Electronic Supplementary Information

High voltage structural evolution and enhanced Na-ion diffusion in P2-$Na_{2/3}Ni_{1/3-x}Mg_xMn_{2/3}O_2$ ($0 \leq x \leq 0.2$) cathodes from diffraction, electrochemical and ab-initio studies

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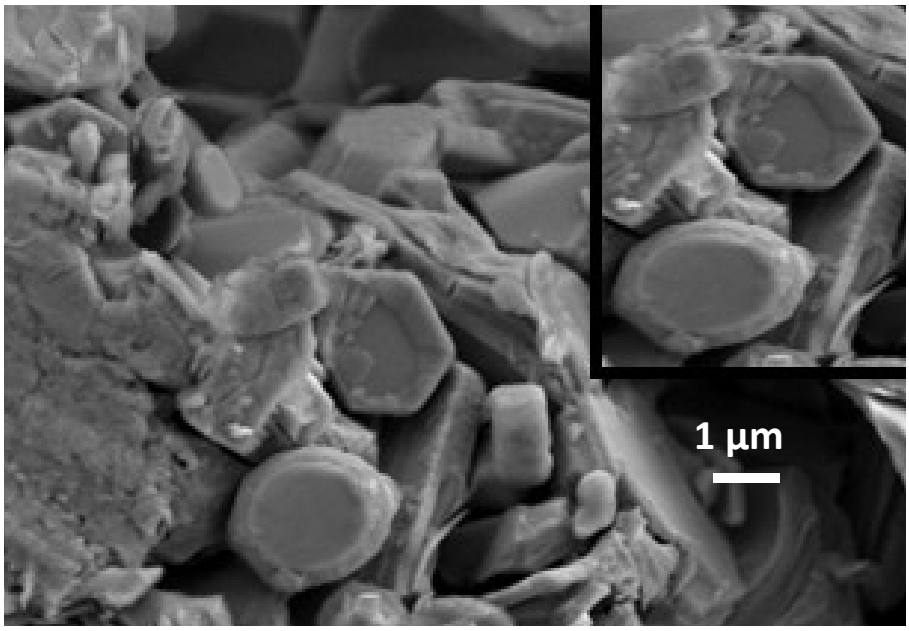

Figure S1. Typical SEM picture of $Na_{2/3}Ni_{1/3-x}Mg_xMn_{2/3}O_2$ (where x = 0.1).

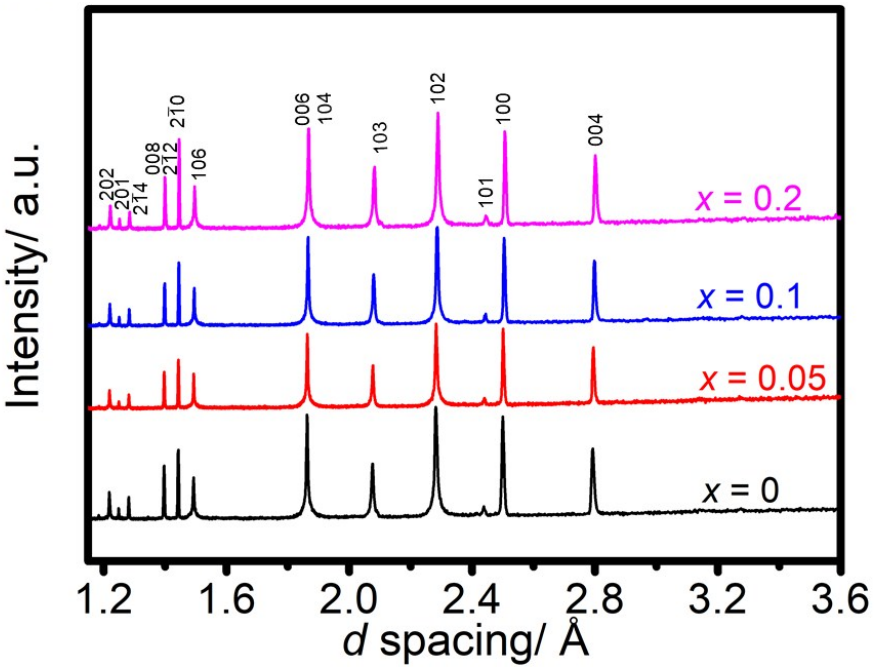

Figure S2. a) Powder X-ray diffraction data of $Na_{2/3}Ni_{1/3-x}Mg_xMn_{2/3}O_2$, where $0 \leq x \leq 0.2$ showing *hkl* indexing based on $P6_3/mmc$ space group.

