Supporting Information

Metal-Doped Fullerene: Promising Electrocatalysts for Hydrogen and Oxygen Evolution Reactions

*Sougata Saha, Swapan K. Pati**

Theoretical Sciences Unit, School of Advanced Materials (SAMat), Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, 560064

Computational details

To determine the stability, we have calculated the formation energy (E_f) of each TM-Ful system according to the following equation[1],

$$E_f = E_{catalyst} - E_{substrate} - \mu_{TM} \qquad (1)$$

where, $E_{catalyst}$ represents the energy of a single transition metal (TM)-doped fullerene systems, $E_{substrate}$ denotes the energy of the defected fullerene, and μ_{TM} is the chemical potential of the transition metals in their stable structures.

Under standard electrocatalytic conditions, the overall pathway of the HER can be expressed as,

$$H^+ + e^- \rightarrow \tfrac{1}{2} H_2\,(g) \qquad (2)$$

This reaction involves two elementary steps,

$$H^+ + e^- + * \rightarrow H^* \qquad (3)$$

$$H^* \rightarrow \tfrac{1}{2} H_2\,(g) \qquad (4)$$

In the HER, the reactants and products pass through an intermediate adsorbed hydrogen (H*). Therefore, the catalytic activity of HER can be characterised by the Gibbs free energy of hydrogen adsorption (ΔG_H), obtained from the Equation (5)

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} + T\Delta S_H \qquad (5)$$

where ΔE_H is the hydrogen adsorption energy, ΔE_{ZPE} represents the zero-point energy difference between adsorbed hydrogen and gas-phase hydrogen, and ΔS_H shows the entropy difference between gas phase and adsorbed state. T indicates a temperature of 298.15 K. Furthermore, the ΔE_{ZPE} and $T\Delta S_H$ values can be measured through the vibrational frequencies of the system. For the H_2 and H_2O molecules, the frequency and zero-point energy (ZPE) values were obtained from the NIST database, as DFT calculations cannot provide accurate frequency values for molecular systems. ΔE_H is defined as,

$$\Delta E_H = E_H - E_{catal} - \tfrac{1}{2} E_{H2} \qquad (6)$$

where E_H represents the calculated adsorption energies of TM-Ful systems with adsorption of one H atom and E_{catal} signifies the energy of the TM-Ful system.

The theoretical exchange current (i_o) at pH= 0, was calculated based on Equation 7.[2]

$$i_0 = -\frac{ek_0}{1 + exp^{[70]}(\frac{|\Delta G_H|}{K_B T})} \qquad (7)$$

where k_0 is the rate constant, K_B is the Boltzmann constant and T is the temperature.

In standard acidic conditions, the OER can be divided into the following four elementary steps.[3]

$$H_2O\ (l) + * \rightarrow *OH + (H^+ + e^-) \qquad (8)$$

$$*OH \rightarrow *O + (H^+ + e^-) \qquad (9)$$

$$*O + H_2O\ (l) \rightarrow *OOH + (H^+ + e^-) \qquad (10)$$

$$*OOH \rightarrow O_2\ (g) + * + (H^+ + e^-) \qquad (11)$$

In each elementary step of the OER, the free energy can be calculated based on the approach proposed by Nørskov et al.[5] The difference of free energy between the initial state and the final state of the reactions has been defined as follows[4]

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_U \qquad (12)$$

where ΔE, ΔE_{ZPE}, and ΔS represent the total energy changes from DFT calculations, the zero-point energy, and the entropy difference between the reactants and products, respectively. T is set to 298.15 K in our calculations. ΔG_{pH} accounts for the free energy correction due to the difference in pH (H^+ concentration) of the solution, calculated using the formula $\Delta G_{pH} = 2.303 K_B T pH$, where K_B is the Boltzmann constant. We assume a pH of zero under acidic conditions. ΔG_U represents the free energy correction due to the difference in electrode potential, and can be expressed as $\Delta G_U = -neU$, where n is the number of electrons transferred, e is the charge, and U is the applied electrode potential.

The changes of free energy between the elementary steps in OER can be described as follows,

$$\Delta G_1 = \Delta G_{OH} \qquad (13)$$

$$\Delta G_2 = \Delta G_O - \Delta G_{OH} \qquad (14)$$

$$\Delta G_3 = \Delta G_{OOH} - \Delta G_O \qquad (15)$$

$$\Delta G_4 = 4.92 - \Delta G_{OOH} \qquad (16)$$

The efficiency of OER can be expressed by the overpotential (η_{OER}) value.

$$\eta_{OER} = \max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}/e - 1.23 \qquad (17)$$

where 1.23 V represents the equilibrium potential.

