

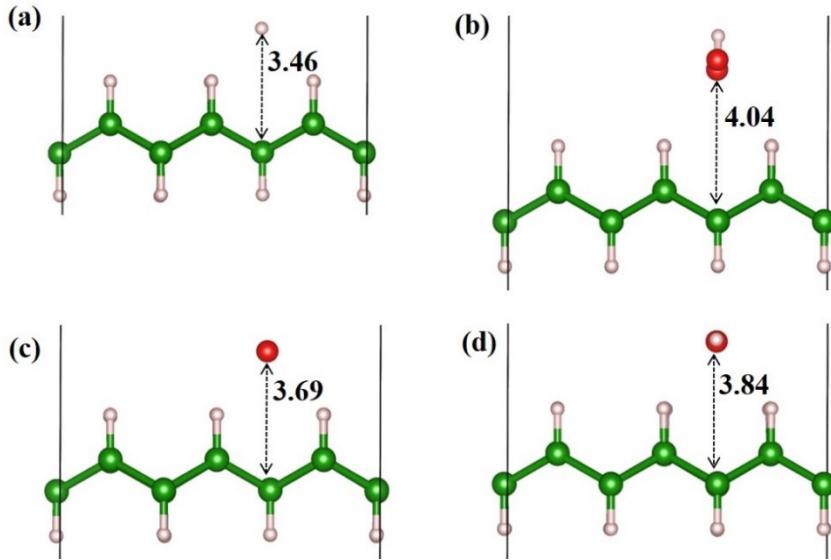
## **Supporting Information (SI)**

**Table S1.** Standard dissolution potential for pure metals ( $U_{diss}$ ) and reaction free energies corresponding to equation (7), (8), and (9) of the paper. n is the number of electrons transferred in the reaction. Positive values in bold are corresponding to the TM-BH systems that are stable against dissolution at pH=0. pH<sub>min</sub> is the minimum pH value for Gibbs free energy of eq (7) ( $\Delta G_{diss}$ ) is zero. Maximum and minimum pH values are set as 16.0 and -2.0, respectively, beyond which the values are unrealistic.

TM	$U_{diss}$ (V) <sup>1</sup>	n	$\Delta G_a$ (eV)	$\Delta G_b=nU_{diss}$ (eV)	$\Delta G_{diss}$ at pH=0	pH <sub>min</sub>
Sc	-2.08	3	2.99	-6.24	-3.25	>16.0
Ti	-1.63	2	2.28	-3.26	-0.98	8.33
V	-1.18	2	1.28	-2.36	-1.08	9.14
Cr	-0.91	2	0.84	-1.82	-0.98	8.25
Mn	-1.18	2	0.99	-2.36	-1.37	11.61
Fe	-0.45	2	0.83	-0.90	-0.07	0.63
<b>Co</b>	-0.28	2	0.89	-0.56	<b>0.33</b>	-2.80
Ni	-0.26	2	0.86	-0.52	<b>0.34</b>	-2.88
<b>Cu</b>	0.34	2	0.37	0.68	<b>1.05</b>	-8.84
Y	-2.37	3	3.23	-7.11	-3.88	>16.0
<b>Zr</b>	-1.45	4	11.67	-5.80	<b>5.87</b>	<-2.0
<b>Nb</b>	-1.10	3	4.26	-3.30	<b>0.96</b>	<-2.0
<b>Ru</b>	0.46	2	0.35	0.92	<b>1.27</b>	<-2.0
<b>Rh</b>	0.60	2	0.43	1.20	<b>1.63</b>	<-2.0
<b>Pd</b>	0.95	2	0.08	1.90	<b>1.98</b>	<-2.0
<b>Ag</b>	0.80	1	-0.72	0.80	<b>0.08</b>	-1.40
Hf	-1.55	4	4.27	-6.20	-1.93	8.16
Ta	-0.60	3	0.28	-1.80	-1.52	8.54
W	0.10	3	-0.81	0.30	-0.51	2.85
<b>Re</b>	0.30	3	-0.89	0.90	<b>0.01</b>	-0.08
<b>Ir</b>	1.16	3	-0.24	3.48	<b>3.24</b>	<-2.0
<b>Pt</b>	1.18	2	-0.18	2.36	<b>2.18</b>	<-2.0
<b>Au</b>	1.50	3	-1.50	4.50	<b>3.00</b>	<-2.0

**Table S2.** The bond lengths of a transition metal with boron along the zigzag direction ( $d_{\text{TM-B1}}$ ) and perpendicular to the zigzag direction ( $d_{\text{TM-B2}}$ ) of all the considered transition metal-doped borophane (TM-BH).  $E_b$  denotes the binding energy,  $\delta q$  represent the Bader charge on transition metal atom and  $\mu$  is the magnetic moment associated with the TM-BH system.