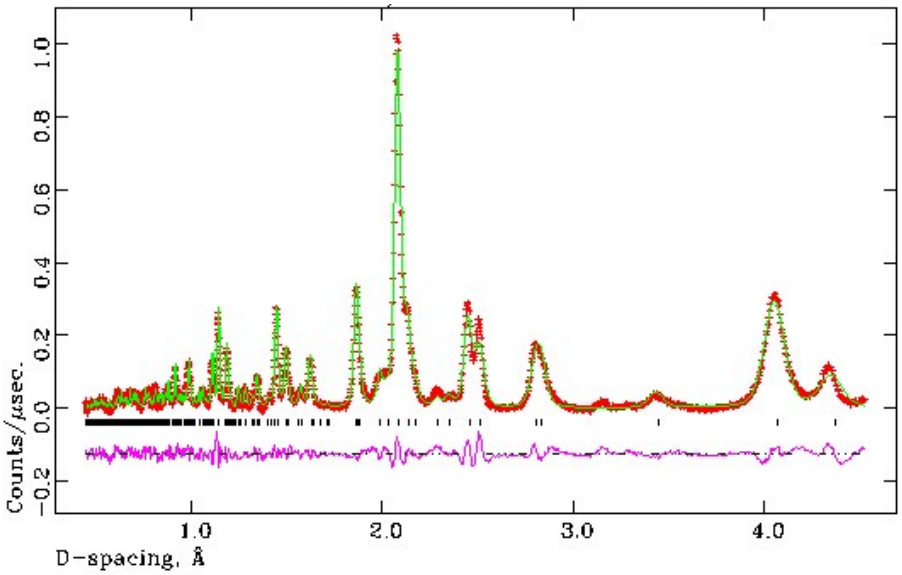

Figure S3. Rietveld refined fit from ToF neutron data collected on Bank 3 (45 °) of pristine P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ at room temperature. Data are shown in red, calculated pattern is shown in green and the difference plot is shown in purple. Bragg peak positions are shown in black.

