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SUPPLEMENTARY MATERIAL

Bifunctional Diatomic Site Catalysts Supported by β_{12}-Borophene for Efficient Oxygen Evolution and Reduction Reactions

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Computational Details for OER and ORR:

The OER progress of a catalyst mainly consists of the following four steps: (i) an H_2O molecule dissociates into an OH^* group adsorbed on the surface and release a pair of protons and electrons; (ii) proton-electron pairs are continuously separated from OH^*, forming an isolated O^*; (iii) another H_2O molecule in the solvent randomly reacts with O^*, releasing another pair of protons and electrons, forming OOH^*; (iv) another proton-electron pair is released from OOH^*, and the final products ($O_2(g)$) formed and released (as shown in Fig. S1). These four basic steps can be described by the following equations:

$$H_2O(l) + * \rightarrow OH^* + H^+ + e^- \qquad (S1)$$

$$OH^* \rightarrow O^* + H^+ + e^- \qquad (S2)$$

$$H_2O(l) + O^* \rightarrow OOH^* + H^+ + e^- \qquad (S3)$$

$$OOH^* \rightarrow O_2(g) + * + H^+ + e^- \qquad (S4)$$

, where $*$, H^+ and e^- represent the substrate, protons and electrons, respectively. In this paper, the energy of O_2 gas is obtained by the experimental reaction energy of $2H_2O \rightarrow 2H_2 + O_2$ (4.92 eV).[1] Furthermore, the free energy of the ($H^+ + e^-$) pair can be replaced by half of that of an H_2 molecule, so the Gibbs free energy change at each step can be described as

$$\Delta G_1 = \Delta G_{OH^*} - eU + \Delta G_{pH} \qquad (S5)$$

$$\Delta G_2 = \Delta G_{O^*} - \Delta G_{OH^*} - eU + \Delta G_{pH} \qquad (S6)$$

$$\Delta G_3 = \Delta G_{OOH^*} - \Delta G_{O^*} - eU + \Delta G_{pH} \qquad (S7)$$

$$\Delta G_4 = 4.92 - \Delta G_{OOH^*} - eU + \Delta G_{pH} \qquad (S8)$$

, where ΔG_{OH^*}, ΔG_{O^*} and ΔG_{OOH^*} represent the Gibbs free energy changes of the OH^*, O^* and OOH^* intermediates when they are adsorbed, respectively. U is the potential measured against normal hydrogen electrode (NHE) at standard conditions (T = 298.15 K, P = 1 bar, pH = 0). The free-energy change of the protons relative to the NHE at nonzero pH is described by the Nernst equation as $\Delta G_{pH} = -k_BT\,ln(10) \times pH$. The effect of U and pH was not taken into account in our study (U =0, pH = 0). To calculate the free energy change (ΔG) for the intermediates when they are adsorbed, we used the computational hydrogen electrode (CHE) model developed by Nørskov et al.[1] According to this model, the free energy changes of the corresponding intermediates are expressed as

$$\Delta G_{OH^*} = \mu_{OH^*} - \mu^* - [\mu_{H_2O} - 1/2 \times \mu_{H_2}] \qquad (S9)$$

$$\Delta G_{O^*} = \mu_{O^*} - \mu^* - [\mu_{H_2O} - \mu_{H_2}] \qquad (S10)$$

$$\Delta G_{OOH^*} = \mu_{OOH^*} - \mu^* - [2 * \mu_{H_2O} - 3/2 \times \mu_{H_2}] \qquad (S11)$$

, where μ_{OH^*}, μ_{O^*}, μ_{OOH^*}, μ^*, μ_{H_2O}, μ_{H_2} represent the chemical potentials of OH^*, O^*, OOH^*, substrate, H_2O molecule and H_2 molecule, respectively. And the chemical potential (μ) of each species is defined as follows,

$$\mu = E_{DFT} + ZPE - TS \qquad (S12)$$

, where E_{DFT}, ZPE and S are the calculated total energy of species, zero point energy and the entropy at 298.15 K.

The maximum free energy change between these steps will determine the reaction rate, to be referred to as the potential-determining step (PDS). To describe the catalytic activity, the OER overpotential (η_{OER}) is defined as

$$\eta_{OER} = \frac{\max\{\Delta G_1,\Delta G_2,\Delta G_3,\Delta G_4\}}{e} - 1.23 \qquad (S13)$$

, where e is the charge of one electron. Traditionally, the lower the η_{OER} value, the better the catalytic activity.

