Supporting Information

A novel strategy to significantly enhance initial voltage and suppress voltage fading of Li- and Mn-rich Layered Oxide Cathode Material for lithium-ion batteries†

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XRD refinement process: In order to further explore the crystal structure of the $Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O_2$-x$LiNiO_2$ material with varying x, the Rietveld refinements of the XRD data of the $LiNiO_2$-0, $LiNiO_2$-10, $LiNiO_2$-20 and $LiNiO_2$-40 samples were carried out by a General Structure Analysis System (GSAS) software package. The Rietveld refinements of the XRD data are based on a three-phase model system with the trigonal layered $LiMO_2$(R-3m) phase, monoclinic layered Li_2MnO_3(C2/m) phase and spinel-like LiM_2O_4 phase. Due to the similar ionic radii of Ni^{2+} with the Li^+, we performed the Ni^{2+} to occupy the Li^+ sites, and the goal of this refinement is in order to get possible sites of Ni^{2+} substituting the Li^+ sites and the corresponding to qualitative value of Ni/Li occupancies in the Li slab and metal slab. This refinement on the Ni/Li occupancies was carried out for both the R-3m space group, C2/m space group and Fd-3m. Firstly, we set the theory occupies as 0.000% of Ni^{2+} in the Li^+ 3b sites of R-3m space group, in the Li^+ 2b, Li^+ 2c and Li^+ 4h sites for the C2/m space group and in the Li^+ 8a sites of the Fd-3m space group. Then the real occupies were refined step by step until they reached a reliable value.

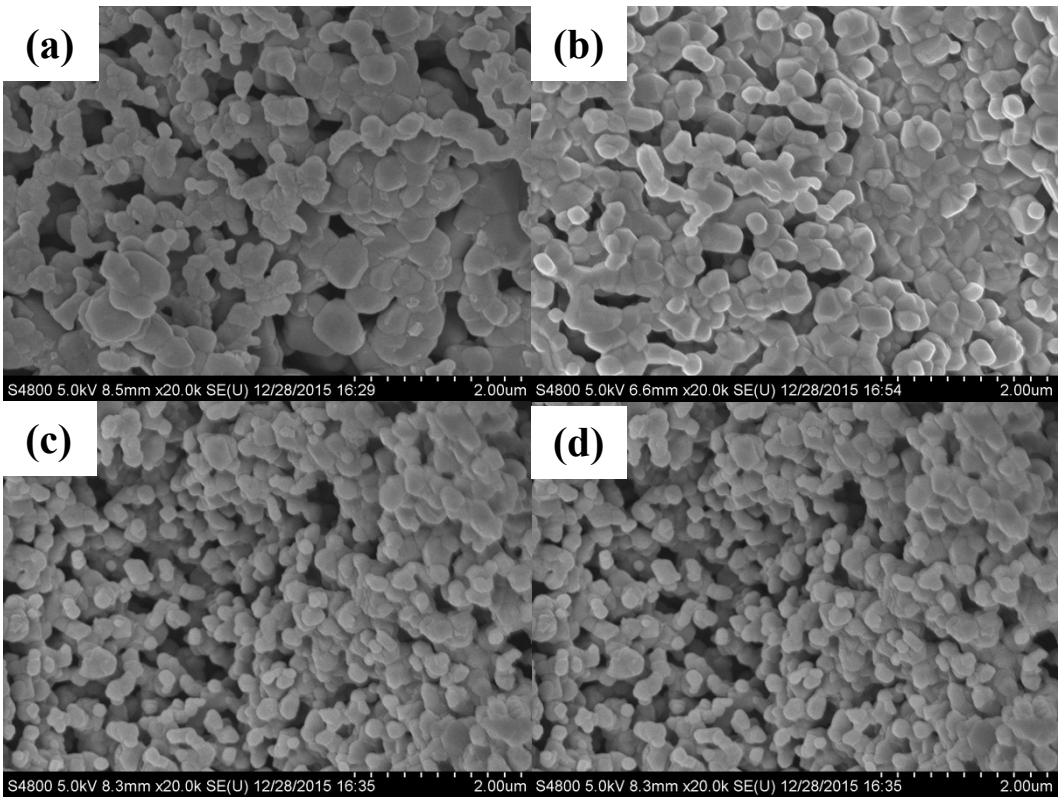

Fig. S1 SEM images of the LiNiO-0, LiNiO-10, LiNiO-20 and LiNiO-40 samples.