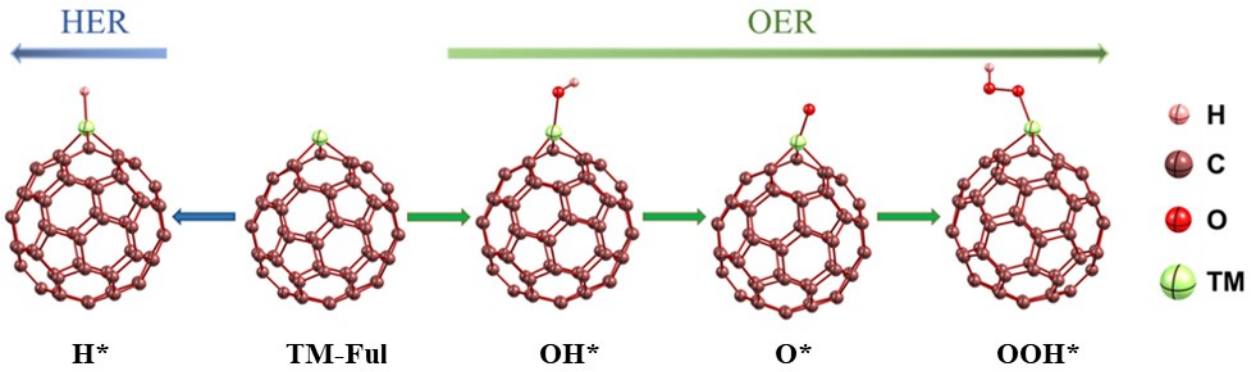

Fig. S1. Schematic picture of the transition metal-doped fullerene (TM-Ful), with the involved intermediates for HER (left) and OER (right).

Table S1. The calculated Bader charge values of the doped transition metals (TM) in the H -adsorbed TM-Ful systems.

TM	Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt
Bader Charge	1.29	0.84	0.89	0.94	0.56	0.64	1.81	0.98	0.68

Table S2. The TM-H bond distance in *H intermediate.

TM	Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt
TM-H bond	1.60	1.56	1.49	1.71	1.69	1.61	1.71	1.68	1.64

(Å)									

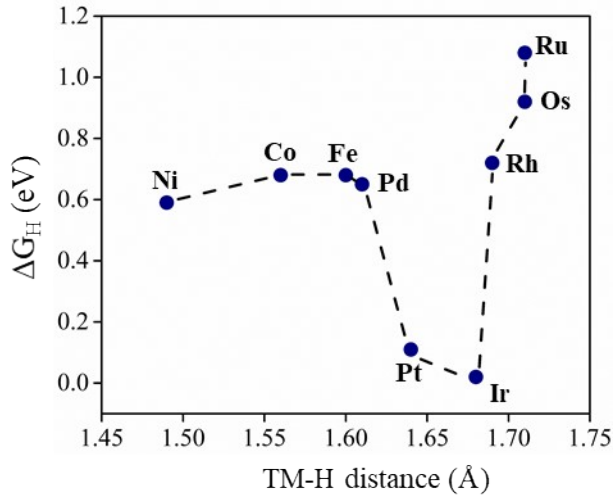

Fig. S2. Distribution of ΔG_H with the TM-H bond distance.

Table S3. The reaction free energy for each elementary step of the OER and the overpotential values for different TM-Ful.

TM-Ful	**ΔG_{OH} (eV)**	**ΔG_O (eV)**	**ΔG_{OOH} (eV)**	**η_{OER} (V)**
Fe-Ful	-0.45	0.90	2.86	0.83
Co-Ful	-0.31	1.39	2.65	1.04
Ni-Ful	-0.17	1.02	2.96	0.73
Ru-Ful	0.19	1.55	3.26	0.48
Rh-Ful	0.08	1.89	3.08	0.61
Pd-Ful	0.26	1.61	3.35	0.51
Os-Ful	-0.46	0.78	2.72	0.97
Ir-Ful	-0.66	1.03	2.42	1.27

Pt-Ful	-0.20	0.52	2.91	1.16

Table S4. U-J values[5] for the different TMs.

