Supplementary Materials for

Phase transitions in the "spinel-layered" $Li_{1+x}Ni_{0.5}Mn_{1.5}O_4$ (x = 0, 0.5, 1) cathodes upon (de)lithiation studied with *operando* synchrotron X-ray powder diffraction.

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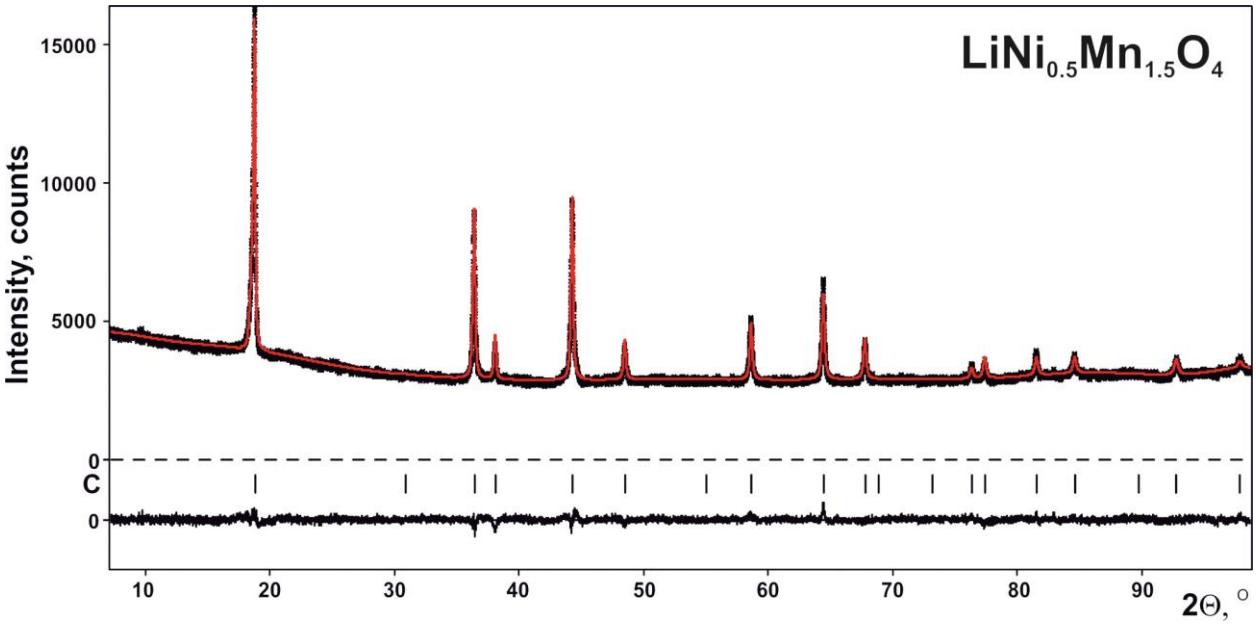


Figure S1. Experimental, calculated (red) and difference PXRD (λ = 1.540598 Å) patterns for $LiNi_{0.5}Mn_{0.5}O_4$ sample. PXRD data were refined by Rietveld method using JANA 2006 software as $LiNi_{0.5}Mn_{0.5}O_4$ cubic spinel (C) (sp. gr. $Fd\bar{3}m$, Z = 8, a = 8.1710(3) Å, V = 545.54(2) Å^3, R_F = 0.047, R_P = 0.018, wR_P = 0.023, GOF = 1.31). The used structure model was the follow: Li 8*a*

(⅛,⅛,⅛) 1[1]; Ni/Mn 16*d* (½, ½, ½) 0.25/0.75[1]; O 32*e* (0.2632, 0.2632, 0.2632) 1[1] [S1]. The 16*d* site occupancy was fixed in accordance with Ni:Mn ratio founded by EDX.

[1]site occupancy

[S1] W. Branford, M. A. Green, D. A. Neumann, Chem. Mat., 14 (2002) 1649–1656.