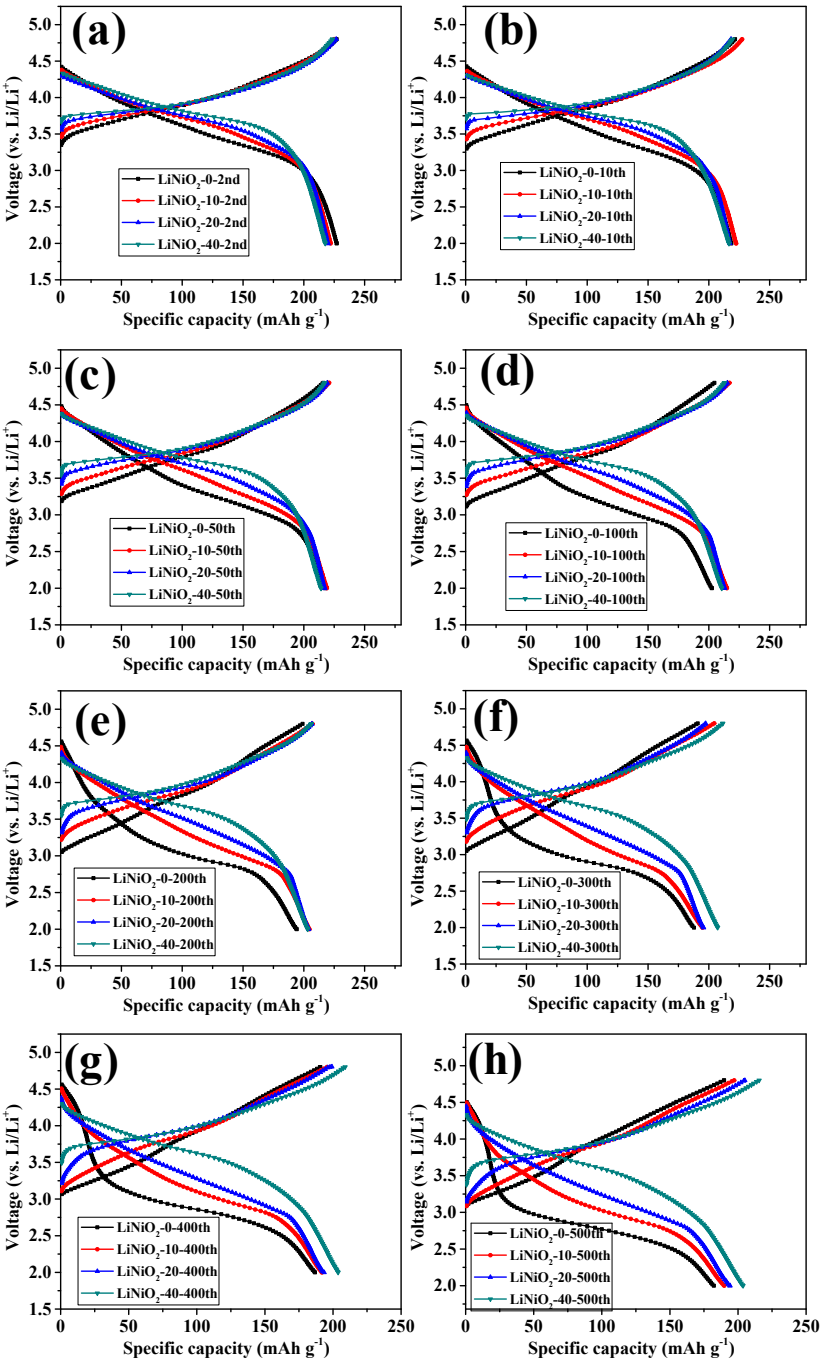

Fig. S2 Comparisons of charge and discharge curves of the $LiNiO_2$-0, $LiNiO_2$-10, $LiNiO_2$-20 and $LiNiO_2$-40 electrodes in the range of 2.0 to 4.8 V vs. Li/Li^+ at 200 mA g^{-1} under 30°C.

