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Comparative Analysis of M_a Site Elements in Fe-Based Prussian Blue Frame Materials for Ammonium Ion Battery Applications: A First-Principles Study

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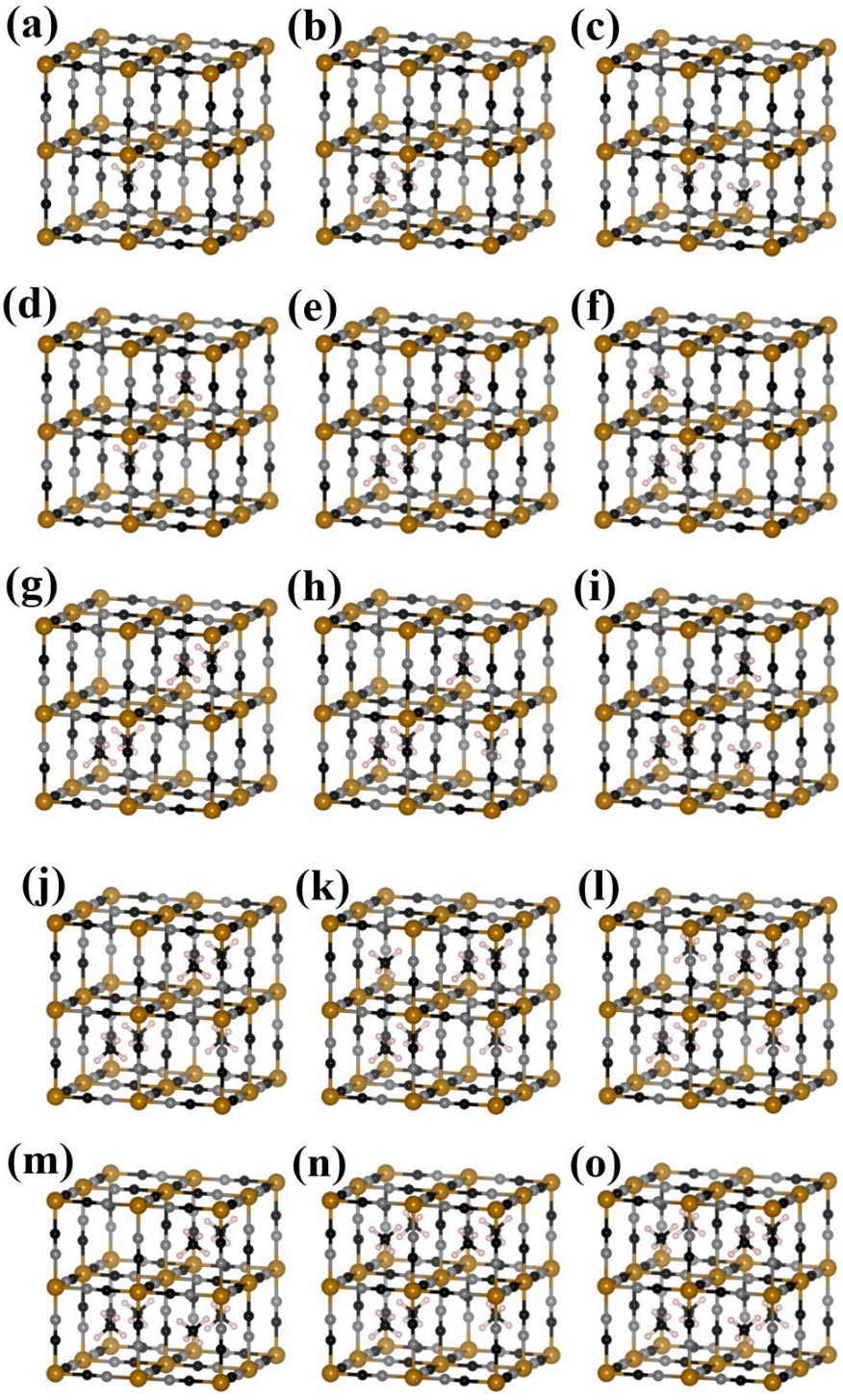

Fig. S1 The considered configurations of NH_4^+ embedding in $Fe[Fe(CN)_6]$. (a) 1 NH_4^+, (b-d) 2 NH_4^+, (e-f) 3 NH_4^+, (g-i) 4 NH_4^+, (j) 5 NH_4^+, (k-m) 6 NH_4^+, (n) 7 NH_4^+, (o) 8 NH_4^+.

