Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Density Distribution of Mn-N bond by Tuning effect through partial Replacement of Mn by Co or Ni in Sodium-rich Hexacyanoferrate and its influence on the Stability as Cathode for Na-ion Batteries

M. Oliver-Tolentino, G. Ramos-Sánchez, M. González M., H. Osiry, I. González

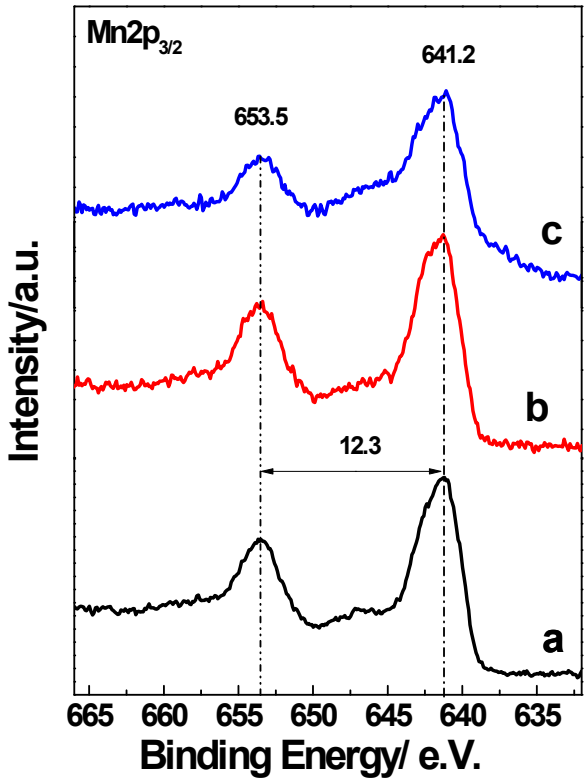

Figure S1. Manganese High resolution X-ray Photon Spectroscopy of a) MnFe, b) MnCoFe and c) MnNiFe.

