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Supporting Information

High performance P2 sodium layered oxides: an in-depth study into the effect of rationally selected stoichiometry

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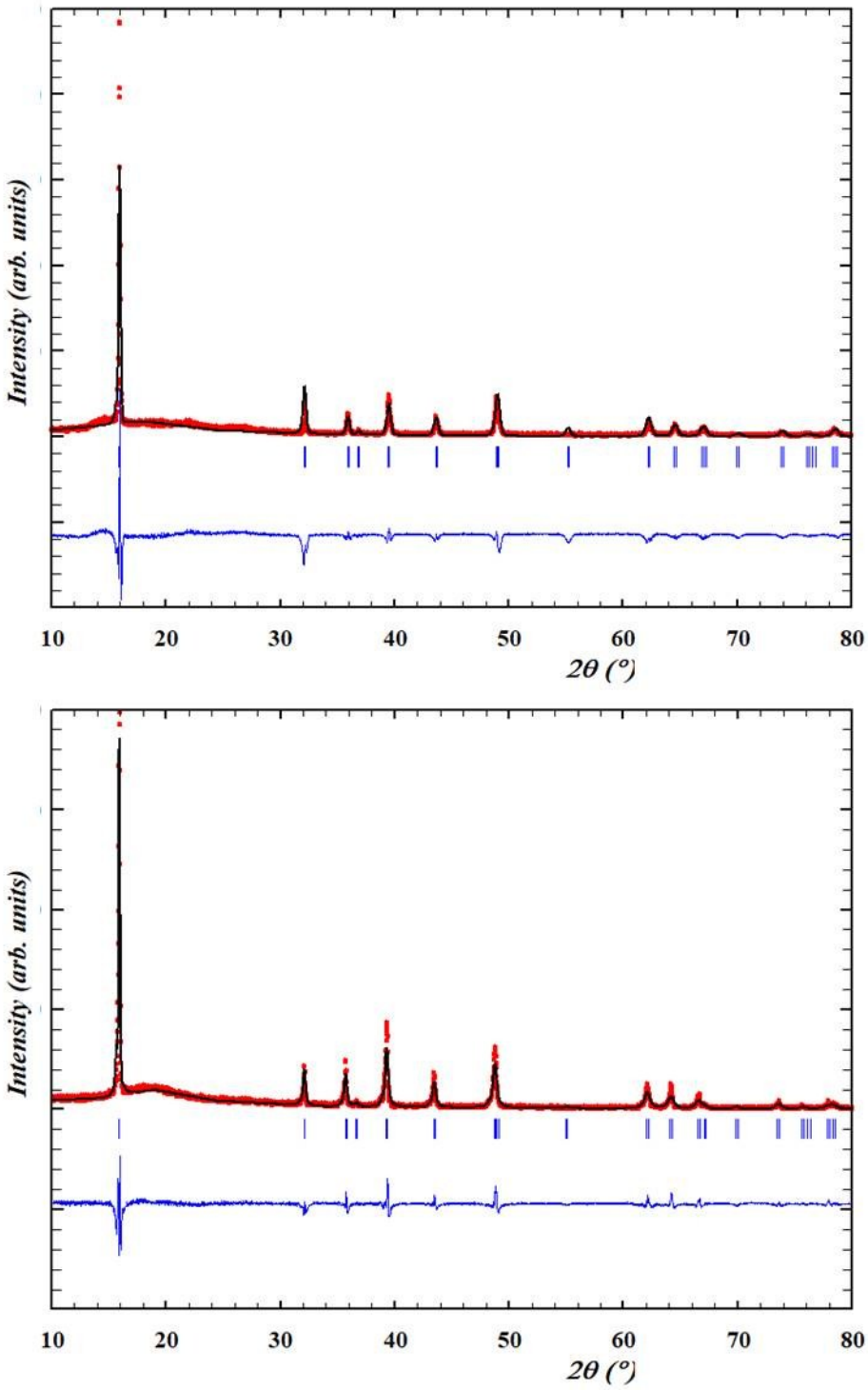

Figure S1. Structure and Le Bail fit for the XRD pattern of a) Ni10% and b) Ni20%. Data are shown as red circles, the calculated model as a black line through the data, and the difference between the data and the model as the blue line below the data.

Table S1a. Crystallographic parameters for P2- $Na_{2/3}Mn_{0.8}Fe_{0.05}Ti_{0.05}Ni_{0.1}O_2$ as determined from Rietveld analysis of neutron powder diffraction data ($P6_3/mmc$).

Atom	Wyckoff	X	y	z	SOF [a]	Isotropic ADP [a] (×100/Å^2)
Na(1)	2b	0	0	0.25	0.25(1)	6.6*
Na(2)	2d	1/3	2/3	0.75	0.37(2)	5.7*
Mn	2a	0	0	0	0.8	1.4*,#
Ni	2a	0	0	0	0.1	1.4*,#
Fe	2a	0	0	0	0.05	1.4*,#
Ti	2a	0	0	0	0.05	1.4*,#
O	4f	1/3	2/3	0.0915(1)	1	2.2*

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Refined alternatively to SOFs, refined and fixed. # Constrained to be equal. Space group $P6_3/mmc$, R_p = 4.2%, wR_p = 5.3%, a = 2.9015(1) Å, c =11.1833(7) Å.

Table S1b. Crystallographic parameters for P2- $Na_{2/3}Mn_{0.7}Fe_{0.05}Ti_{0.05}Ni_{0.2}O_2$ as determined from Rietveld analysis of neutron powder diffraction ($P6_3/mmc$).

Atom	Wyckoff	X	y	z	SOF [a]	Isotropic ADP [a] (×100/Å^2)
Na(1)	2b	0	0	0.25	0.23(1)	5.3*
Na(2)	2d	1/3	2/3	0.75	0.39(1)	4.8*
Mn	2a	0	0	0	0.7	1.5*,#
Ni	2a	0	0	0	0.2	1.5*,#
Fe	2a	0	0	0	0.05	1.5*,#
Ti	2a	0	0	0	0.05	1.5*,#
O	4f	1/3	2/3	0.0921(2)	1	1.6*

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Refined alternatively to SOFs, refined and fixed. # Constrained to be equal. Space group $P6_3/mmc$, R_p = 6.3%, wR_p = 8.8%, a = 2.89346(7) Å, c =11.2003(6) Å.

Table S2. Crystallographic parameters for P2- $Na_{0.61(9)}Mn_{0.76(3)}Ni_{0.24(5)}O_2$, used as a starting model for the Rietveld analysis of neutron powder diffraction data for P2- $Na_{2/3}Mn_{0.7}Fe_{0.05}Ti_{0.05}Ni_{0.2}O_2$ ($P6_3$).

Atom	Wyckoff	X	y	z	SOF [a]	Isotropic ADP [a, *] (×100/Å^2)
Na(1)	6c	0.310(5)	0.012(6)	0.372(2)	0.35(1)	2.3
Na(2)	2b	1/3	2/3	0.384(3)	0.50(2)	4.1
Na(3)	2b	2/3	1/3	0.350(3)	0.28(2)	1.1
Mn/Ni(1)	2a	0	0	0.12(1)	0.80(1)/0.20(1)	1.6
Mn/Ni(2)	2b	1/3	2/3	0.0840(7)	1.0/0.0	2.6
Mn/Ni(3)	2b	1/3	2/3	0.5828(8)	0.47(1)/0.53(1)	3.2
O(1)	6c	0.334(2)	0.0123(8)	-0.292(1)	1.0	0.57
O(2)	6c	0.689(2)	0.022(1)	0.523(1)	1.0	1.8

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Refined alternatively to SOFs, refined and fixed. Space group $P6_3$, R_p = 4.2%, wR_p = 5.4%, a = 5.0121(1)Å, c =11.1992(4)Å.