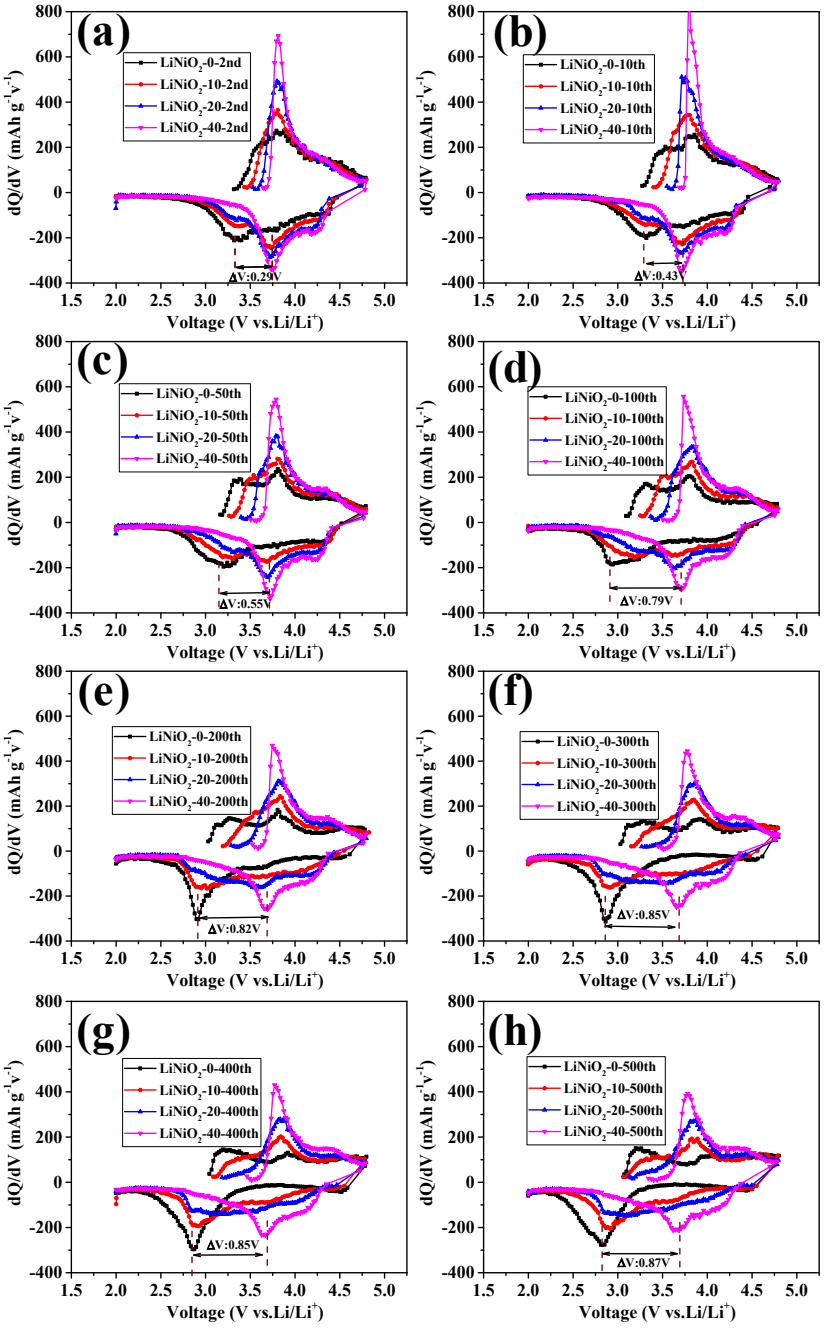

Fig. S3 Comparisons of the dQ/dV profiles for curves of the $LiNiO_2$-0, $LiNiO_2$-10, $LiNiO_2$-20 and $LiNiO_2$-40 electrodes in the range of 2.0 to 4.8 V vs. Li/Li^+ at 200 mA g^{-1} under 30°C.