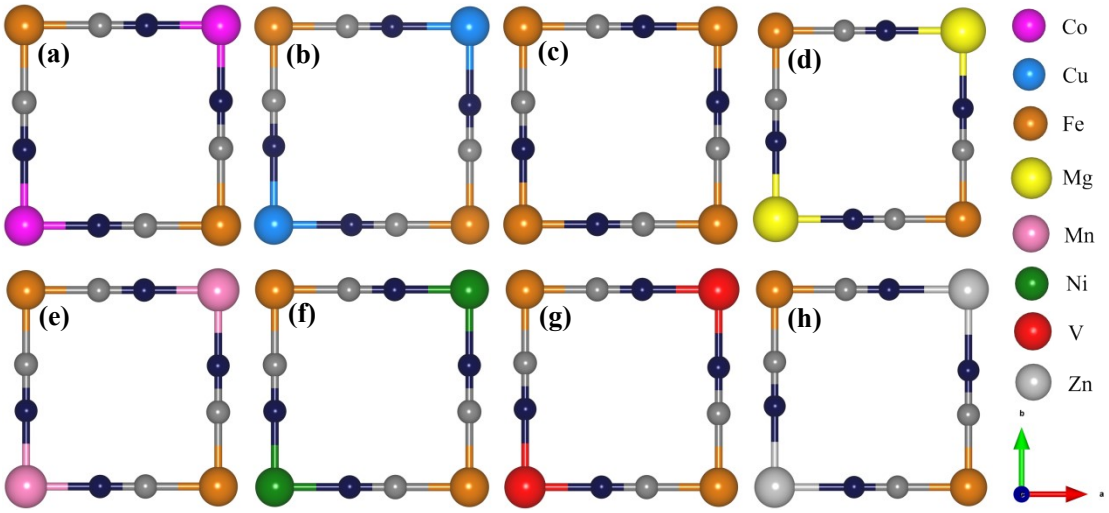

Fig. S2 Front view of $M_a[Fe(CN)_6]$ (M_aFe PBAs) local models with different M_a elements. And M_a = (a) Co, (b) Cu, (c) Fe, (d) Mg, (e) Mn, (f) Ni, (g) V, (h) Zn.

Tab. S1 Average atomic distances of M_aFe PBAs for different M_a elements (M_a = Co, Cu, Fe, Mg, Mn, Ni, V, Zn).

M_a	M_a-Fe (Å)	M_a-N (Å)	N-C (Å)	C-Fe (Å)
Cu	5.09	2.02	1.17	1.91
Co	4.94	1.87	1.17	1.90
Fe	4.95	1.89	1.17	1.89
Mg	5.24	2.16	1.17	1.91
Mn	4.97	1.91	1.17	1.88
Ni	4.98	1.92	1.17	1.89
V	5.04	1.99	1.18	1.87
Zn	5.22	2.14	1.17	1.91