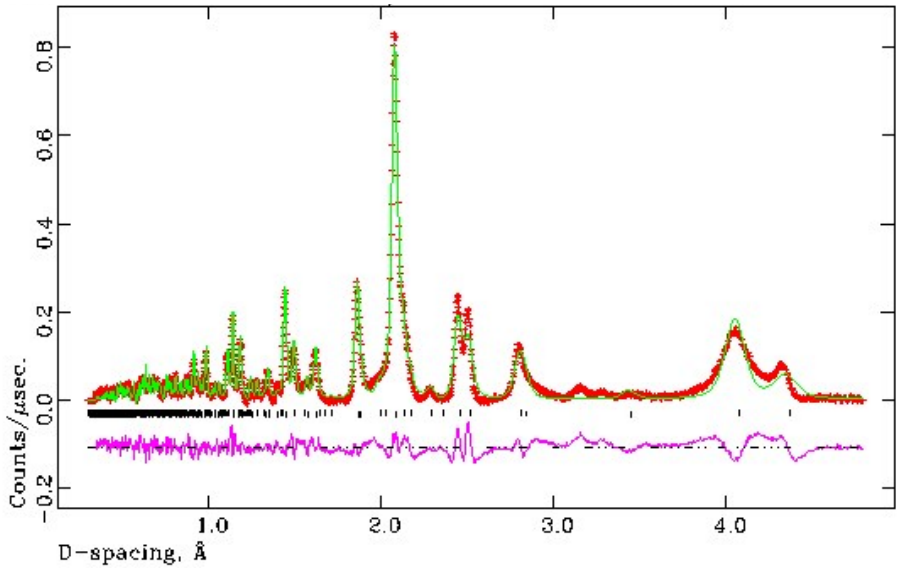

Figure S4. Rietveld refined fit from ToF neutron data collected on Bank 3 (45 °) of pristine P2-$Na_{2/3}Ni_{0.28}Mg_{0.05}Mn_{2/3}O_2$ at room temperature. Data are shown in red, calculated pattern is shown in green and the difference plot is shown in purple. Bragg peak positions are shown in black.

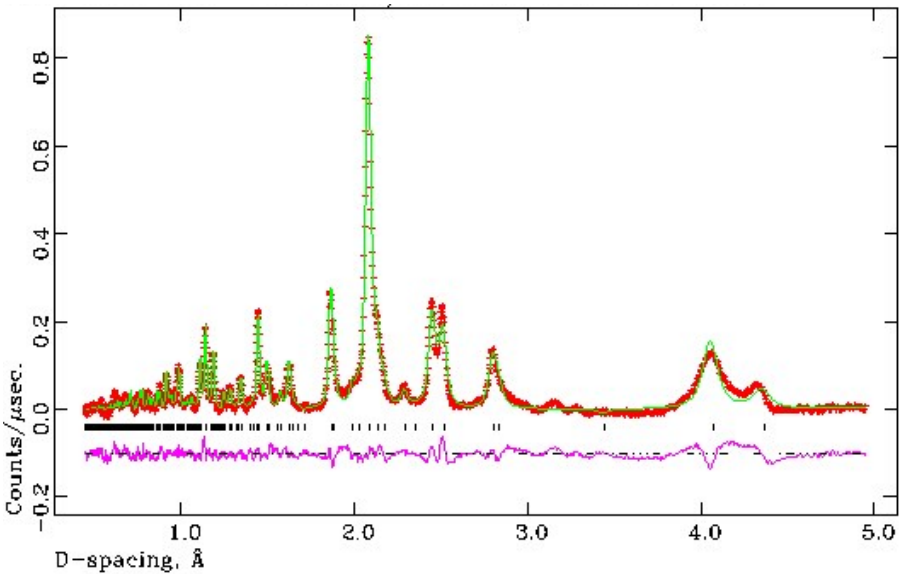

Figure S5. Rietveld refined fit from ToF neutron data collected on Bank 3 (45 °) of pristine P2-$Na_{2/3}Ni_{0.23}Mg_{0.1}Mn_{2/3}O_2$ at room temperature. Data are shown in red, calculated pattern is shown in green and the difference plot is shown in purple. Bragg peak positions are shown in black.