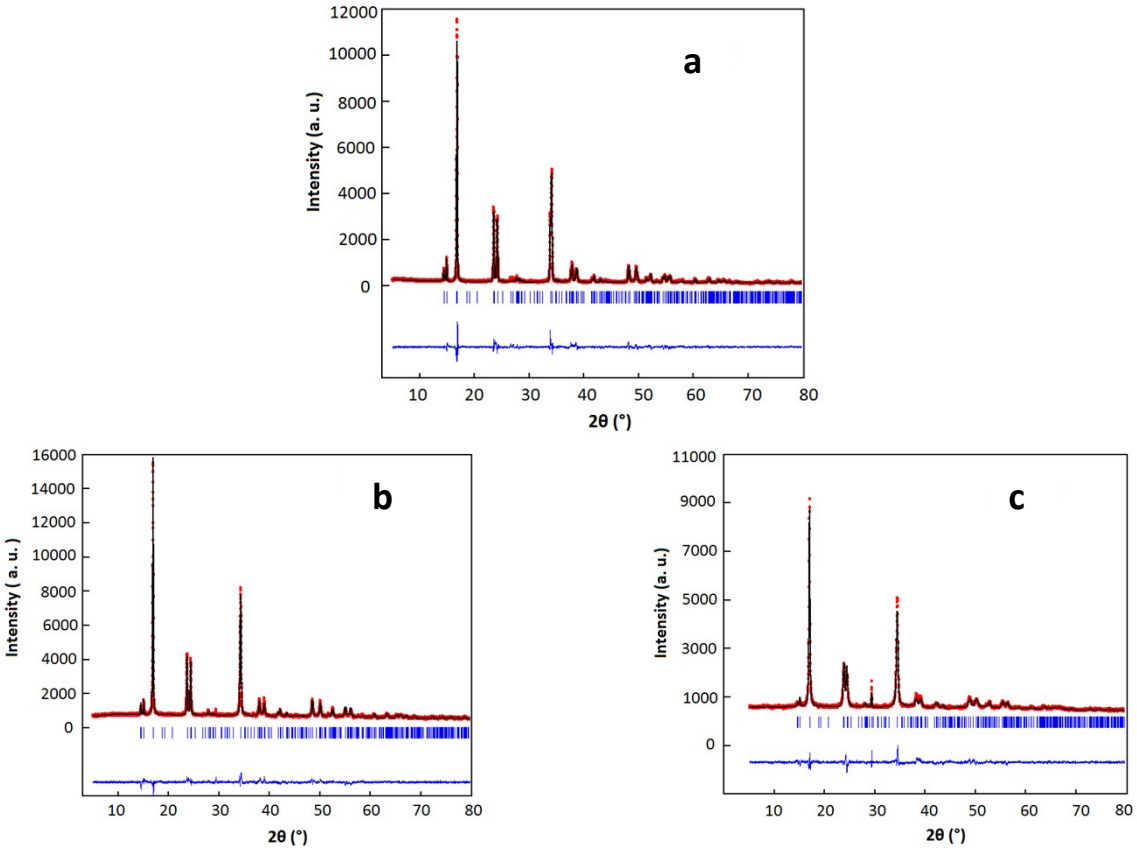

Figure S2. XRD pattern of a) MnFe, b) MnCoFe and c) MnNiFe, its fitting according to the refined structural model, and their difference.

Table S1. Details of data collection, crystal data and structure refinement.

	MnFe	**MnCoFe**	**MnNiFe**
Diffractometer	D8 Adavnced	D8 Adavnced	D8 Adavnced
Radiation	Cu$K_{\alpha 1}$	Cu$K_{\alpha 1}$	Cu$K_{\alpha 1}$
2θ range [°]	5 – 80	5 – 80	5 – 80
Step scan [°]	0.008	0.008	0.008
Count time [s/step]	10	10	10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P* $2_1/n$	*P* $2_1/n$	*P* $2_1/n$
a [Å]	10.5726(2)	10.4693(5)	10.391(2)
b [Å]	7.5240(3)	7.4961(6)	7.475(11)
c [Å]	7.3264(3)	7.2769(5)	7.227(1)
β (°)	92.114(3)	92.33(5)	91.66(9)
V [Å^3]	582.41(4)	570.62(7)	561.7(1)
Z	2	2	2
Number of observations	388	383	409
Number of reflections	159	144	119
Number of structural parameters refined	34	34	34
Number of profile parameters refined	10	10	10
Number of distance restrictions	9	9	9
R_{exp}	5.999	3.486	3.846
R_{wp}	10.118	5.365	5.731
R_B	7.367	10.645	6.098
S	1.685	1.53	1.489

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for MnFe.

Atom	**Wyck.**	**x**	**y**	**z**	**Uiso*/Ueq**
Mn	2a	0.5	0.5	0.5	0.0374(3)
Fe	2d	0.5	0	1	0.037(3)
C1	4e	0.5057(3)	0.1911(2)	0.8242(2)	0.050(5)
C2	4e	0.1835(1)	0.5017(3)	0.5025(2)	0.050(5)
C3	4e	0.5024(3)	0.1798(3)	0.1888(2)	0.050(5)
N1	4e	0.4994(2)	0.3042(2)	0.7220(2)	0.050(5)
N2	4e	0.2907(1)	0.4968(2)	0.4971(2)	0.050(5)
N3	4e	0.4993(2)	0.2905(2)	0.2950(2)	0.050(5)
O1	4e	0.2507(2)	0.2125(1)	0.2915(1)	0.050(5)
Na	4e	0.2488(7)	0.4401(8)	0.0418(8)	0.081(2)

Table S3. Atomic coordinates and equivalent isotropic displacement parameters for MnCoFe.

