# Electronegativity principle for hydrogen evolution activity using firstprinciples calculations

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# 1. Supplementary Tables and Figures

Catalyst	$\Delta G_{\rm H}({\rm eV})$	Reference	$j_0 ({ m mA \ cm^{-2}})$	Reference
Pt	-0.03	1	2.34	10
Co	-0.27	2	4.79×10 <sup>-3</sup>	10
Re	-0.32	2	1.35	10
Pd	-0.14	2	1	11
Rh	-0.1	2	0.251	11
Ir	0.03	2	0.12	11
Cu	0.19	2	4.27×10-3	10
Ni	-0.27	2	6.31×10 <sup>-3</sup>	11
Au (111)	0.45	2	3.98×10 <sup>-3</sup>	11
Ag (111)	0.51	2	1.58×10 <sup>-5</sup>	10
Nb (110)	-0.56	2	1.58×10 <sup>-4</sup>	11
Mo (110)	-0.37	2	8.51×10-5	10
W (110)	-0.43	2	1.26×10-3	11
VC	0.314	3	3.13×10 <sup>-2</sup>	12
MoC	0.14	4	0. 1	4
Mo <sub>2</sub> C	-0.24	5	3.3×10 <sup>-2</sup>	13
MoP	-0.389	6	4.15×10 <sup>-3</sup>	14
$2H-MoS_2-V_S$	0.02	7	4.49×10 <sup>-2</sup>	7
1T-WS <sub>2</sub> (6.25%)	0.28	8	2×10-2	8
2H-MoS <sub>2</sub> -edge	0.09	9	1.84×10 <sup>-2</sup>	15

**TABLE S1.** Reported exchange current density  $j_0$  (mA cm<sup>-2</sup>) and  $\Delta G_{\rm H}$  for catalysts in Fig. 1.

Catalyst	Hydrogen coverage	TOF $(s^{-1})$	$j_0 ({ m mA \ cm^{-2}})$	Reference
Pt (111)	87.5%→100%	/	2.344	10
Pd (111)	87.5%→100%	/	0.47	16
1T-MoS <sub>2</sub> -bp	25.0%→37.5%	0.02	/	17
MoC(001)	75%→83%	/	0.033	13
2H-MoS <sub>2</sub> -edge	0→25.0%	0.013	/	15
1T-WS <sub>2</sub> -bp	0→6.25%	0.043	/	8
2H-VS <sub>2</sub> -bp	0→12.5%	/	/	18
2H-MoS <sub>2</sub> -Vs	$1 \text{ H} \rightarrow 2 \text{ H}$	0.06	/	19
Pt(pH=13)	0→25%	/	0.08	20
Ir(pH=13)	0→33.3%	/	0.66	21
N-doped graphene	83.33%→100%	/	0.00007	22

**TABLE S2.** Hydrogen coverage, TOF and exchange current density  $j_0$  for catalysts in Fig. 4.

**TABLE S3.** The calculated hydrogen desorption barriers  $(\Delta G^{\ddagger}_{des})$  and their corresponding ratedetermining steps (RDS)

	$2H-VS_2/H_2O$	$1T-MoS_2/H_2O$	$2H\text{-}MoS_2\text{-}V_S/H_2O$	Pt(111)/H <sub>2</sub> O
$\Delta G^{\ddagger}_{des} \left( \mathrm{eV} \right)$	1.05	0.95	0.80	0.67
RDS	Heyrovsky	Tafel	Heyrovsky	Tafel



**Fig. S1**. Structural evolution and reaction energy pathway at the  $2\text{H-VS}_2/\text{H}_2\text{O}$  interface. (a) the Volmer reaction, (b) the Heyrovsky reaction, (c) the Tafel reaction and (d) linearly fitted Tafel reaction barriers at different potentials. Structures of initial state (IS) and final state (FS) are given for each of the reactions. For the Volmer and the Heyrovsky reactions, the initial states have an electrode potential of  $U_{\text{SHE}} = -0.03$  V. For the Tafel reaction, the initial state has an electrode potential of  $U_{\text{SHE}} = -0.65$  V.<sup>18</sup> All the energies along the reaction pathways are corrected using the charge extrapolation scheme.<sup>23</sup> Protons participating in the reactions are labelled by green. Imaginary frequencies for transition states (TS) are given in parentheses.