TM	Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt
U-J (eV)	3.00	3.00	3.00	2.79	3.04	3.33	2.51	2.74	2.95

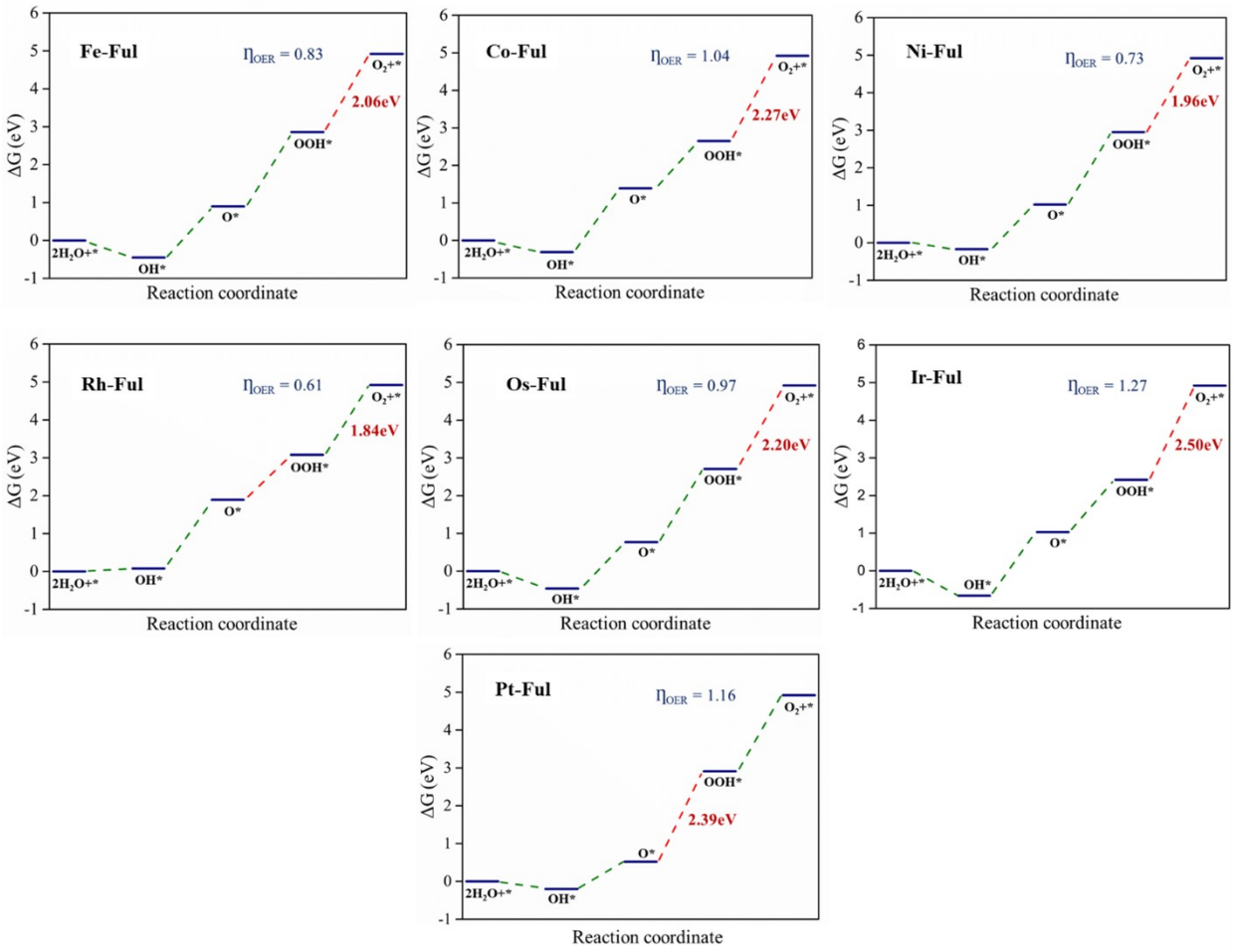

Fig. S3. Free energy diagrams of OER for different transition metals (Fe, Co, Ni, Rh, Os, Ir, Pt) doped fullerene.

