Supporting Information

Structural and Electrochemical Analyses on the Transformation of CaFe$_2$O$_4$-Type LiMn$_2$O$_4$ from Spinel-Type LiMn$_2$O$_4$

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Figure S1: XRD patterns of the (a) SP-LMO($x=0$), (b) SP-LMO($x=0.1$), (c) SP-LMO($x=0.2$), and (d) SP-LMO($x=0.333$) samples. The SP-LMO($x=0.333$) sample contains 12.1 wt% of the impurity, Li$_2$MnO$_3$, as determined by Rietveld analysis.
Figure S2: Cubic lattice parameters ($a_c$s) of the SP-LMO samples; i.e., $a_c$ as a function of $x$ in Li[Li$_x$Mn$_{2-x}$]O$_4$. The $a_c$ values were determined by Rietveld analyses.
Figure S3: XRD patterns of (a) HP($x=0$,6GPa,1000°C), (b) HP($x=0$,8GPa,1000°C), and (c) HP($x=0$,1000°C) samples.
Figure S4: SEM images of the (a) HP($x=0$,RT), (b) HP($x=0$,400°C), and (c) HP($x=0$,800°C) samples.
Figure S5: Results of the Rietveld analyses for the (a) HP($x=0,400^\circ$C), (b) HP($x=0,600^\circ$C), and (c) HP($x=0,800^\circ$C) samples.
Table S1: Structural parameters of the HP($x=0.400^\circ$C) sample determined by Rietveld analyses.

| Space group  | Atom  | Wyckoff position | Occupancy $(g)$ | $x$  | $y$  | $z$  | $B_{iso}$ $(\text{Å}^2)$ |
|-------------|-------|------------------|----------------|------|------|------|--------------------------|
| $Fd\overline{3}m$ (SP-LMO) | Li1   | 8$a$             | 1.0            | 0.125| 0.125| 0.125| 1.0(1)                   |
|             | Mn1   | 16$d$            | 1.0            | 0.5  | 0.5  | 0.5  | 0.8(1)                   |
|             | O1    | 32$e$            | 1.0            | 0.262(1)| 0.262(1)| 0.262(1)| 1.7(1)                  |
|             |        |                  |                |      |      |      |                          |
| $a_c = 8.2236(3)$ Å, $R_{wp} = 8.25$ % and $S = 1.21$ |

Table S2: Structural parameters of the HP($x=0.600^\circ$C) sample determined by Rietveld analyses.

| Space group  | Atom  | Wyckoff position | Occupancy $(g)$ | $x$  | $y$  | $z$  | $B_{iso}$ $(\text{Å}^2)$ |
|-------------|-------|------------------|----------------|------|------|------|--------------------------|
| $C2/m$ (Li$_2$MnO$_3$) 31.8 wt% | Li11  | 2$b$            | 1.0            | 0    | 0.5  | 0    | 1.0(1)                   |
|             | Li12  | 2$c$            | 1.0            | 0    | 0    | 0.5  | 1.0(1)                   |