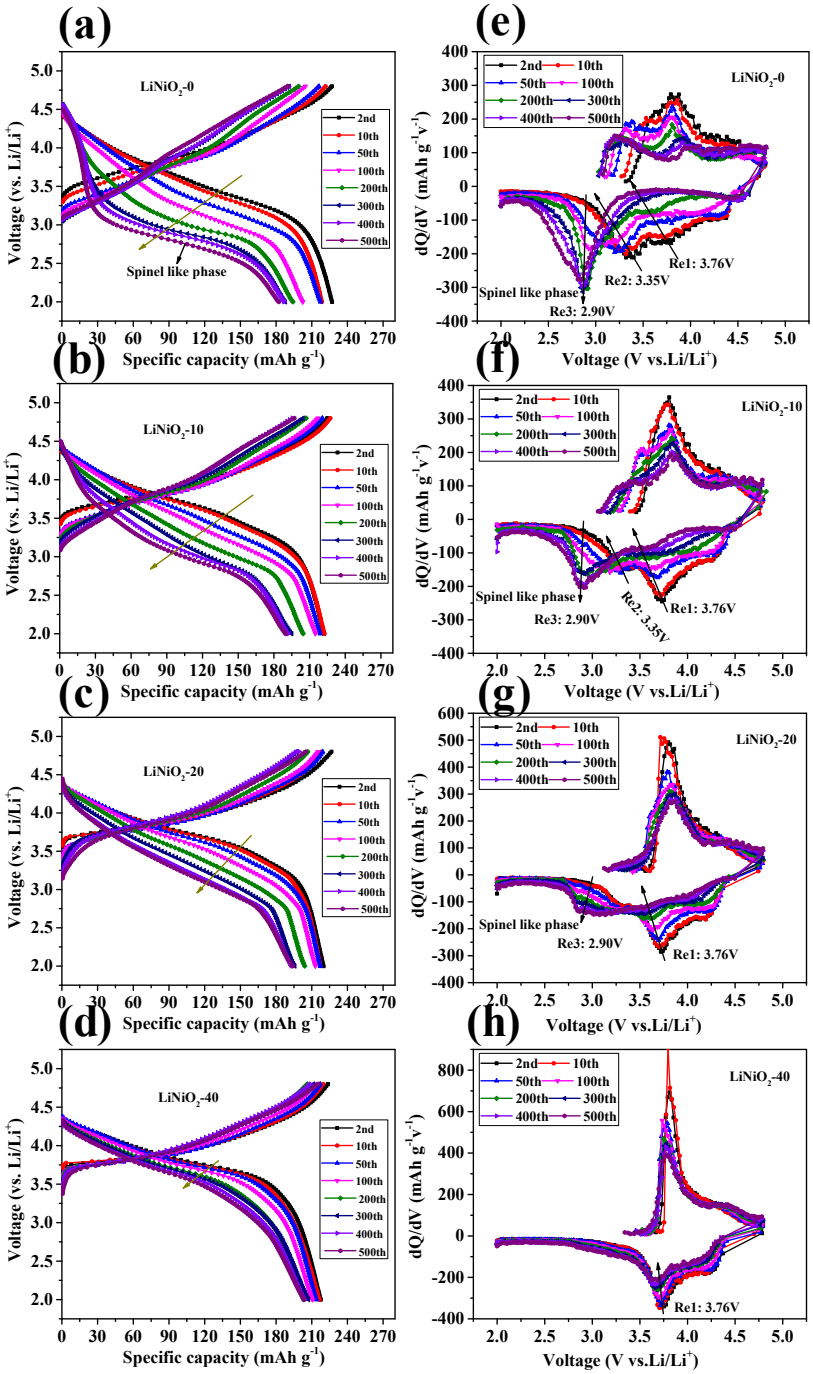

Fig. S4 (a-d) Charge and discharge curves of $LiNiO_2$-0, $LiNiO_2$-10, $LiNiO_2$-20 and $LiNiO_2$-40 electrodes in the range of 2.0 to 4.8 V vs. Li/Li^+ at 200 mA g^{-1} under 30°C. (e-h) dQ/dV profiles of $LiNiO_2$-0, $LiNiO_2$-10, $LiNiO_2$-20 and $LiNiO_2$-40 electrodes in the range of 2.0 to 4.8 V vs. Li/Li^+ at 200 mA g^{-1} under 30°C.

