(7) | 1 | 0.56(4) |
| O3 | 8*d* | 0.1651(3) | 0.0455(4) | 0.2783(4) | 1 | 0.56(4) |
| *a* = 10.39131(7) Å, *b* = 6.05416(4) Å, *c* = 4.71783(4) Å, *V* = 296.802(4) Å3 | | | | | | |

TABLE SI-VI. Structural & metric parameters of the reference Li0.5Mn0.5Fe0.5PO4 (*Pnma*) used in the multi-fraction models, *Rbragg* = 1.946%. Determined by chemically delithiated ssr-LiMn0.5Fe0.5PO4.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| site | Wyckoff  position | *x* | *y* | *z* | *sof* | *Biso* (Å2) |
| Li1 | 4*a* | 0 | 0 | 0 | 0.5 | 0.47(2) |
| Mn1 | 4*c* | 0.27953(8) | ¼ | 0.9663(2) | 0.5 | 0.47(2) |
| Fe1 | 0.5 | 0.47(2) |
| P1 | 4*c* | 0.0963(1) | ¼ | 0.4122(3) | 1 | 0.58(3) |
| O1 | 4*c* | 0.1133(3) | ¼ | 0.7273(7) | 1 | 0.96(4) |
| O2 | 4*c* | 0.4500(4) | ¼ | 0.1796(6) | 1 | 0.96(4) |
| O3 | 8*d* | 0.1696(3) | 0.0476(4) | 0.2709(4) | 1 | 0.96(4) |
| *a* = 10.1441(1) Å, *b* = 5.96917(5) Å, *c* = 4.79509(5) Å, *V* = 290.352(5) Å3 | | | | | | |

TABLE SI-VII. Structural & metric parameters of the reference NaMn0.5Fe0.5PO4 (*Pnma*) used in the multi-fraction models, *Rbragg* = 1.472%. Determined by a molten salt product NaMn0.5Fe0.5PO4.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| site | Wyckoff  position | *x* | *y* | *z* | *sof* | *Biso* (Å2) |
| Na1 | 4*a* | 0 | 0 | 0 | 1 | 0.83(4) |
| Mn1 | 4*c* | 0.2864(1) | ¼ | 0.9894(4) | 0.5 | 0.83(4) |
| Fe1 | 0.5 | 0.83(4) |
| P1 | 4*c* | 0.1085(2) | ¼ | 0.4412(4) | 1 | 0.58(6) |
| O1 | 4*c* | 0.1160(5) | ¼ | 0.7433(9) | 1 | 0.88(7) |
| O2 | 4*c* | 0.4656(5) | ¼ | 0.1625(9) | 1 | 0.88(7) |
| O3 | 8*d* | 0.1767(4) | 0.0545(6) | 0.3134(6) | 1 | 0.88(7) |
| *a* = 10.4820(3) Å, *b* = 6.2835(2) Å, *c* = 4.9799(2) Å, *V* = 328.00(2) Å3 | | | | | | |

TABLE SI-VIII. Structural & metric parameters of the reference Na0.5Mn0.5Fe0.5PO4 (*Pnma*) used in the multi-fraction models, *Rbragg* = 1.843%. Determined by chemical desodiation of the molten salt compound.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| site | Wyckoff  position | *x* | *y* | *z* | *sof* | *Biso* (Å2) |
| Na1 | 4*a* | 0 | 0 | 0 | 0.5 | 1.07(4) |
| Mn1 | 4*c* | 0.2829(1) | ¼ | 0.9829(3) | 0.5 | 1.07(4) |
| Fe1 | 0.5 | 1.07(4) |
| P1 | 4*c* | 0.1064(2) | ¼ | 0.4378(5) | 1 | 1.26(7) |
| O1 | 4*c* | 0.1201(5) | ¼ | 0.736(1) | 1 | 1.99(8) |
| O2 | 4*c* | 0.4553(7) | ¼ | 0.159(1) | 1 | 1.99(8) |
| O3 | 8*d* | 0.1742(4) | 0.0556(6) | 0.3010(7) | 1 | 1.99(8) |
| *a* = 10.2670(3) Å, *b* = 6.1139(2) Å, *c* = 4.9811(2) Å, *V* = 312.67(2) Å3 | | | | | | |

TABLE SI-IX. Overview of the parameters used in the Rietveld refinements for the references and fractions in multi- fraction models.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| parameters | determination of reference | usage of reference | single fraction of the 11 or 36 fraction model | single fraction of the 121 fraction model |
| Instrumental broadening & emission profile | fixed | fixed | fixed | fixed |
| background of the total scan | refined1 | refined1 | refined1 | refined1 |
| scaling factor | refined | set to 0 | refined | refined by constraint2 |
| lattice parameters | refined | fixed | interpolated | interpolated |
| microstructural parameters | refined3 | refined3,4 | constrained to values of the reference phases | constrained to values of the reference phases |
| atomic positions | refined | fixed | interpolated | interpolated |
| thermal vibration factors | refined isotropic5 | refined isotropic5 | constrained to values of the reference phases | constrained to values of the reference phases |
| *sof* | fixed to known value | fixed | interpolated | interpolated |
| March Dollase parameter | refined | refined4 | constrained to reference phases | constrained to reference phases |

1refined by a Chebychev polynomial of 15th order

2refined by constraining with a bimodal bivariate normality

3refined by a double-Voigt model

4refined but constrained to the same parameter(s) for all reference phases

5refining one isotropic *B* value for all phases and all atoms of the same type, thermal vibration factor of alkaline metal and transition metal were constrained to the same value



Figure SI-1. Comparison of different fit routines applied on the compound Li0.49Na0.51Mn0.5Fe0.5PO4 (step 5). Measured data (black), calculated curve using one phase Li0.5Na0.5Mn0.5Fe0.5PO4 with an isotropic model of microstructure (red), calculated curve using one phase Li0.5Na0.5Mn0.5Fe0.5PO4 with Stephens’ model (green), and calculated curve using the 121 fraction model (blue).



Figure SI-2. Rietveld plot of the reference compound Li0.5Co0.5Fe0.5PO4 (step 1) refined with one phase: Experimental data in black (dotted), calculated curve in red (cross), difference curve in grey, and *hkl* markers in blue.



Figure SI-3. Rietveld plot of the compound Li0.25Na0.51Co0.5Fe0.5PO4 (step 6) refined with the 121 fraction model: Experimental data in black (dotted), calculated curve in red (cross), and difference curve in grey.



Figure SI-4. Rietveld plot of the compound Li0.49Na0.51Mn0.5Fe0.5PO4 (step 5) refined with the 121 fraction model: Experimental data in black (dotted), calculated curve in red (cross), and difference curve in grey.