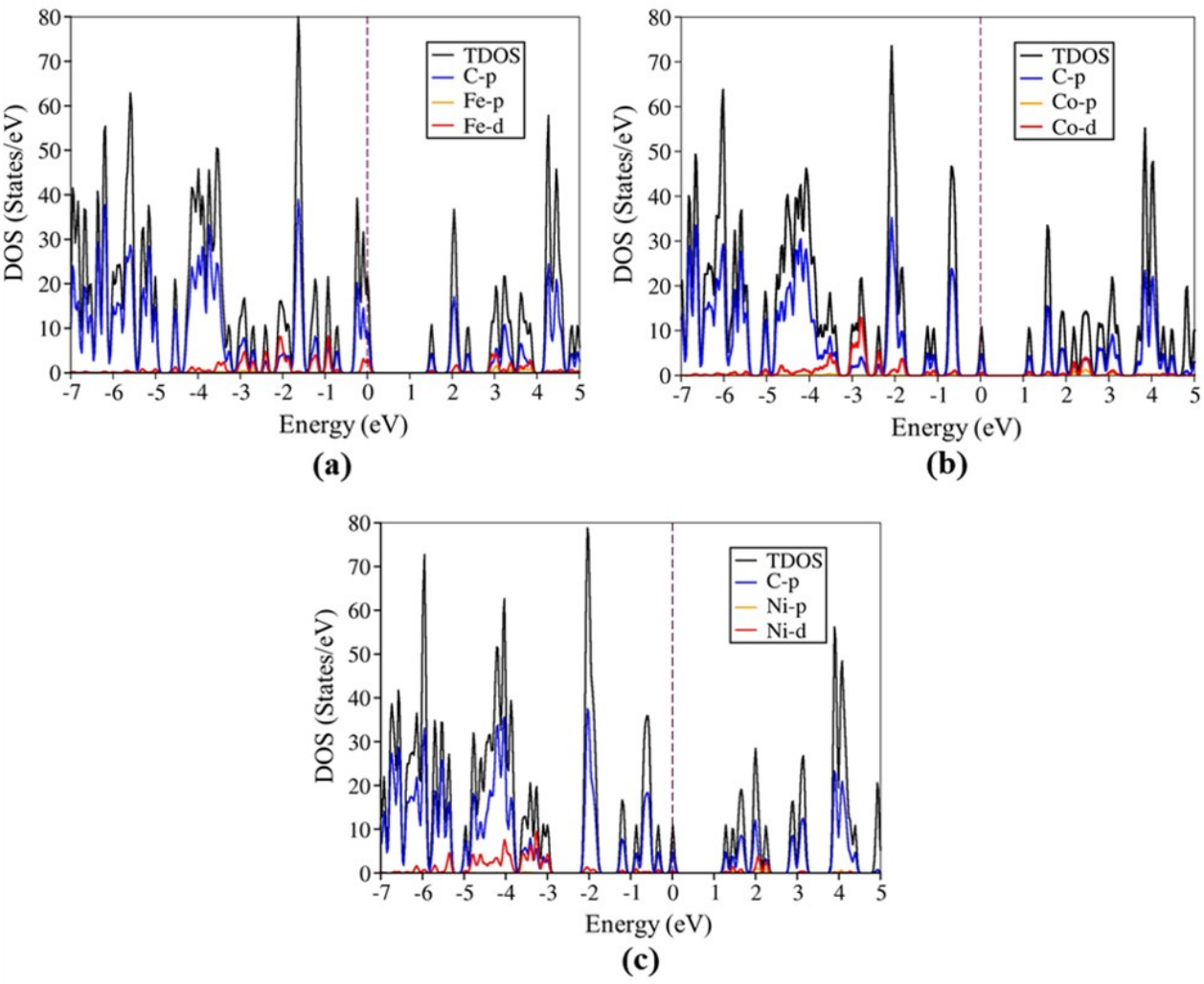

Fig. S4. Density of States (DOS) of (a) Fe-Ful, (b) Co-Ful and (c) Ni-Ful. The Fermi levels are set to zero, as indicated by the dashed lines.