Fig. S2. Structural evolution and reaction energy pathway at the 1T-MoS<sub>2</sub>/H<sub>2</sub>O interface. (a) the Volmer reaction, (b) the Heyrovsky reaction, (c) the Tafel reaction and (d) linearly fitted Heyrovsky reaction barriers at different potentials. Structures of IS and FS are given for each of the reactions. For the Volmer reaction, the IS has an electrode potential of  $U_{\text{SHE}} = 0.15$  V. For the Heyrovsky reaction, the IS has an electrode potential of  $U_{\text{SHE}} = -0.63$  V. The IS of the Tafel reaction has an electrode potential of  $U_{\text{SHE}} = 0.09$  V.<sup>24</sup> All the energies along the reaction pathways are corrected using the charge extrapolation scheme.<sup>23</sup> Protons participating in the reactions are labelled by green. Imaginary frequencies for transition states (TS) are given in parentheses.



Fig. S3. Structural evolution and reaction energy pathway at the 2H-MoS<sub>2</sub>-V<sub>S</sub>/H<sub>2</sub>O interface. (a) Proton transfer from a surface O site to water, (b) the Vomer reaction and Tafel reaction, (c) the Heyrovsky reaction. Structures of IS and FS are given for each of the reactions. The initial potential is  $U_{\text{SHE}} = -0.20 \text{ V}.^{25}$  All the energies along the reaction pathways are corrected using the charge extrapolation scheme.<sup>23</sup> Protons participating in the reactions are labelled by green.



**Fig. S4**. Structural evolution and reaction energy pathway at the  $Pt(111)/H_2O$  interface. (a) The Tafel reaction and (b) the Heyrovsky reaction. Structures of IS and FS are given for each of the reactions. The IS has an electrode potential of  $U_{SHE} = 0$  V. All the energies along the reaction pathways are corrected using the charge extrapolation scheme.<sup>23</sup> Protons participating in the reactions are labelled by green. Imaginary frequencies for transition states (TS) are given in parentheses.



Fig. S5. Slab surface models for the catalysts discussed in Fig. 4. For the  $2H-MoS_2$  edge structure, we give the top and side views of the models. For all the structures, H and O atoms are shown with grey and red spheres.



Fig. S6. Hydrogen adsorption energy  $\Delta G_{\rm H}$  as a function of hydrogen coverage on MoC(001).

## 2. Calculations Details for Free Energies

The free energy data shown in Fig. S1 were obtained by correcting the DFT calculated energies with the contribution of zero-point energies and entropies.

$$\Delta G_0 = \Delta E + \Delta Z P E - T \Delta S_{.} \quad (S1)$$

Zero-point energies were obtained by calculating the Hessian matrix using the finite difference method.<sup>26</sup> We corrected zero-point energies for excess protons involving hydroniums and adsorbed protons. By examining a series of interfacial structures with different proton concentrations and water networks, we found that the zero-point energy contribution of a proton to the total free energy was rather small (*ca.* 2 meV). Consequently, we ignored zero-point energy correction for all free energy data.

Entropic correction was performed for both hydroniums and adsorbed protons, following the way of Norskov.<sup>27</sup> The entropy for an adsorbed proton was taken to be zero because the vibrational entropy was quite small.<sup>27</sup> Hydroniums were also addressed in a similar way because they were bound to an ice-like water network with little freedom. This leads to an entropic change of *ca*. -0.20 eV for a proton, which is then normalized to be *ca*. -0.01 eV for one water molecule.