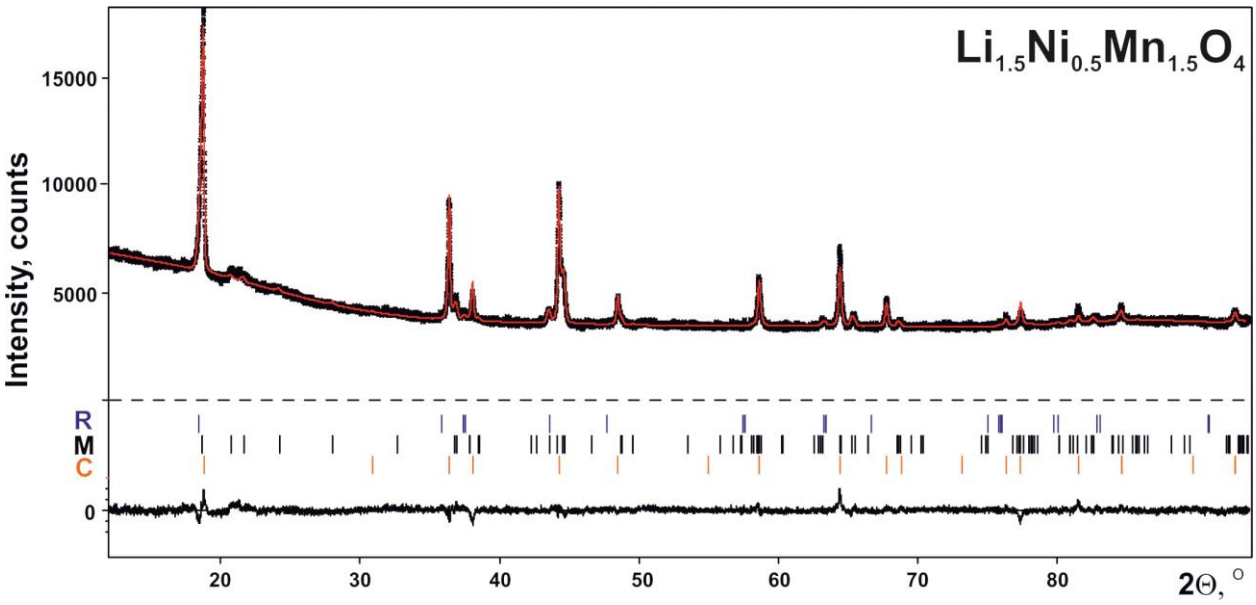


Figure S2. Experimental, calculated (red) and difference PXRD (λ = 1.540598 Å) patterns for $Li_{1.5}Ni_{0.5}Mn_{0.5}O_4$ sample. PXRD data were refined by Rietveld method using JANA 2006 software as three phase mixture of:

C - $LiNi_{0.5}Mn_{0.5}O_4$ (sp. gr. $Fd\bar{3}m$, Z = 8, a = 8.1720(3) Å, V = 545.7(1) Å^3, R_F = 0.088, 60(2) wt. %),

M – $Li(Li_{0.28}Mn_{0.64}Ni_{0.08})O_2$ (sp. gr. $C2/m$, Z = 4, a = 4.950(3) Å, b = 8.543(5) Å, c = 5.028(2) Å, β = 109.25(5)°, V = 200.7(1) Å^3, R_F = 0.098, 34(2) wt. %),

R – $Li_{0.5}Ni_{1.21}Mn_{0.26}O_2$ (sp. gr. $R\bar{3}m$, Z = 3, a = 2.932(3) Å, c = 14.41(3) Å, V = 107.3(1) Å^3, R_F = 0.11, 5.2(6) wt. %) with R_P = 0.018, wR_P = 0.024, GOF = 1.58.

The used structure models were the follow:

$LiNi_{0.5}Mn_{0.5}O_4$: similar to aforementioned one.

