Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Transition Metal Oxynitrides Catalysts for Electrochemical Reduction of Nitrogen to Ammonia

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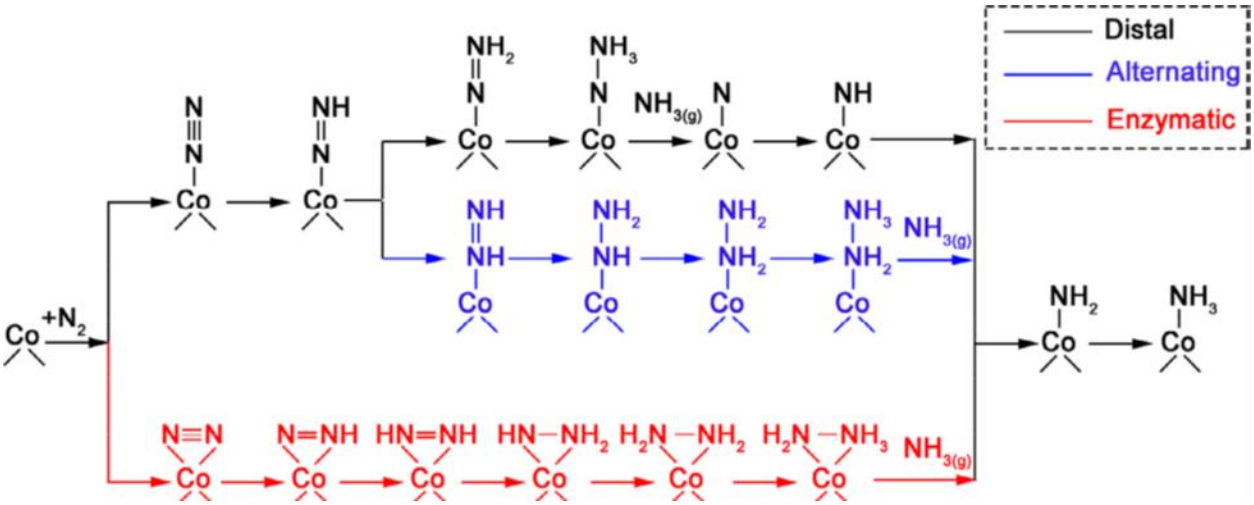


Figure S1. Three main pathways for ENRR: (i) distal, (ii) alternating, and (iii) enzymatic. (Figure adapted from ref.[1] with permission).