|             | Li13  | 4$h$            | 1.0            | 0    | 0.694(1)| 0.5(1)| 1.0(1)                   |
|             | Mn11  | 4$g$            | 1.0            | 0    | 0.169(1)| 0   | 1.3(1)                   |
|             | O11   | 4$i$            | 1.0            | 0.300(2)| 0    | 0.206(2)| 1.3(1)                   |
|             | O12   | 4$j$            | 1.0            | 0.269(1)| 0.336(1)| 0.234(1)| 1.3(1)                   |
| $a_m = 4.9332(17)$ Å, $b_m = 8.5339(23)$ Å, $c_m = 5.0145(18)$ Å, and $\beta_m = 109.32(75)$ ° |
| $P4_2/mnm$ (MnO$_2$) 24.1 wt% | Mn21  | 2$a$            | 1.0            | 0    | 0    | 0    | 1.3(1)                   |
|             | O21   | 4$f$            | 1.0            | 0.299(3)| 0.299(3)| 0   | 1.3(1)                   |
| $a_t = 4.4020(67)$ Å and $c_t = 2.8813(44)$ Å |
| $Pbca$ (Mn$_2$O$_3$) 44.1 wt% | Mn31  | 4$a$            | 1.0            | 0    | 0    | 0    | 1.3(1)                   |
|             | Mn32  | 4$b$            | 1.0            | 0    | 0    | 0.5  | 1.3(1)                   |
|             | Mn33  | 8$c$            | 1.0            | 0.253(3)| 0.287(2)| 0.001(3)| 1.3(1)                   |
|             | Mn34  | 8$c$            | 1.0            | 0.999(3)| 0.255(3)| 0.287(2)| 1.3(1)                   |
|             | Mn35  | 8$c$            | 1.0            | 0.276(1)| 0.998(3)| 0.25(3) | 1.3(1)                   |
|             | O31   | 8$c$            | 1.0            | 0.150(5)| 0.917(5)| 0.139(5)| 1.3(1)                   |
|             | O32   | 8$c$            | 1.0            | 0.108(3)| 0.112(3)| 0.872(4)| 1.3(1)                   |
|             | O33   | 8$c$            | 1.0            | 0.918(6)| 0.133(4)| 0.127(4)| 1.3(1)                   |
|             | O34   | 8$c$            | 1.0            | 0.667(6)| 0.435(6)| 0.624(6)| 1.3(1)                   |
|             | O35   | 8$c$            | 1.0            | 0.617(6)| 0.641(5)| 0.432(5)| 1.3(1)                   |
|             | O36   | 8$c$            | 1.0            | 0.434(6)| 0.620(6)| 0.660(6)| 1.3(1)                   |
| $a_o = 9.4505(12)$ Å, $b_o = 9.4108(14)$ Å, and $c_o = 9.3990(24)$ Å |
| $R_B$(Li$_2$MnO$_3$) = 4.78 %, $R_B$(MnO$_2$) = 4.44 %, $R_B$(Mn$_2$O$_3$) = 6.06 %, $R_{wp}$ = 10.39 %, and $S = 1.50$ |
Table S3: Structural parameters of the HP(\(x=0.800^\circ\text{C}\)) sample determined by Rietveld analyses.

