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SUPPLEMENTARY INFORMATION

Introducing Na-sufficient P3-Na_{0.9}Fe_{0.5}Mn_{0.5}O₂ as cathode material for Na-ion batteries

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Note added after first publication: This supplementary information file replaces that originally published on 31 July 2020. There were originally some errors in Table S2. The lattice parameter values and the z value for the O1 atom site have been corrected in this updated version.

Figures and Tables:



Figure S1: Sodiation curve of pristine P3-Na_{0.9}Fe_{0.5}Mn_{0.5}O₂



Figure S2: FESEM images of P3-NFM at different magnifications (a) 100 μ m, (b) 10 μ m and (c) 1 μ m.



Figure S3: Galvanostatic curves of P3-NFM for different voltage windows and C-rates : (a) Cycle 1, 5 and 10 for 4.1-2.5 V at 0.2C (0.2 C = 0.02 A/g), (b) Discharge curves at 0.2C, 0.5C, 1C and 2C for 4.1-2.5 V, (c) Cycle 1, 5 and 10 for 4.2-2.5 V at 0.2C (0.2 C = 0.02 A/g), (d) Discharge curves at 0.2C, 0.5C, 1C and 2C for 4.2-2.5 V, (e) Cycle 1, 5 and 10 for 4.4-1.5 V at 0.2C (0.2 C = 0.02 A/g), and (f) Discharge curves at 0.2C, 0.5C, 1C and 2C for 4.4-1.5 V. 1M NaClO₄ in PC was used as electrolyte.



Figure S4: Discharge voltage in various voltage windows and modified protocol at 0.2C, 0.5C, 1C and 2C for P3-NFM half-cells



Figure S5:: (a) Comparison of pristine P3-NFM's Fe-Kedge with that of Fe_2O_3 and $(CH_3COO)_2Fe$ (b) Comparison of pristine P3-NFM's Mn K-edge with that of MnCO₃ (Mn(II)_1), (CH_3COO)_2Mn(Mn(II)_2), Mn_2O_3(Mn(III)_1), LiMnO_2(Mn(III)_2), Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O_2(Mn(IV)_1)



Figure S6: Ex-situ XANES curves for electrode samples at (a) Fe K-edge and (b) Mn K edge.
Magnified Ex-situ XANES curves for (c) Fe K-egde and (d) Mn K-edge. (e) Centroids of pre edge peaks for Fe K-edge and Mn K-edge. Pristine – Pristine electrode, C420_1 – Charged up to 4.2 V at the first cycle, C440_1 – Charged up to 4.4 V at the first cycle, D200_1 – Discharged up to 2.0 V at the first cycle, C420_2 – Charged up to 4.2 V at the second cycle, , D200_2 – Discharged up to 2.0 V at the second cycle.

Table S1: ICP results of pristine P3-Na_{0.9}Fe_{0.5}Mn_{0.5}O₂

	Observed (wt/wt%)	Expected (wt/wt%)
Na/Fe	0.727	0.741
Na/Mn	0.762	0.753

Table S2. Rietveld refinement results of pristine P3-Na_{0.9}Fe_{0.5}Mn_{0.5}O₂ XRD patterns.

Space group: R3m; $R_{exp} = 4.06$; $R_{wp} = 6.28$; $Chi^2 = 1.54$

Atom Sites	X	У	Z	Occ	Beq
Na1	0	0	0.1763(5)	0.88(3)	1
Mn1	0	0	0	0.49(2)	1
Fe1	0	0	0	0.50(3)	1
01	0	0	0.3991(6)	1	1
O2	0	0	0.6051(9)	1	1

Lattice parameters a = 2.9180 (7) Å, c =16.9525 (10) Å

Methods:

