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Toward high energy density cathode materials for sodium-ion batteries: investigating the beneficial effect of Aluminum doping on the P2-type structure

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Supplementary information

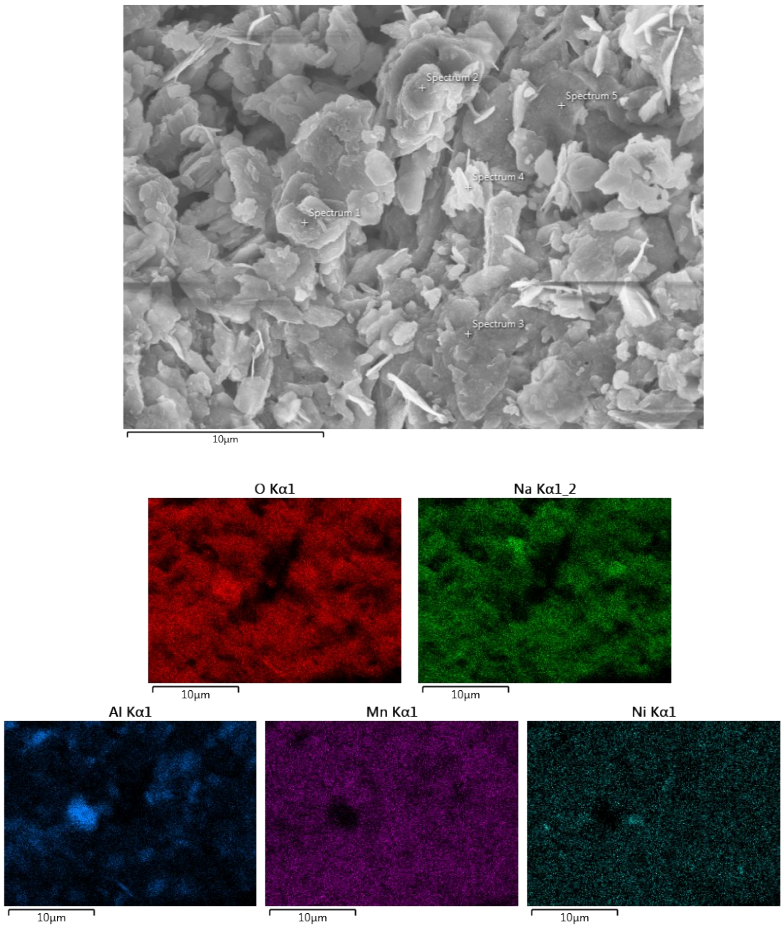


Figure S1. Elemental mapping by energy dispersive X-ray spectroscopy (EDX) of oxygen, sodium, aluminum, manganese and nickel for the $Na_{0.6}Ni_{0.22}Al_{0.11}Mn_{0.66}O_2$ material. EDX images reveal a homogeneous distribution of Na, Mn, Ni and O, with spot-like agglomeration of aluminum-based compounds.