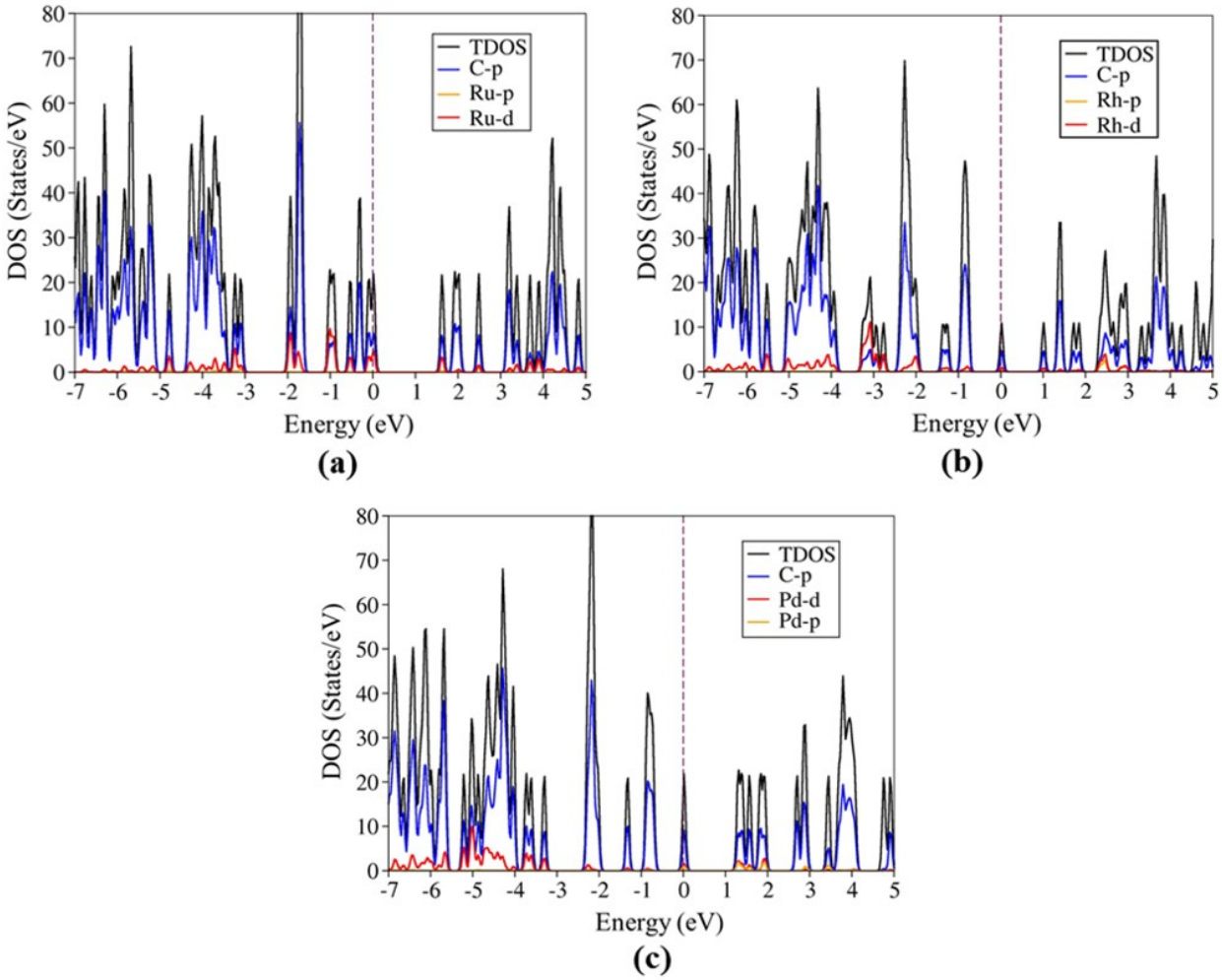

Fig. S5. Density of States (DOS) of (a) Ru-Ful, (b) Rh-Ful and (c) Pd-Ful. The Fermi levels are set to zero, as indicated by the dashed lines.