Synthesis and Characterization

P3-NFM was synthesized using a simple solution-based synthesis. In a typical synthesis, stoichiometric amounts of Na₂CO₃ (Alfa Aesar, 98%), CH₃(COO)₂Fe (Alfa Aesar, 97%), and MnCO₃ (Alfa Aesar, 98+%) was added in the aqueous solution of citric acid (amount of citric acid was equal to the molar equivalent of total transition metals). The pH of the solution at this stage was c.a. 3.85. NH₄OH solution (Alfa Aesar, 50% v/v) was added to adjust the pH to c.a. 8.8-9.0. The resultant solution was mixed for 24 h, followed by drying on a hot-plate at 120 °C for 8-10 h. The dried powder was crushed and mixed well in mortar-pestle and finally calcined in ambient air. A two-step calcination was employed which includes calcining at 900 °C for 15 h followed by further calcination at 500 °C for 2 h, finally quenching the product in air at 250-300 °C, ramp rate for cooling/heating was maintained at 5 °C/min.

Powder XRD was recorded using Bruker Advance which uses Cu-K α radiation (Voltage = 40 kV and Current = 40mA). Rietveld refinement was performed using TOPAS V6. Field Emission Scanning Electron Microscopy data was collected using JEOL-JSM 7000F for morphology studies.

Electrochemical Methods

2016 coin cells were assembled for Galvanostatic testing in both full cell and half cell formats. Half cells were tested against Na-metal as the counter electrode. P3-Na_{0.9}Fe_{0.5}Mn_{0.5}O₂ (P3-NFM) electrodes were prepared by making a slurry of P3-NFM powder, Super P (Alfa Aesar) conductive carbon and PVDF (Kureha) powder in N-methyl-2-pyrrolidone (Sigma Aldrich) in the wt./wt. ratio of 80:10:10 respectively. The slurry was coated on an aluminium foil and dried in vacuum at 110 °C for 6h. The coated electrodes were roll pressed at 4kN and disks of 1cm² were punched out of them. The active material loading of these electrodes were in the range of 6-7 mg/cm². These electrode disks were dried in antechamber at 110 °C in vacuum before cell assembly. Coin cell assembly was done in Argon filled Glovebox (MBraun) with

 H_2O and O_2 concentration lower than 1ppm. Whatman Glass Fibre (Sigma Aldrich) separators were used as separators during coin cell assembly and 1M NaClO₄ in Propylene Carbonate (Sigma Aldrich) was used as electrolyte for both full cells and half cells.

Full cells were assembled with Hard carbon composite electrodes (95% Hard carbon, 5% Sodium salt of carboxy-methyl cellulose). The cathode to anode active material ratio was fixed as 1.65. All galvanostatic testing was carried out on Arbin testers. Operando XRD was performed in a hermetically sealed cell with a beryllium window in variable slit-width mode using a Bruker Advance.

Ex-situ X-ray Absorption Near Edge Spectroscopy(XANES) Methods

Electrodes at various SoCs and DoDs were disassembled in the glovebox and sandwiched between Kapton tapes to avoid air exposure during measurement. The prepared samples were stored in an air tight argon filled box inside the glovebox. The air exposure prior to beamline measurement was thus avoided.

X-ray absorption spectroscopy (XAS) measurements were conducted at the Singapore Synchrotron Light Source (SSLS) using the X-ray absorption fine structure for catalysis (XAFCA) beamline in transmission mode.¹ The electron storage ring at the SSLS was operated at 700 MeV and 200 mA, and a Si(111) monochromator was used for varying the energy. Software packages – Athena and Artemis by Ravel et al.² – were used for XAS data analyses.² The inflection point was set as E_0 for normalization; energy calibration was made using XAS spectra of metal foils (Fe and Mn), which was measured under the same conditions.

References:

1. Y. Du, Y. Zhu, S. Xi, P. Yang, H. O. Moser, M. B. H. Breese and A. Borgna, J. Synchrotron Radiat., 2015, 22(3), 839–843.

2. B. Ravel and M. Newville, J. Synchrotron Radiat., 2005, 12(4), 537-541.