Table S3. Refinement statistics as determined from Rietveld analysis of neutron powder diffraction data upon introduction of Fe and Ti onto different sites of the starting model, P2- $Na_{0.61}Mn_{0.76}Ni_{0.24}O_2$. Site occupancy factors for Mn/Ni were adjusted to achieve the composition P2- $Na_{0.61}Mn_{0.7}Ti_{0.05}Fe_{0.05}Ni_{0.2}O_2$ (space group $P6_3$).

	Model 1	Model 2*	Model 3	Model 4	Model 5	Model 6	Model 7	Model 8	Model 9	Model 10
2a	Fe, Ti			Fe	Fe	Ti	Ti			0.5(Fe, Ti)
2b		Fe, Ti		Ti		Fe		Fe	Ti	
2b'			Fe, Ti		Ti		Fe	Ti	Fe	0.5(Fe, Ti)
wR_p	5.38	-	5.40	5.37 (5.33)	5.61	6.51	5.67	6.88	5.37 (5.37)	5.39
R_p	4.24	-	4.25	4.24 (4.21)	4.44	5.01	4.37	5.20	4.24 (4.23)	4.24
χ^2	5.35	-	5.38	5.33 (5.28)	5.80	7.81	5.90	8.74	5.33 (5.33)	5.35

*Incompatible combination to achieve the composition P2- $Na_{0.61}Mn_{0.7}Ti_{0.05}Fe_{0.05}Ni_{0.2}O_2$. Highlighted columns show the statistically best models, further optimised values are given in brackets.

Table S4. Crystallographic parameters for P2- $Na_{0.6(1)}Mn_{0.68(4)}Ti_{0.04(1)}Fe_{0.04(1)}Ni_{0.20(2)}O_2$ as determined from Rietveld analysis of neutron powder diffraction data ($P6_3$, model 4).

Atom	Wyckoff	X	y	z	SOF [a]	Isotropic ADP [a, *] (×100/Å^2)
Na(1)	6c	0.306(5)	0.012(6)	0.372(2)	0.35(1)	2.3
Na(2)	2b	1/3	2/3	0.386(3)	0.54(2)	4.1
Na(3)	2b	2/3	1/3	0.353(4)	0.24(2)	1.3
Mn/Ni/Fe(1)	2a	0	0	0.12(1)	0.75(2)/0.05(1)/0.13(1)	1.6
Mn/Ni/Ti(2)	2b	1/3	2/3	0.083(2)	0.80(1)/0.0/0.13(1)	2.0
Mn/Ni(3)	2b	1/3	2/3	0.582(2)	0.5(1)/0.53(1)	2.0
O(1)	6c	0.335(2)	0.0126(9)	-0.293(3)	1.0	0.57
O(2)	6c	0.688(2)	0.022(1)	0.522(1)	1.0	1.9

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Refined alternatively to SOFs, refined and fixed. [#] Constrained to be equal. Space group $P6_3$, R_p = 4.2%, wR_p = 5.3%, a = 5.0123(1)Å, c =11.1991(4)Å.

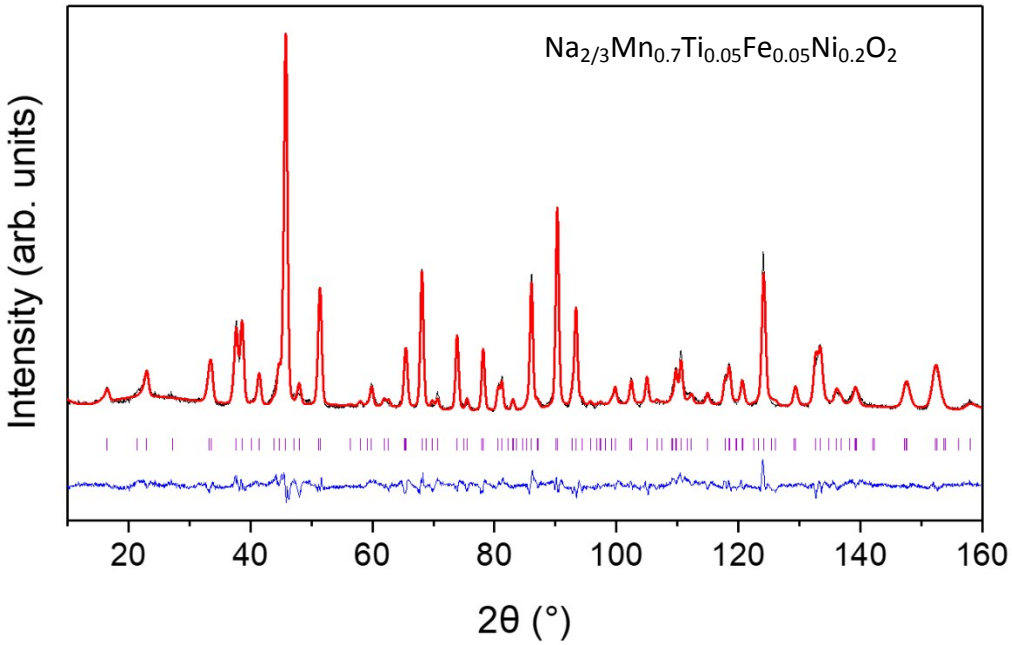

Figure S2. Rietveld refined fit, using a $P6_3$ unit cell, of the neutron diffraction data collected at room temperature for the pristine P2- $Na_{2/3}Mn_{0.7}Fe_{0.05}Ti_{0.05}Ni_{0.2}O_2$ powder. Observed, calculated and difference are shown by a solid black line, a solid red line and a solid blue line respectively.

Table S5. Crystallographic parameters for P2- $Na_{0.6(2)}Mn_{0.91(1)}Ni_{0.09(4)}O_2$, used as a starting model for the Rietveld analysis of neutron powder diffraction data for P2- $Na_{2/3}Mn_{0.8}Fe_{0.05}Ti_{0.05}Ni_{0.1}O_2$ ($P6_3$).

Atom	Wyckoff	X	y	z	SOF [a]	Isotropic ADP [a, #] (×100/Å^2)
Na(1)	6c	0.345(5)	0.057(3)	0.355(5)	0.36(1)	2.7
Na(2)	2b	1/3	2/3	0.370(7)	0.58(4)	5.1
Na(3)	2b	2/3	1/3	0.35(2)	0.12(3)	1.5
Mn/Ni(1)	2a	0	0	0.12*	1.0/0.0	2.7
Mn/Ni(2)	2b	1/3	2/3	0.0840*	1.0/0.0	9.6
Mn/Ni(3)	2b	1/3	2/3	0.583*	0.73(1)/0.27(1)	3.2

O(1)	6c	0.333(2)	0.0071(3)	-0.296(3)	1.0	1.5
O(2)	6c	0.683(2)	0.014(2)	0.521(3)	1.0	2.0

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). [#] Refined alternatively to SOFs, refined and fixed. Space group $P6_3$, R_p = 3.2%, wR_p = 4.1%, a = 5.0258(1)Å, c =11.1840(5)Å. * Fixed to values from P2-$Na_{0.61}Mn_{0.76}Ni_{0.24}O_2$ refinement due to tendency of atoms to drift.

Table S6. Refinement statistics as determined from Rietveld analysis of neutron powder diffraction data upon introduction of Fe and Ti onto different sites of the starting model, P2- $Na_{0.59}Mn_{0.91}Ni_{0.09}O_2$. Site occupancy factors for Mn/Ni were adjusted to achieve the composition P2- $Na_{0.59}Mn_{0.8}Ti_{0.05}Fe_{0.05}Ni_{0.1}O_2$ (space group $P6_3$).