There are two ORR response pathways that we studied, four-electron (1.23 V vs. RHE) and two-electron (0.70 V vs. RHE) ORR. The four-electron ORR (4e ORR) is just reverse reaction of OER, as shown in Fig. S2. The overpotential of four-electron ORR (η_{ORR}) is defined as

$$\eta_{ORR} = \frac{\max\{-\Delta G_1,-\Delta G_2,-\Delta G_3,-\Delta G_4\}}{e} + 1.23 \qquad (S14)$$

we mainly focus on the 4e ORR reaction pathway. The higher the overpotential, the harder the reaction, and vice versa. Therefore, a good ORR catalyst must have a low overpotential, and the reaction path is displayed in Fig. S2.

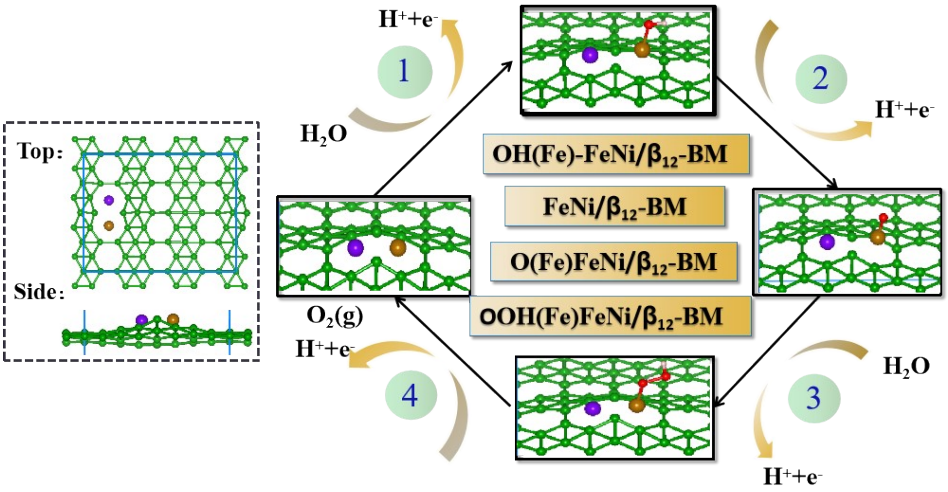

Fig. S1. Reaction pathways of the OER for FeNi/β_{12}-BM.

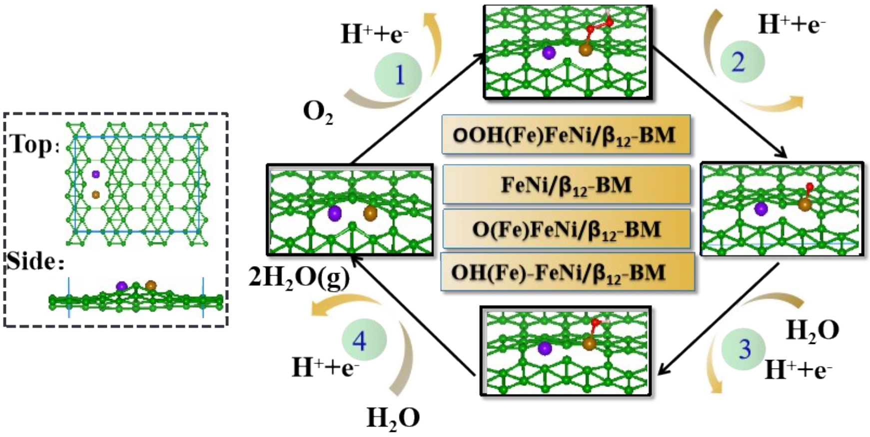

Fig. S2. Reaction pathways of the ORR for FeNi/β_{12}-BM.