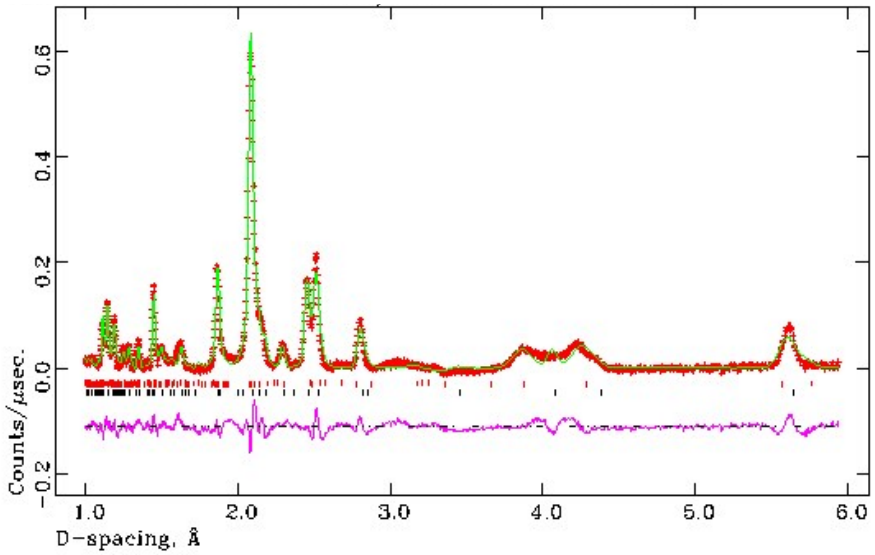

Figure S6. Rietveld refined fit from ToF neutron data collected on Bank 3 (45 °) of pristine P2-$Na_{2/3}Ni_{0.13}Mg_{0.2}Mn_{2/3}O_2$ at room temperature. Data are shown in red, calculated pattern is shown in green and the difference plot is shown in purple. Black tickmarks represent the P2 phase with $P6_3$ space group and red tickmarks represent the P2 phase with $P6_3/m$ space group.