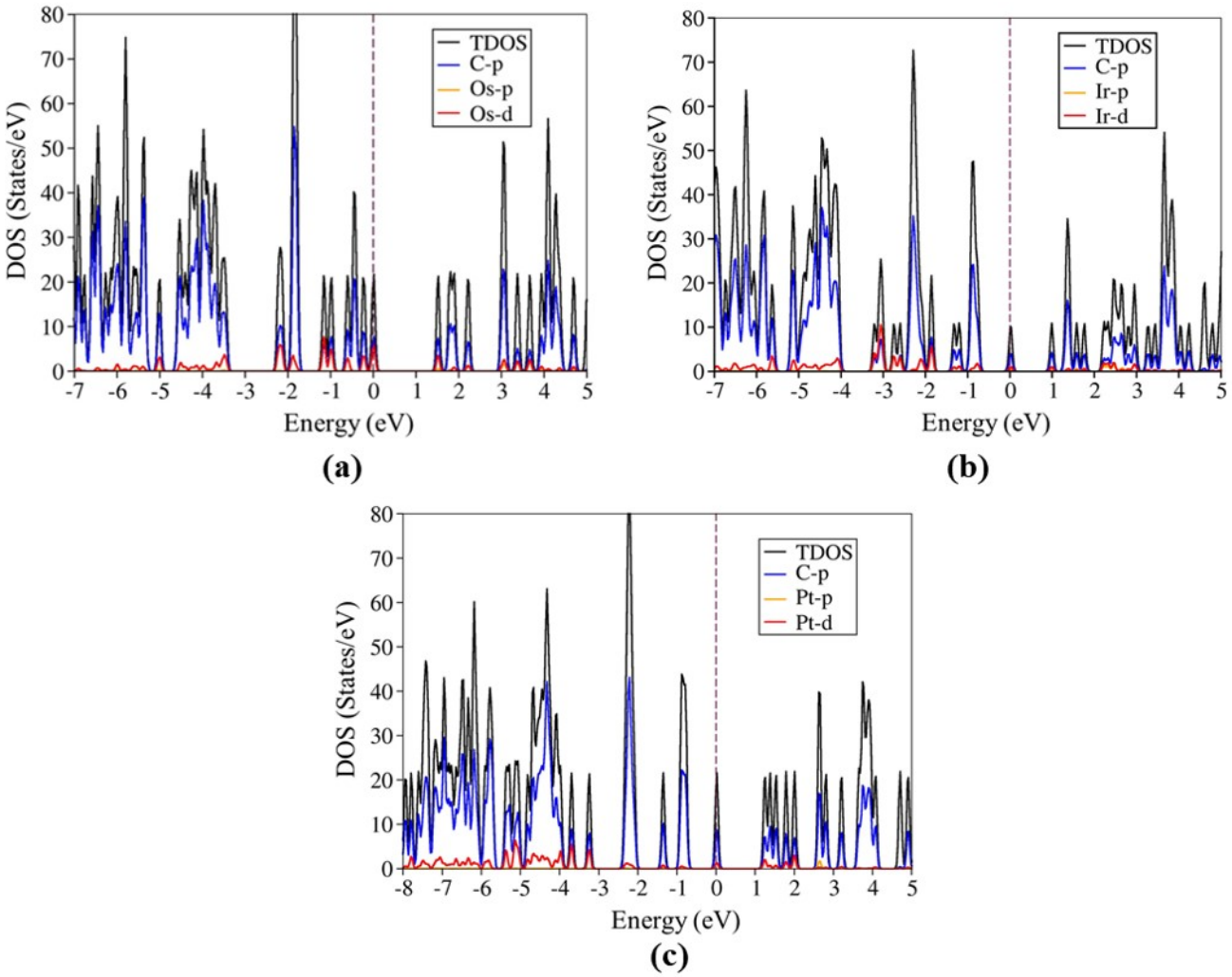

Fig. S6. Density of States (DOS) of (a) Os-Ful, (b) Ir-Ful and (c) Pt-Ful. The Fermi levels are set to zero, as indicated by the dashed lines.

Table S5. The calculated Bader charge values on the doped transition metals (TM) in the TM-Ful systems.

TM	Fe	Co	Ni	Ru	Rh	Pd	Os	Ir	Pt
Bader Charge	1.34	1.02	0.91	0.95	0.71	0.68	1.80	1.05	0.68

Table S6. d-band and p-band center of the TM-Ful systems.

TM-Ful	**d-band center (eV)**	**p-band center (eV)**
Fe-Ful	-0.43	1.77
Co-Ful	-0.85	-5.06
Ni-Ful	-0.83	-3.97
Ru-Ful	0.21	6.69
Rh-Ful	-0.71	-6.95

Pd-Ful	-0.60	14.15
Os-Ful	-0.02	6.66
Ir-Ful	-0.61	-13.91
Pt-Ful	-0.84	7.65

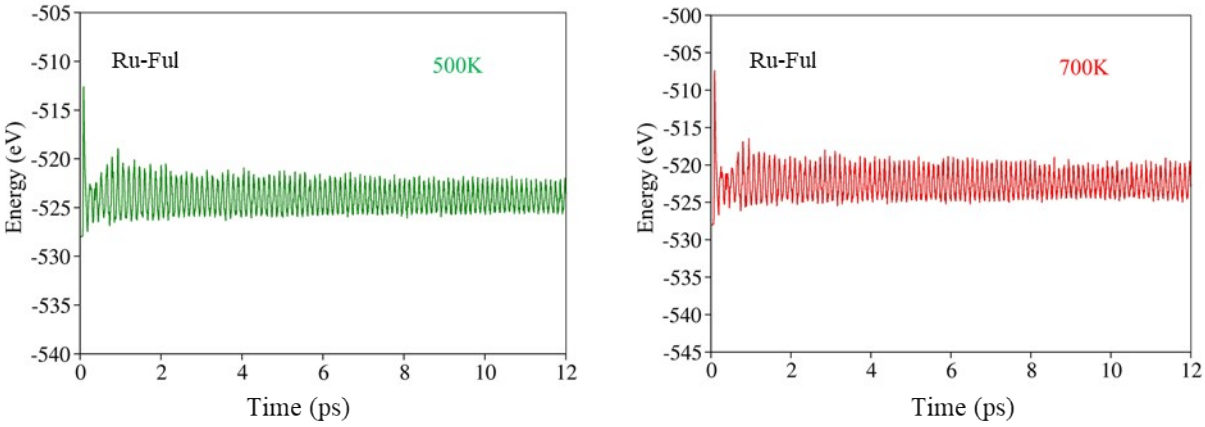

Fig. S7. The variation of total energy with time under AIMD simulations at target temperatures of 500 K, and 700 K for the Ru-Ful.