	Model 1	Model 2	Model 3	Model 4	Model 5	Model 6	Model 7	Model 8	Model 9	Model 10
2a	Fe, Ti			Fe	Fe	Ti	Ti			0.5(Fe, Ti)
2b		Fe, Ti		Ti		Fe		Fe	Ti	
2b'			Fe, Ti		Ti		Fe	Ti	Fe	0.5(Fe, Ti)
wR_p	4.42 (4.28)	4.43 (4.30)	4.95	4.68	4.69	4.42 (4.29)	4.93	4.43 (4.40)	4.91	4.65
R_p	3.44 (3.37)	3.44 (3.32)	3.83	3.58	3.59	3.43 (3.33)	3.81	3.44 (3.39)	3.8	3.58
χ^2	3.43 (3.21)	3.44 (3.25)	4.29	3.85	3.86	3.43 (3.25)	4.25	3.44 (3.40)	4.23	3.79

Highlighted columns show the statistically best models, further optimised values are given in brackets.

Table S7. Crystallographic parameters for P2- $Na_{0.59}Mn_{0.81}Ti_{0.05}Fe_{0.05}Ni_{0.09}O_2$* as determined from Rietveld analysis of neutron powder diffraction data ($P6_3$, model 1).

Atom	Wyckoff	X	y	z	SOF [a, *]	Isotropic ADP [a] (×100/Å^2)
Na(1)	6c	0.345	0.057	0.355	0.36	2.7
Na(2)	2b	1/3	2/3	0.363	0.58	5.1
Na(3)	2b	2/3	1/3	0.35	0.12	1.5
Mn/Ni/Fe/Ti(1)	2a	0	0	0.12	0.70/0.0/0.15/0.15	2.7
Mn/Ni(2)	2b	1/3	2/3	0.0840	1.0/0.0	9.6
Mn/Ni(3)	2b	1/3	2/3	0.583	0.73/0.27	3.2
O(1)	6c	0.337(2)	0.009(2)	-0.302(2)	1.0	1.0
O(2)	6c	0.688(1)	0.017(1)	0.513(2)	1.0	2.9

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). Space group $P6_3$, R_p = 3.4%, wR_p = 4.3%, a = 5.0265(2)Å, c =11.1834(6)Å. * Values fixed for refinement, therefore no errors are given.

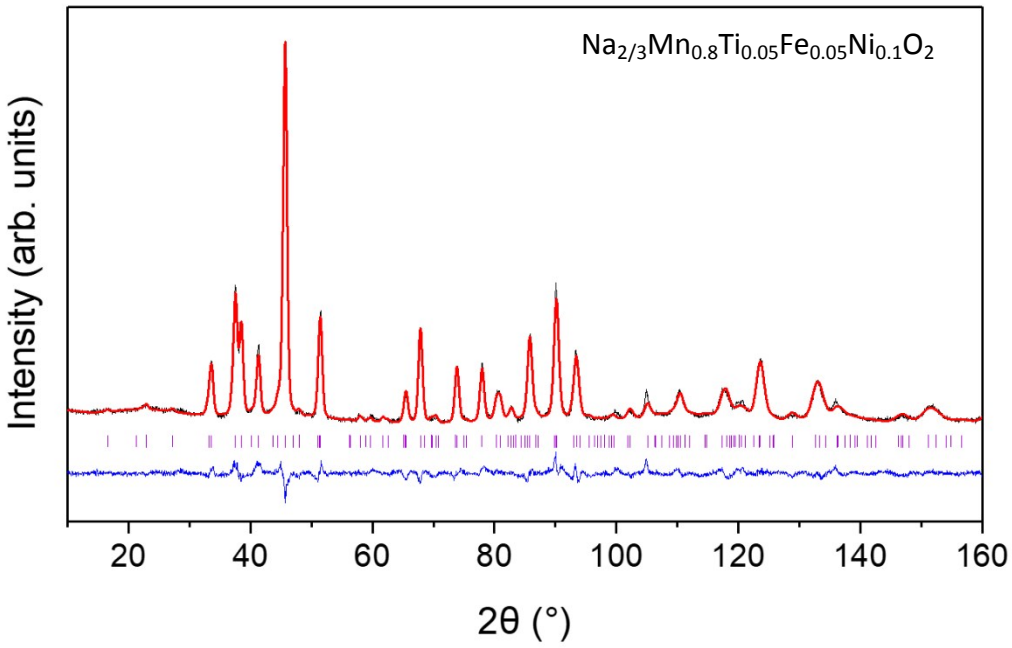

Figure S3. Rietveld refined fit, using a $P6_3$ unit cell, of the neutron diffraction data collected at room temperature for the pristine P2- $Na_{2/3}Mn_{0.8}Fe_{0.05}Ti_{0.05}Ni_{0.1}O_2$ powder. Observed, calculated and difference are shown by a solid black line, a solid red line and a solid blue line respectively.

Table S8. Crystallographic parameters for P2- $Na_{2/3}Mn_{0.8}Fe_{0.05}Ti_{0.05}Ni_{0.1}O_2$ as determined from Rietveld analysis of *operando* XRD data before cycling.

Atom	Wyckoff	x	y	z	SOF [a]	Isotropic ADP [a] (×100/Å^2)
Na(1)	2b	0	0	0.25	0.10(1)	4.8*
Na(2)	2d	1/3	2/3	0.75	0.48(1)	4.8*
Mn	2a	0	0	0	0.8	2.9*,#
Fe	2a	0	0	0	0.05	2.9*,#
Ti	2a	0	0	0	0.05	2.9*,#
Ni	2a	0	0	0	0.1	2.9*,#
O	4f	1/3	2/3	0.1013(8)	1	3.1*

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Refined alternatively to SOFs, refined and fixed. # Constrained to be equal. Space group $P6_3/mmc$, 13 refinement parameters, $\chi^2 = 2.31$ $R_p = 21.4\%$, $wR_p = 27.3\%$, $a = 2.8984(7)$ Å, $c = 11.2132(8)$ Å.

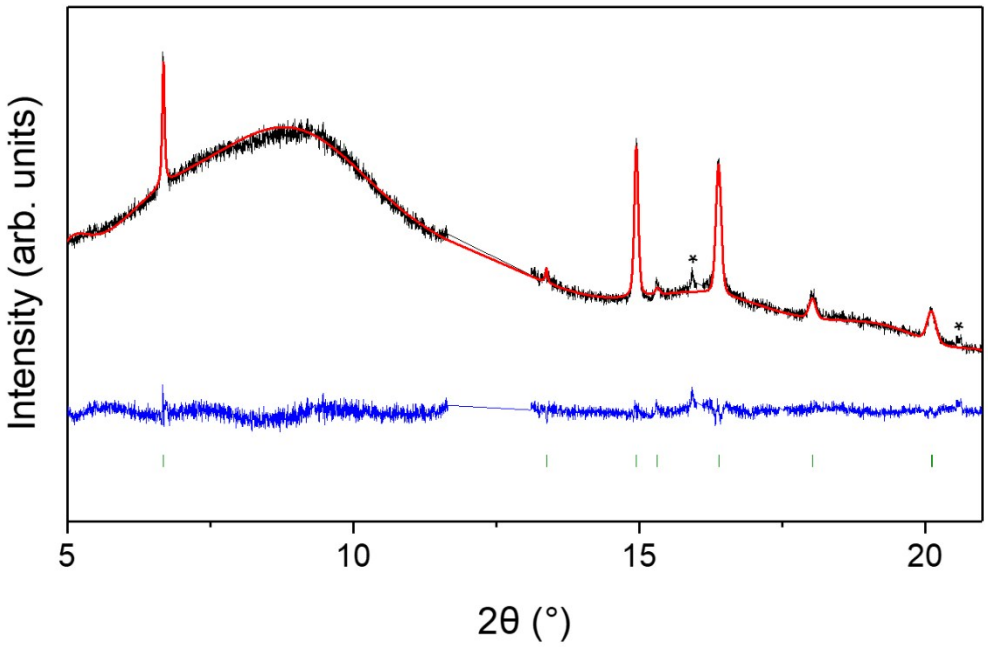

Figure S4. Rietveld refined fit of the P2- $Na_{2/3}Mn_{0.8}Fe_{0.05}Ti_{0.05}Ni_{0.1}O_2$ electrode in the operando coin cell. Observed, calculated and difference are shown by a solid black line, a solid red line and a solid blue line respectively. Reflections corresponding to Na and Al-foil are excluded, asterisks indicate electrochemically inactive reflections.