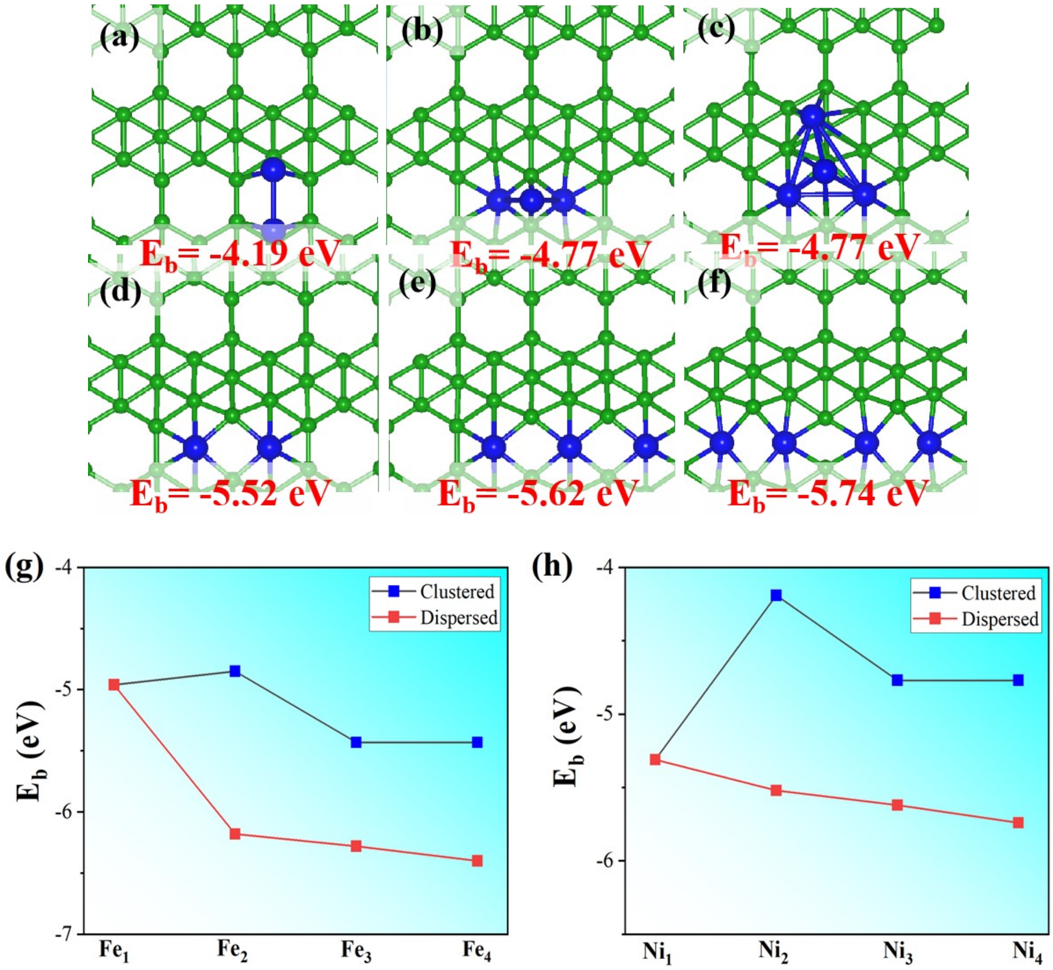

Fig. S3. (a-c) The structures for Ni_n (n = 2 - 4) clusters adsorbed on β_{12}-BM and their (d-f) dispersed counterparts. The average binding energies in the two modes for (g) Ni_n (n = 2 - 4) and (h) Fe_n (n = 2 - 4) on β_{12}-BM .