Atom	**Wyck.**	**x**	**y**	**z**	**Uiso*/Ueq**
Mn	2a	0.5	0.5	0.5	0.038(8)
Co	2a	0.5	0.5	0.5	0.038(8)
Fe	2d	0.5	0	1	0.0380(8)
C1	4e	0.4985(5)	0.1800(4)	0.8104(4)	0.05066
C2	4e	0.1850(3)	0.5018(4)	0.4936(4)	0.050(8)
C3	4e	0.5058(4)	0.1852(4)	0.1867(4)	0.050(8)
N1	4e	0.4993(4)	0.2894(4)	0.7014(4)	0.050(8)
N2	4e	0.2934(2)	0.5007(3)	0.4929(3)	0.050(8)
N3	4e	0.5037(4)	0.2914(4)	0.2939(4)	0.050(8)
O1	4e	0.2537(3)	0.2305(3)	0.2793(2)	0.050(8)
Na	4e	0.2511(8)	0.4529(8)	0.0303(9)	0.050(1)

Table S4. Atomic coordinates and equivalent isotropic displacement parameters for MnNiFe.

Atom	**Wyck.**	**x**	**y**	**z**	**Uiso*/Ueq**
Mn	2a	0.5	0.5	0.5	0.037(9)
Ni	2a	0.5	0.5	0.5	0.037(9)
Fe	2d	0.5	0	1	0.037(9)
C1	4e	0.5126(5)	0.1810(7)	0.8085(7)	0.049(1)
C2	4e	0.1869(3)	0.5115(6)	0.5101(6)	0.049(1)
C3	4e	0.5040(6)	0.1848(7)	0.1895(7)	0.049(1)
N1	4e	0.5098(4)	0.2969(5)	0.7062(6)	0.049(1)
N2	4e	0.2960(3)	0.5068(4)	0.5077(4)	0.049(1)
N3	4e	0.5031(5)	0.2944(6)	0.2972(6)	0.049(1)
O1	4e	0.2390(4)	0.2252(4)	0.2636(4)	0.049(1)
Na	4e	0.2658(2)	0.4554(1)	-0.0022(2)	0.071(2)

Table S5. Selected bond lengths (Å) and bond angle (°) for MnFe.

Bond distances (Å)			
Fe – C1	1.932(15)	Mn – N1	2.194(15)
Fe – C2^{i}	1.939(11)	Mn – N2	2.212(11)
Fe – C3^{ii}	1.934(19)	Mn – N3	2.177(15)
C1 – N1	1.134(2)	C3 – N3	1.141(2)
C2 – N2	1.136(15)		
Interatomic distances (Å)			
Na - Na	4.843(8)	Mn – Mn	10.573(2)
Bond Angles (°)			
Fe - C1 - N1	174.81(17)	N1 – Mn – N3	91.44(10)
Fe - C2^{i} - N2^{i}	176.62(12)	N1 – Mn – N3^{iii}	88.56(10)
Fe - C3^{ii} - N3^{ii}	176.52(18)	N2 – Mn – N3	89.57(9)
N1 – Mn – N2	88.26(9)	N2^{iii} – Mn – N3	90.43(10)
N1 – Mn – N2^{iii}	91.74(10)		

Symmetry codes: (i) x+1/2, -y+1/2, z+1/2; (ii) x, y, z+1/2; (iii) –x+1, -y+1, −z+1.

Table S6. Selected bond lengths (Å) and bond angle (°) for MnCoFe.

Bond distances (Å)			
Fe – C1	1.930(3)	Mn/Co – N1	2.154(3)
Fe – C2^{i}	1.939(3)	Mn/Co – N2	2.161(2)
Fe – C3^{ii}	1.942(3)	Mn/Co – N3	2.168(3)
C1 – N1	1.141(4)	C3 – N3	1.115(4)
C2 – N2	1.135(4)		
Interatomic distances (Å)			
Na - Na	4.926(9)	Mn – Mn	10.469(3)
Bond Angles (°)			
Fe - C1 - N1	178.2(3)	N1 – Mn/Co – N3	86.87(19)
Fe - C2^{i} - N2^{i}	178.6(3)	N1 – Mn/Co – N3^{iii}	93.13(20)
Fe - C3^{ii} - N3^{ii}	177.1(3)	N2 – Mn/Co – N3	91.84(19)
N1 – Mn/Co – N2	89.20(18)	N2^{iii} – Mn/Co – N3	88.16(18)
N1 – Mn/Co – N2^{iii}	90.80(19)		

Symmetry codes: (i) x+1/2, -y+1/2, z+1/2; (ii) x, y, z+1/2; (iii) –x+1, -y+1, −z+1.