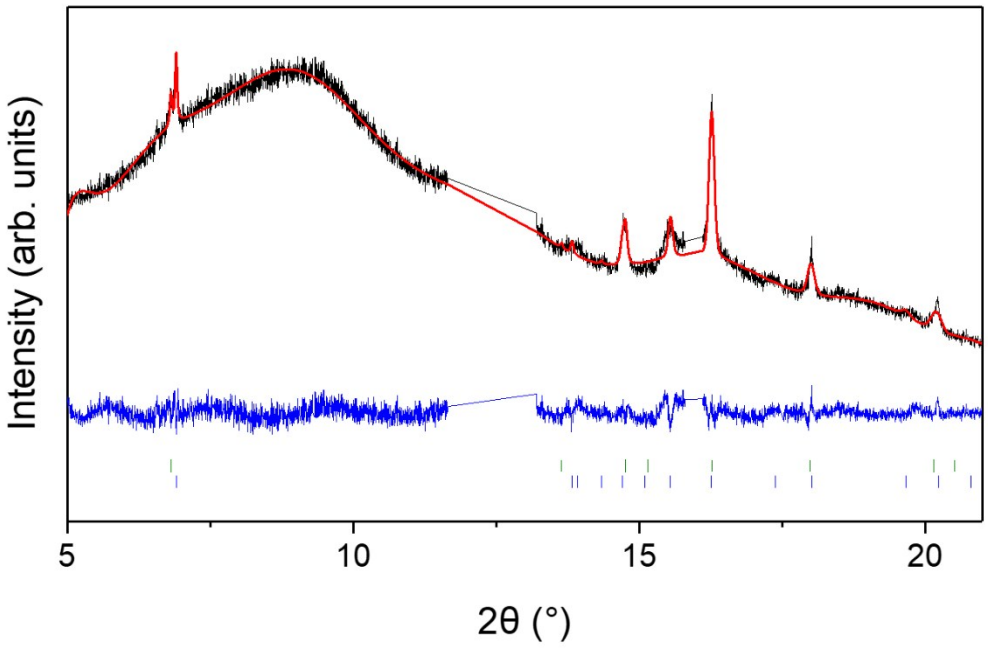

Figure S5. Rietveld refined fit of the P2/P'2- $Na_{2/3}Mn_{0.8}Fe_{0.05}Ti_{0.05}Ni_{0.1}O_2$ electrode in the operando coin cell at 1.5 V. Observed, calculated and difference are shown by a solid black line, a solid red line and a solid blue line respectively. $P6_3/mmc$ and Cmcm reflections are shown in green and blue respectively. Reflections corresponding to Na and Al-foil and electrochemically inactive reflections are excluded.

Table S9. Crystallographic parameters for P2- $Na_{2/3}Mn_{0.8}Fe_{0.05}Ti_{0.05}Ni_{0.1}O_2$ as determined from Rietveld analysis of *operando* XRD data at 1.5 V.

Atom	Wyckoff	x	y	z	SOF [a]	Isotropic ADP [a] (×100/Å²)
Na(1)	2b	0	0	0.25	0.12(7)	5.0*
Na(2)	2d	1/3	2/3	0.75	0.92(8)	5.0*
Mn	2a	0	0	0	0.8	2.9*,#
Fe	2a	0	0	0	0.05	2.9*,#
Ti	2a	0	0	0	0.05	2.9*,#
Ni	2a	0	0	0	0.1	2.9*,#
O	4f	1/3	2/3	0.105(5)	1	3.1*

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Refined alternatively to SOFs, refined and fixed. # Constrained to be equal. Space group $P6_3/mmc$, R_p = 2.3%, wR_p = 4.1%, a = 2.9374(3) Å, c =10.981(4) Å.

Table S10. Crystallographic parameters for P'2- $Na_{2/3}Mn_{0.8}Fe_{0.05}Ti_{0.05}Ni_{0.1}O_2$ as determined from Rietveld analysis of *operando* XRD data at 1.5 V.

Atom	Wyckoff	X	y	z	SOF [a]	Isotropic ADP [a] (×100/Å²)
Na	4c	0	0.347(3)	0.25	0.95(4)	1.5*
Mn	4a	0	0	0	0.8	5.5*,#
Fe	4a	0	0	0	0.05	5.5*,#
Ti	4a	0	0	0	0.05	5.5*,#
Ni	4a	0	0	0	0.1	5.5*,#
O	8f	0	0.656(4)	0.870(1)	1	1.3*

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Refined alternatively to SOFs, refined and fixed. # Constrained to be equal. Space group *Cmcm*, R_p = 2.3%, wR_p = 4.1%, a = 2.8950(5) Å, c =10.853(2) Å.

Table S11. Crystallographic parameters for P2- $Na_{2/3}Mn_{0.7}Fe_{0.05}Ti_{0.05}Ni_{0.2}O_2$ as determined from Rietveld analysis of *operando* XRD data before cycling.

Atom	Wyckoff	x	y	z	SOF [a]	Isotropic ADP [a] (×100/Å²)
Na(1)	2b	0	0	0.25	0.20(1)	7.2*
Na(2)	2d	1/3	2/3	0.75	0.33(1)	7.2*
Mn	2a	0	0	0	0.8	1.0*,#
Fe	2a	0	0	0	0.05	1.0*,#
Ti	2a	0	0	0	0.05	1.0*,#
Ni	2a	0	0	0	0.1	1.0*,#
O	4f	1/3	2/3	0.0967(7)	1	2.4*

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Refined alternatively to SOFs, refined and fixed. # Constrained to be equal. Space group $P6_3/mmc$, R_p = 2.3%, wR_p = 3.0%, a = 2.8948(3) Å, c =11.2040(3) Å.