| Space group | Atom          | Wyckoff position | Occupancy | \(x\)      | \(y\)      | \(z\)      | \(B_{\text{iso}}\) / Å\(^2\) |
|-------------|---------------|------------------|-----------|------------|------------|------------|-----------------------------|
| \(Pnma\)   | Li11          | 4c               | 1.0       | 0.256(3)   | 0.25       | 0.348(3)   | 1.4(2)                     |
| (CF-LMO)    | Mn11          | 4c               | 1.0       | 0.062(1)   | 0.25       | 0.119(1)   | 0.2(1)                     |
| 35.0 wt%    | Mn12          | 4c               | 1.0       | 0.085(1)   | 0.25       | 0.600(1)   | 0.2(1)                     |
|            | O11           | 4c               | 1.0       | 0.305(1)   | 0.25       | 0.666(1)   | 0.3(1)                     |
|            | O12           | 4c               | 1.0       | 0.380(1)   | 0.25       | 0.974(1)   | 0.3(1)                     |
|            | O13           | 4c               | 1.0       | 0.468(1)   | 0.25       | 0.207(1)   | 0.3(1)                     |
|            | O14           | 4c               | 1.0       | 0.067(1)   | 0.25       | 0.926(1)   | 0.3(1)                     |
|            | \(a_o = 8.8030(5)\) Å, \(b_o = 2.8326(2)\) Å, and \(c_o = 10.6333(6)\) Å |
| \(C2/m\)   | Li21          | 2b               | 1.0       | 0          | 0.5        | 0          | 1.4(2)                     |
| (Li\(_2\)MnO\(_3\)) | Li22        | 2c               | 1.0       | 0          | 0.5        | 0          | 1.4(2)                     |
| 21.9 wt%    | Li23          | 4h               | 1.0       | 0          | 0.688(1)   | 0          | 1.4(2)                     |
|            | Mn21          | 4g               | 1.0       | 0          | 0.170(1)   | 0          | 0.2(1)                     |
|            | O21           | 4i               | 1.0       | 0.280(1)   | 0          | 0.208(1)   | 0.3(1)                     |
|            | O22           | 8j               | 1.0       | 0.242(1)   | 0.342(1)   | 0.231(1)   | 0.3(1)                     |
|            | \(a_m = 4.9279(8)\) Å, \(b_m = 8.5258(9)\) Å, \(c_m = 5.0029(7)\) Å, and \(\beta_m = 109.02(1)^\circ\) |
| \(P4_2/mnm\)| Mn31          | 2a               | 1.0       | 0          | 0          | 0          | 0.2(1)                     |
| (MnO\(_2\)) | O31           | 4f               | 1.0       | 0.300(1)   | 0.300(1)   | 0          | 0.3(1)                     |
| 15.5 wt%    | \(a_t = 4.3972(4)\) Å and \(c_t = 2.8766(3)\) Å |
| \(Pbca\)   | Mn41          | 4a               | 1.0       | 0          | 0          | 0          | 0.2(1)                     |
| (Mn\(_2\)O\(_3\)) | Mn42       | 4b               | 1.0       | 0          | 0          | 0          | 0.2(1)                     |
| 27.6 wt%    | Mn43          | 8c               | 1.0       | 0.254(7)   | 0.283(3)   | 0.997(7)   | 0.2(1)                     |
|            | Mn44          | 8c               | 1.0       | 0.000(6)   | 0.254(7)   | 0.284(3)   | 0.2(1)                     |
|            | Mn45          | 8c               | 1.0       | 0.284(3)   | 0.999(8)   | 0.256(5)   | 0.2(1)                     |
|            | O41           | 8c               | 1.0       | 0.141(3)   | 0.918(6)   | 0.131(6)   | 0.3(1)                     |
|            | O42           | 8c               | 1.0       | 0.139(5)   | 0.145(4)   | 0.895(7)   | 0.3(1)                     |
|            | O43           | 8c               | 1.0       | 0.910(4)   | 0.132(5)   | 0.134(3)   | 0.3(1)                     |
|            | O44           | 8c               | 1.0       | 0.658(6)   | 0.426(5)   | 0.621(5)   | 0.3(1)                     |
|            | O45           | 8c               | 1.0       | 0.630(3)   | 0.658(3)   | 0.411(5)   | 0.3(1)                     |
|            | O46           | 8c               | 1.0       | 0.425(5)   | 0.624(7)   | 0.249(5)   | 0.3(1)                     |
| \(a_o = 9.3944(21)\) Å, \(b_o = 9.4007(22)\) Å, and \(c_o = 9.4146(14)\) Å |
| \(R_B(\text{CF-LMO}) = 4.52\%\), \(R_B(\text{Li}_2\text{MnO}_3) = 4.41\%\), \(R_B(\text{MnO}_2) = 3.53\%\), and \(R_B(\text{Mn}_2\text{O}_3) = 3.89\%\) |
| \(R_{wp} = 8.20\%\) and \(S = 1.23\) |
Figure S6: Temperature dependence of magnetic susceptibility ($\chi$) of the HP(x=0,1000°C) sample. $\chi$ was measured in a field-cooling (FC) mode under a magnetic field of 10 kOe. The red line represents the fitting result using a Curie-Weiss equation.
Figure S7: Results of the Rietveld analyses for the (a) HP(x=0.2,1000°C) and (b) HP(x=0.333,1000°C) samples.
Table S4: Structural parameters of the HP($x$=0.2,1000°C) sample determined by Rietveld analyses.