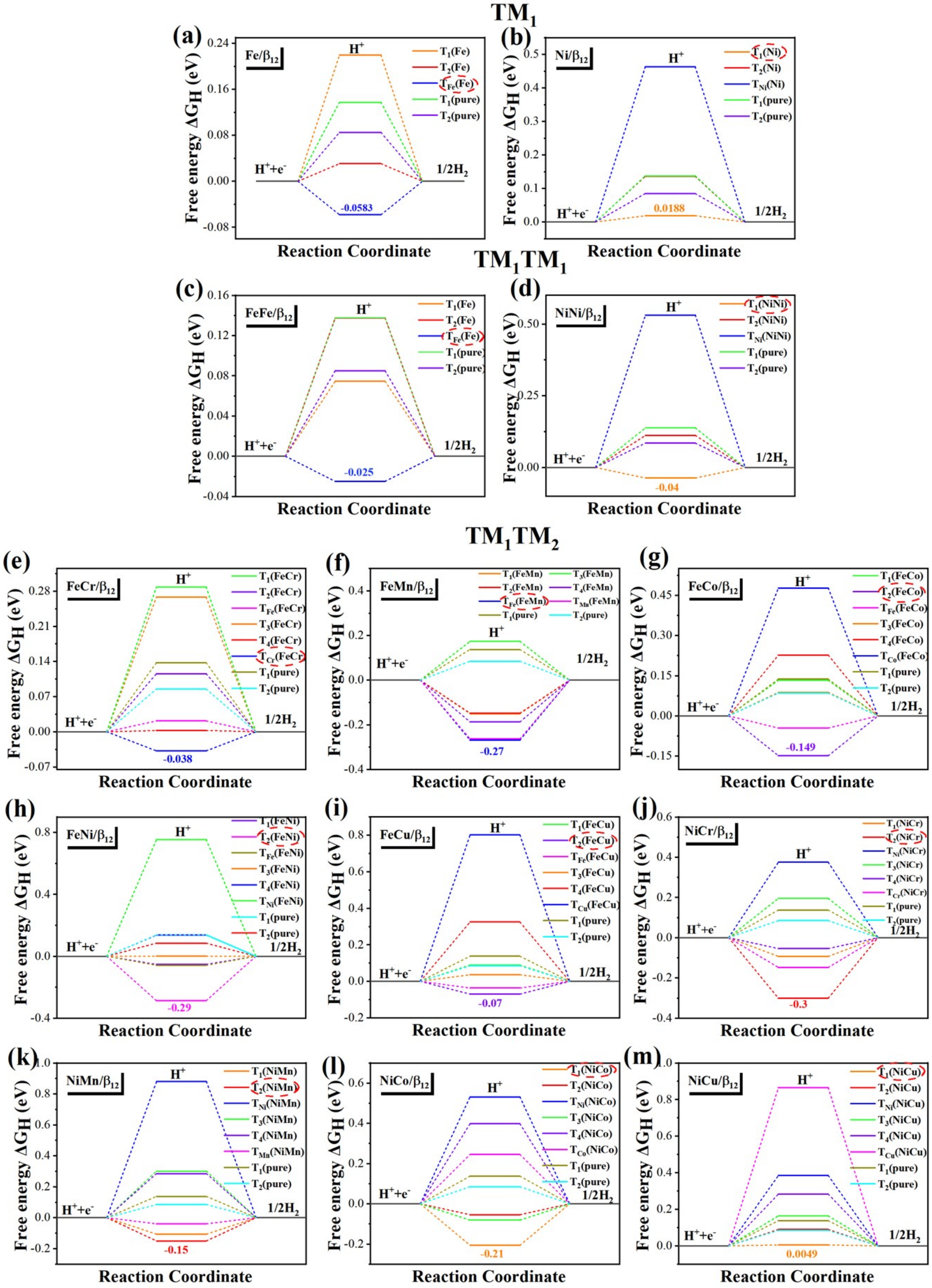

Fig. S4. HER free energy step diagram of TM_1/β_{12}-BM and TM_1TM_2/β_{12}-BM (TM_1=Fe/Ni, TM_2= Cr~Cu) systems.