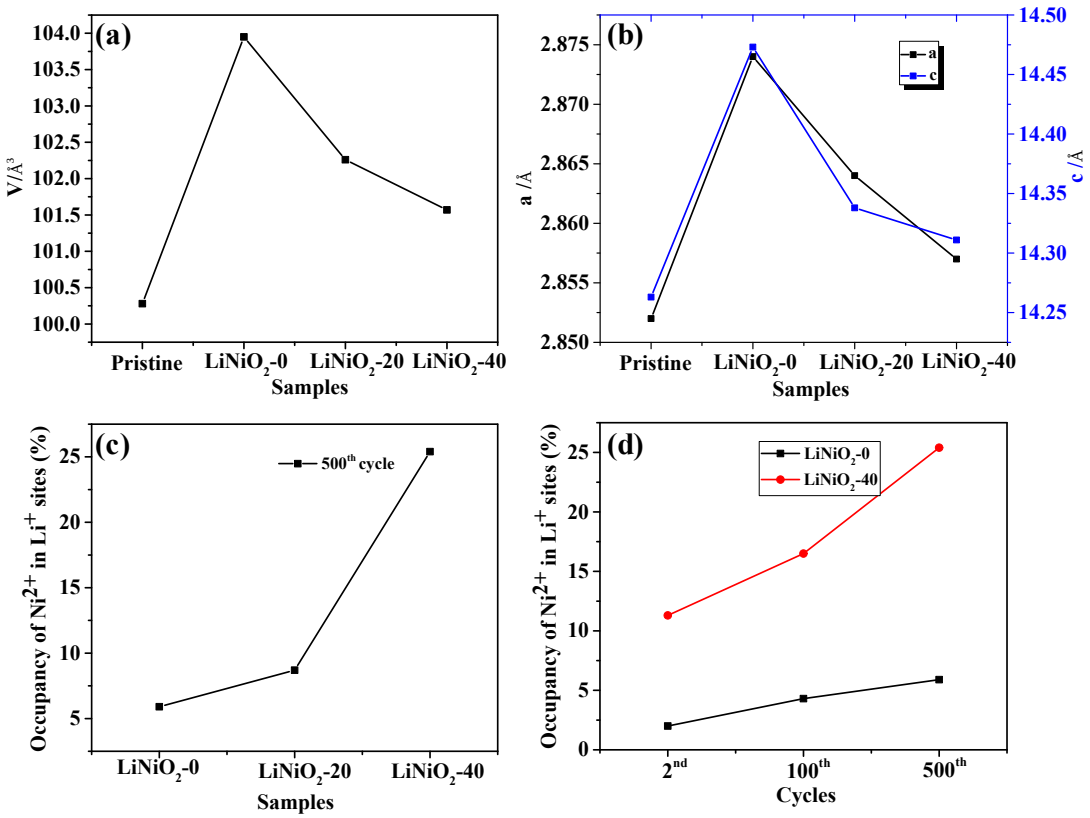

Fig. S5 (a, b) Refined lattice parameters of the $LiNiO_2$-0, $LiNiO_2$-20 and $LiNiO_2$-40 electrodes after 500 cycles. (c, d) The occupancy of the Ni^{2+} ions in the Li^+ ions sites of the $LiNiO_2$-0, $LiNiO_2$-20 and $LiNiO_2$-40 electrodes at different cycles.

Table S1 Experimental and theoretical results of Li/Ni/Co/Mn mole ratios of the $Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O_2$-$xLiNiO_2$ materials.

Samples	Li:Ni:Co:Mn	
	Theoretical	Experimental
$LiNiO_2$-0	1.20: 0.13:0.13:0.54	1.1950:0.1312:0.1291:0.5384
$LiNiO_2$-10	1.18: 0.217:0.117:0.486	1.1780:0.2190:0.1184:0.4832
$LiNiO_2$-20	1.16: 0.304:0.104:0.432	1.1540: 0.3071:0.1011:0.4301
$LiNiO_2$-40	1.12: 0.478:0.078:0.324	1.1151: 0.4802:0.0791:0.3239

Table S2 Crystallographic parameters obtained from the results of the Rietveld refinement: (a) for the $LiMO_2$ (R-3m) phase and (b) for the Li_2MO_3(C2/m) phase of the $LiNiO_2$-0 sample.

(a)$LiNiO_2$-0 (54.9 wt.%)			*R-3m*		χ^2=1.085 R_{wp}=0.0133 R_p=0.0099	
