Supplementary Material (ESI) for Journal of Materials Chemistry

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NMR, PDF and RMC Study of the Positive Electrode Material $Li(NiMn)_{0.5}O_2$ Synthesized by Ion-Exchange Methods

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Table S1 Rietveld refinement results for the $Na(NiMn)_{0.5}O_2$-II neutron diffraction pattern. Simultaneous refinement using six different histograms, corresponding to banks 1 to 6 of the GPPD detector, with the same parameters, were performed.

	$Na(NiMn)_{0.5}O_2$	NiO impurity[18]
Space group	R-3m	Fm-3m
a (Å)	2.95803(2)	4.1812(2)
c (Å)	15.9419(2)	-
V (Å^3)	120.803(1)	73.10(1)
z (O)	0.23199(2)	-
Na occupancy	0.986(2)	-
Ni occupancy	0.494(1)	-
Mn occupancy	0.506(1)	-
100**Uiso* (Å^2) Na (3a) Ni, Mn (3b) O (6c)	 1.54(5) 0.31(3) 0.59(3)	 Ni (0,0,0): 1.5 O (1/2,1/2,1/2):0.25
Weight Fraction	98.0 %	2.0 %
Bank 1 (145º)	R_{wp} = 4.48 %	
Bank 2 (125º)	R_{wp} = 4.82 %	
Bank 3 (107º)	R_{wp} = 4.35 %	
Bank 4 (90º)	R_{wp} = 4.68 %	
Bank 5 (53º)	R_{wp} = 5.27 %	
Bank 6 (30º)	R_{wp} = 3.11 %	

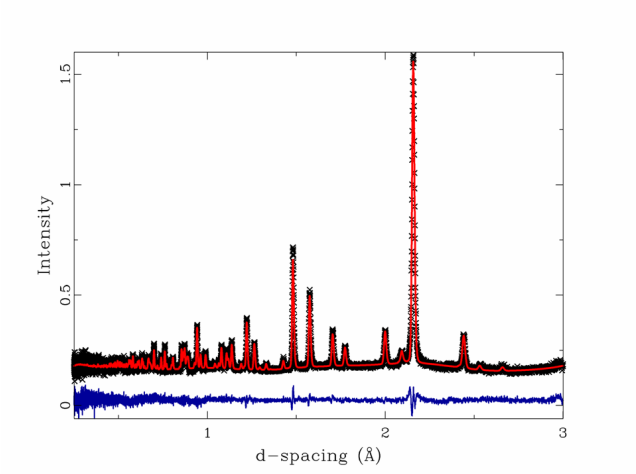

Fig. S2 Rietveld refinement using the neutron diffraction pattern (bank 4 -90º- of the GPPD detector) of $Na(NiMn)_{0.5}O_2$-II. The crosses and the solid red line represent the experimental and the calculated patterns, respectively. The difference is shown between the two patterns is shown in blue below the data. The structural parameters are given in Table S1.

Table S3 Number of Ni/Mn pairs in the transition metal layers (*ab* plane) of $Na(NiMn)_{0.5}O_2$-II and occupational correlation results before and after the RMC calculations, for 12×12×2 cluster size and for the first and second coordination shells.

	R-3m space group 12×12×2 cluster			
	1st coordination shell		2nd coordination shell	
	Before (Random)	**After**	Before (Random)	**After**
% Ni-Ni pairs	23.1 %	19.8 %	23.6 %	26.0 %
% Ni-Mn pairs	49.8 %	56.5 %	48.9 %	44.1 %
% Mn-Mn pairs	27.1 %	23.7 %	27.5 %	29.9 %
Total	100 %	100 %	100 %	100 %
Correlation c_{NiMn}[a]	0.00	-0.16	0.02	+0.10

[a] The correlation coefficient c_{ij} between a pair of sites i and j is given by the statistical definition[24] of the correlation: $c_{ij} = (P_{ij} - \theta^2)/(\theta(1-\theta))$, where P_{ij} is the probability that both sites i and j are occupied by the same atom type and θ is its overall occupancy. Negative values of c_{ij} indicate that the sites i and j tend to be occupied by different atom types.