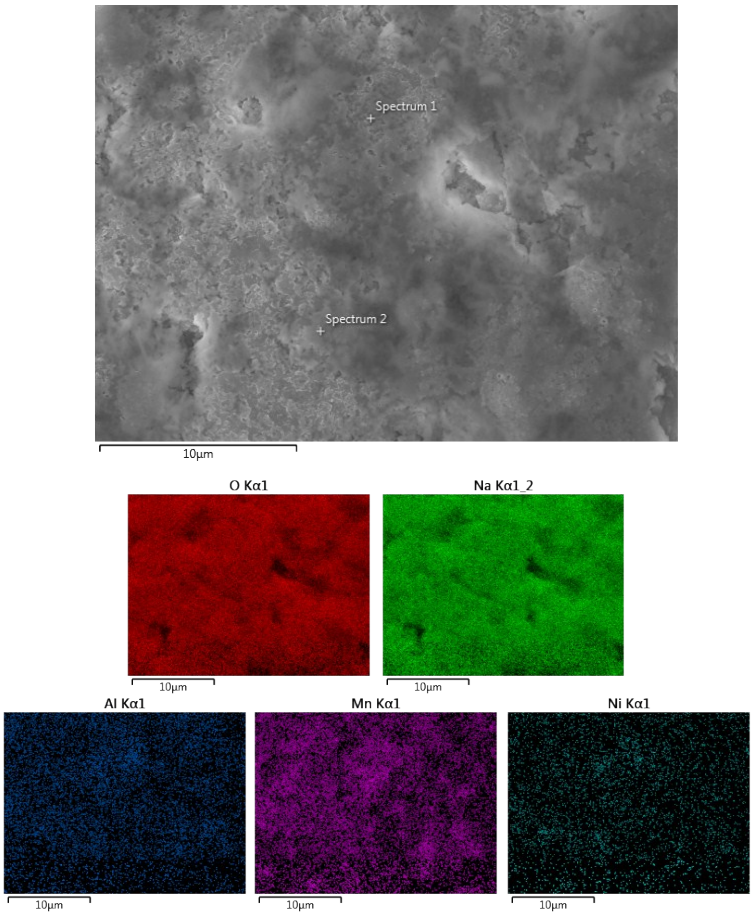


Figure S2. Elemental mapping via energy dispersive X-ray spectroscopy (EDX) of oxygen, sodium, aluminum, manganese and nickel for the co-precipitated hydroxide precursor mixed with 0.685 equivalent of NaOH. EDX images reveal a homogeneous distribution of the metal elements.

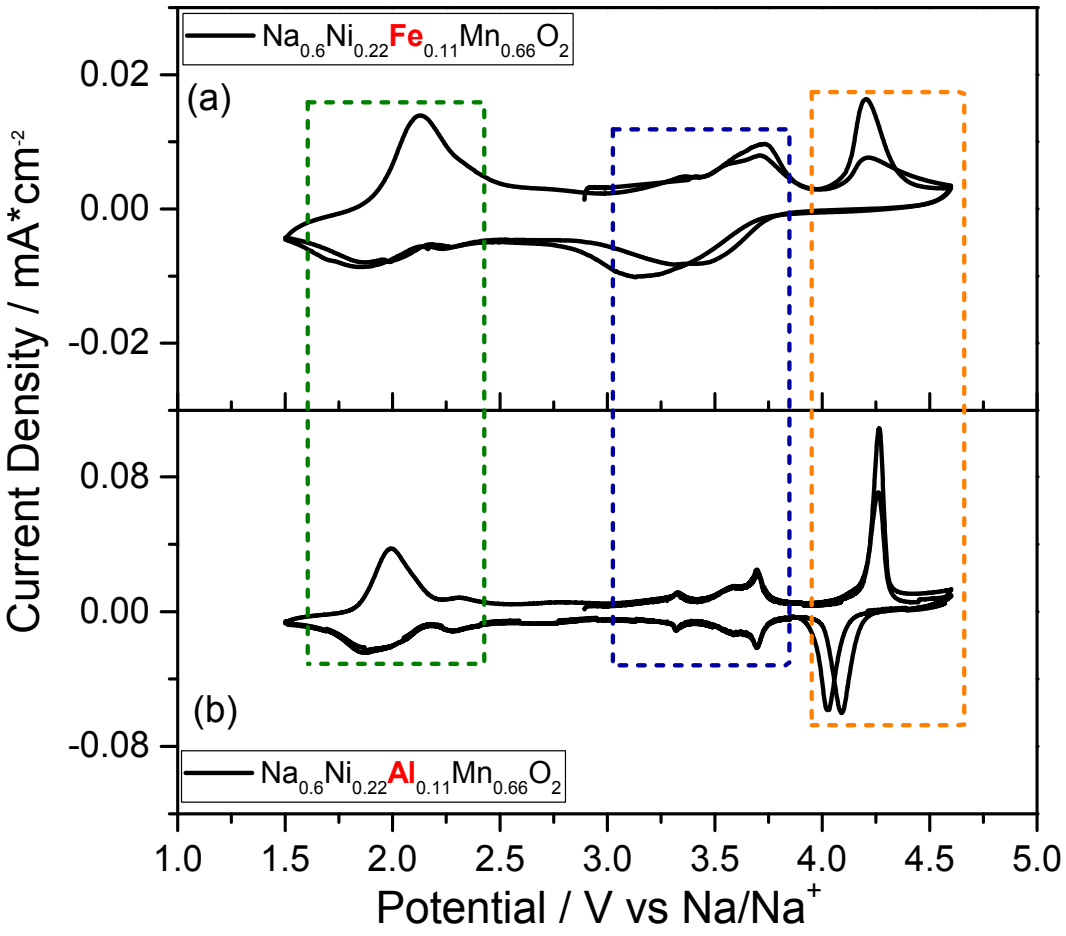


Figure S3. Comparison of the cyclic voltammograms of $Na_{0.6}Ni_{0.22}Fe_{0.11}Mn_{0.66}O_2$ (a) and $Na_{0.6}Ni_{0.22}Al_{0.11}Mn_{0.66}O_2$ (b) electrode materials in sodium half-cells within the 4.6-1.5V vs Na/Na^+ potential range. Temperature: 20°C ± 2 °C. Electrolyte: 1M $NaPF_6$ in PC. Scan rate: 0.1 mV sec^{-1}.