| Space group | Atom | Wyckoff position | Occupancy | $x$    | $y$    | $z$    | $B_{iso}$ / Å² |
|-------------|------|------------------|-----------|--------|--------|--------|----------------|
| $Pnma$      | Li11 | 4c               | 1.0       | 0.236(5) | 0.25   | 0.254(5) | 1.0(1)         |
| (CF-LMO) 37.2 wt% | Mn11 | 4c               | 1.0       | 0.062(1) | 0.25   | 0.118(1) | 0.3(1)         |
|             | Mn12 | 4c               | 1.0       | 0.087(1) | 0.25   | 0.601(1) | 0.3(1)         |
|             | O11  | 4c               | 1.0       | 0.288(1) | 0.25   | 0.664(1) | 0.9(1)         |
|             | O12  | 4c               | 1.0       | 0.373(1) | 0.25   | 0.978(1) | 0.9(1)         |
|             | O13  | 4c               | 1.0       | 0.475(1) | 0.25   | 0.208(1) | 0.9(1)         |
|             | O14  | 4c               | 1.0       | 0.092(1) | 0.25   | 0.923(1) | 0.9(1)         |
|             |      |                  |           |        |        |        |                 |
|             |      |                  |           |        |        |        |                 |
|             |      |                  |           |        |        |        |                 |
|             |      |                  |           |        |        |        |                 |
| $C2/m$      | Li21 | 2b               | 1.0       | 0      | 0.5    | 0      | 1.0(2)         |
| (Li$_2$MnO$_3$) 19.4 wt% | Li22 | 2c               | 1.0       | 0      | 0      | 0.5    | 1.0(2)         |
|             | Li23 | 4h               | 1.0       | 0      | 0.686(1) | 0.5    | 1.0(2)         |
|             | Mn21 | 4g               | 1.0       | 0      | 0.171(1) | 0      | 0.3(1)         |
|             | O21  | 4i               | 1.0       | 0.267(4) | 0      | 0.229(5) | 0.9(1)         |
|             | O22  | 8j               | 1.0       | 0.243(6) | 0.338(5) | 0.234(3) | 0.9(1)         |
|             |      |                  |           |        |        |        |                 |
|             |      |                  |           |        |        |        |                 |
|             |      |                  |           |        |        |        |                 |
| $P4_2/mnm$  | Mn31 | 2a               | 1.0       | 0      | 0      | 0      | 0.2(1)         |
| (MnO$_2$) 22.1 wt% | O31  | 4f               | 1.0       | 0.294(2) | 0.294(2) | 0      | 0.9(1)         |
|             |      |                  |           |        |        |        |                 |
|             |      |                  |           |        |        |        |                 |
| $Pbcn$      | Mn41 | 4a               | 1.0       | 0      | 0      | 0      | 0.2(1)         |
| (Mn$_2$O$_3$) 21.3 wt% | Mn42 | 4b               | 1.0       | 0      | 0      | 0      | 0.3(1)         |
|             | Mn43 | 8c               | 1.0       | 0.375(7) | 0.199(3) | 0.945(6) | 0.3(1)         |
|             | Mn44 | 8c               | 1.0       | −0.196(4) | 0.346(4) | 0.267(5) | 0.3(1)         |
|             | Mn45 | 8c               | 1.0       | 0.391(5) | 0.003(4) | 0.339(5) | 0.3(1)         |
|             | O41  | 8c               | 1.0       | 0.273(4) | 0.959(4) | 0.257(5) | 0.9(1)         |
|             | O42  | 8c               | 1.0       | 0.921(6) | 0.590(4) | 0.816(5) | 0.9(1)         |
|             | O43  | 8c               | 1.0       | 0.030(5) | 0.335(5) | 0.865(7) | 0.9(1)         |
|             | O44  | 8c               | 1.0       | 0.724(6) | 0.456(6) | 0.233(5) | 0.9(1)         |
|             | O45  | 8c               | 1.0       | 0.669(7) | 0.178(4) | 0.388(5) | 0.9(1)         |
|             | O46  | 8c               | 1.0       | 0.416(5) | 0.553(6) | 0.761(5) | 0.9(1)         |
|             |      |                  |           |        |        |        |                 |