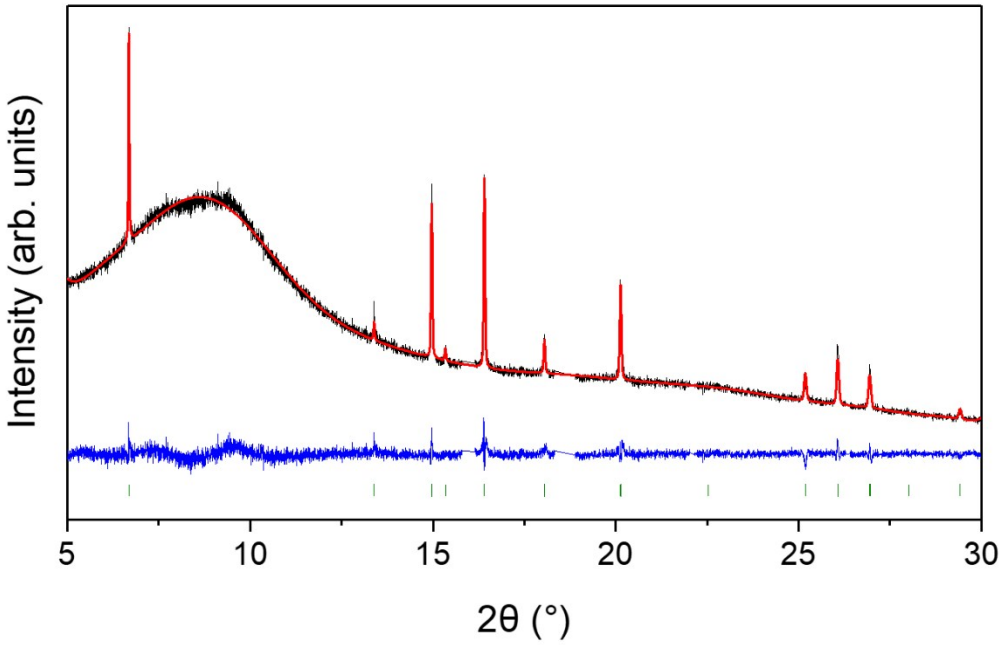

Figure S6. Rietveld refined fit of the P2- $Na_{2/3}Mn_{0.7}Fe_{0.05}Ti_{0.05}Ni_{0.2}O_2$ electrode in the operando coin cell. Observed, calculated and difference are shown by a solid black line, a solid red line and a solid blue line respectively. Reflections corresponding to Al-foil are excluded, asterisks indicate electrochemically inactive reflections.

Table S12. Compositional data obtained via ICP-OES for the synthesized materials.

ICP-OES					
Material	Elemental ratio				
	Na	Mn	Fe	Ti	Ni
Ni 10%	0.63	0.8	0.027	0.045	0.082
Ni 20%	0.63	0.7	0.0172	0.049	0.176

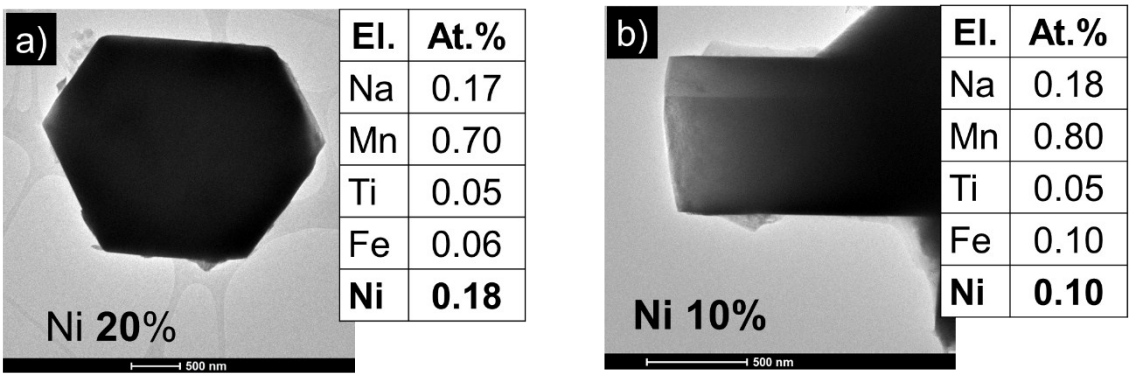

Figure S7. Characterization of composition by EDX-TEM for a Ni20% (a) and a Ni10% (b) particles. The atomic percentages (At.%) were normalized with respect to the manganese at.%.

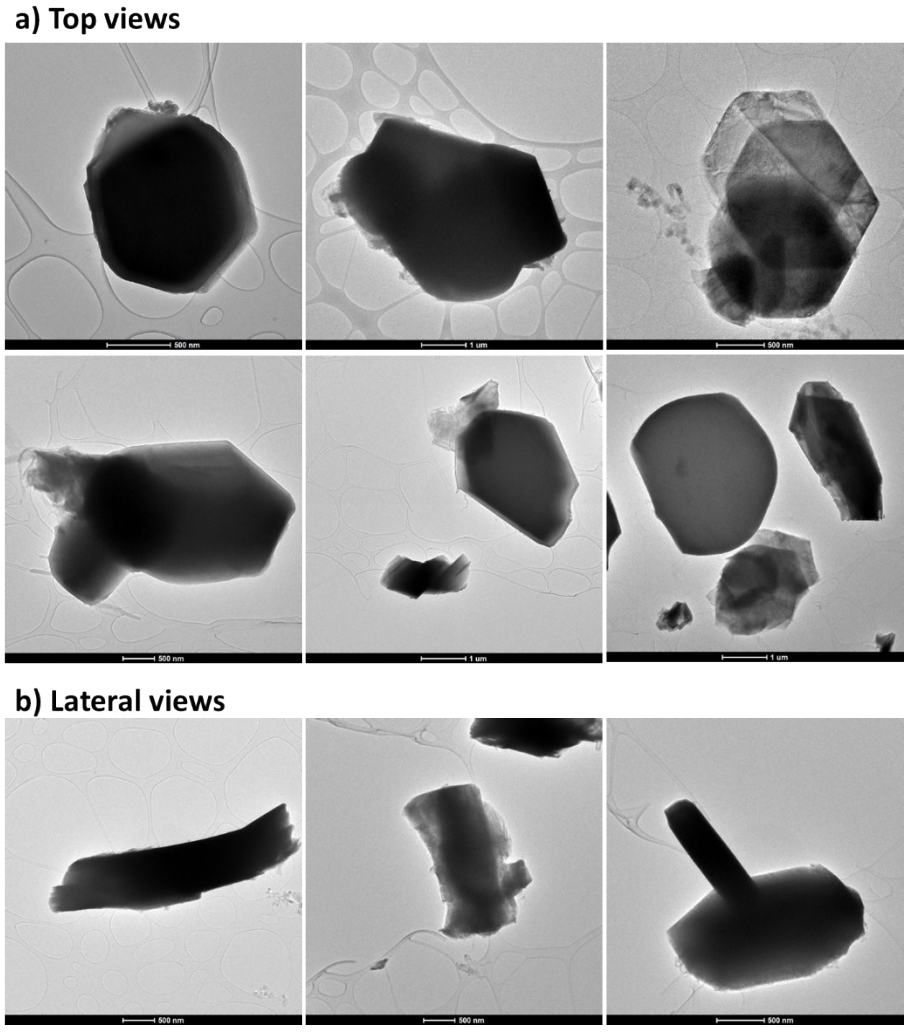

Figure S8. TEM on different Ni20% single particles. Top views reveal the presence of facets in the particles and the hexagonal shape in the ones ranging on sizes around hundreds of nanometers, Lateral view corroborate the flake-like shape of the particles.