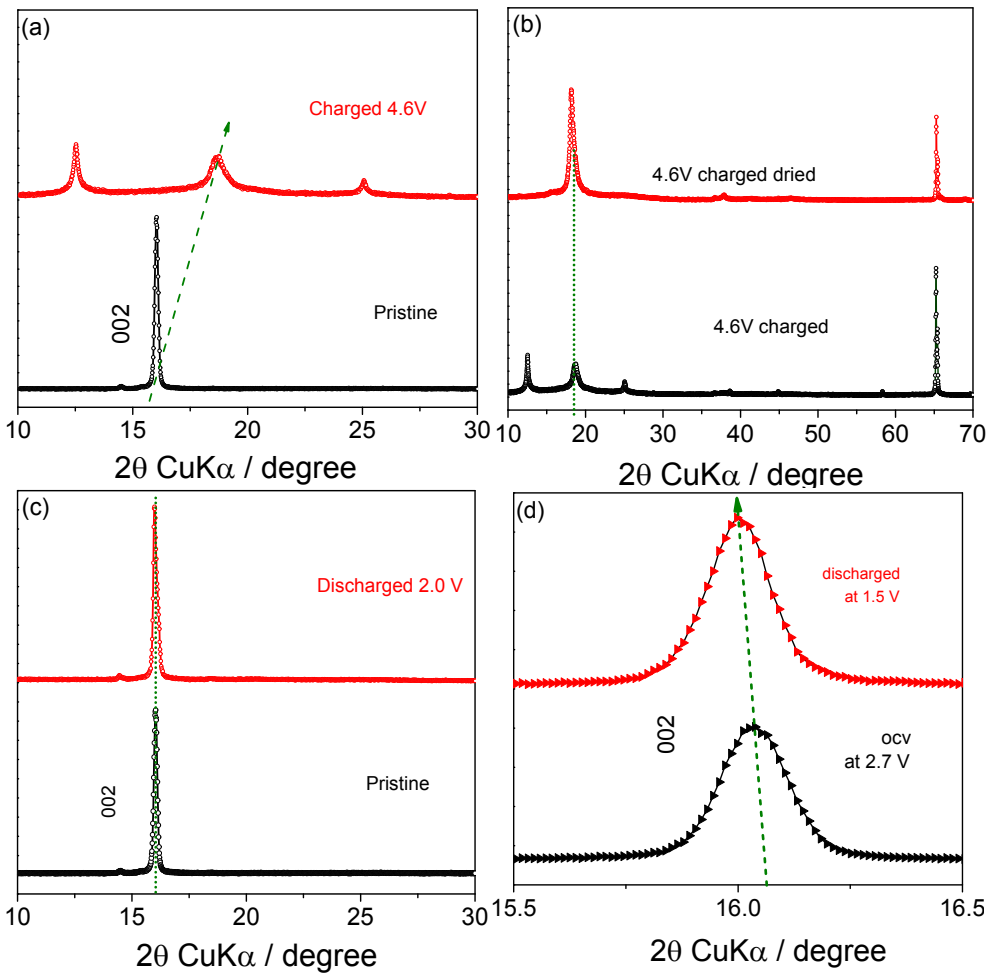
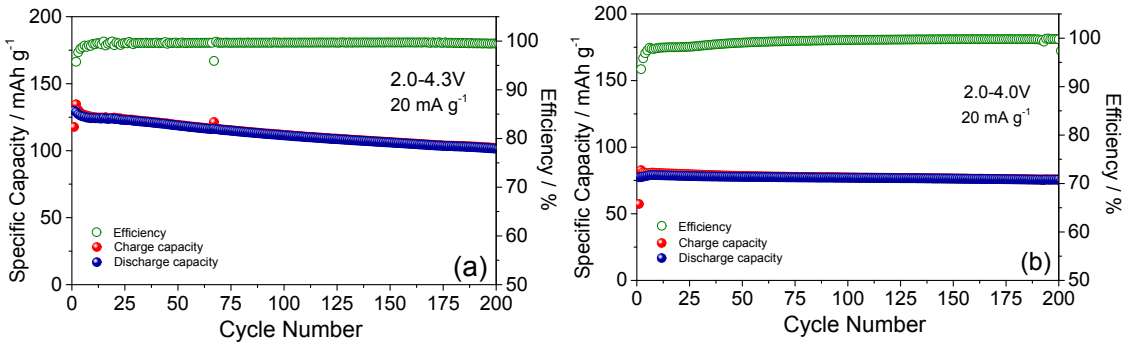