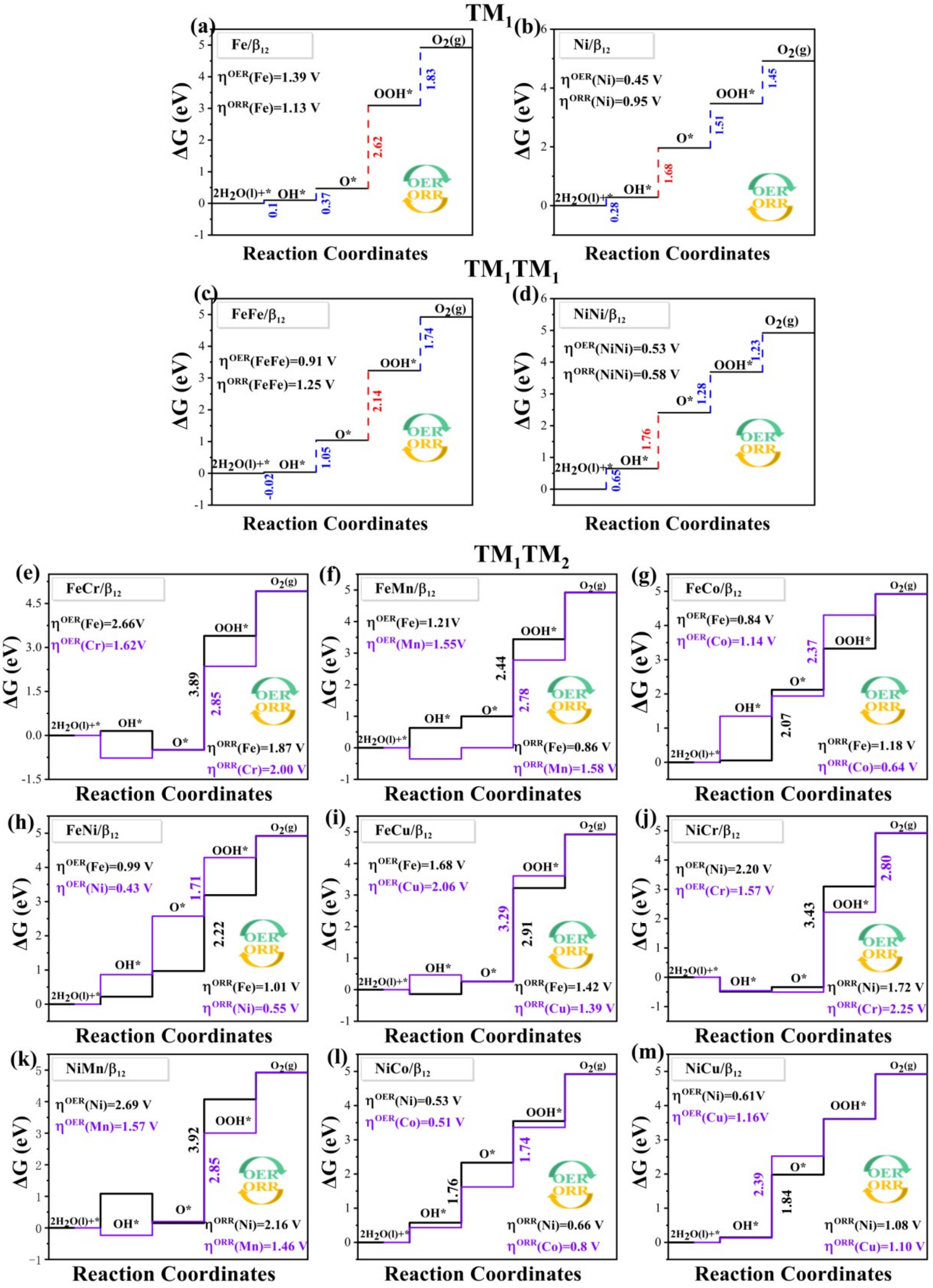

Fig. S5. OER and ORR free energy step diagrams of TM_1/β_{12}-BM and TM_1TM_2/β_{12}-BM (TM_1=Fe/Ni, TM_2= Cr~Cu) systems.