System	$d_{\text{TM-B1}} (\text{\AA})$	$d_{\text{TM-B2}} (\text{\AA})$	$E_b (\text{eV})$	$\delta q (\text{e})$	$\mu$
Sc-BH	2.48	2.25	-2.37	1.67	0.44
Ti-BH	2.31	2.16	-1.96	1.32	0.00
V-BH	2.25	2.10	-1.42	0.26	1.36
Cr-BH	2.19	2.04	-1.01	-0.21	2.04
Mn-BH	2.20	2.07	-1.11	0.68	3.44
<b>Fe-BH</b>	<b>2.14</b>	<b>1.99</b>	<b>-1.01</b>	<b>-1.42</b>	<b>2.12</b>
<b>Co-BH</b>	<b>2.13</b>	<b>2.01</b>	<b>-1.08</b>	<b>-0.76</b>	<b>1.63</b>
Ni-BH	2.12	1.99	-1.05	-0.32	0.00
Cu-BH	2.09	2.02	-0.56	-0.88	0.00
Y-BH	2.66	2.39	-2.05	1.73	0.28
Zr-BH	2.47	2.30	-1.71	2.19	0.00
Nb-BH	2.37	2.23	-0.82	0.99	1.02
Ru-BH	2.20	2.06	-0.54	-0.34	0.00
<b>Rh-BH</b>	<b>2.19</b>	<b>2.07</b>	<b>-0.62</b>	<b>-1.08</b>	<b>0.00</b>
Pd-BH	2.24	2.12	-0.26	-0.07	0.00
Ag-BH	2.87	2.40	0.60	0.48	0.00
Hf-BH	2.43	2.26	-1.56	0.89	0.00
Ta-BH	2.36	2.22	-0.59	0.68	1.01
W-BH	2.26	2.13	0.47	-1.81	0.00
Re-BH	2.21	2.10	0.55	0.18	0.00
Os-BH	2.20	2.08	-0.09	-2.65	0.00
Ir-BH	2.19	2.08	-0.11	-1.54	0.00
Pt-BH	2.23	2.09	0.00	-1.88	0.00
Au-BH	2.33	2.16	1.18	-1.18	0.00



**Figure S1.** Optimized structure of reaction intermediates (OOH, O, OH) and H on the surface of pristine borophane.

### Catalytic Inertness of Pristine Borophane

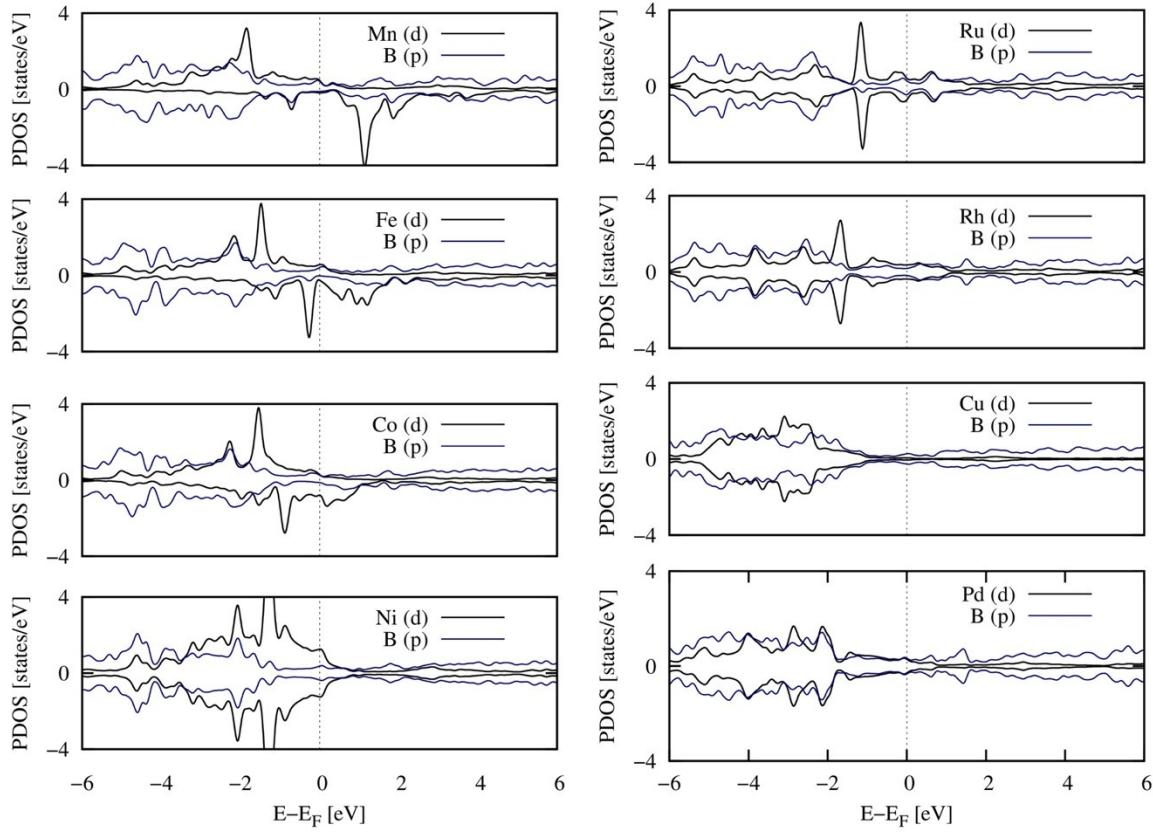
In order to test the catalytic inertness of the surface of borophane (BH) towards ORR/OER, we perform full structural relaxation by keeping reaction intermediates close to the surface of BH. As can be seen from Figure S1., ORR/OER reaction intermediates including H atom doesn't bind covalently to the surface of BH. Adsorption energies presented in Table S3., of all the intermediates, are calculated using the following relations,<sup>2,3</sup>