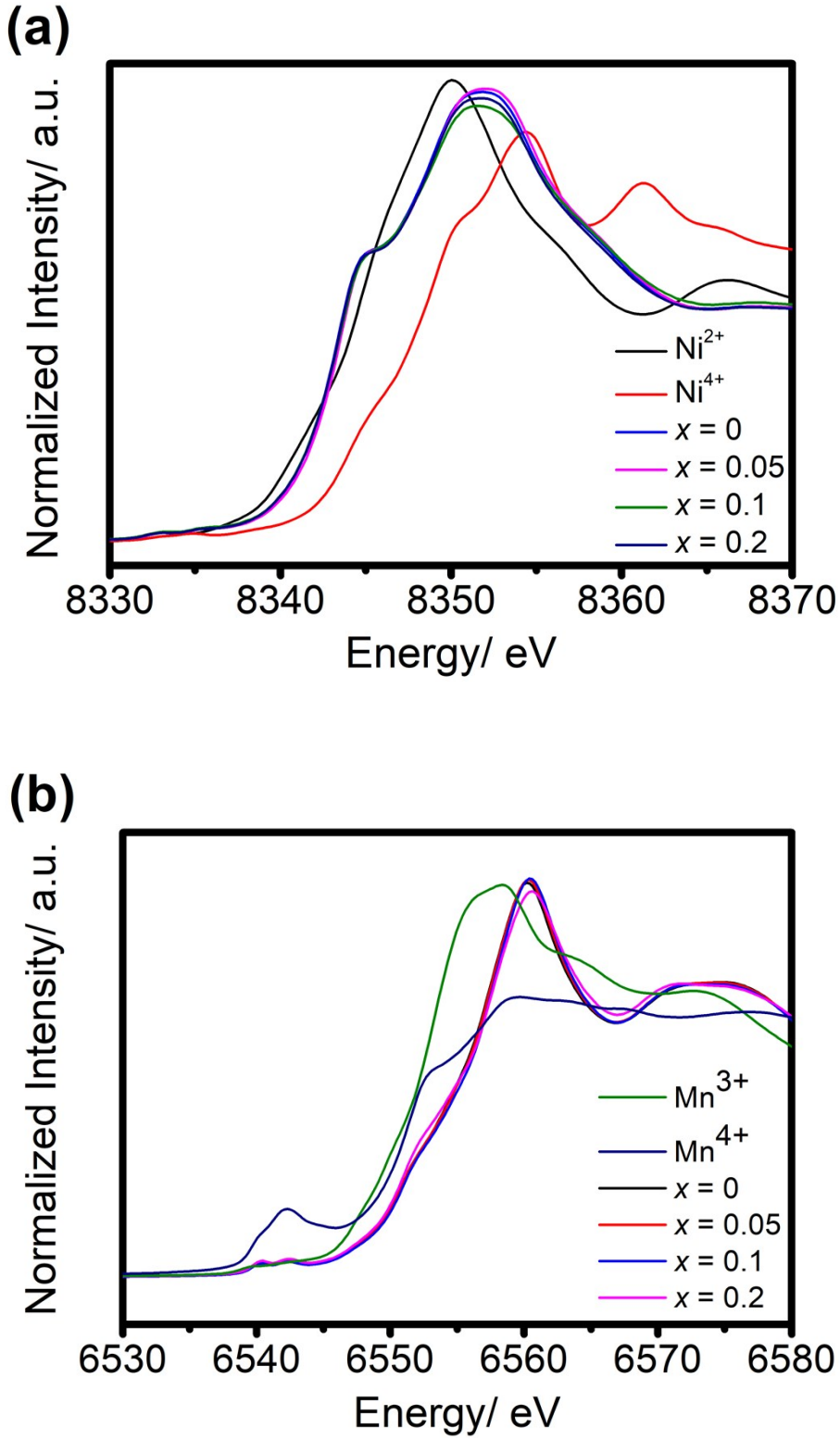

Figure S7. X-ray absorption spectra at a) Ni K-edge and b) Mn K-edge of the pristine P2-$Na_{2/3}Ni_{1/3-x}Mg_xMn_{2/3}O_2$ ($0 \leq x \leq 0.2$) materials. Reference spectra of NiO (Ni^{2+}) and K_2NiF_6 (Ni^{4+}) and Mn_2O_3 (Mn^{3+}) and MnO_2 (Mn^{4+}) standard materials were obtained to identify by direct comparison the oxidation states of the investigated materials.

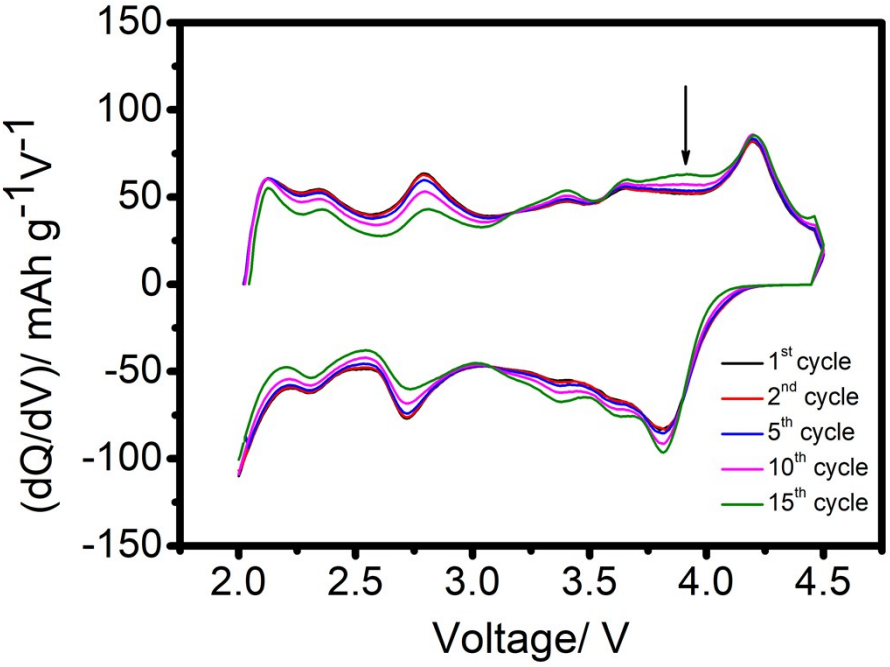

Figure S8. Differential capacity curves for P2-$Na_{2/3}Ni_{0.13}Mg_{0.2}Mn_{2/3}O_2$ in the voltage range 2-4.5 V at 10 mA g^{-1} for cycles 1, 2, 5, 10 and 15.