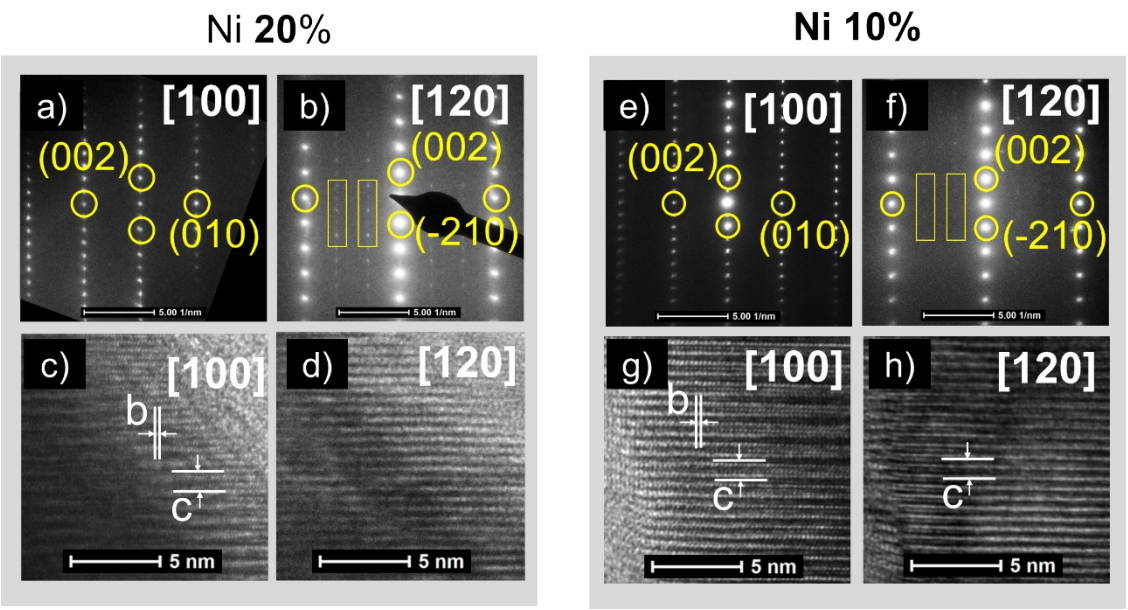

Figure S9. SAED and HRTEM for Ni20% (a-d) and Ni 10%(e-h) taken at two zone of axis [100] and [120]. SAEDs at [120] show some extra peaks at 1/3 and 2/3 of the distance between the origin and the (-210) reflection, as indicated by the rectangles in the patterns.

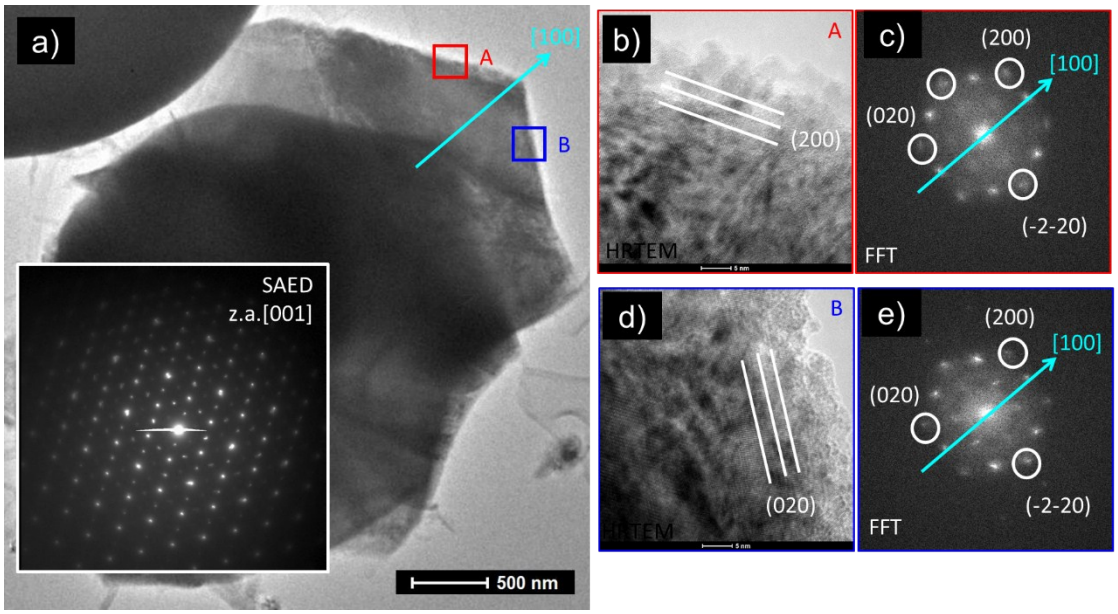

Figure S10. a) Top view TEM image of a Ni20% particle with a SAED (inset) taken in an area close to the particle edge. (b,d) HRTEM at A and B positions and their FFT (c,d) respectively. Indexation of FFTs shows that the facets of particles correspond the planes (h00) and (0k0).

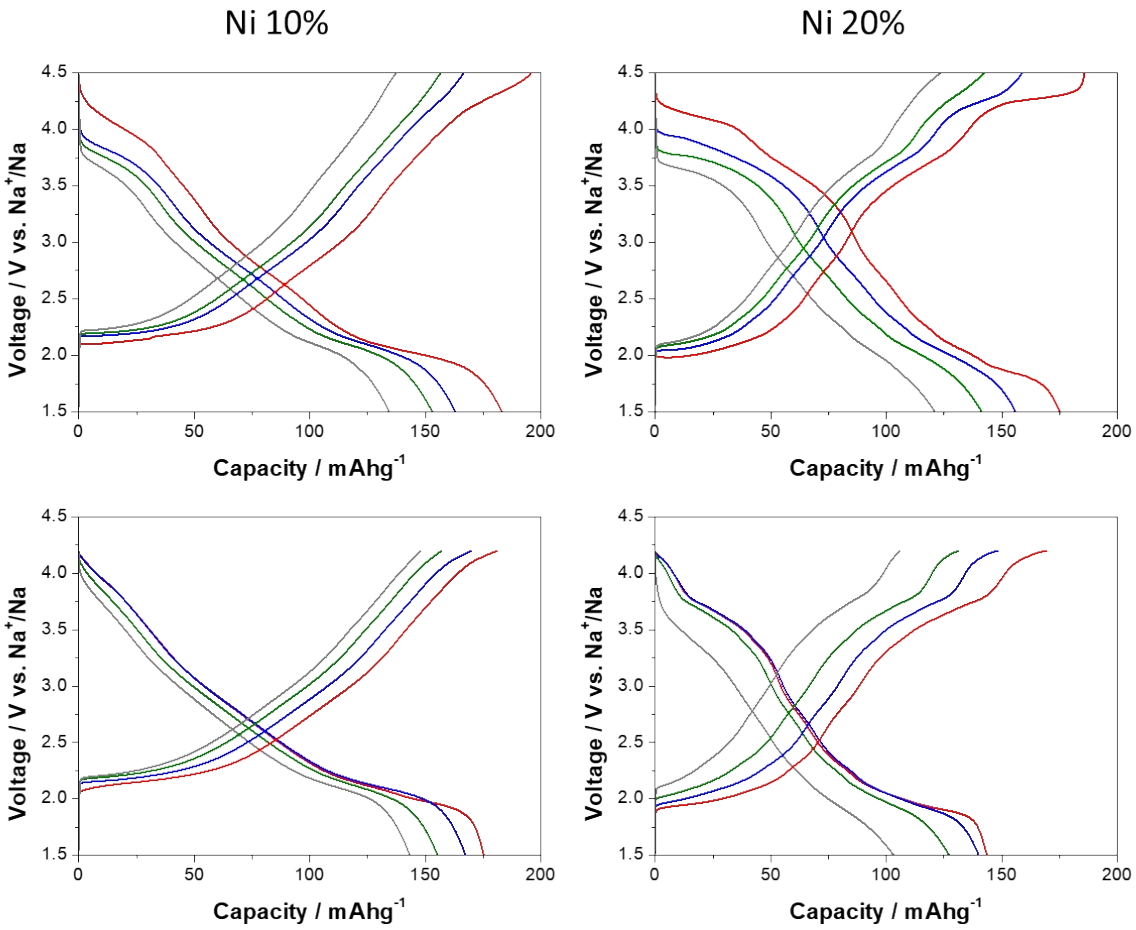

Figure S11. Load curves of Ni 10% and 20% taken at cycles 2, 10, 25, and 50.

Table S13. Tabulated values for Ni 10% and Ni 20%, at C/10 and 1C for a range of voltage windows, including: discharge capacities; cycle 50 capacity retention figures; 2nd cycle charge and discharge energy densities; 2nd cycle charge capacity values and the average voltages calculated from these.