Table S7. Selected bond lengths (Å) and bond angle (°) for MnNiFe.

Bond distances (Å)			
Fe – C1	1.943(5)	Mn/Ni – N1	2.128(4)
Fe – C2^{i}	1.945(3)	Mn/Ni – N2	2.125(3)
Fe – C3^{ii}	1.945(5)	Mn/Ni – N3	2.125(4)
C1 – N1	1.139(7)	C3 – N3	1.130(7)
C2 – N2	1.136(4)		
Interatomic distances (Å)			
Na - Na	5.237(17)	Mn – Mn	10.401(2)
Bond Angles (°)			
Fe - C1 - N1	172.5(5)	N1 – Mn/Ni – N3	88.0(3)
Fe - C2^{i} - N2^{i}	174.7(4)	N1 – Mn/Ni – N3^{iii}	92.0(3)
Fe - C3^{ii} - N3^{ii}	177.9(5)	N2 – Mn/Ni – N3	94.0(3)
N1 – Mn/Ni – N2	91.5(12)	N2^{iii} – Mn/Ni – N3	86.0(3)
N1 – Mn/Ni – N2^{iii}	88.5(2)		

Symmetry codes: (i) x+1/2, -y+1/2, z+1/2; (ii) x, y, z+1/2; (iii) –x+1, -y+1, −z+1.

Magnetic Properties

The Curie constant (C/emu K/Mn-mol) obtained from least squares fit of Figure 3 curve *i* were 1.97, this higher Curie constant value obtained at near room temperature indicates an increase in the effective paramagnetic moment (P_{eff}). In the *quasi* paramagnetic region, the Curie constant is written as equation 1.

$$C = \frac{N_s P_{eff}^2 \mu_B^2}{3k_B} \quad \text{.....(1)}$$

where N_S, μ_B and k_B are the number of ions, the Bohr magneton and the Boltzmann constant, respectively.

The 2 K field dependence of the magnetization, M(H), shows a higher increase with increasing field H (Fig. S3a) as predicted by the Brillouin expression, this suggests weak ferromagnetic ordering at low temperatures, also displayed by the low temperature region of the μeff Vs T plots (see figure 3).

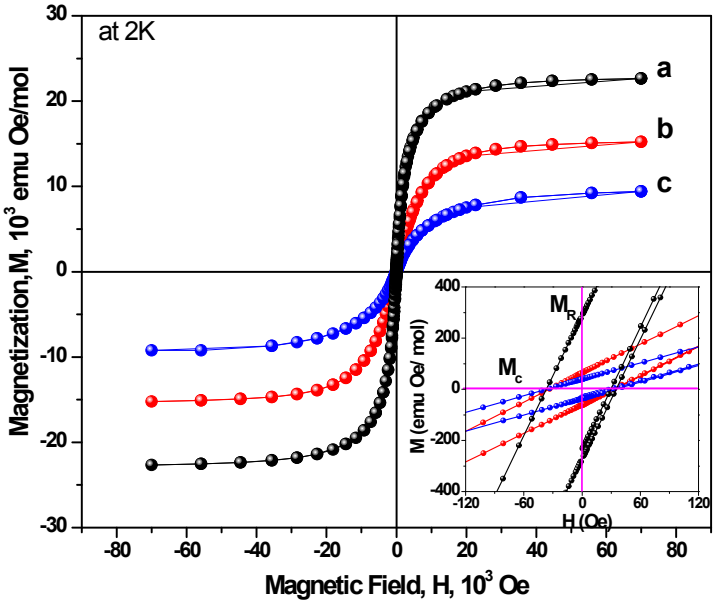

Figure S3 M vs H. The increasing of magnetization with increasing field with respect to the expectation from the Brillouin expression in all samples is suggestive of magnetic ordering. Zoom: The coercitive field and remanent magnetization of a) MnFe, b) MnCoFe and c) MnNiFe.