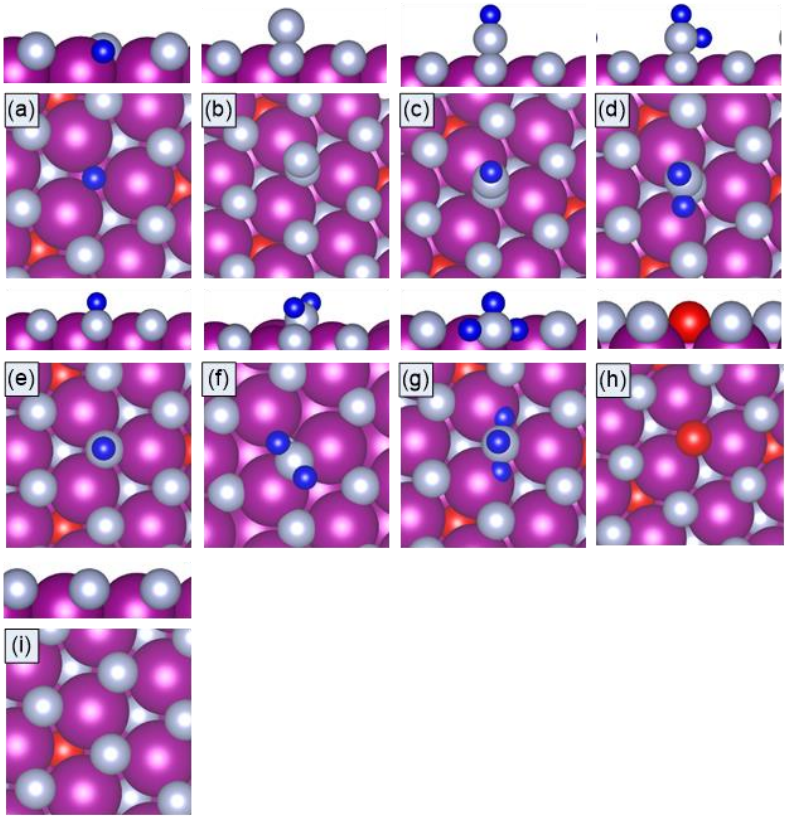
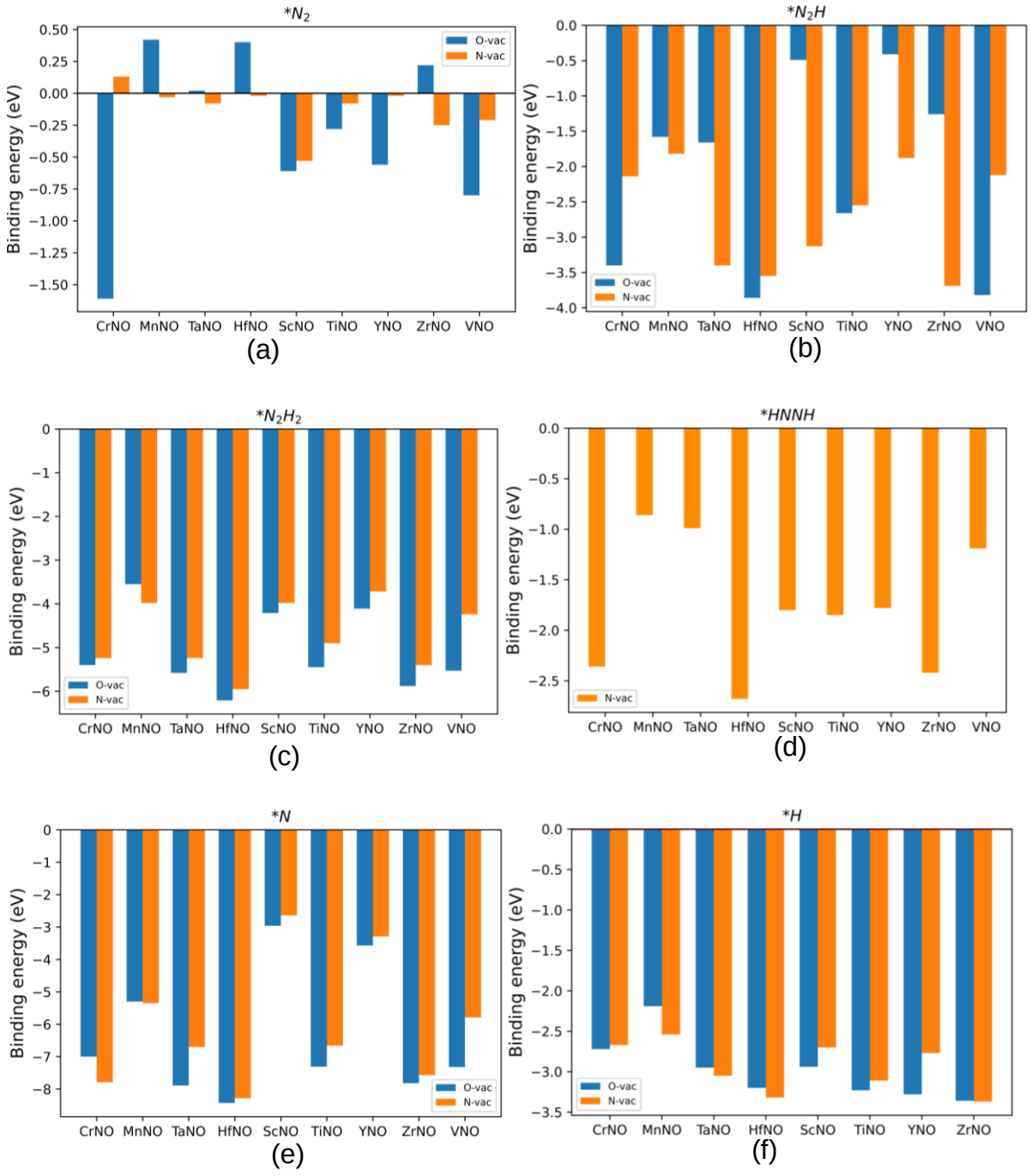