Material		Voltage window (V)	Discharge capacity at cycle ($mAhg^{-1}$) 2	10	50	Cycle 50 capacity retention (%)	2nd cycle charge capacity ($mAhg^{-1}$)	Energy density charge ($Wh\ kg^{-1}$)	Energy density discharge ($Wh\ kg^{-1}$)	Average Voltage (V)
Ni 10%	C/10	1.5 - 4.2	175.24	167.44	143.38	81.82	181.10	511.05	468.64	2.82
		1.5 - 4.5	183.06	162.93	134.35	73.39	195.86	586.02	506.85	2.99
Ni 20%	C/10	1.5 - 4.2	143.63	140.07	103.37	71.97	169.32	494.10	390.74	2.92
		1.5 - 4.5	175.08	155.87	121.07	69.15	185.89	588.89	520.83	3.17
Ni 10%	1C	1.5 - 4.2	149.00	136.17	115.46	77.49	154.85	446.27	384.07	2.88
		1.5 - 4.5	163.08	147.50	87.43	53.61	180.93	597.89	462.98	3.30
Ni 20%	1C	1.5 - 4.2	71.86	73.30	73.12	101.75	132.045	393.94	345.89	2.98
		1.5 - 4.5	163.09	143.32	88.13	54.04	170.07	560.69	492.14	3.30

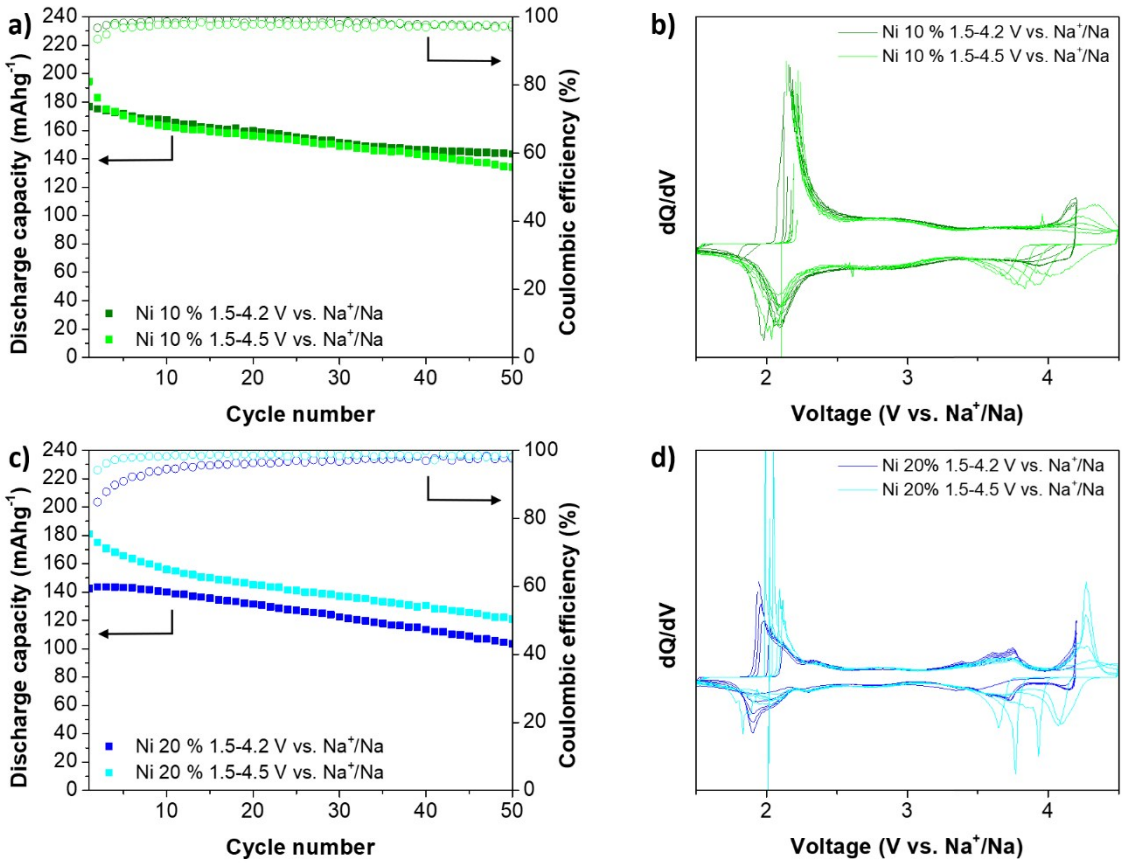

Figure S12. a) and c) cyclability plots for Ni 10% and 20% at C/10 using discharge capacities; b) and d) dQ/dV plots of cycles 2, 5, 10, 25, and 50, for Ni 10% and 20% at C/10.

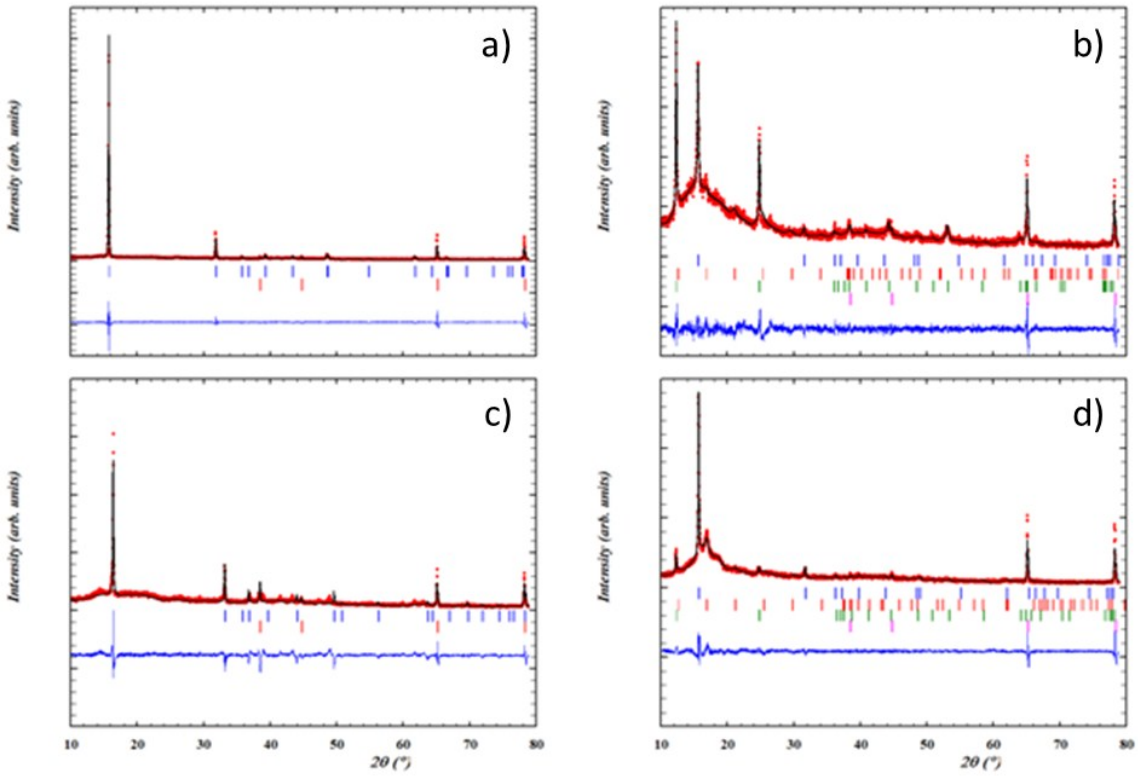

Figure S13. Le Bail fit of the Ni 10% *ex situ* X-Ray Diffractograms a) pristine electrode, b) charged to 4.2V, c) charged to 4.2V and discharged to 1.5V d)charged to 4.5V. Aluminium current collector has been refined as one more phase.

