Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Title: Identification and Characterisation of High Energy Density P2-Type $Na_{2/3}[Ni_{1/3-y/2}Mn_{2/3-y/2}Fe_y]O_2$ Compounds for Na-ion Batteries

Authors: J. W. Somerville, R. A. House, N. Tapia-Ruiz, A. Sobkowiak, S. Ramos, A. V. Chadwick, M. R. Roberts, U. Maitra, and P. G. Bruce

Methods:

Synthesis: All $NaMO_2$ materials were prepared by solid state synthesis under flowing O_2 gas for 10 hours. 13 mm pellets of precursors, 5% excess Na_2CO_3 (Sigma Aldrich, ≥ 99.7%), MnO_2 (Sigma Aldrich, ≥ 99.0%), Fe_2O_3 (Sigma Aldrich, nanopowder), and NiO (Sigma Aldrich, ≥ 99.8%), were pressed and placed in an alumina boat in a tube furnace. For the ternary phase-composition diagram, the in-house materials were heated to 900°C except for $Na_{2/3}[Ni_{1/6}Mn_{1/2}Fe_{1/3}]O_2$ which needed an elevated temperature of 1030°C to eliminate a very slight O3 minority phase (~5%). For samples prepared for further characterization (ie. Electrochemistry, SEM, ICP-MS, XANES), $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ and $Na_{2/3}[Ni_{1/4}Mn_{7/12}Fe_{1/6}]O_2$ were heated at 950°C and $Na_{2/3}[Ni_{1/6}Mn_{1/2}Fe_{1/3}]O_2$ was heated at 1030°C.

Electrochemistry: Electrodes were prepared by casting a mixture of active material, Carbon Super S (TIMCAL), and PVDF (Kynar) binder in a 75/15/10 ratio in NMP solvent (Sigma Aldrich) onto an aluminum current collector, then dried at 80°C under vacuum. Coin cells were assembled with a Na metal counter electrode and glass fiber separator with the electrolyte, 1M $NaPF_6$ (Alfa Aesar, ≥ 99.0%) in battery grade 1:1 ethylene carbonate/diethyl carbonate (EC/DEC) solvent (BASF Selectilyte). Cells were cycled at a rate of 10 mA g^{-1} between 1.5 and 4.5 V vs. Na/Na^+.

X-Ray Diffraction: Patterns were recorded on a 9KW Rigaku Smartlab diffractmeter using Cu Kα1 radiation. Phase fractions were refined using the Rietveld method with the program, GSAS[1], using the EXPGUI interface[2].

ICP-MS: Samples were dissolved a solution of HNO_3 and HCl (1:3) and diluted appropriately. A Perkin Elmer Elan 6100 DRC inductively coupled plasma – mass spectrometer was used for composition validation.

SEM/EDX: Powders of pristine samples were dispersed onto a Cu tape. A Zeiss Gemini SEM-500 was used for identifying particle morphology. Energy dispersive X-ray (EDX) spectroscopy was performed on a built in Oxford Instruments X-Max 150 Silicon drift detector and analyzed with the Aztec software package.

X-ray Absorption Spectroscopy: Ex situ electrodes were washed dimethyl carbonate (DMC), dried under vacuum and sealed in a pouch bag for direct measurement. All XAS measurements were carried out at beamline B18 at the Diamond Light Source, Harwell, UK. The spectra were collected in transmission mode with intensities of incident and transmitted X-ray beams measured using gas-filled ionization chambers. Scans were normalized using the program, Athena[3].

