Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information for:

Structure of the High Voltage Phase of Layered P2-$Na_x[Mn_{1/2}Fe_{1/2}]O_2$ and the Positive Effect of Ni Substitution on its Stability

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Table S1: Atomic parameters and unit cell constants of $Na_{0.67}[Mn_{0.6}Ni_{0.1}Fe_{0.3}]O_2$ and $Na_{0.67}[Mn_{0.65}Ni_{0.15}Fe_{0.2}]O_2$ calculated from combined Rietveld refinement of the neutron and X-ray powder diffraction data.

		$Na_{2/3}Mn_{0.6}Fe_{0.3}Ni_{0.1}O_2$	$Na_{2/3}Mn_{0.65}Fe_{0.2}Ni_{0.15}O_2$
	Space Group	*P6₃/mmc*	*P6₃/mmc*
	χ^2 (XRPD/NPD)	10.1/6.04	12.6/14.4
	R_{bragg} (XRPD/NPD) (%)	4.71/4.72	3.58/4.87
	a (Å)	2.9276(1)	2.9207(1)
	c (Å)	11.1690(2)	11.1598(8)
	Cell Volume (Å^3)	82.904(6)	82.444(6)
Mn/Fe/Ni (2a) (0, 0, 0)	- $U_{11} = U_{22}$ (Å^2)	0.014(2)	0.016(2)
	- U_{33} (Å^2)	0.023(2)	0.021(2)
	- U_{12} (Å^2)	0.007(2)	0.008(2)
Na_e (6h) (x, 2x, 1/4)	- x	0.623(4)	0.621(5)
	- Occupancy	0.154(4)	0.150(5)
	- U_{iso} (Å^2)	0.015(5)	0.02(1)
Na_f (6h) (x, 2x, 1/4)	- x	0.04(2)	0.03(2)
	- Occupancy	0.069(4)	0.074(5)
	- U_{iso} (Å^2)	0.02(2)	0.02(1)
O (4f) (1/3, 2/3, z)	- z	0.0925(2)	0.0926(3)
	- $U_{11} = U_{22}$ (Å^2)	0.013(2)	0.015(2)
	- U_{33} (Å^2)	0.011(2)	0.013(2)
	- U_{12} (Å^2)	0.007(2)	0.007(2)