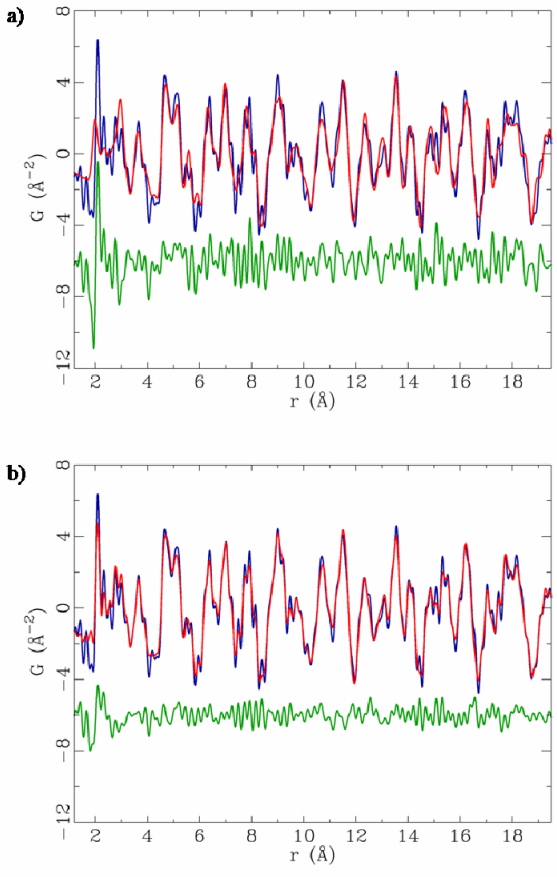

Fig. S4 Reverse Monte Carlo (RMC) results for the $Na(NiMn)_{0.5}O_2$-II precursor: (a) is the fit before the RMC calculations with the initial random cluster model and (b) is after. The blue line represents the experimental data and the red line the calculated PDF. The difference between the calculated and experimental PDFs is shown in green.

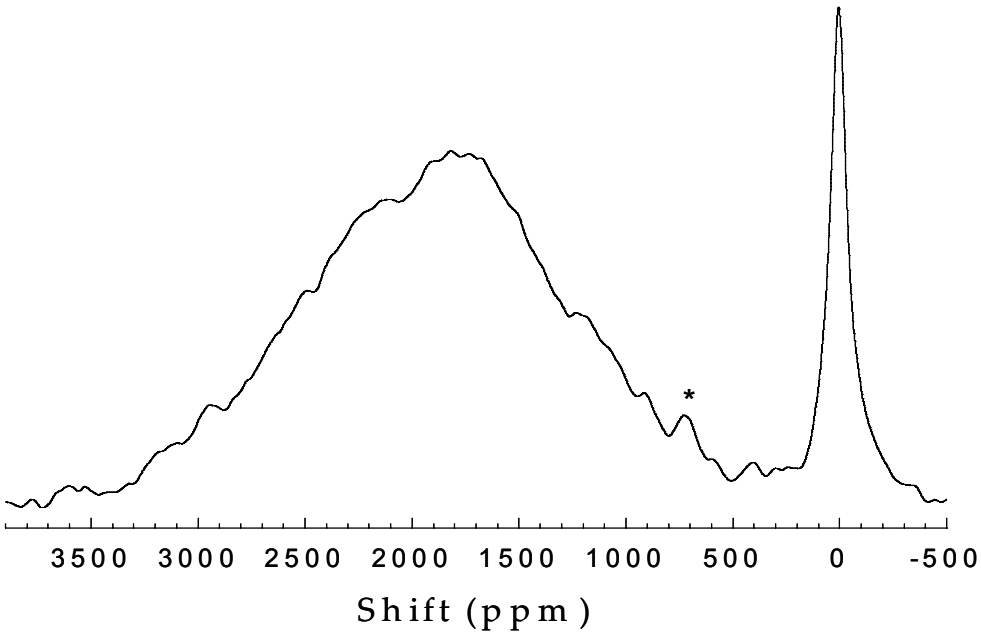

Fig. S5 ^{23}Na MAS NMR spectra of Na($Ni_{0.5}Mn_{0.5}$) O2-I. The extremely large width of the peak (150 kHz) is the result of the overlap of the sidebands and the isotropic shift(s) even while spinning at the highest speeds that can be reached in our setup (38-40 kHz). The resonance at 0 ppm arises from diamagnetic impurities (most probably, unreacted Na_2CO_3), and the asterisk indicates its corresponding sideband.