Figure S4. Ex-situ XRD study of the $Na_{0.6}Ni_{0.22}Al_{0.11}Mn_{0.66}O_2$ electrode upon charge/discharge in sodium cell (magnified regions taken from Fig. 5 of the manuscript). XRD patterns of (a) pristine and charged electrodes. (b) charged and dried electrode at 4.6 V. (c) pristine and discharged electrode at 2.0 V. (d) pristine and discharged electrode at 1.5 V.



Voltage range	Capacity at 200th cycle	Capacity retention at 200th cycle	Average working voltage at the 2nd cycle	Voltage efficiency after 200 cycles at 20 mA g^{-1}	Total cycling test time / hours
2.0-4.3 V	102 mAh g^{-1}	79%	3.6 V	89 %	2250 h
2.0-4.0 V	75 mAh g^{-1}	97 %	3.1 V	93 %	1150 h

Figure S5. Long-term cycling behavior of Na/PC, 1M $NaPF_6$/P2-$Na_{0.6}Ni_{0.22}Al_{0.11}Mn_{0.66}O_2$ cells galvanostatically cycled at a constant current value of 20 mA g^{-1} within the (a) 4.3-2.0 V and (b) 4.0-2.0V vs Na/Na^+ potential ranges. Table resumes the electrochemical performance parameters.

The developed electrode material reveals good cycling stability and satisfactory capacity retention after 200 cycles in both cases, i.e within the 4.3-2.0 V (Fig. S5 a) and 4.0-2.0 V (Fig. S5 b) potential range. In addition, the average working voltage calculated at the 2nd cycle is about 3.6 V and 3.1 V, which are remarkable values within the state of art of Mn-based P2-type layered cathodes for sodium-ion cells. The total amounts of hours of the cycling tests represent a preliminary encouraging result for long term and stable cycling performance.