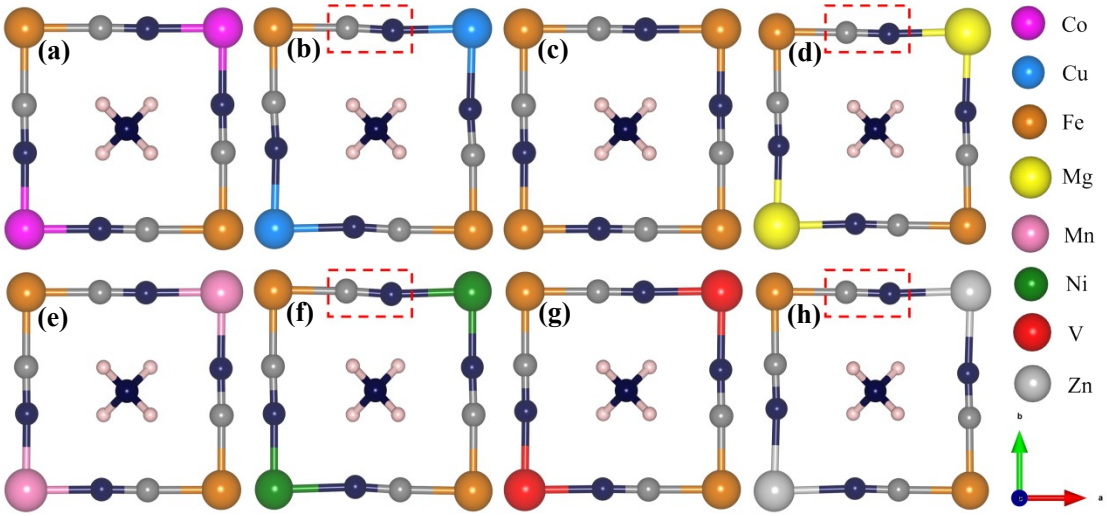

Fig. S3 Front view of $M_a[Fe(CN)_6]$ (M_aFe PBAs) local models with different Ma elements after inserting an NH_4^+ ion. And M_a = (a) Co, (b) Cu, (c) Fe, (d) Mg, (e) Mn, (f) Ni, (g) V, (h) Zn.

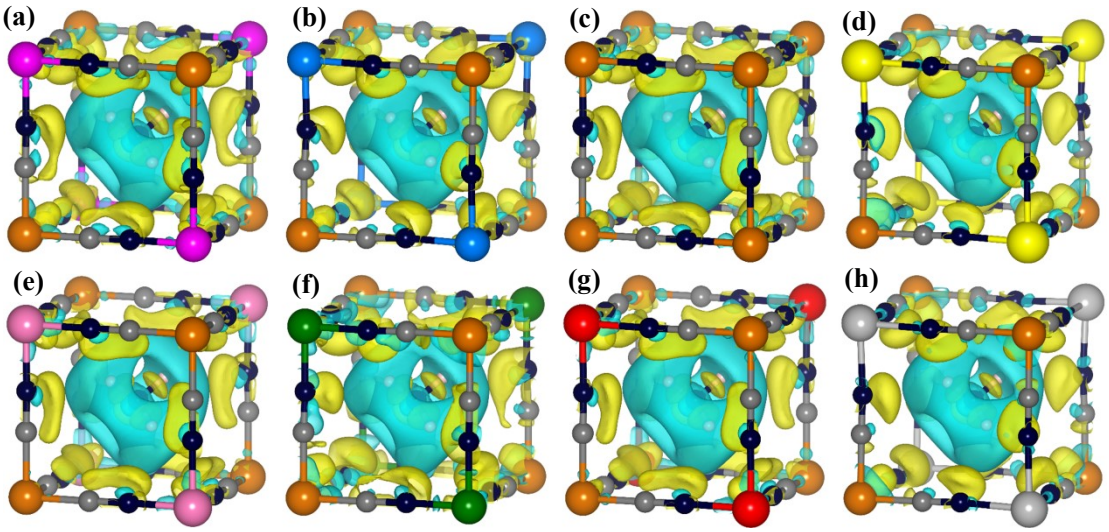

Fig. S4 Charge Density Difference (CDD) of different $NH_4 \cdot M_aFe$ PBAs local models. M_a = (a) Co, (b) Cu, (c) Fe, (d) Mg, (e) Mn, (f) Ni, (g) V, (h) Zn.