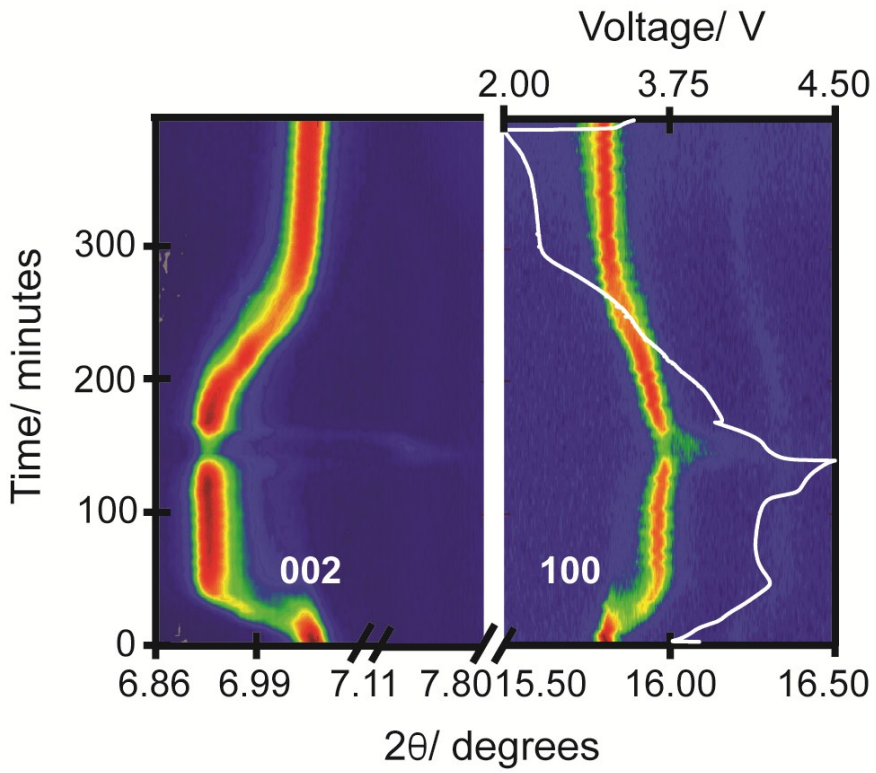

Figure S9. Selected 2θ regions of *in operando* synchrotron XRD data highlighting the evolution of the (002) and (100) reflections for $Na_{2/3}Ni_{0.23}Mg_{0.1}Mn_{2/3}O_2$. The colour scale represents reflection intensity and the potential profiles are included.

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Table S1. Nominal compositions for $Na_{2/3}Ni_{1/3-x}Mg_xMn_{2/3}O_2$ ($0 \leq x \leq 0.2$) obtained from ICP/MS.

x in $Na_{2/3}Ni_{1/3-x}Mg_xMn_{2/3}O_2$				
Molar fraction	**0**	**0.05**	**0.1**	**0.2**
Na	0.66	0.67	0.66	0.67
Ni	0.33	0.29	0.23	0.14
Mg	0	0.04	0.1	0.19
Mn	0.66	0.67	0.68	0.66

Table S2. Structural information obtained from ToF ND collected on Bank 3 (45 °) at room temperature for P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$

$Na_{0.64}Ni_{1/3}Mn_{2/3}O_2$ Space group: $P6_3$ (nº 173) a = 5.0067(7) Å; c = 11.160(1) Å R_{wp} = 0.0746; χ^2 = 4.4						
Atom	**Wyckoff site**	**x**	**y**	**z**	**SOF**	**100 x UISO/ Å²**
Mn(1)	2a	0	0	0	1	3.83(8)*
Mn(2)	2b	1/3	2/3	1/2	1	3.83(8)*
Ni	2b	1/3	2/3	0	1	3.83(8)*
O(1)	6c	0.3207(8)	-0.021(1)	-0.3914(6)	1	1.60(8)^
O(2)	6c	0.6823(5)	-0.035(1)	0.4240(6)	1	1.60(8)^
Na(1)	2a	0	0	1/4	0.141(4)	7.9(3)#
Na(2)	6c	1/3	0	1/4	0.491(1)	7.9(3)#
Na(3)	2b	1/3	2/3	1/4	0.152(3)	7.9(3)#
Na(4)	2b	2/3	1/3	1/4	0.146(3)	7.9(3)#

*, ^ and # are constrained to be equal.