Figure S2. DFT optimized geometries of (a) *H, (b) *N_2, (c) *N_2H, (d) *N_2H_2, (e) *NH, (f) *NH_2, (g) *NH_3, (h) *O, and (i) *N adsorbed on O-vac of MnNO(111). Mn: purple, N: gray, O: red, H: blue.

Table S1. ZPE and TS values of the adsorbed species.

species	ZPE/eV	TS/eV
*N_2	0.18	0.18
*N_2H	0.51	0.08
*N_2H_2	0.87	0.11
*HNNH	0.84	0.15
*N	0.10	0.02
*H	0.18	0.00
*NH	0.38	0.04
*NH_2	0.67	0.07
*NH_3	1.01	0.12
H_2(g)	0.27	0.41
N_2(g)	0.15	0.60
NH_3(g)	0.89	0.74
H_2O(g)	0.58	0.65


*N2
*N2H
*N2H2
*HNNH
*N
*H
Binding energy (eV)
O-vac
N-vac
CrNO MnNO TaNO HfNO ScNO TiNO YNO ZrNO VNO
(a)
(b)
(c)
(d)
(e)
(f)

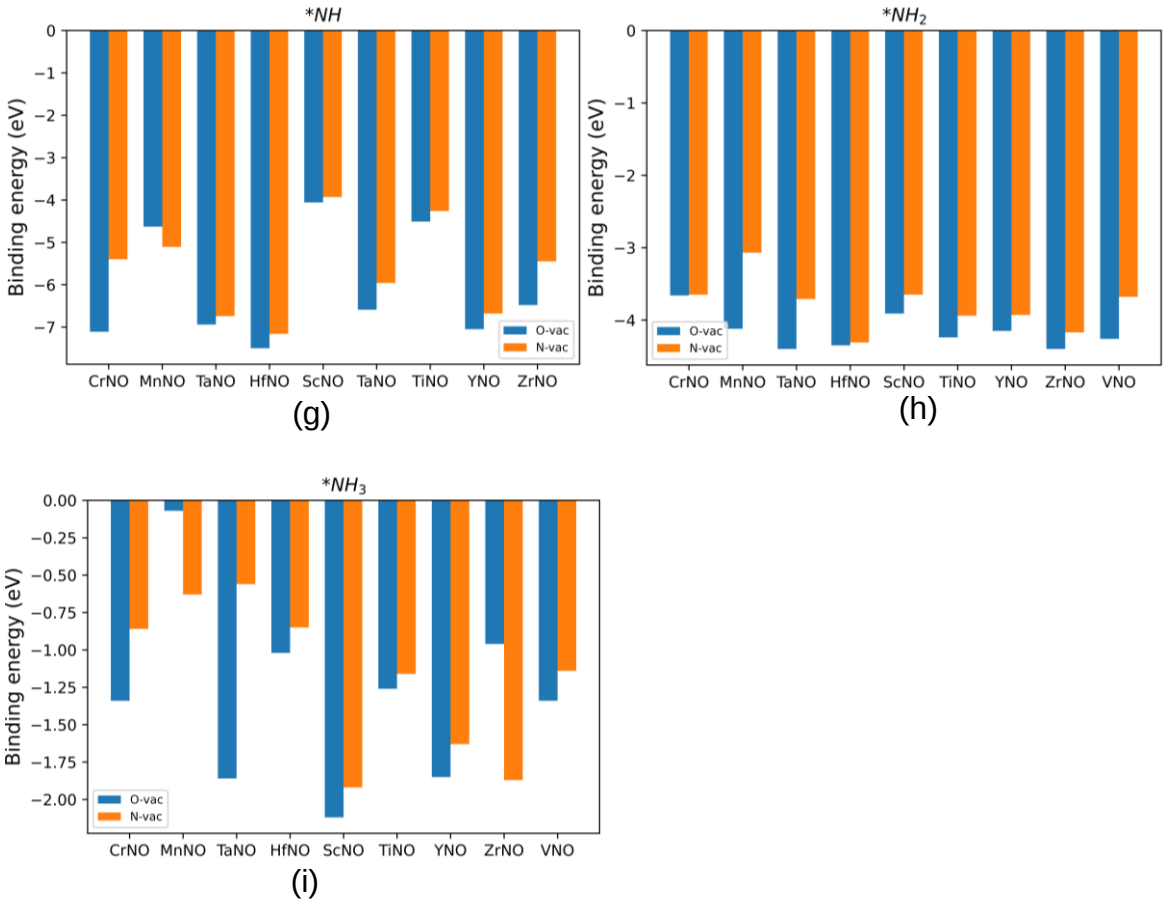


Figure S3. DFT calculated binding energies of reaction intermediates on N-vac and O-vac.

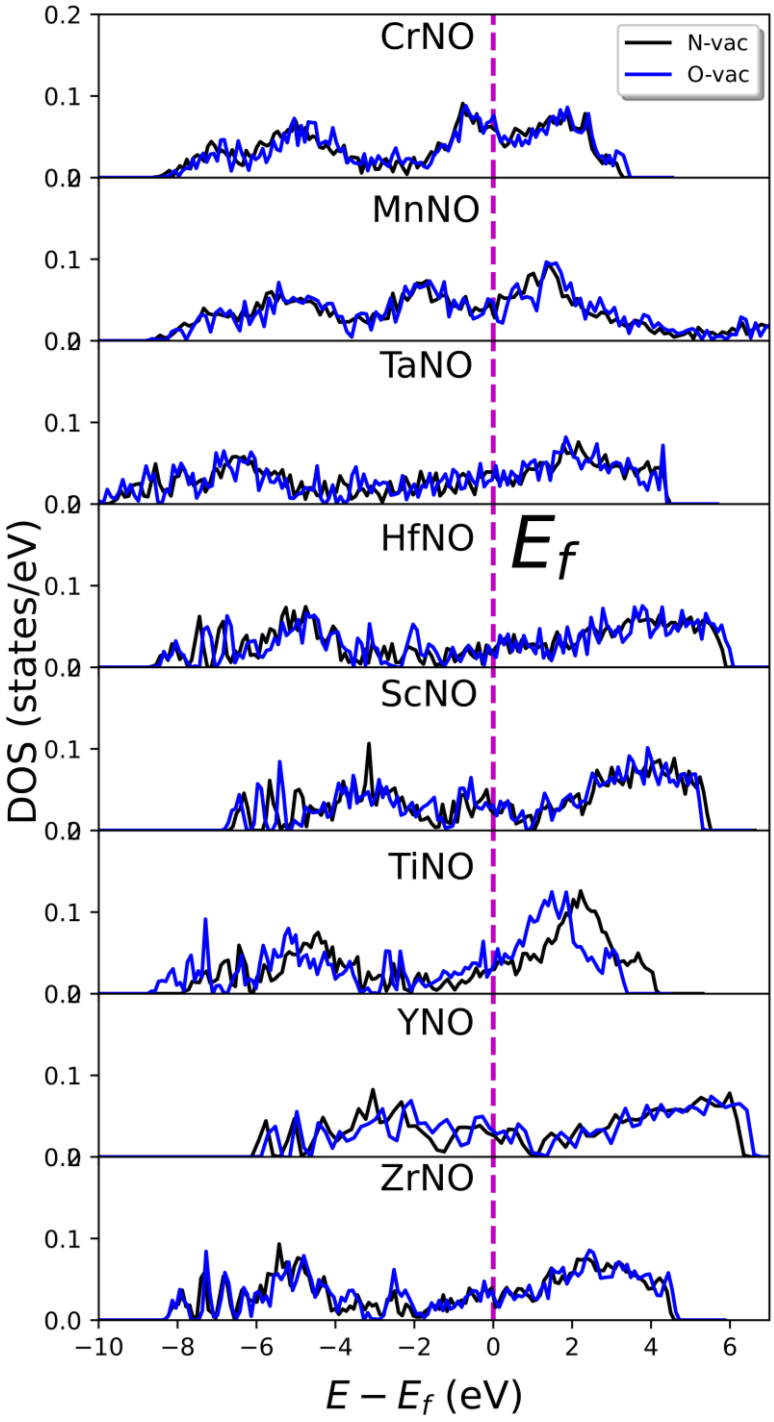


Figure S4. Density of state (DOS) plots for all the TMNO on N-vac and O-vac.