Supporting Results:

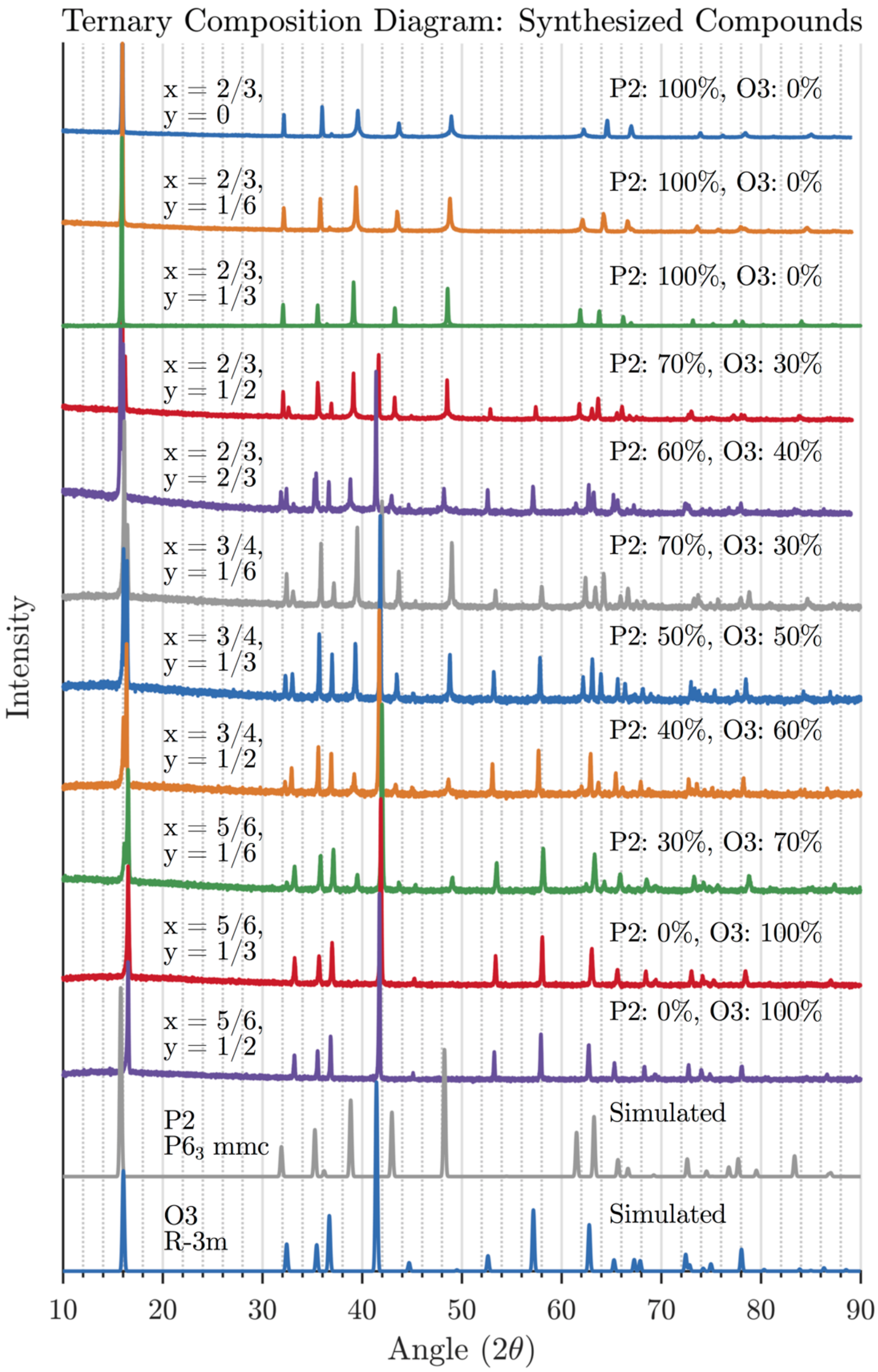