$Li(Li_{0.28}Mn_{0.64}Ni_{0.08})O_2$: Li1/Mn1/Ni1 2*b* (0, ½, 0) 0.64/0.32/0.04[1]; Li2/Mn2/Ni2 4*g* (0, 0.1687, 0) 0.1/0.81/0.1[1]; Li3 2*c* (0, 0, ½) 1[1]; Li4 4*h* (0, 0.319, ½) 1[1]; O1 4*i* (0.224, 0, 0.225) 1[1]; O2 8*j* (0.253, 0.323, 0.2275) 1[1] [S2].

At the first refinement attempt the ordered Li_2MnO_3 structure model (Li1 2*b*; Li2 2*c*; Li3 4*h*, Mn1 4*g*; O1 4*i*; O2 8*j*) was used. Strong disagreement for experimental and calculated intensities of several diffraction maxima together with EDX data was the reason to use the disordered model with Li/M (M = $Mn_{0.89}Ni_{0.11}$) statistic occupation of cation sites [S2]. The refined values of atomic displacement parameters were used as a hint for presence of Li/M statistic occupation for certain positions. Finally, Li/Mn/Ni joint occupancy for 2*b* and 4*g* sites was refined.

$Li_{0.5}Ni_{1.21}Mn_{0.26}O_2$: Li1/Ni1/Mn1 3*b* (0, 0, ½) 0.252/0.600/0.132[1]; Li2/Ni2/Mn2 3*a* (0, 0, 0) 0.252/0.600/0.135[2], O 6*c* (0, 0, 0.2458) 1[1] [S3].

The site occupancies were fixed in accordance with EDX data.

[1]site occupancies

[S2] A. Boulineau, L. Croguennec, C. Delmas, F. Weill, Chem. Mat., 21 (2009) 4216–4222.

W. Li, J.N. Reimers, J.R. Dahn, Phys. Rev. B, 46 (1992) 3236–3246.

[S3] W. Li, J.N. Reimers, J.R. Dahn, Crystal structure of $Li_xNi_{2-x}O_2$ and a lattice-gas model for the ordered-disordered transition, Phys. Rev. B, 46 (1992) 3236–3246.