				a =b= 2.852 Å, c = 14.237 Å,		
atom	**site**	**x**	**y**	**z**	**Occ.$_{theo}$**	**Occ.$_{refined}$**
Li	3a	0	0	0	1.0000	0.9933
Ni	3a	0	0	0	0.0000	**0.0067**
Mn	3b	0	0	0.5	0.5400	0.5400
Ni	3b	0	0	0.5	0.1330	0.1267
Co	3b	0	0	0.5	0.1330	0.1330
Li	3b	0	0	0.5	0.2000	0.2033
O	6c	0	0	0.243	1.0000	1.0000
(b)$LiNiO_2$-0 (45.1 wt.%)			*C2/m*		χ^2=1.085 R_{wp}=0.0133 R_p=0.0099	
		a = 4.94 Å,	*b = 8.52 Å,*	*c = 5.022 Å,*	*β = 108.99°*	
atom	**site**	**x**	**y**	**z**	**Occ.$_{theo}$**	**Occ.$_{refined}$**
Mn	4g	0	0.173	0	0.6760	0.6760
Ni	4g	0	0.173	0	0.1620	0.1547
Co	4g	0	0.173	0	0.1620	0.1620
Li	4g	0	0.173	0	0.0000	0.0073
Ni	2b	0	0.5	0	0.0000	**0.1056**
Li	2b	0	0.5	0	1.0000	0.8944
Li	2c	0	0	0.5	1.0000	0.9803
Ni	2c	0	0	0.5	0.0000	**0.0197**
Ni	4h	0	0.715	0.5	0.0000	**0.0912**
Li	4h	0	0.715	0.5	1.0000	0.9088
O	4i	0.238	0	0.219	1.0000	1.0000
O	8j	0.253	0.320	0.258	1.0000	1.0000

Table S3 Crystallographic parameters obtained from the results of the Rietveld refinement: (a) for the $LiMO_2$ (R-3m) phase and (b) for the Li_2MO_3(C2/m) phase of the $LiNiO_2$-10 sample.