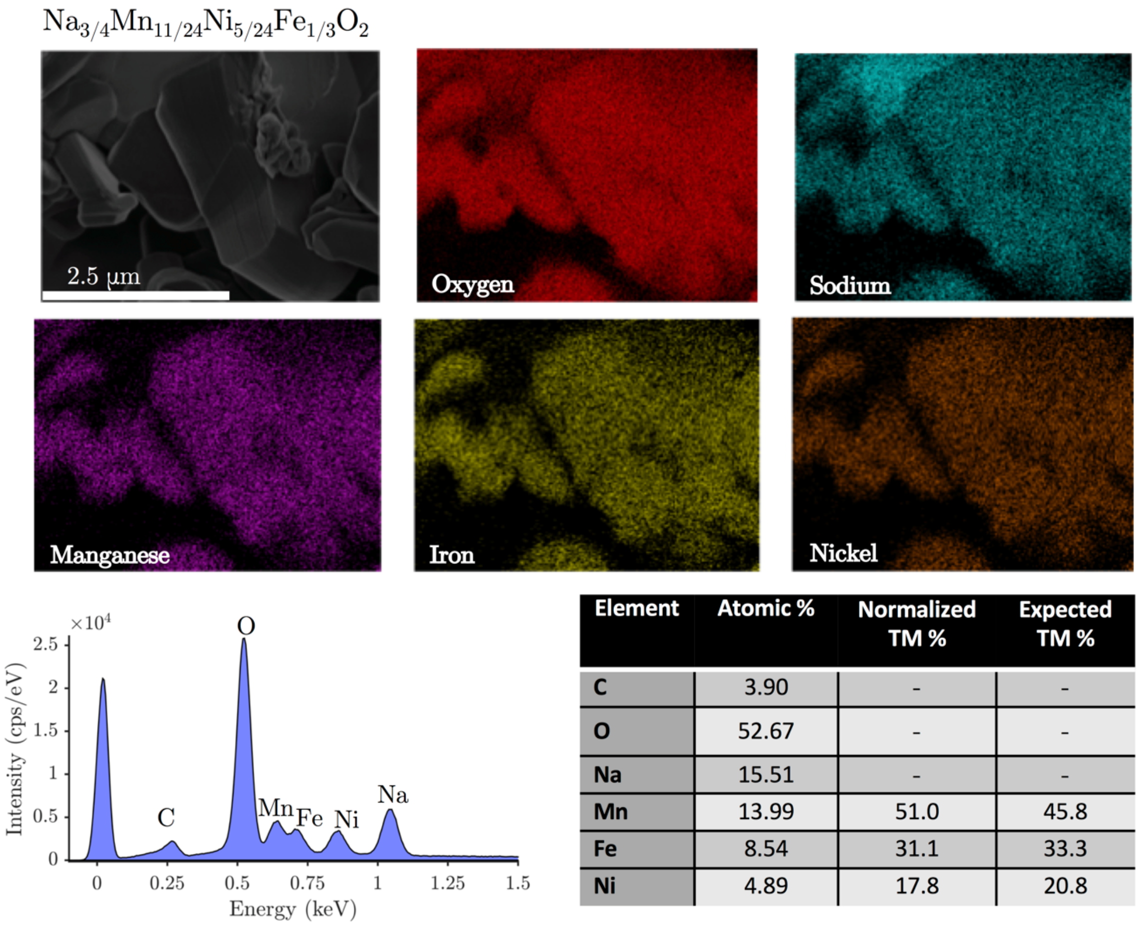