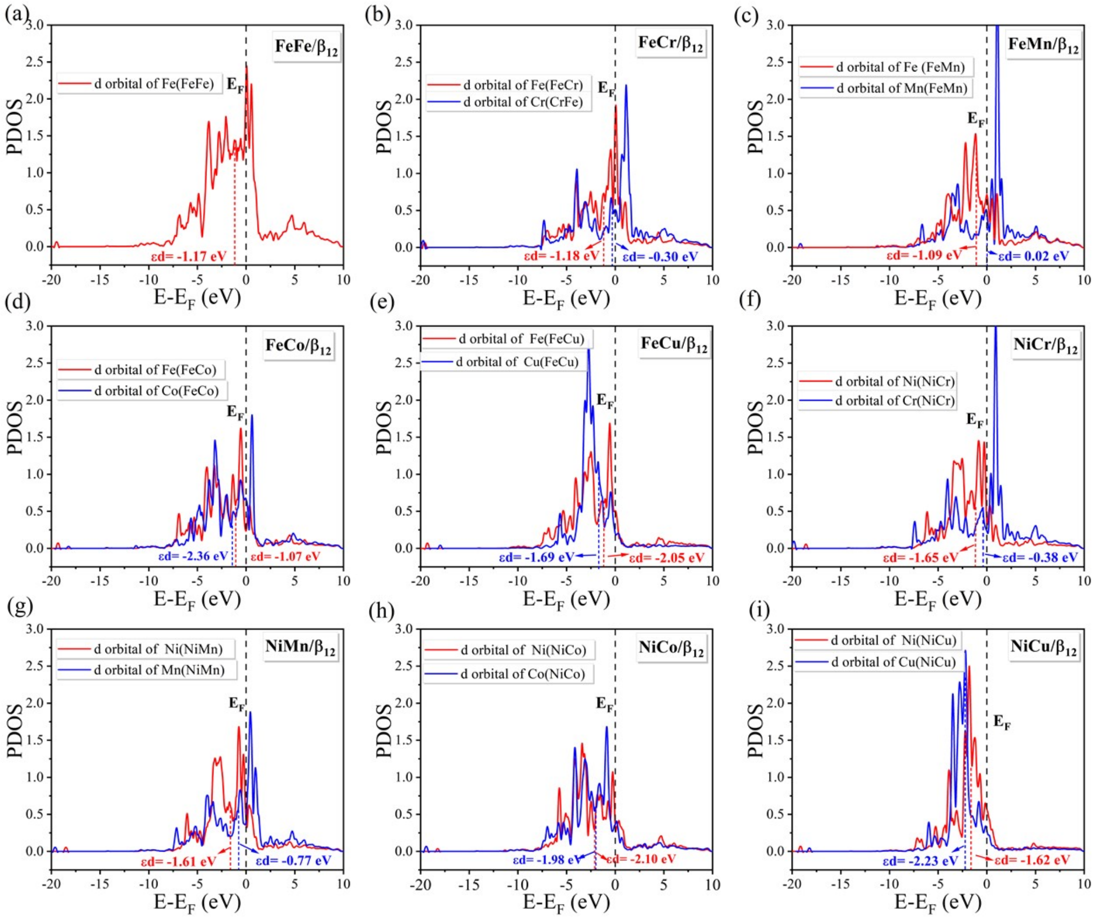

Fig. S6. The project density of states (PDOS) of the d-orbitals of the transition metal(TM) atoms in TM_1-OH/β_{12}-BM and TM_1TM_2-OH/β_{12}-BM systems. Dotted line denotes the d-band centers of transition metal atoms.

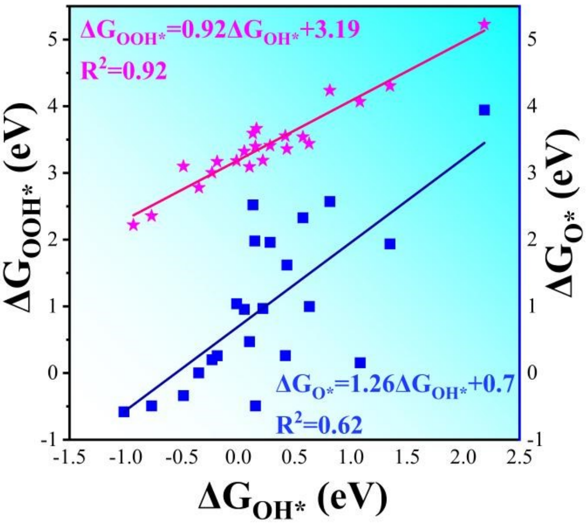

Fig. S7. Linear relationship between the absorption free energies of intermediates ΔG_{OOH^*} *vs.* ΔG_{OH^*} (in purple) and ΔG_{O^*} *vs.* ΔG_{OH^*} (in blue) for TM_1TM_2/β_{12}-BM systems.