(a)$LiNiO_2$-10 (60.2 wt.%)		*R-3m*		χ^2=1.313 R_{wp}=0.0154 R_p=0.0115		
				a =b=2.858 Å, c = 14.240 Å,		
atom	**site**	**x**	**y**	**z**	**Occ.$_{theo}$**	**Occ.$_{refined}$**
Li	3a	0	0	0	1.0000	0.9888
Ni	3a	0	0	0	0.0000	**0.0112**
Mn	3b	0	0	0.5	0.4900	0.4900
Ni	3b	0	0	0.5	0.2091	0.1949
Co	3b	0	0	0.5	0.1181	0.1181
Li	3b	0	0	0.5	0.1800	0.1942
O	6c	0	0	0.244	1.0000	1.0000
(b)$LiNiO_2$-10 (39.8 wt.%)		*C2/m*		χ^2=1.313 R_{wp}=0.0154 R_p=0.0115		
		a = 4.974 Å, b = 8.499 Å,		*c = 5.034 Å,*	*β = 109.340°*	
atom	**site**	**x**	**y**	**z**	**Occ.$_{theo}$**	**Occ.$_{refined}$**
Mn	4g	0	0.1784	0	0.5970	0.5970
Ni	4g	0	0.1784	0	0.2590	0.2583
Co	4g	0	0.1784	0	0.1440	0.1440
Li	4g	0	0.1784	0	0.0000	0.0007
Ni	2b	0	0.5	0	0.0000	**0.1142**
Li	2b	0	0.5	0	1.0000	0.8858
Li	2c	0	0	0.5	1.0000	0.9596
Ni	2c	0	0	0.5	0.0000	**0.0404**
Ni	4h	0	0.702	0.5	0.0000	**0.1035**
Li	4h	0	0.702	0.5	1.0000	0.8965
O	4i	0.200	0	0.210	1.0000	1.0000
O	8j	0.261	0.312	0.269	1.0000	1.0000

Table S4 Crystallographic parameters obtained from the results of the Rietveld refinement: (a) for the $LiMO_2$ (R-3m) phase, (b) for the Li_2MO_3(C2/m) phase and (c) for the $LiNi_yMn_{2-y}O_4$ (Fd-3m) phase of the $LiNiO_2$-20 sample.

(a)$LiNiO_2$-20 (74.5 wt.%)		*R-3m*		χ^2=1.528 R_{wp}=0.0164 R_p=0.0123		
				a =b= 2.861 Å, c = 14.242 Å,		
atom	**site**	**x**	**y**	**z**	**Occ.$_{theo}$**	**Occ.$_{refined}$**
Li	3a	0	0	0	1.0000	0.9861
Ni	3a	0	0	0	0.0000	**0.0139**
Mn	3b	0	0	0.5	0.4500	0.4500
Ni	3b	0	0	0.5	0.2750	0.2611
Co	3b	0	0	0.5	0.1080	0.1080
Li	3b	0	0	0.5	0.1700	0.1839
O	6c	0	0	0.243	1.0000	1.0000
(b)$LiNiO_2$-20 (23.1 wt%)		*C2/m*		χ^2=1.528 R_{wp}=0.0164 R_p=0.0123		
		a = 4.961 Å, b = 8.516 Å, c = 5.0211 Å,		*β = 109.014°*		
atom	**site**	**x**	**y**	**z**	**Occ.$_{theo}$**	**Occ.$_{refined}$**
Mn	4g	0	0.175	0	0.5422	0.5422
Ni	4g	0	0.175	0	0.3310	0.3302
Co	4g	0	0.175	0	0.1301	0.1301
Li	4g	0	0.175	0	0.0000	0.0008
Ni	2b	0	0.5	0	0.0000	**0. 1160**
Li	2b	0	0.5	0	1.0000	0.884
Li	2c	0	0	0.5	1.0000	09262
Ni	2c	0	0	0.5	0.0000	**0.0738**
Ni	4h	0	0.698	0.5	0.0000	**0.1230**
Li	4h	0	0.698	0.5	1.0000	0.8770
O	4i	0.239	0	0.213	1.0000	1.0000
O	8j	0.250	0.321	0.265	1.0000	1.0000
(c)$LiNiO_2$-20 (2.4 wt.%)		*Fd-3m*		χ^2=1.528 R_{wp}=0.0164 R_p=0.0123		
				a =b=c= 7.74Å		
atom	**site**	**x**	**y**	**z**	**Occ.$_{theo}$**	**Occ.$_{refined}$**
Li	8a	0	0	0	1.0000	0.9069
Ni	8a	0.625	0.625	0.625	0.00	**0.0931**
Mn	16d	0.625	0.625	0.625	0.7500	0.7500
Ni	16d	0.625	0.625	0.625	0.2500	0.2210
Li	16d	0.625	0.625	0.625	0.0000	0.0290
O	32e	0.388	0.388	0.388	1.0000	1.0000