Figure S1. Stacked X-ray diffraction patterns of the compositions from phase diagram in Figure 1 which were used to refine the phase fractions annotated on the figure. The compositions are labeled with x and y, referring to the formula: $Na_x[Ni_{(x-y)/2}Mn_{(1-x-y)/2}Fe_y]O_2$.



Element	Atomic %	Normalized TM %	Expected TM %
C	3.90	-	-
O	52.67	-	-
Na	15.51	-	-
Mn	13.99	51.0	45.8
Fe	8.54	31.1	33.3
Ni	4.89	17.8	20.8

Figure S2: The composition, $Na_{3/4}[Mn_{11/24}Ni_{5/24}Fe_{1/3}]O_2$, was measured by SEM/EDX to identify any inhomogeneous transition metal ratios that might have occurred alongside the P2/O3 phase segregation as refined from XRD. Representative images are shown above. No such distribution could be seen, and the transition metal ratios are close to expected values. This does not rule the possibility, however, of a P2/O3 intergrowth which might not be visible on the length scales probed.

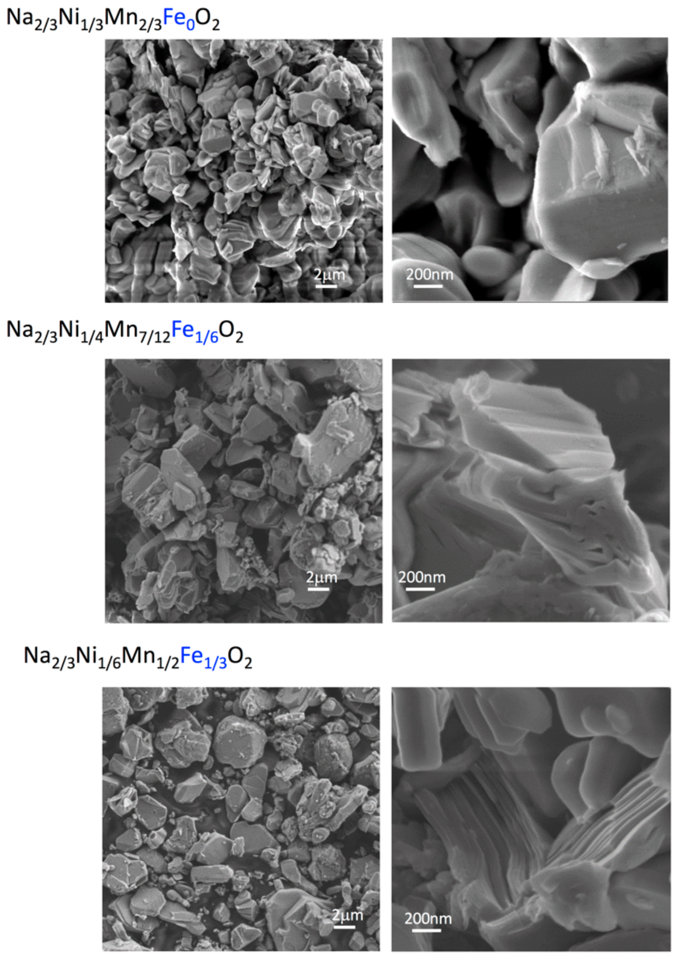


Figure S3: SEM images show all three samples have well defined flat plate like morphology with particles in the ranges 0.5 µm -5 µm. While, $Na_{2/3}Ni_{1/3}Mn_{2/3}Fe_0O_2$ has majority of the particles with average dimension of around 2 µm, for $Na_{2/3}Ni_{1/4}Mn_{7/12}Fe_{1/6}O_2$ and $Na_{2/3}Ni_{1/6}Mn_{1/2}Fe_{1/3}O_2$ majority of the particles have average dimension of 4-5 µm. High resolution SEM images on the right panel shows that each of these flat plate like particles have layer like morphology.

Table S1. ICP-MS results

Sample	**Na**	**Ni**	**Mn**	**Fe**
$Na_{2/3}Ni_{1/4}Mn_{7/12}Fe_{1/6}O_2$	0.70(3)	0.24	0.60	0.16
$Na_{2/3}Ni_{1/6}Mn_{1/2}Fe_{1/3}O_2$	0.73(3)	0.16	0.54	0.31