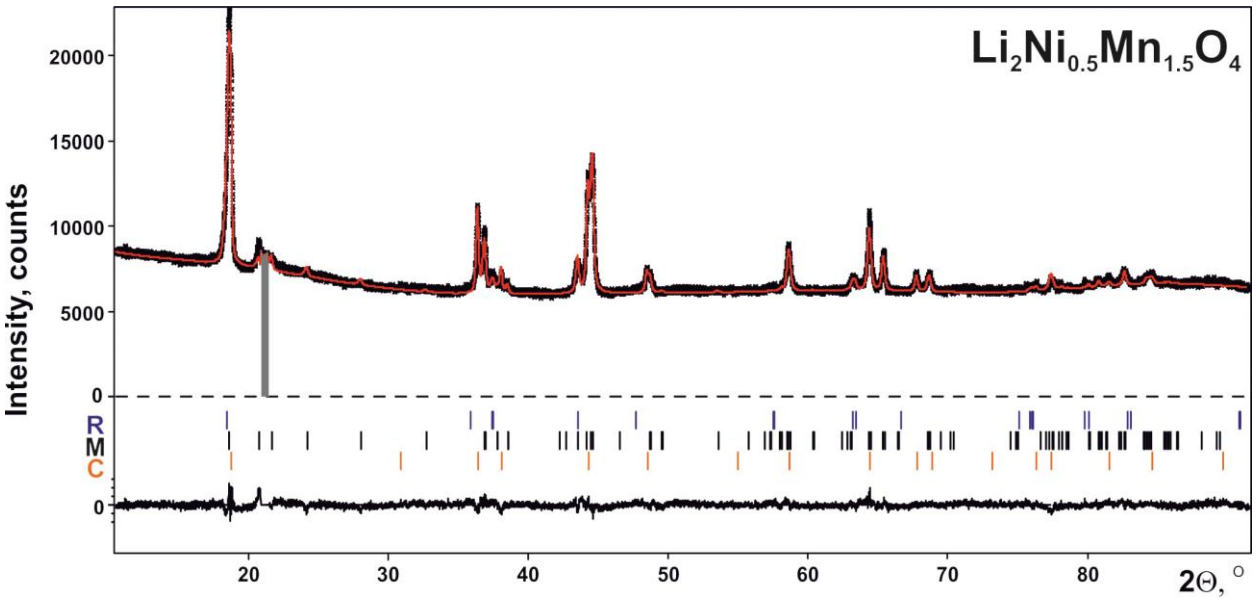


Figure S3. Experimental, calculated (red) and difference PXRD (λ = 1.54598 Å) patterns for $Li_2Ni_{0.5}Mn_{0.5}O_4$ sample. PXRD data were refined by Rietveld method using JANA 2006 software as three phase mixture of:

C – $LiNi_{0.5}Mn_{0.5}O_4$ cubic spinel (sp. gr. $Fd\bar{3}m$, Z = 8, a = 8.1692(4) Å, V = 545.2(1) Å^3, R_F = 0.071, 28(1) wt. %),

M – $Li(Li_{0.28}Mn_{0.64}Ni_{0.08})O_2$ (sp. gr. $C2/m$, Z = 4, a = 4.940(1) Å, b = 8.542(2) Å, c = 5.034(1) Å, β = 109.28(2)°, V = 200.5(1) Å^3, R_F = 0.080, 63(1) wt. %.

R – $Li_{0.5}Ni_{1.21}Mn_{0.26}O_2$ (sp. gr. $R\bar{3}m$, Z = 3, a = 2.930(1) Å, c = 14.41(1) Å, V = 107.1(1) Å^3, R_F = 0.073, 9.0(4) wt. %) with R_P = 0.017, wR_P = 0.020, GOF = 1.68.

The used structure models were similar to aforementioned ones.

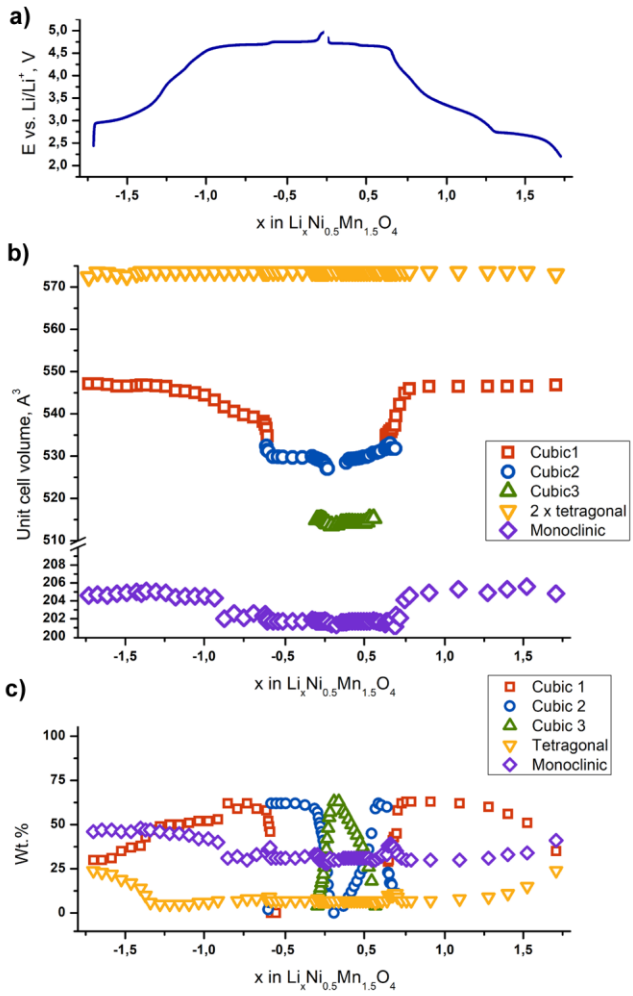


Figure S4. E–x curves (a) and variation of the unit cell volumes (b) and weight fractions of the phases (c) for the $Li_{1.5}Ni_{0.5}Mn_{1.5}O_4$ sample