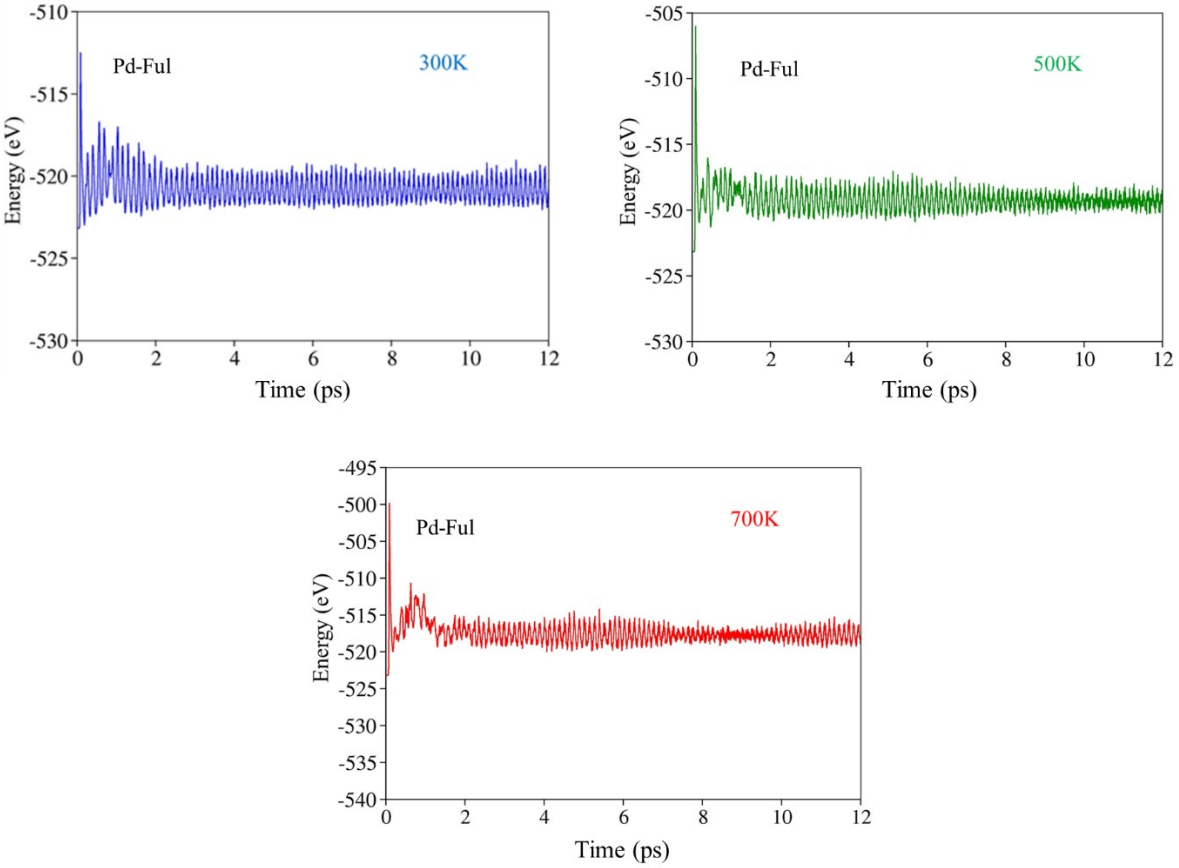

Fig. S8. The variation of total energy with time under AIMD simulations at target temperatures of 300 K, 500 K, and 700 K for the Pd-Ful.

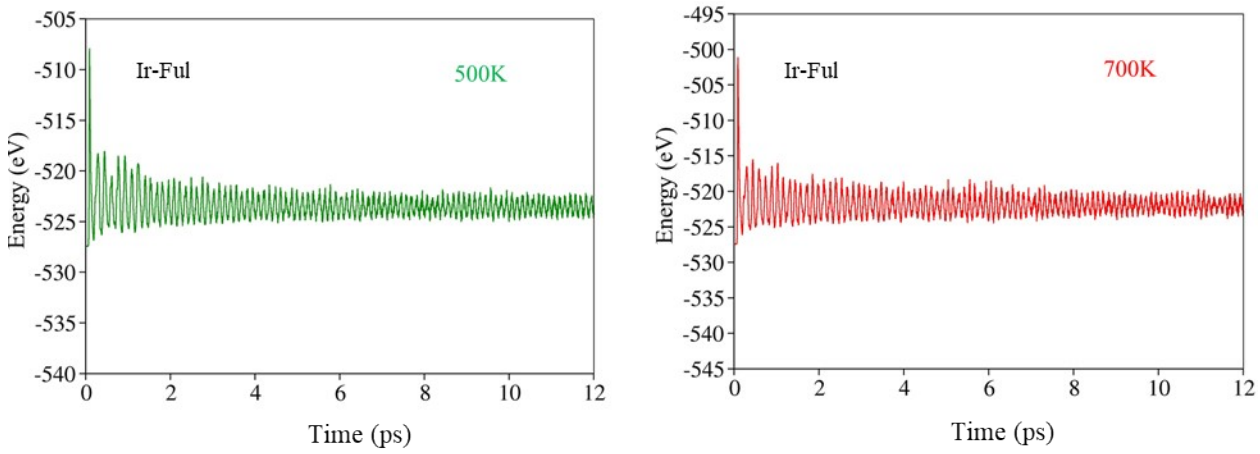

Fig. S9. The variation of total energy with time under AIMD simulations at target temperatures of 500 K, and 700 K for the Ir-Ful.