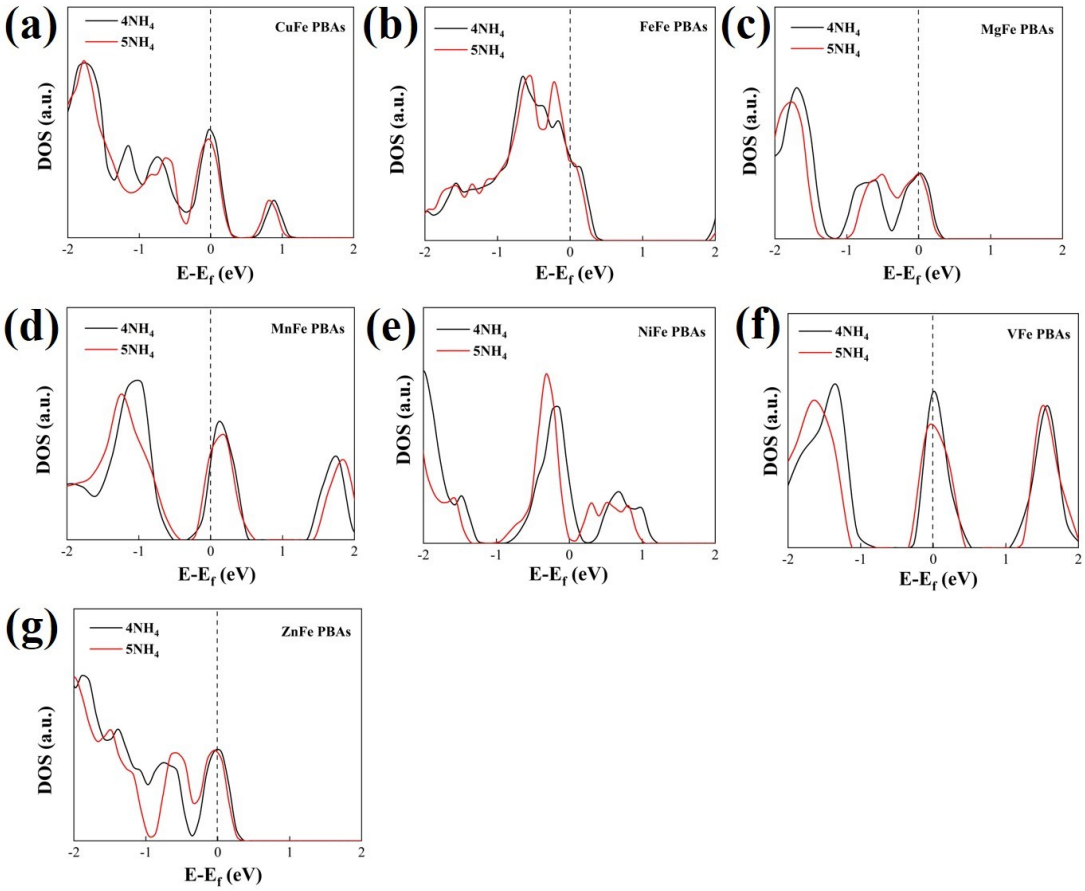

Fig. S5 The electron state density of M_aFe PBAs model with 4 and 5 NH_4^+ inserted. M_a = Cu, Fe, Mg, Mn, Ni, V, Zn.

Tab. S2 Nominal battery voltage for M_aFe PBAs models with different amounts of NH_4^+ inserted. M_a = Co, Cu, Fe, Mg, Mn, Ni, V, Zn.

Voltage	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**Potential range**
(V)	**NH_4^+**	**NH_4^+**	**NH_4^+**	**NH_4^+**	**NH_4^+**	**NH_4^+**	**NH_4^+**	**NH_4^+**	**(V)**
Co	4.19	4.24	4.00	3.99	2.57	2.66	2.63	2.94	1.67
Cu	4.62	5.14	4.90	4.88	4.40	4.35	4.27	4.20	0.94
Fe	4.05	4.09	3.83	3.81	3.52	3.48	3.19	3.07	1.02
Mg	5.07	4.89	4.62	4.54	4.29	4.22	4.00	3.90	1.17
Mn	3.64	3.52	3.22	3.14	2.88	2.82	2.45	2.44	1.20
Ni	4.70	4.53	4.16	4.21	4.04	4.05	4.16	4.06	0.66
V	3.69	3.61	3.34	3.26	2.93	2.81	2.45	2.28	1.41
Zn	5.07	4.86	4.63	4.52	4.31	4.19	4.03	3.87	1.19

Tab. S3 Voltage ranges and specific capacities @ current densities of reported PBAs used as electrode materials for aqueous ammonium ion batteries.

Electrode	Potential range (V)	Specific capacity ($mAh \cdot g^{-1}$) @ current density ($mA \cdot g^{-1}$)	Ref.
CuHCF	1.24	55@500	[1]
NiHCF	0.6	38@500	[2]
N-CuHCF	0.5	53.1@1000	[3]
MnHCF	1.0	104@100	[4]
$K_{0.9}Cu_{1.3}Fe(CN)_6$	1.0	60@50	[5]
$NaFe[Fe(CN)_6]$	0.6	60@250	[6]
$Na_{1.45}Fe[Fe(CN)_6]_{0.93}$	1.0	75@250	[7]
$(NH_4)_2Cu[Fe(CN)_6]$	0.8	77.8@150	[2]
K-V-Fe PBAs	1.2	93.4@2000	[8]
$Na_{0.73}Ni[Fe(CN)_6]_{0.88}$	0.6	92.5@100	[9]
$Ni_2Fe(CN)_6$	0.4	57.4@556	[10]

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