Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Sucrose-induced structural changes in $LiNi_{0.5}Mn_{1.5}O_4$

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1 Experimental Section

Pristine ordered $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) was synthesized by a modified solid state reaction from carbonate precursor.[1] 40 mmol of $MnSO_4 \cdot H_2O$ and 20 ml of ethanol were dissoveled in 100 ml of distilled water. 120 mmol of NH_4HCO_3 and 20 ml of ethanol were dissolved in 100 mL of distilled water and poured into $MnSO_4$ solution under vigorous stirring. The mixed solution was kept stirring for 1 hour at room temperature and the products were collected by centrifugation, washed by ethanol and distilled water for three times. The synthesized products were dried at 80 ºC for 24 h, and then calcined at 400 ºC for 5 h. 30 mmol of as-obtained MnO_2 and desired amount of $Ni(CH_3COO)_2 \cdot 4H_2O$ and $LiCH_3COO \cdot 2H_2O$ (5% extra) were dispersed in 15 mL of ethanol. The ethanol was removed slowly under stirring at room temperature. The obtained-mixture was ground manually for 15 minutes and then calcined at 700 ºC for 6 h in air.

2 Rietveld Refinement

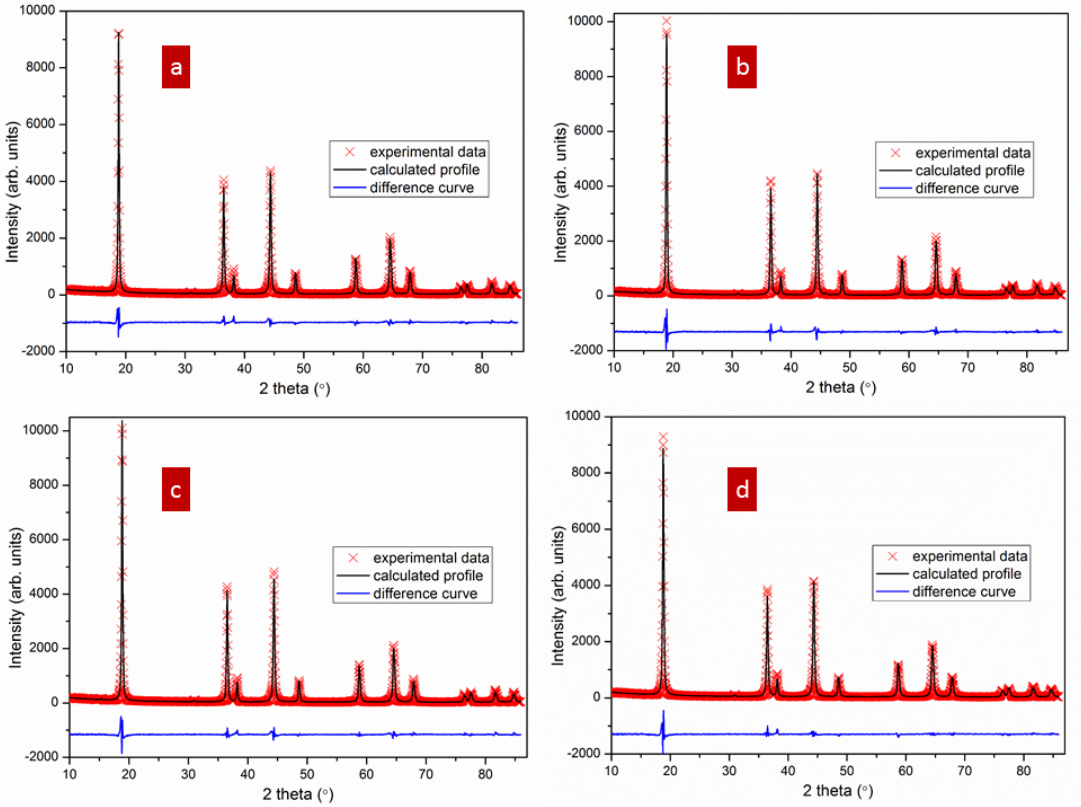

Figure S1. Rietveld refined XRD patterns with experimental data (red crosses), calculated profile (black lines) and difference curves (blue lines). Sucrose treated LNMO (2.5g). a) 0g sucrose(C1); b) 0.025g sucrose(C2); c) 0.1g sucrose(C3); d) 0.42g sucrose(C4).