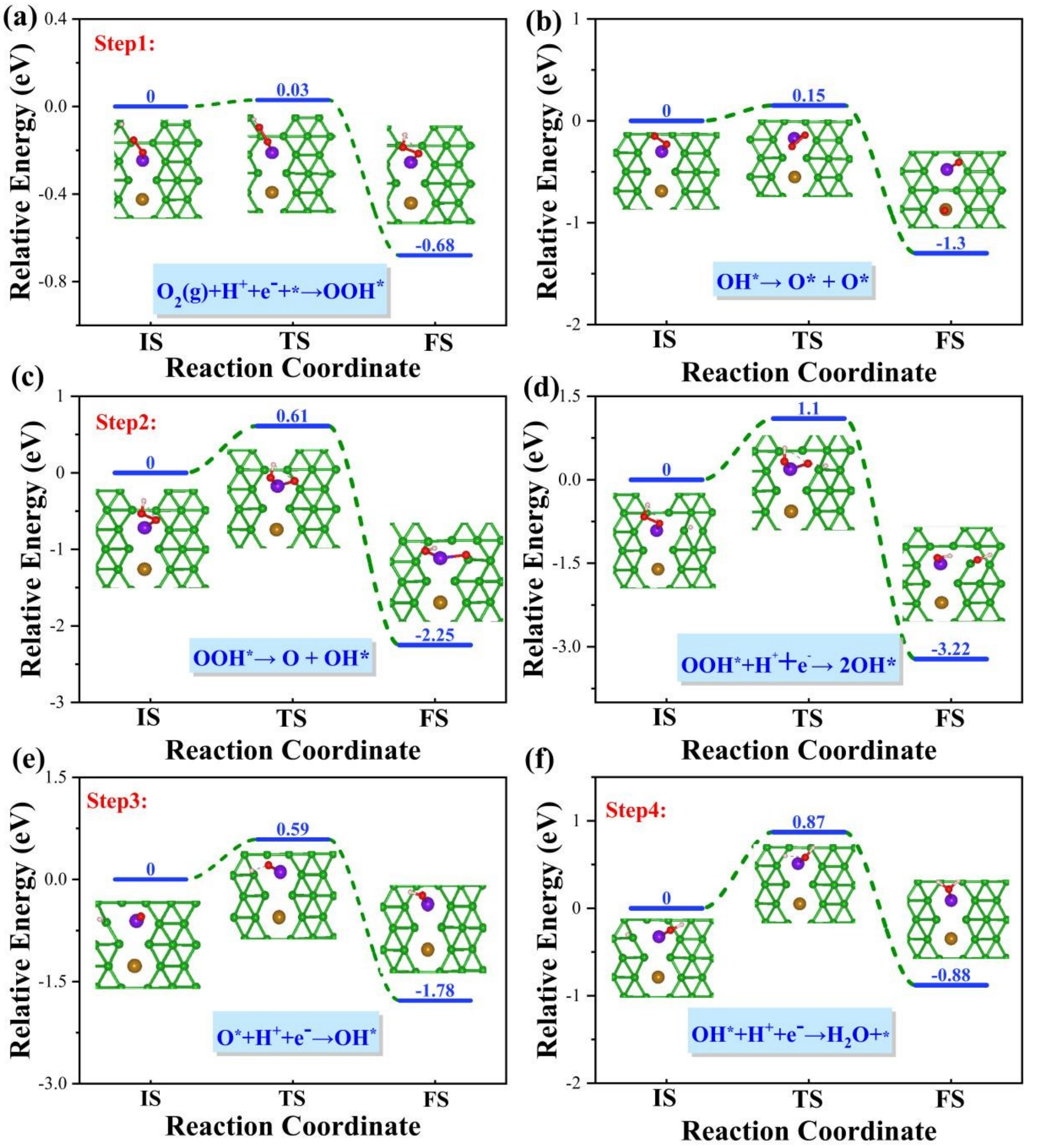

Fig. S8. Optimized structures of the initial state (IS), transition state (TS), and final state (FS) of ORR elemental steps on Ni(FeNi)/β_{12}-BM and the corresponding energy barriers for the reactions: (a) O_2 (g)+ H^+ + e^-+*→OOH*; (b) OH* → O* + O*; (c) OOH* →O + OH* ; (d) OOH*+ H^+ + e^-→2OH*; (e) O* + H^+ +e^-→OH*; (f) OH* + H^++ e^-→H_2O+*.

Table S1 The calculated free energies of HER for TM_1/β_{12}-BM and TM_1TM_2/β_{12}-BM (TM_1=Fe/Ni, TM_2= Cr~Cu) systems.

System	**E(eV)**	**ZPE-298.15Svib(eV)**	**ΔG**
T_1(Fe)	-391.807	0.198	0.220
T_2(Fe)	-391.100	0.201	0.0306
T_{Fe}(Fe)	-392.040	0.152	-0.0583
T_1(FeFe)	-400.819	0.198	0.0746
T_2(FeFe)	-400.700	0.201	0.1376
T_{Fe}(FeFe)	-400.841	0.152	-0.025
T_1(Fe)	-400.819	0.198	0.0746
T_1(FeCr)	-401.745	0.241	0.288
T_2(FeCr)	-401.871	0.192	0.116
T_{Fe}(FeCr)	-401.935	0.162	0.0217
T_3(FeCr)	-401.759	0.233	0.268
T_4(FeCr)	-401.971	0.180	0.0025
T_{Cr}(FeCr)	-401.996	0.163	-0.038
T_1(FeMn)	-401.669	0.232	-0.150
T_2(FeMn)	-401.620	0.186	-0.148
T_{Fe}(FeMn)	-401.721	0.166	-0.269
T_3(FeMn)	-401.313	0.201	0.174
T_4(FeMn)	-401.644	0.171	-0.189
T_{Mn}(FeMn)	-401.706	0.157	-0.263
T_1(FeCo)	-399.751	0.232	0.133
T_2(FeCo)	-400.022	0.221	-0.149
T_{Fe}(FeCo)	-399.856	0.159	-0.0455
T_3(FeCo)	-399.806	0.088	0.0878
T_4(FeCo)	-399.642	0.227	0.227
T_{Co}(FeCo)	-399.319	0.478	0.478
T_1(FeNi)	-398.274	0.195	-0.0525
T_2(FeNi)	-398.538	0.224	-0.287
T_{Fe}(FeNi)	-398.248	0.162	-0.059
T_3(FeNi)	-398.269	0.243	0.0009
T_4(FeNi)	-398.114	0.224	0.138
T_{Ni}(FeNi)	-397.382	0.109	0.754
T_1(FeCu)	-395.699	0.235	0.0889
T_2(FeCu)	-395.848	0.225	-0.0699
T_{Fe}(FeCu)	-395.743	0.153	-0.0366
T_3(FeCu)	-395.761	0.244	0.0361
T_4(FeCu)	-395.433	0.205	0.325