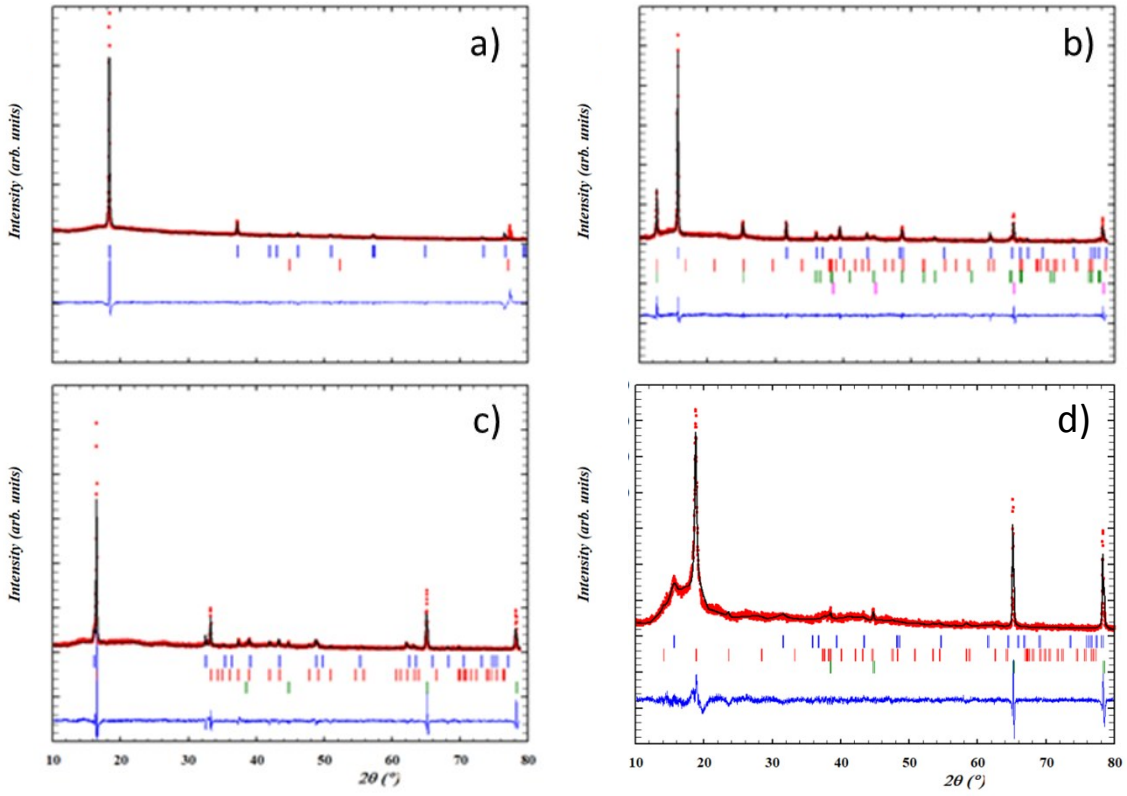

Figure S14. Le Bail fit of the Ni 20% *ex situ* X-Ray Diffractograms a) pristine electrode, b) charged to 4.2V, c) charged to 4.2V and discharged to 1.5V, d) charged to 4.5V.

Table S14. Refined parameters of Ni 10%:

a) pristine and charged states.

Ni 10%	Phase 1		Phase 2		Phase 3	
	P2 (S.G. $P6_3/mmc$) α=β=90 ; γ=120		OP4 (S.G. P-6m2) α=β=90 ; γ=120		Hydrated (S.G. $P6_3/mmc$) α=β=90 ; γ=120	
	Cell parameters		Cell parameters		Cell parameters	
	a	c	a	c	a	c
Pristine	2.8986(8)	11.241(3)	-	-	-	-
Charged to 4.2V	2.872(4)	11.346(2)	2.736(1)	21.086(2)	2.874(1)	14.344(1)
Charged to 4.5V	2.859(2)	11.279(1)	2.777(6)	20.97(2)	2.845(5)	14.373(6)

b) discharged state.

Ni 10%	Phase 1		Phase 2		
	P2 (S.G. $P6_3/mmc$) α=β=90 ; γ=120		P´2 (S.G. Cmcm) α=β=γ=90		
	Cell parameters		Cell parameters		
	a	c	a	b	c
Discharged to 1.5V	2.889(1)	10.7884(1)	2.8915(7)	5.404(1)	10.919(2)

Table S15. Refined parameters of Ni 20%:

a) pristine and charged states.

Ni 20%	Phase 1		Phase 2		Phase 3	
	P2 (S.G. $P6_3/mmc$) α=β=90 ; γ=120		OP4 (S.G. P-6m2) α=β=90 ; γ=120		Hydrated (S.G. $P6_3/mmc$) α=β=90 ; γ=120	
	Cell parameters		Cell parameters		Cell parameters	
	a	c	a	c	a	C
Pristine	2.8881(7)	11.221(2)	-	-	-	-
Charged to 4.2V	2.8761(2)	11.3188(6)	2.7434(2)	21.1492(8)	2.8851(7)	14.118(3)
Charged to 4.5V	2.89(1)	11.34(3)	2.786(4)	18.86(1)	-	-

b) discharged state.

Ni 20%	Phase 1		Phase 2		
	P2 (S.G. $P6_3/mmc$) α=β=90 ; γ=120		P´2 (S.G. Cmcm) α=β=γ=90		
	Cell parameters		Cell parameters		
	a	c	a	b	c
Discharged to 1.5V	2.933(1)	10.999(2)	2.916(1)	5.387(1)	10.762(1)

Figures S12 and **S13** show the structural analysis carried out on the X-Ray Diffraction data of the Ni 10% and Ni 20% pristine electrodes, charged to 4.2 and 4.5 V and discharged to 1.5 V. Aluminium reflections due to the current have been found in all the diffractograms and has been refined as one more phase. Ni 10% and Ni 20% pristine electrodes (Figures S12a and S13a, **Tables S14** and **S15**) exhibited very similar cell parameters as those presented in **Table 1**. Ex situ XRD of the charged electrodes show the presence of several phases (Figures S12b, d; S13b, d), not only the initial P2 phase but also the OP4 phase appears, which is more evident in the 4.2V diffractograms (Figures S12b and S13b). A hydrated phase[1] was also found which unfortunately overlaps with OP4 phase for Ni 10% at 4.2V and 4.5V charged states and for Ni 20% at 4.2V. This hydrated phase could be formed during the electrode washing procedure after opening the cells, as previously reported.[2] In the *ex situ* XRD of the discharged electrodes (Figures S12c, S13c), a P2 phase coexists with an orthorhombic *Cmcm* phase - as has been well reported for other P2 materials.[3] (See Table S14b and S15b).

Bibliography

1. Han M. H., Gonzalo E., Sharma N., Lopez del Amo JM., Armand M., Avdeev M., Saiz Garitaonandia JJ., Rojo T., High-Performance P2-Phase $Na_{2/3}Mn_{0.8}Fe_{0.1}Ti_{0.1}O_2$ Cathode Material for Ambient-Temperature Sodium-Ion Batteries. *Chem. Mater.* 28, 106–116 (2016).

2. Han M. H., Sharma N., Gonzalo E., Pramudita JC., Brand HEA., del Amo JML, Rojo T. Moisture exposed layered oxide electrodes as Na-ion battery cathodes. Journal of Materials Chemistry A 4 (48), 18963-18975

3. Gonzalo E, Han MH, del Amo JML, Acebedo B, Casas-Cabanas M, Rojo T. Synthesis and characterization of pure P2-and O3-Na 2/3 Fe 2/3 Mn 1/3 O 2 as cathode materials for Na ion batteries. Journal of Materials Chemistry A 2 (43), 18523-18530