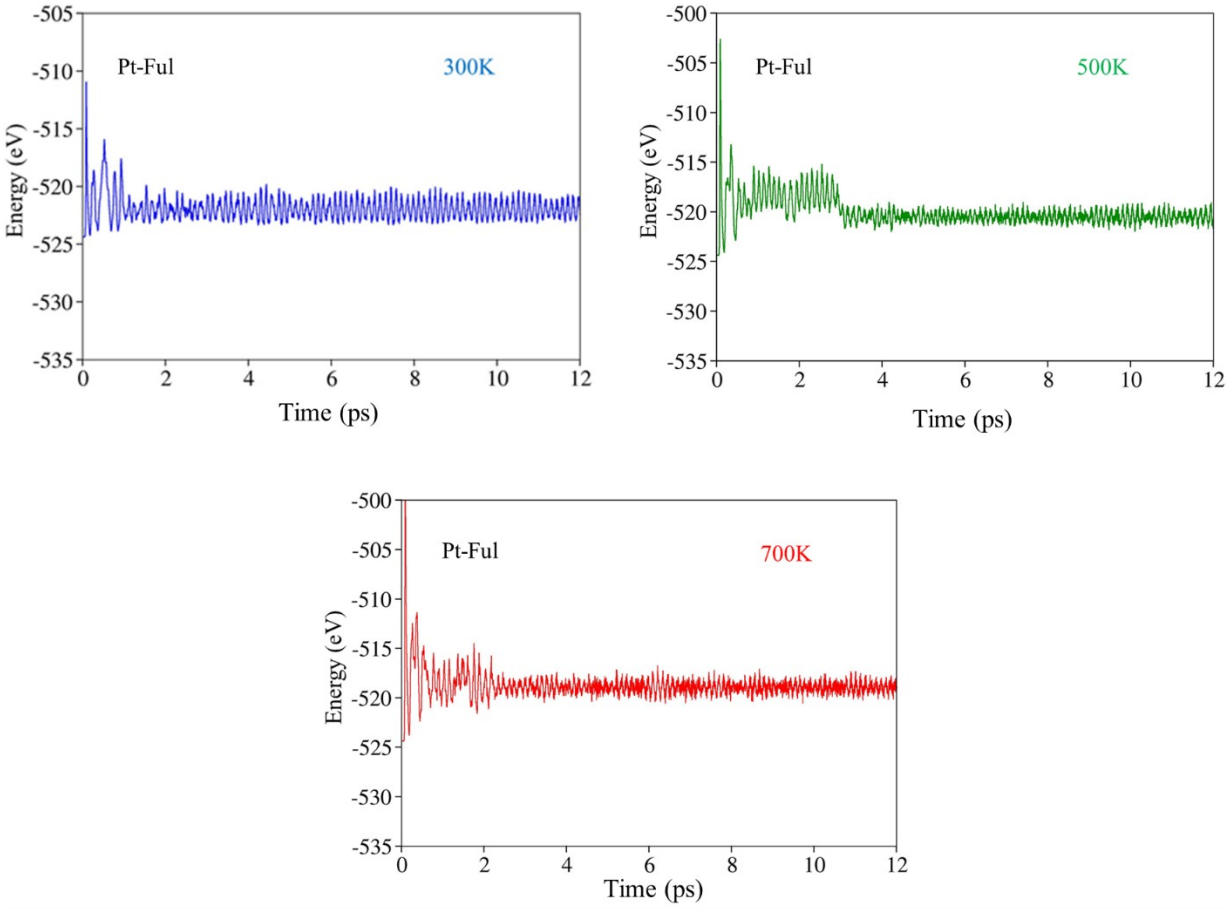

Fig. S10. The variation of total energy with time under AIMD simulations at target temperatures of 300 K, 500 K, and 700 K for the Pt-Ful.

References:

1) V. Fung, G. Hu, Z. Wu and D. E. Jiang, J. Phys. Chem. C, 2020, **124**, 19571–19578.

2) J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, J. Electrochem. Soc., 2005, **152**, J23–J26.

3) I. C. Man, H. Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov and J. Rossmeisl, ChemCatChem, 2011, **3**, 1159–1165

4) J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, J. Phys. Chem. B, 2004, **108**, 17886–17892

5) I. Barlocco, L. A. Cipriano, G. Di Liberto and G. Pacchioni, Adv. Theory. Simul. 2023, **6**, 2200513