Table S3. Structural information obtained from ToF ND collected on Bank 3 (45 °) at room temperature for P2-$Na_{2/3}Ni_{0.28}Mg_{0.05}Mn_{2/3}O_2$

$Na_{0.64}Ni_{0.28}Mg_{0.05}Mn_{2/3}O_2$ Space group: $P6_3$ (nº 173) a = 5.0082(3) Å; c = 11.168(1) Å R_{wp} = 0.0764; χ^2 = 4.07						
Atom	**Wyckoff site**	**x**	**y**	**z**	**SOF**	**100 x UISO/ Å²**
Mn(1)	2a	0	0	0	1	3.87(9)*
Mn(2)	2b	1/3	2/3	1/2	1	3.87(9)*
Ni	2b	1/3	2/3	0	0.85	3.87(9)*
Mg	2b	1/3	2/3	0	0.15	3.87(9)*
O(1)	6c	0.3152(8)	-0.0114(8)	-0.4136(8)	1	1.45(5)^
O(2)	6c	0.6608(8)	-0.0348(7)	0.4034(7)	1	1.45(5)^
Na(1)	2a	0	0	1/4	0.16(5)	7.6(4)#
Na(2)	6c	1/3	0	1/4	0.479(3)	7.6(4)#
Na(3)	2b	1/3	2/3	1/4	0.18(4)	7.6(4)#
Na(4)	2b	2/3	1/3	1/4	0.15(3)	7.6(4)#

*, ^ and # are constrained to be equal.

Table S4. Structural information obtained from ToF ND collected on Bank 3 (45 °) at room temperature for P2- $Na_{2/3}Ni_{0.23}Mg_{0.1}Mn_{2/3}O_2$

$Na_{0.65}Ni_{0.23}Mg_{0.1}Mn_{2/3}O_2$ Space group: *P*6$_3$ (nº 173) *a* = 5.0109(3) Å; *c* = 11.172(1) Å R_{wp} = 0.0766; χ^2 = 3.273						
Atom	**Wyckoff site**	**x**	**y**	**z**	**SOF**	**100 x UISO/ Å²**
Mn(1)	2a	0	0	0	1	3.9(1)*
Mn(2)	2b	1/3	2/3	1/2	1	3.9 (1)*
Ni	2b	1/3	2/3	0	0.7	3.9(1)*
Mg	2b	1/3	2/3	0	0.3	3.9(1)*
O(1)	6c	0.3152(8)	-0.0104(7)	-0.4152(8)	1	1.42(5)^
O(2)	6c	0.6618(8)	-0.0337(8)	0.4022(7)	1	1.42(5)^
Na(1)	2a	0	0	1/4	0.18(1)	8.3(4)#
Na(2)	6c	1/3	0	1/4	0.493(8)	8.3(4)#
Na(3)	2b	1/3	2/3	1/4	0.13(1)	8.3(4)#
Na(4)	2b	2/3	1/3	1/4	0.15(3)	8.3(4)#

*, ^ and # are constrained to be equal.

Table S5. Structural information obtained from ToF ND collected on Bank 3 (45 °) at room temperature for P2- $Na_{2/3}Ni_{0.13}Mg_{0.2}Mn_{2/3}O_2$

$Na_{0.67}Ni_{0.13}Mg_{0.2}Mn_{2/3}O_2$ Space group: *P*6$_3$ (nº 173) *a* = 5.023(1) Å; *c* = 11.189(3) Å R_{wp} = 0.0771; χ^2 = 4.671						
Atom	**Wyckoff site**	**x**	**y**	**z**	**SOF**	**UISO/ Å²**
Mn(1)	2a	0	0	0	1	4.3(5)*
Mn(2)	2b	1/3	2/3	1/2	1	4.3(5)*
Ni	2b	1/3	2/3	0	0.4	4.3(5)*
Mg	2b	1/3	2/3	0	0.6	4.3(5)*
O(1)	6c	0.3183(1)	-0.028(1)	-0.3938(7)	1	1.5(1)^
O(2)	6c	0.682(1)	-0.028(1)	0.4186(7)	1	1.5(1)^
Na(1)	2a	0	0	1/4	0.16(3)	7.5(5)#
Na(2)	6c	1/3	0	1/4	0.52(1)	7.5(5)#
Na(3)	2b	1/3	2/3	1/4	0.15(3)	7.5(5)#
Na(4)	2b	2/3	1/3	1/4	0.15(2)	7.5(5)#

*, ^ and # are constrained to be equal.