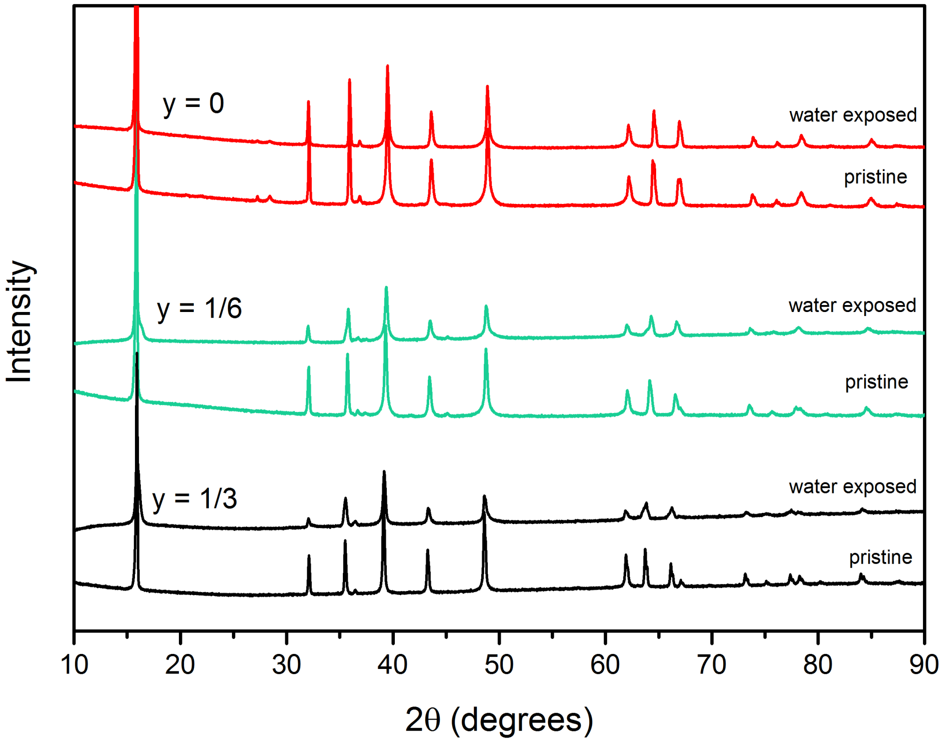


Figure S4. To test the stability of each sample against water, each of the samples were exposed to water and subsequently dried. The X-ray diffraction patterns show that the structure of $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ is not affected by the water exposure. However, both of the Fe containing samples develop an asymmetry on many of the Bragg reflections after water exposure demonstrating that they are water sensitive.

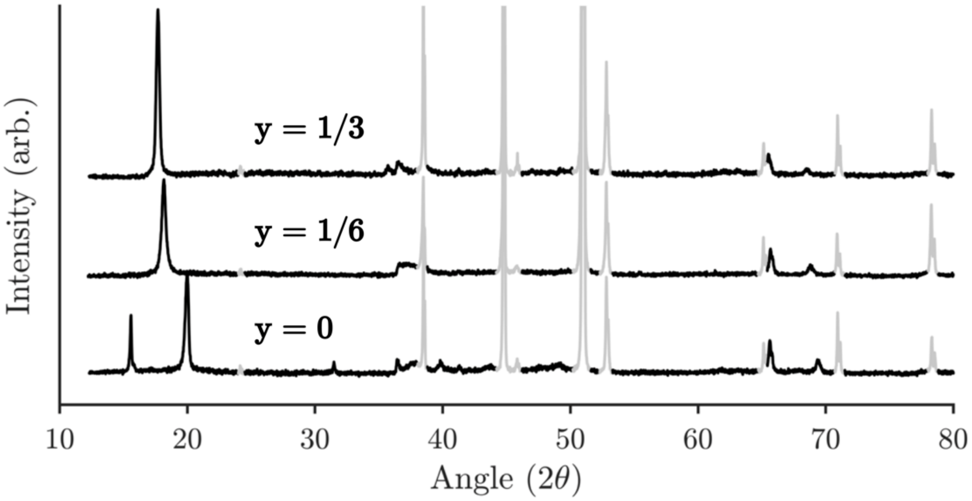


Figure S5. XRD patterns for all three relevant compositions, $Na_{2/3}[Ni_{1/3-y/2}Mn_{2/3-y/2}Fe_y]O_2$ (y = 0,1/6,1/3), charged to 4.5 V vs Na/Na^+ are shown. Peaks from the air sensitive cell are marked in grey. The data shows that end of charge sample for $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ is a mixed phase with characteristic peaks of the P2 and O2 phases. On the other hand, $Na_{2/3}[Ni_{1/4}Mn_{7/12}Fe_{1/6}]O_2$ and $Na_{2/3}[Ni_{1/6}Mn_{1/2}Fe_{1/3}]O_2$ appear to be a single phase, previously described in literature as the Z-phase.