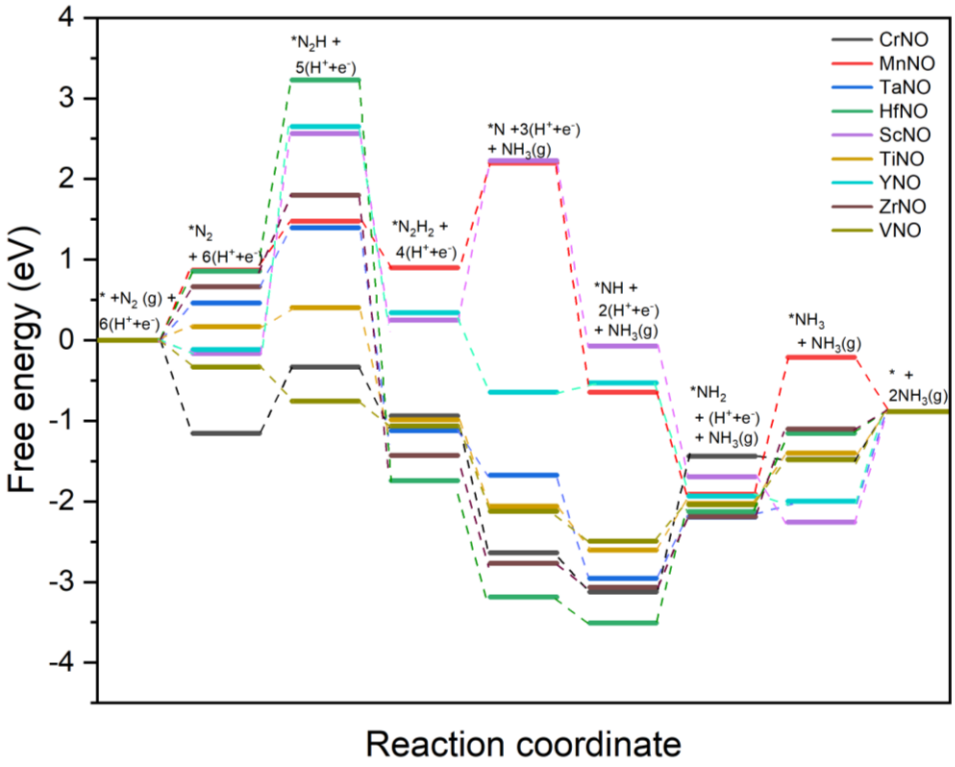


Figure S5. DFT calculated free energy diagrams at U = 0 V along the associative N_2H_2 pathway on O-vacancy.