Table S5 Crystallographic parameters obtained from the results of the Rietveld refinement: (a) for the $LiMO_2$ (R-3m) phase, (b) for the Li_2MO_3(C2/m) phase and (c) for the $LiNi_yMn_{2-y}O_4$ (Fd-3m) phase of the $LiNiO_2$-40 sample.

(a)$LiNiO_2$-40 (78.7 wt.%)		*R-3m*		χ^2=1.769 R_{wp}=0.0168 R_p=0.0109		
				a =b= 2.868 Å, c = 14.253 Å,		
atom	**site**	**x**	**y**	**z**	**Occ.$_{theo}$**	**Occ.$_{refined}$**
Li	3a	0	0	0	1.0000	0.9770
Ni	3a	0	0	0	0.0000	**0.0230**
Mn	3b	0	0	0.5	0.3860	0.3860
Ni	3b	0	0	0.5	0.3790	0.3560
Co	3b	0	0	0.5	0.0950	0.0950
Li	3b	0	0	0.5	0.1400	0.1430
O	6c	0	0	0.243	1.0000	1.0000
(b)$LiNiO_2$-40 (15.2 wt.%)		*C2/m*		χ^2=1.769 R_{wp}=0.0168 R_p=0.0109		
		a = 5.021 Å, b = 8.374 Å,		*c = 4.962 Å,*	*β = 108.703°*	
atom	**site**	**x**	**y**	**z**	**Occ.$_{theo}$**	**Occ.$_{refined}$**
Mn	4g	0	0.168	0	0.4488	0.4488
Ni	4g	0	0.168	0	0.4406	0.4397
Co	4g	0	0.168	0	0.1106	0.1106
Li	4g	0	0.168	0	0.0000	0.0009
Ni	2b	0	0.5	0	0.0000	**0.1298**
Li	2b	0	0.5	0	1.0000	0.8944
Li	2c	0	0	0.5	1.0000	0.8901
Ni	2c	0	0	0.5	0.0000	**0.1099**
Ni	4h	0	0.687	0.5	0.0000	**0.1783**
Li	4h	0	0.687	0.5	1.0000	0.8217
O	4i	0.241	0	0.229	1.0000	1.0000
O	8j	0.274	0.325	0.285	1.0000	1.0000
(c)$LiNiO_2$-40 (6.1 wt.%)		*Fd-3m*		χ^2=1.769 R_{wp}=0.0168 R_p=0.0109		
				a =b=c= 7.74Å		
atom	**site**	**x**	**y**	**z**	**Occ.$_{theo}$**	**Occ.$_{refined}$**
Li	8a	0	0	0	1.0000	0.8575
Ni	8a	0.625	0.625	0.625	0.00	**0.1425**
Mn	16d	0.625	0.625	0.625	0.7500	0.7500
Ni	16d	0.625	0.625	0.625	0.2500	0.2330
Li	16d	0.625	0.625	0.625	0.0000	0.0170
O	32e	0.388	0.388	0.388	1.0000	1.0000