$$\Delta E_{*OOH} = E_{*OOH} - E(*) - \left[ 2E_{H_2O} - \frac{3}{2}E_{H_2} \right] \quad (1)$$

$$\Delta E_{*O} = E_{*O} - E(*) - [E_{H_2O} - E_{H_2}] \quad (2)$$

$$\Delta E_{*OH} = E_{*OH} - E(*) - \left[ E_{H_2O} - \frac{1}{2}E_{H_2} \right] \quad (3)$$

$$\text{and, } \Delta E_{*H} = E_{*H} - E(*) - \frac{1}{2}E_{H_2} \quad (4)$$



**Figure S2.** The partial density of states (PDOS) of Mn-, Fe-, Co-, Ni-, Cu-, Rh-, Ru- and Pd-BH systems. The vertical dashed lines correspond to the Fermi level which is rescaled to zero. Black and blue lines represent the d-orbital of transition metal and p-orbital of boron atom, respectively.

**Table S3.** Binding energies (eV) of ORR/OER reaction intermediates and H on pristine borophane.

$\Delta E_{*OOH}$	4.74
$\Delta E_{*O}$	4.85
$\Delta E_{*OH}$	2.54
$\Delta E_{*H}$	2.23

### Two-electron ( $2e^-$ ) reduction mechanism on TM-BH systems

The ORR process sometimes proceeds via a  $2e^-$  reduction pathway, where the second hydrogen adsorbs on the un-hydrogenated O site of  $*OOH$ , yielding a stable  $H_2O_2$  molecule that leaves the surface of the catalyst, for example, see Figure 7 (g) of the paper. The  $2e^-$  and  $4e^-$  reduction pathways compete with each other depending upon on the Gibbs free-energy change in the second protonation step to form either  $*O$  with a molecule of water ( $\Delta G_2$ ) or  $H_2O_2$  ( $\Delta G_5 = (G_{*H_2O_2} - G(*) - G(H_2O_2))$ ). On comparing free energy changes during second protonation step, we found  $\Delta G_2$  much larger than  $\Delta G_5$  in almost all the TM-

BH systems as shown in Table S4. which thermodynamically support \*O formation and discard 2e<sup>-</sup> process over 4e<sup>-</sup> reduction pathway.

**Table S4.** Gibbs free-energy change ( $\Delta G$ , eV) values of all the ORR intermediate steps on selected transition metal-doped borophane (TM-BH) at U=0 V.  $\eta^{\text{ORR}}$  and  $\eta^{\text{OER}}$  are the ORR and OER overpotentials associated with respective systems (in volts).

System	$\Delta G_1$	$\Delta G_2$	$\Delta G_3$	$\Delta G_4$	$\Delta G_5$	$\eta^{\text{ORR}}$	$\eta^{\text{OER}}$
<b>Cr-BH</b>	1.63	3.00	0.06	0.23	0.27	1.17	1.77
<b>Mn-BH</b>	1.33	2.32	0.67	0.60	0.14	0.63	1.09
<b>Fe-BH</b>	1.17	1.78	1.18	0.80	0.4	<b>0.43</b>	0.55
<b>Co-BH</b>	0.58	1.60	1.20	1.54	0.32	0.65	<b>0.37</b>
<b>Ni-BH</b>	0.23	1.26	1.46	1.97	0.34	1.00	0.74
<b>Cu-BH</b>	0.26	0.89	1.84	1.93	0.31	0.97	0.70
<b>Ru-BH</b>	0.76	2.25	0.59	1.32	0.32	0.64	1.02
<b>Rh-BH</b>	0.76	1.37	1.47	1.32	0.26	<b>0.47</b>	<b>0.24</b>
<b>Ag-BH</b>	0.57	0.59	2.21	1.55	0.16	0.66	0.98

## References

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