Table S1. Refined parameters of sucrose-treated LNMO

sample	*a(Å)*	*atom*	*x*	*y*	*z*	*occupancy*	*Uiso* *(Å²*100)*	R_p(%)	R_{wp}(%)
C1	8.1734(1)	Li	0	0	0	1	0.8	7.7	10.2
($P4_332$)		Ni1/Mn1	5/8	5/8	5/8	0.25/0.75	1.09(5)		
		Ni2/Mn2	1/8	0.374	0.876	0.25/0.75	1.09(5)		
		O1	0.3788(7)	0.3788(7)	0.3788(7)	1	2.46(9)		
		O2	0.1090(6)	0.1120(6)	0.3961(6)	1	2.46(9)		
C2	8.1647(1)	Li	0	0	0	1	0.8	8.4	10.8
($P4_332$)		Ni1/Mn1	5/8	5/8	5/8	0.25/0.75	1.1(2)		
		Ni2/Mn2	1/8	0.374	0.876	0.25/0.75	1.1(2)		
		O1	0.3855(7)	0.3855(7)	0.3855(7)	1	2.70(9)		
		O2	0.1036(6)	0.1206(6)	0.3885(6)	1	2.70(9)		
C3	8.1718(1)	Li	0	0	0	1	0.8	7.7	10.4
($P4_332$)		Ni1/Mn1	5/8	5/8	5/8	0.25/0.75	1.72(5)		
		Ni2/Mn2	1/8	0.374	0.876	0.25/0.75	1.72(5)		
		O1	0.3897(7)	0.3897(7)	0.3897(7)	1	2.69(9)		
		O2	0.1065(6)	0.1236(6)	0.3877(6)	1	2.69(9)		
C4	8.1753(1)	Li	1/8	1/8	1/8	1	0.8	6.7	8.4
($Fd\bar{3}m$)		Ni/Mn	1/2	1/2	1/2	0.25/0.75	1.76(4)		
		O	0.2618(2)	0.2618(2)	0.2618(2)	1	2.82(8)		

3 Best Fit Results Obtained by EXAFS Analysis for Sucrose-Treated LNMO

Table S2. Bond lengths and mean square relative displacements (σ^2) derived from EXAFS analysis of sucrose-treated LNMO at Ni K edge.

$S_0^2 = 0.83, \Delta E_0 = 2.1 \pm 0.3\ eV, Reduced\ \chi^2 = 32.6$

Samples	First shell(Ni-O)		Second shell(Ni-Mn/Ni)		Fitting R-factor
	R (Å)	σ^2 (10^{-3} Å^2)	R (Å)	σ^2 (10^{-3} Å^2)	
C1	2.038 ± 0.005	5.2 ± 0.3	2.917 ± 0.002	5.1 ± 0.2	0.2%
C2	2.039 ± 0.007	5.2 ± 0.4	2.917 ± 0.002	5.4 ± 0.3	0.4%
C3	2.040 ± 0.009	5.6 ± 0.5	2.916 ± 0.002	4.7 ± 0.3	0.3%
C4	2.025 ± 0.006	5.9 ± 0.4	2.910 ± 0.002	5.4 ± 0.3	0.2%