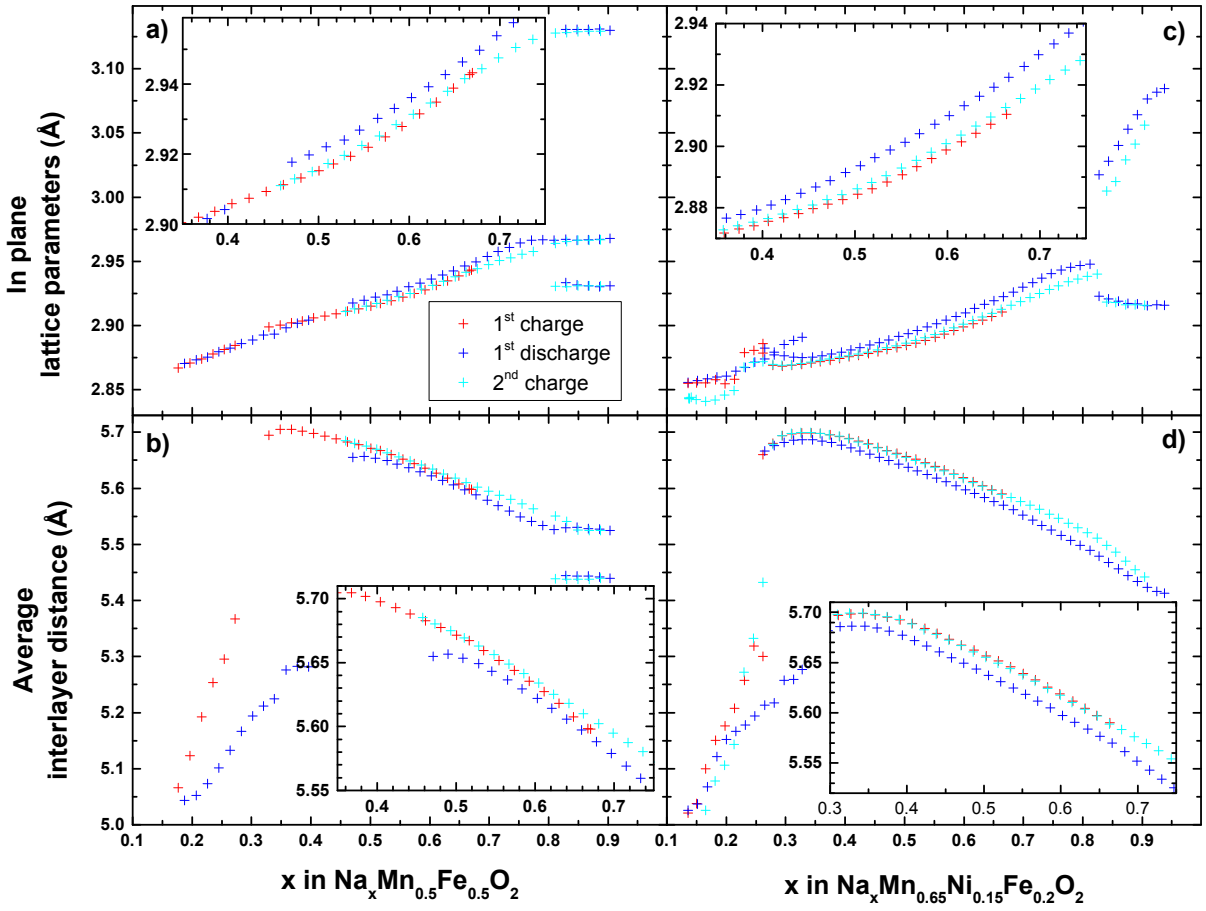

Figure S1: Evolution of lattice parameters, in plane a), c) and out of plane b), d) of $Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$ a), b) and $Na_{0.67}Fe_{0.2}Mn_{0.65}Ni_{0.15}O_2$ as a function of the sodium content for the first cycle and a half (charge-discharge-charge). For the sake of clarity, phase identification is not reported on this figure: please see Figure 6 in the main text. The insets show expanded views of the stability domain of the P2 phase, highlighting the perfect reversibility of the system, since the cell parameter measured on second charge overlap perfectly with the ones extracted on first charge (red and cyan crosses).

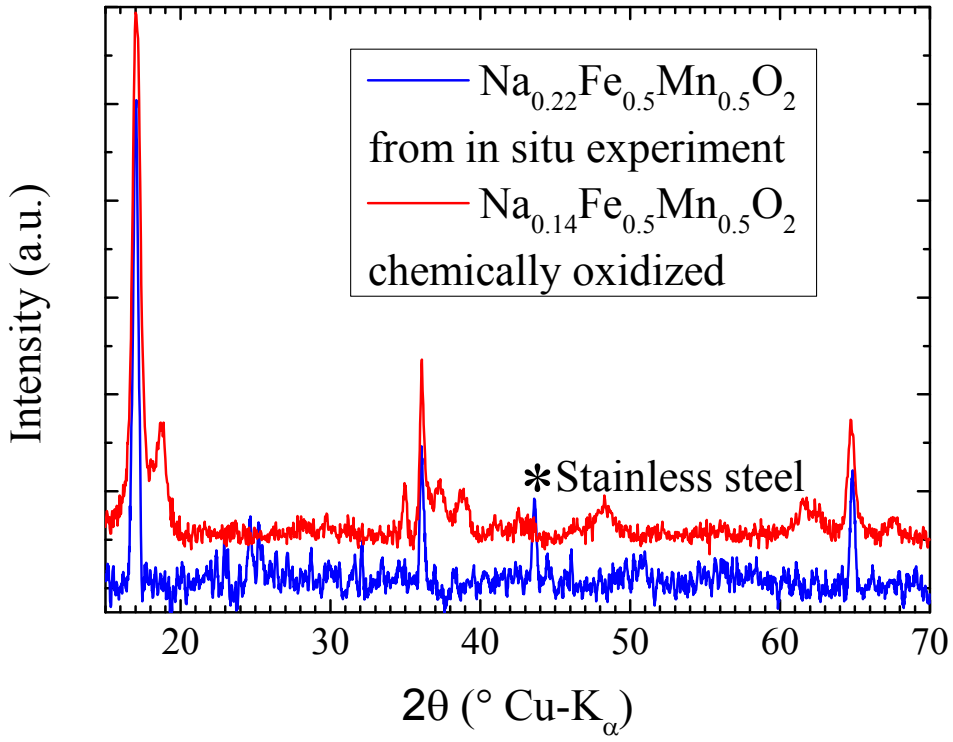

Figure S2: Comparison of the X-ray diffraction patterns of the high potential phase obtained *via* electrochemical oxidation and chemical oxidation.