Table S7. Refined crystallographic parameters of P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ obtained from the synchrotron XRD pattern collected at room temperature before cycling.

Space group: *P*6$_3$/*mmc* (nº 194) *a* = 2.8878(1) Å; *c* = 11.1604(6) Å R_{wp} = 0.0519; χ^2 = 1.796						
Atom	**Wyckoff site**	**x**	**y**	**z**	**SOF**	**UISO/ Å²**
Mn	2	0	0	0	2/3	1.1*^
Ni	2	0	0	0	1/3	1.1*^
O	4	1/3	2/3	0.071(1)	1	0.48*
Na(1)	2	0	0	1/4	0.30(1)#	1.2*
Na(2)	2	1/3	2/3	3/4	0.37(1)#	8.8*

* Refined alternatively to SOFs and refined and fixed; ^ Constrained to be equal; #Total sodium content constrained to equal 0.67.

Table S8. Refined crystallographic parameters of P2-$Na_{2/3}Ni_{0.23}Mg_{0.1}Mn_{2/3}O_2$ obtained from the synchrotron XRD pattern collected at room temperature before cycling.

Space group: *P*6$_3$/*mmc* (nº 194) *a* = 2.88735(6) Å; *c* = 11.11843(1) Å R_{wp} = 0.0393; χ^2 = 3.676						
Atom	**Wyckoff site**	**x**	**y**	**z**	**SOF**	**UISO/ Å²**
Mn	2	0	0	0	2/3	1.5*^
Ni	2	0	0	0	0.23	1.5*^
Mg	2	0	0	0	0.1	1.5*^
O	4	1/3	2/3	0.0698(5)	1	0.75*
Na(1)	2	0	0	1/4	0.279(7)#	2.5*
Na(2)	2	1/3	2/3	3/4	0.387(7)#	6.5*

* Refined alternatively to SOFs and refined and fixed; ^ Constrained to be equal; #Total sodium content constrained to equal 0.67.

Table S9. Refined crystallographic parameters of P2-$Na_{2/3}Ni_{0.13}Mg_{0.2}Mn_{2/3}O_2$ obtained from the synchrotron XRD pattern collected at room temperature before cycling.

Space group: *P*6$_3$/*mmc* (nº 194) *a* = 2.89793(6) Å; *c* = 11.1681(1) Å R_{wp} = 0.0415; χ^2 = 3.802						
Atom	**Wyckoff site**	**x**	**y**	**z**	**SOF**	**UISO/Å²**
Mn	2	0	0	0	2/3	2.8*^
Ni	2	0	0	0	0.13	2.8*^
Mg	2	0	0	0	0.2	2.8*^
O	4	1/3	2/3	0.0589(6)	1	4.1*
Na(1)	2	0	0	1/4	0.316(8)#	6.4*
Na(2)	2	1/3	2/3	3/4	0.350(8)#	7.3*

* Refined alternatively to SOFs and refined and fixed; ^ Constrained to be equal; #Total sodium content constrained to equal 0.67.

Table S10. Range of R_{wp} and χ^2 for sequential Rietveld refinements of P2-$Na_{2/3}Ni_{1/3-x}Mg_xMn_{2/3}O_2$ obtained from the synchrotron XRD patterns.

x	R_{wp} range	χ^2 range
0	0.0422 – 0.0543	1.180 – 1.969
0.1	0.0370 – 0.0502	3.402 – 5.972
0.2	0.0403 – 0.0601	3.608 – 4.997