P2-type Cathode material	Current density / mA g^{-1}	Voltage range / V	1st discharge capacity / mAh g^{-1}	Capacity retention / %	Electrolyte	Reference
$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$	13	1.5-4.2	190	After 30 cycles 150 mAh g^{-1} (79%)	1M $NaClO_4$ in PC +2%vol FEC	[1]
$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$	0.1C 	2.0-4.2 2.0-4.0 1.5-4.0 1.5-4.2	~140 85 ~140 184	After 80 cycles 40 mAh g^{-1} (28%) After 80 cycles 60 mAh g^{-1} (70%) After 80 cycles 28 mAh g^{-1} (20%) After 80 cycles 100 mAh g^{-1} (54%)	1M $NaClO_4$ in PC +2%w FEC	[2]
$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$	1.73 8.65 34.6	2.3-4.5 2.3-4.1 2.3-4.1	135 90 80	After 30 cycles 50 mAh g^{-1} (37%) After 50 cycles ~90 mAh g^{-1} (~100%) After 50 cycles ~80 mAh g^{-1} (~100%)	1M $NaPF_6$ in DEC:EC 67:33 vol%	[3]
$Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$	10	1.5-4.4	220	After 30 cycles 150 mAh g^{-1} (68%)	1M $NaClO_4$ in PC:DMC +2%vol FEC	[4]
$Na_{7/9}Cu_{2/9}Fe_{1/9}Mn_{2/3}O_2$	10	2.5-4.2	89	After 150 cycles at 1C (100 mA g^{-1}) From 68 to 59.5 mAh g^{-1} (87%)	0.8M $NaPF_6$ in PC	[5]
$Na_{0.5}[Ni_{0.23}Fe_{0.13}Mn_{0.63}]O_2$	15	1.5-4.6	200	After 70 cycles 150 mAh g^{-1} (75%)	1M $NaPF_6$ in PC	[6]
$Na_{0.6}Ni_{0.22}Fe_{0.11}Mn_{0.66}O_2$	15	1.5-4.6	205	After 30 cycles 178 mAh g^{-1} (87%)	1M $NaPF_6$ in PC	[7]
$Na_{2/3}Mn_{1/3}Fe_{1/3}Co_{1/3}O_2$	10	1.5-4.0 2.5-4.3 2.5-4.1	126 110 78	After 20 cycles 120 mAh g^{-1} (95%) After 20 cycles 80 mAh g^{-1} (72%) After 20 cycles 78 mAh g^{-1} (100%)	1M $NaClO_4$ in PC +2%vol FEC	[8]
$Na_{2/3}Ni_{1/3}Mn_{1/2}Ti_{1/6}O_2$	12	2.5-4.5	127	After 10 cycles 119 mAh g^{-1} (94%)	1M $NaPF_6$ in PC	[9]
$Na_{0.67}Mg_{0.1}Ni_{0.2}Mn_{0.7}O_2$	12	2.0-4.5	130	After 50 cycles ~120 mAh g^{-1} (92%)	1M $NaPF_6$ in DEC:EC 50:50vol%	[10]
$Na_{0.67}Mn_{0.65}Ni_{0.2}Co_{0.15}O_2$	12	1.5-4.2	135	After 100 cycles 105 mAh g^{-1} (77%)	1M $NaClO_4$ in PC	[11]
$Na_{0.45}Ni_{0.22}Co_{0.11}Mn_{0.66}O_2$	12	2.1-4.3	135	After 50 cycles 128 mAh g^{-1} (95%)	0.5M $NaPF_6$ in PC	[12]
$Na_{0.66}Ni_{0.26}Zn_{0.07}Mn_{0.67}O_2$	12	2.0-4.4	140	After 30 cycles 120 mAh g^{-1} (85%)	1M $NaClO_4$ in PC +2%vol FEC	[13]
$Na_{2/3}Mn_{0.7}Ni_{0.1}Fe_{0.1}Mg_{0.1}O_2$	18	2.0-4.3	133	After 50 cycles (at 1C) from 122 to 110 mAh g^{-1} (90%)	1M $NaPF_6$ in PC	[14]
$Na_{0.6}Ni_{0.22}Al_{0.11}Mn_{0.66}O_2$	**20**	**1.5-4.6** **1.5-4.3** **1.5-4.0** **2.0-4.6** **2.0-4.3** **2.0-4.0**	**252.5** **231.6** **183.6** **134.2** **130** **77.4**	After 50 cycles 200.6 mAh g^{-1} **79.5%** After 50 cycles 191.8 mAh g^{-1} **82.8%** After 50 cycles 170.9 mAh g^{-1} **93.1%** After 50 cycles 122.5 mAh g^{-1} **91.2%** After 50 cycles 118.8 mAh g^{-1} **91.5%** After 50 cycles 77.5 mAh g^{-1} **100%**	1M $NaPF_6$ in PC	This work

Table S1. Electrochemical performance comparison of P2-type layered oxides reported in literature and this work. The comparison is influenced by differences in the electrochemical set up such as voltage range, current density and electrolyte solution employed.

This table shows that the material herein studied reveals outstanding specific high capacity in the wider potential range (1.5-4.6 V) of 252 mAh g^{-1}. In fact, the discharge capacity substantially exceeds those of similar compounds, including P2-$Na_{0.6}Ni_{0.22}Fe_{0.11}Mn_{0.66}O_2$[7] and P2-$Na_{2/3}[Mg_{0.28}Mn_{0.72}]O_2$[4] investigated within similar voltage ranges, but with lower current densities.

However, even when cycled in the narrow potential region (1.5-4.0 V), still enabling the manganese redox process, the material herein reported exhibits the outstanding specific capacity of about 180 mAh g^{-1}, which is well above reported values in literature,[8,11] with a good capacity retention after 50 cycles (about 93%). Moreover, the long term cycling stability reported in Figure S5 (2.0-4.3 V potential range) clearly demonstrate the suitability of the materials also in a restricted voltage range, which might be more suitable in view of the obtainment of a full sodium-ion battery.

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