$a_o = 8.7736(7)$ Å, $b_o = 2.8329(3)$ Å, and $c_o = 10.5548(6)$ Å

$a_{m} = 4.9255(9)$ Å, $b_{m} = 8.5205(2)$ Å, $c_{m} = 5.0110(8)$ Å, and $\beta_{m} = 109.18(2)$°

$a_{t} = 4.3959(3)$ Å and $c_{t} = 2.8700(2)$ Å

$R_B$(CF-LMO) = 3.46 %, $R_B$(Li$_2$MnO$_3$) = 3.63 %, $R_B$(MnO$_2$) = 3.15 %, and $R_B$(Mn$_2$O$_3$) = 2.37 %

$R_{wp}$ = 9.52 % and $S$ = 1.55
Table S5: Structural parameters of the HP($x=0.333,1000^\circ\text{C}$) sample determined by Rietveld analyses.

| Space group | Atom     | Wyckoff position | Occupancy ($g$) | $x$    | $y$    | $z$    | $B_{iso}$ / Å$^2$ |
|-------------|----------|------------------|-----------------|-------|-------|-------|------------------|
| $Pnma$      | Li11     | 4c               | 1.0             | 0.236(3) | 0.25 | 0.237(3) | 1.1(2)          |
| (CF-LMO)    | Mn11     | 4c               | 1.0             | 0.064(1) | 0.25 | 0.117(1) | 0.2(1)          |
| 23.5 wt%    | Mn12     | 4c               | 1.0             | 0.095(1) | 0.25 | 0.597(1) | 0.2(1)          |
|             | O11      | 4c               | 1.0             | 0.287(1) | 0.25 | 0.673(1) | 0.7(1)          |
|             | O12      | 4c               | 1.0             | 0.364(1) | 0.25 | 0.974(1) | 0.7(1)          |
|             | O13      | 4c               | 1.0             | 0.481(1) | 0.25 | 0.198(1) | 0.7(1)          |
|             | O14      | 4c               | 1.0             | 0.094(1) | 0.25 | 0.922(1) | 0.7(1)          |
|             |          |                  |                 |        |       |       |                 |
| $C2/m$      | Li21     | 2b               | 1.0             | 0      | 0.5   | 0     | 1.1(2)          |
| (Li$_2$MnO$_3$) | Li22   | 2c               | 1.0             | 0      | 0     | 0.5   | 1.1(2)          |
| 27.4 wt%    | Li23     | 4h               | 1.0             | 0.698(1) | 0.5  | 1.1(2)          |
|             | Mn21     | 4g               | 1.0             | 0      | 0.170(1) | 0     | 0.2(1)          |
|             | O21      | 4i               | 1.0             | 0.267(1) | 0    | 0.223(1) | 0.7(1)          |
|             | O22      | 8j               | 1.0             | 0.244(1) | 0.338(1) | 0.235(1) | 0.7(1)          |
|             |          |                  |                 |        |       |       |                 |
| $P4_2/mnm$  | Mn31     | 2a               | 1.0             | 0      | 0     | 0     | 0.2(1)          |
| (MnO$_2$)   | O31      | 4f               | 1.0             | 0.296(1) | 0.296(1) | 0     | 0.7(1)          |
| 25.3 wt%    |          |                  |                 |        |       |       |                 |
| $Pbca$      | Mn41     | 4a               | 1.0             | 0      | 0     | 0     | 0.2(1)          |
| (Mn$_2$O$_3$) | Mn42   | 4b               | 1.0             | 0      | 0     | 0.5   | 0.2(1)          |
| 23.9 wt%    | Mn43     | 8c               | 1.0             | 0.392(3) | 0.198(6) | 0.948(6) | 0.2(1)          |
|             | Mn44     | 8c               | 1.0             | 0.793(4) | 0.359(4) | 0.272(4) | 0.2(1)          |
|             | Mn45     | 8c               | 1.0             | 0.381(4) | 0.987(5) | 0.346(5) | 0.2(1)          |
|             | O41      | 8c               | 1.0             | 0.306(7) | 0.947(6) | 0.573(3) | 0.7(1)          |
|             | O42      | 8c               | 1.0             | 0.915(5) | 0.582(4) | 0.810(5) | 0.7(1)          |
|             | O43      | 8c               | 1.0             | 0.987(5) | 0.313(4) | 0.872(5) | 0.7(1)          |
|             | O44      | 8c               | 1.0             | 0.762(4) | 0.459(6) | 0.212(5) | 0.7(1)          |
|             | O45      | 8c               | 1.0             | 0.662(5) | 0.206(4) | 0.414(4) | 0.7(1)          |
|             | O46      | 8c               | 1.0             | 0.406(7) | 0.483(5) | 0.684(4) | 0.7(1)          |

$a_o = 8.7878(13)$ Å, $b_o = 2.8357(6)$ Å, and $c_o = 10.5330(14)$ Å

$a_m = 4.9278(8)$ Å, $b_m = 8.5197(10)$ Å, $c_m = 5.01259(7)$ Å, and $\beta_m = 109.02(1)^\circ$

$a_t = 4.3948(4)$ Å and $c_t = 2.8718(3)$ Å

$a_o = 9.2126(40)$ Å, $b_o = 9.4565(5)$ Å, and $c_o = 9.6793(38)$ Å

$R_B$(CF-LMO) = 3.70 %, $R_B$(Li$_2$MnO$_3$) = 4.34 %, $R_B$(MnO$_2$) = 3.02 %, and $R_B$(Mn$_2$O$_3$) = 2.79 %

$R_{wp} = 11.36$ % and $S = 1.78$
Figure S8: XRD patterns of the HP($x=0,1000^\circ$C) sample (a) before (initial) and (b) after cycling test. Enlarged XRD pattern in the 2$\theta$ range between 17 and 30 $^\circ$ is shown in the inset.
Figure S9: Discharge and charge curves of the HP(x=0,1000°C)/Li cell operated in the voltage range between 1.0 and 3.0 V.
Figure S10: Rate performance of the HP\((x=0.1, 1000^{\circ}C)\) sample.