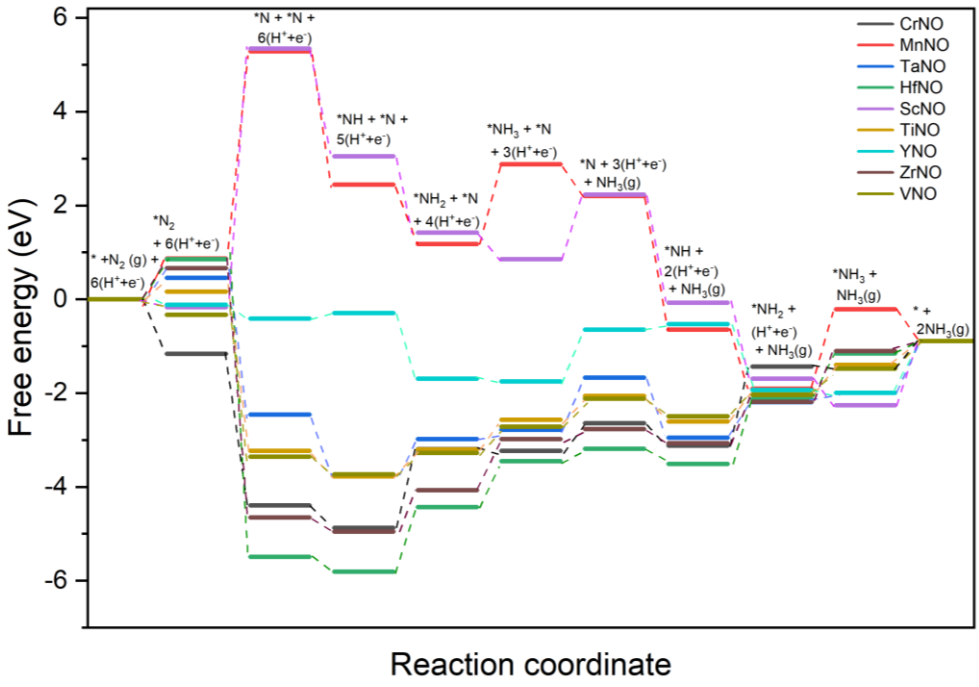


Figure S6. DFT calculated free energy diagrams of ENRR at U = 0 V along the dissociative pathway on O-vac.

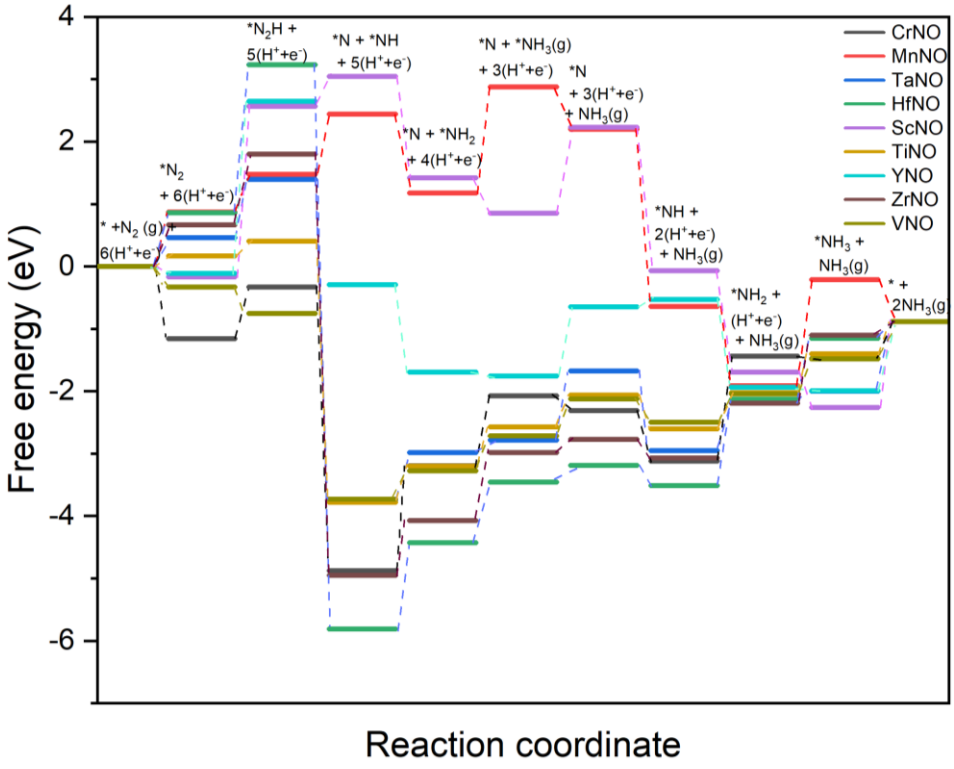


Figure S7. DFT calculated free energy diagrams of ENRR at U = 0 V along the associative N_2H pathway on O-vac.

REFERNCES

1 Z. Wei, Y. Feng and J. Ma, *J. Energy Chem.*, 2020, **48**, 322–327.