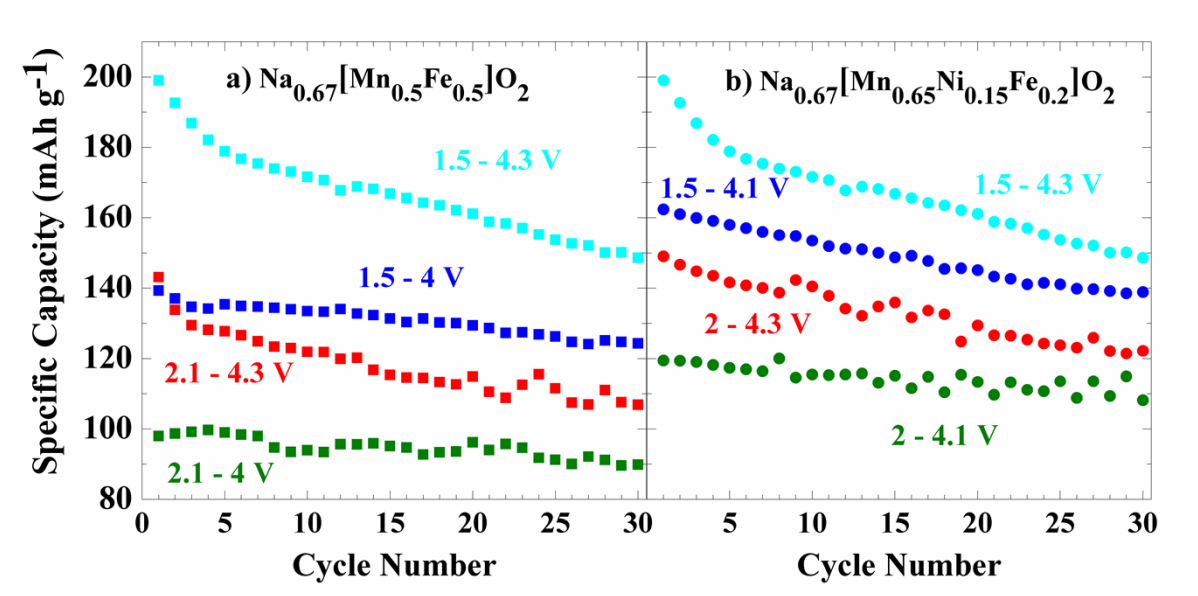

Figure S3: The specific discharge capacity of $Na_{0.67}[Mn_{0.5}Fe_{0.5}]O_2$ and $Na_{0.67}[Mn_{0.65}Ni_{0.15}Fe_{0.2}]O_2$ cycled at C/20 within different voltage ranges.

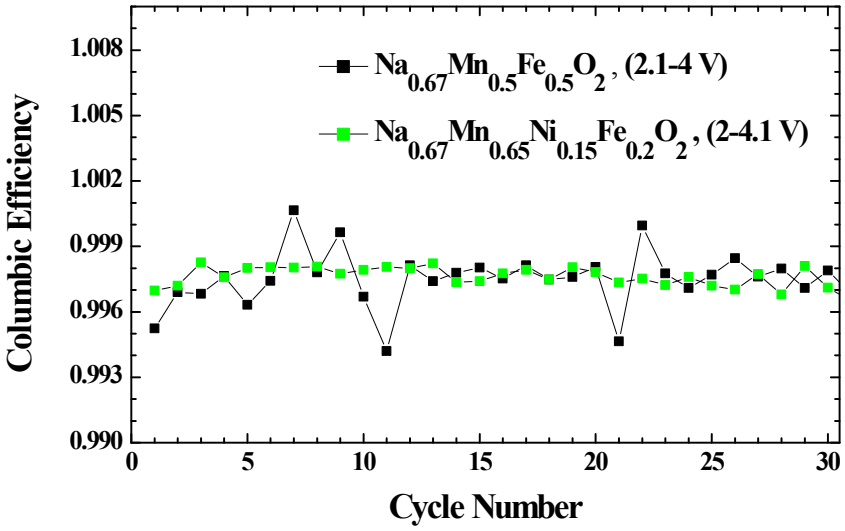

Figure S4: Coulombic efficiency of $Na_{0.67}[Mn_{0.5}Fe_{0.5}]O_2$ and $Na_{0.67}[Mn_{0.65}Ni_{0.15}Fe_{0.2}]O_2$ cycled over P2- phase region at the rate of C/20.