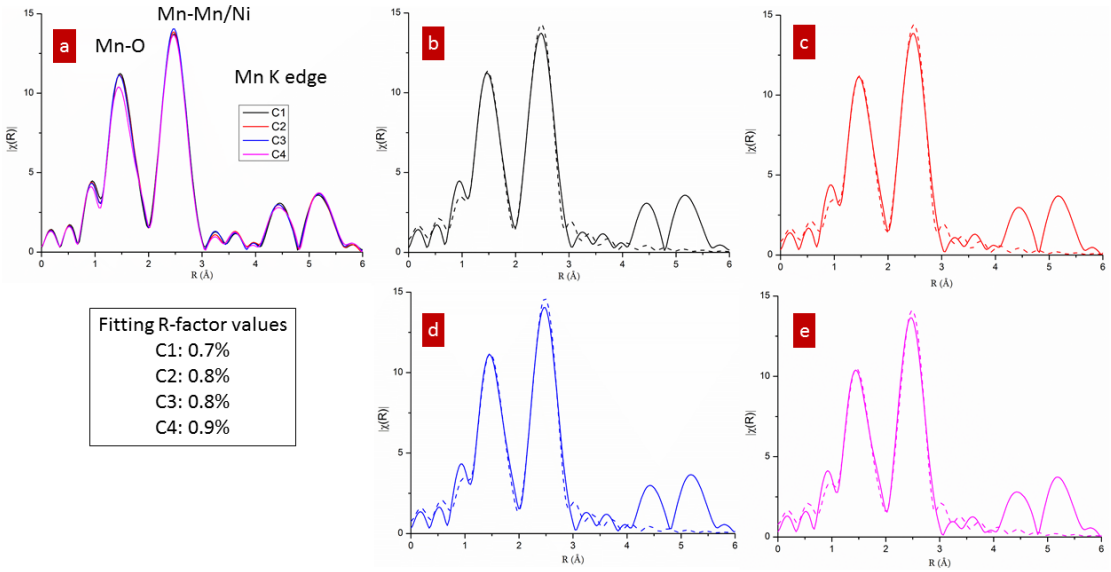

Figure S2. Fourier transform magnitudes of the K edge EXAFS spectra of Mn for a) sucrose treated LNMO, experimental data (solid line) and fits (dashed line) of Mn for b) C1, c) C2, d) C3, and e) C4.

Table S2. Bond lengths and mean square relative displacements (σ^2) derived from EXAFS analysis of sucrose-treated LNMO at Mn K edge.

$S_0^2 = 0.74, \Delta E_0 = -4.3 \pm 0.6\ eV, Reduced\ \chi^2 = 159$

Samples	First shell(Ni-O)		Second shell(Ni-Mn/Ni)		Fitting R-factor
	R (Å)	σ^2 (10^{-3} Å^2)	R (Å)	σ^2 (10^{-3} Å^2)	
C1	1.907 ± 0.004	2.5 ± 1.3	2.884 ± 0.004	2.9 ± 0.3	0.7%
C2	1.906 ± 0.005	2.1 ± 1.6	2.882 ± 0.002	3.9 ± 0.4	0.7%
C3	1.906 ± 0.004	2.2 ± 1.1	2.883 ± 0.002	3.8 ± 0.3	0.8%
C4	1.911 ± 0.010	2.8 ± 1.4	2.888 ± 0.002	4.0 ± 0.3	0.9%

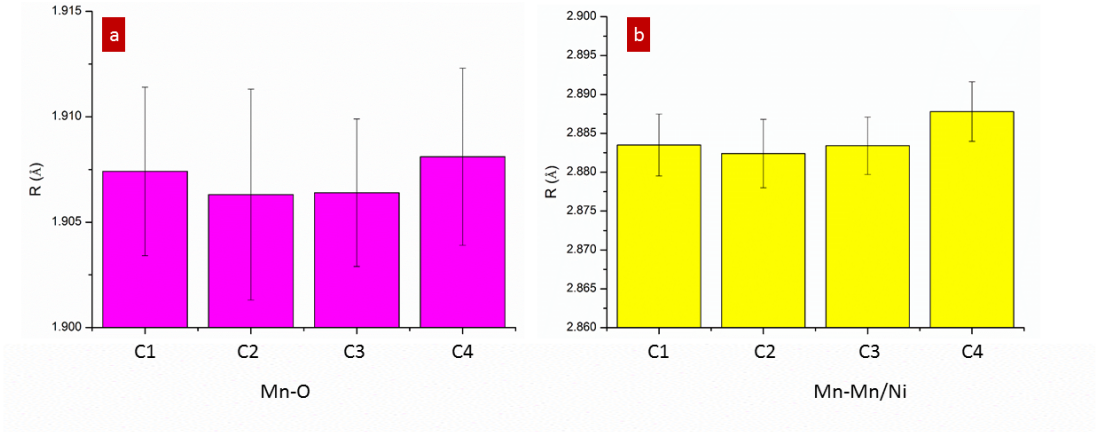

Figure S3. Bond lengths and mean square relative displacements (σ^2) derived from EXAFS analysis of sucrose-treated LNMO at Mn K edge.

1. X. Zhang, F. Cheng, J. Yang and J. Chen, *Nano Lett.*, 2013, **13**, 2822-2825.