T_{Cu}(FeCu)	-394.844	0.0927	0.802
T_1(Ni)	-389.382	0.237	0.0188
T_2(Ni)	-389.246	0.219	0.1363
T_{Ni}(Ni)	-388.809	0.108	0.463
T_1-NiNi	-395.496	0.241	-0.0369
T_2-NiNi	-395.323	0.216	0.1118
T_{Ni}	-394.799	0.112	0.5312
T_1(NiCr)	-399.413	0.243	-0.0931
T_2(NiCr)	-399.584	0.207	-0.3008
T_{Ni}(NiCr)	-398.860	0.159	0.3751
T_3(NiCr)	-399.110	0.229	0.1953
T_4(NiCr)	-399.339	0.209	-0.0541
T_{Cr}(NiCr)	-399.380	0.156	-0.1478
T_1(NiMn)	-399.315	0.234	-0.106
T_2(NiMn)	-399.315	0.189	-0.150
T_{Ni}(NiMn)	-398.248	0.153	0.880
T_3(NiMn)	-398.914	0.240	0.301
T_4(NiMn)	-398.884	0.195	0.285
T_{Mn}(NiMn)	-399.178	0.163	-0.0396
T_1(NiCo)	-397.199	0.242	-0.206
T_2(NiCo)	-397.036	0.226	-0.0545
T_{Ni}(NiCo)	-396.337	0.113	0.532
T_3(NiCo)	-397.075	0.28	-0.0814
T_4(NiCo)	-396.544	0.187	0.398
T_{Co}(NiCo)	-396.643	0.133	0.245
T_1(NiCu)	-392.913	0.234	0.0049
T_2(NiCu)	-392.784	0.189	0.0897
T_{Ni}(NiCu)	-392.453	0.153	0.385
T_3(NiCu)	-392.760	0.240	0.164
T_4(NiCu)	-392.596	0.195	0.283
T_{Cu}(NiCu)	-391.982	0.163	0.865
T_1(pure)	-383.613	0.228	0.138
T_2(pure)	-383.648	0.210	0.0851

Table S2 The calculated overpotentials of OER and 4e ORR for TM_1/β_{12}-BM and TM_1TM_2/β_{12}-BM (TM_1=Fe/Ni, TM_2= Cr~Cu) systems.

System	η_{OER}	η_{ORR}
Fe–β_{12}	1.39	1.13
Cr(FeCr)/β_{12}	1.62	2
Fe(FeCr)/β_{12}	2.66	1.87
Mn(FeMn)/β_{12}	1.55	1.58
Fe(FeMn)/β_{12}	1.21	0.86
FeFe/β_{12}	0.91	1.25
Fe(FeCo)/β_{12}	0.84	1.18
Co(FeCo)/β_{12}	1.14	0.64
Fe(FeNi)/β_{12}	0.99	1.01
Ni(FeNi)/β_{12}	0.43	0.55
Fe(FeCu)/β_{12}	1.68	1.42
Cu(FeCu)/β_{12}	2.06	1.39
Ni–β_{12}	0.45	0.95
Cr(NiCr)/β_{12}	1.57	2.25
Ni(NiCr)/β_{12}	2.20	1.72
Mn(NiMn)/β_{12}	1.57	1.46
Ni(NiMn)/β_{12}	2.69	2.16
Co(NiCo)/β_{12}	0.51	0.8
Ni(NiCo)/β_{12}	0.53	0.66
NiNi/β_{12}	0.53	0.58
Cu(NiCu)/β_{12}	1.16	1.10
Ni(NiCu)/β_{12}	0.61	1.08

Reference

[1] J.K. Nørskov, J. Rossmeisl, A. Logadottir, et al, Origin of the overpotential for oxygen reduction at a fuel-cell cathode, J. Phys. Chem. B. 2004, 108(46): 17886-17892, https://doi.org/10.1021/jp047349j.