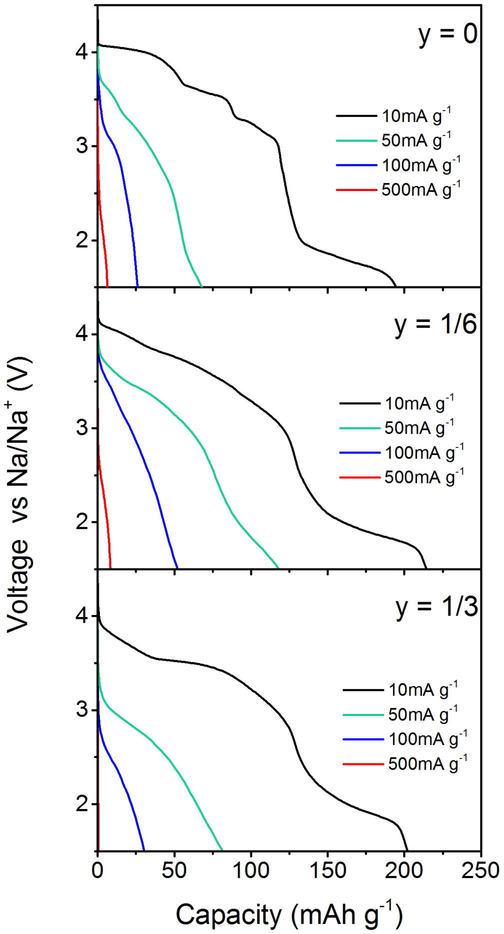


Figure S6. The rate performance is show for $Na_{2/3}[Ni_{1/3-y/2}Mn_{2/3-y/2}Fe_y]O_2$ (y = 0, 1/6, 1/3). Capacity is limited when discharged at high rates for all 3 samples. All samples had similar active material loadings and were prepared with 15% carbon Super P additive as explained in the Methods section.

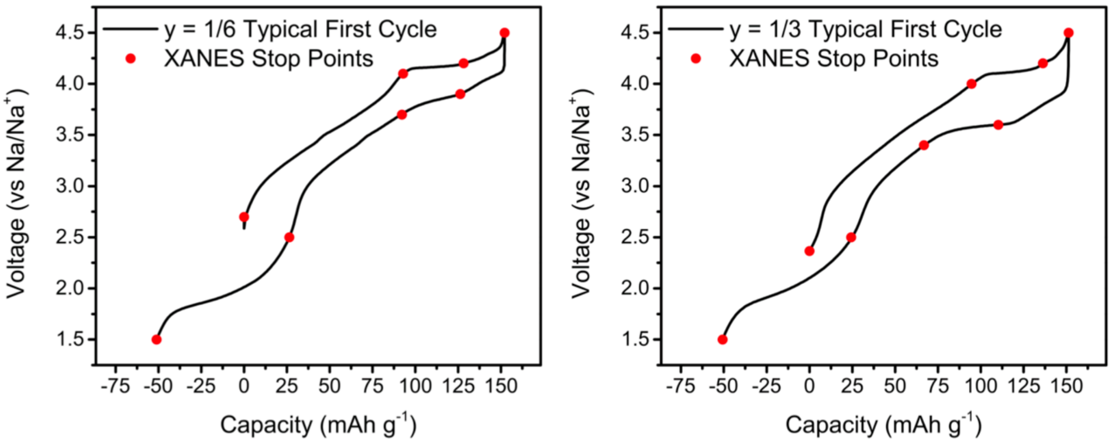


Figure S7. Ex situ extraction points shown for XANES on the electrochemical load curve of the $Na_{2/3}[Ni_{1/4}Mn_{7/12}Fe_{1/6}]O_2$ (y = 1/6) sample (left) and $Na_{2/3}[Ni_{1/6}Mn_{1/2}Fe_{1/3}]O_2$ (y = 1/3) sample (right).