### 3. Evaluation of hydrogen coverages under the SHE condition.

The most reliable method to determine  $H_{SHE}^{\circ}$  for a catalyst is to calculate the surface or interfacial Pourbaix diagram. This has been done for 1T-MoS<sub>2</sub>, 2H-VS<sub>2</sub>, 2H-MoS<sub>2</sub>-Vs and Pt(111) surfaces and the results are collected in Table S2. For the rest systems in Fig. S2, it is computationally too expensive to obtain all the Pourbaix diagrams. Instead, one can approximate the  $H_{SHE}^{\circ}$  by assuming that the permitted maximum hydrogen coverage corresponds to a  $\Delta G_{\rm H}$  of ca. 0.2 eV based on the previous studies.<sup>24, 28, 29</sup> This can greatly save the computational cost and would not lead to large errors. Using this principle, we give a detailed discussion for the rest catalysts in this section and list the results in Table S2.

1T-WS<sub>2</sub> adsorbs H rather weakly, with a  $\Delta G_{\rm H} = 0.37$  eV at 1/8 hydrogen coverage, i.e., the lowest hydrogen coverage for this system. Therefore, we approximately give H%<sub>SHE</sub> = 1/8 though the practical coverage is perhaps lower. The error is represented by the error bar in Fig. 4b.

The H%<sub>SHE</sub> for the MoC(001) surface is determined by calculating the hydrogen coverage dependent  $\Delta G_{\rm H}$ , which is shown in Fig. S3. We estimate that the H%<sub>SHE</sub> lies in between 83% and 92%. 2H-MoS<sub>2</sub>-edge has a H%<sub>SHE</sub> = 0.25, which has been reported by a previous experiment.<sup>9</sup>

Because hydrogen adsorption on Pd(111) is stronger than that on Pt(111) (cf. Fig. 1), one can reasonably estimate that the  $H_{SHE}^{0}$  is 100%.

Previous theoretical and experimental studies demonstrate that the HER on Pt(111) under alkaline conditions is governed by water dissociation and the surface has OH groups adsorbed.<sup>30, 31</sup>We calculate the  $\Delta G_{\rm H}$  for adsorption of one H in the presence of two adsorbed OH groups and find that  $\Delta G_{\rm H} = 0.22$  eV, which approximately corresponds to the permitted maximum hydrogen coverage aforementioned.

Previous studies suggest that Ir(111) has stronger OH adsorption ability than Pt(111).<sup>30</sup> We therefore consider adsorption of one H in the presence of three adsorbed OH groups, which generates a  $\Delta G_{\rm H} = -0.15$  eV. Considering higher OH coverages would move the result to the positive side, which is reflected by the error bar in Fig. 4b.

Au(111) adsorbs H atoms very weakly, we therefore consider the lowest hydrogen coverage of 1/8 as the H%<sub>SHE</sub>, which generates a  $\Delta G_{\rm H} = 0.50$  eV, close to a previous prediction of 0.45 eV.

ZnO(001) has not been reported as an active catalyst and therefore it is meaningless to discuss the H%<sub>SHE</sub>. We use the model in Fig. S2 to represent an inert system with a high- $\chi$  for comparisons.

#### 4. Reaction pathways for the interfacial systems in Table 1

In Table 1 and Fig. 3, we exhibit hydrogen desorption barriers for four interfacial systems. Here, we give the computational details of the reaction pathways in Fig. S1-S4, from which we can identify the rate-determining steps (RDS).

In Fig. S1, we show the three elementary reaction steps at the interface of  $2\text{H-VS}_2/\text{H}_2\text{O}$ , i.e., the Volmer and Heyrovsky reactions at  $U_{\text{SHE}} = -0.03$  V and the Tafel reaction at  $U_{\text{SHE}} = -0.65$  V. The reason why we do not give the result of the Tafel reaction around the equilibrium potential is that the surface hydrogen coverage under the SHE condition is only 1/8, which do not favor the direct Tafel manner. From Fig. S1, one can see that the Volmer reaction takes place when a proton in the water layer is transferred to the catalyst surface. This takes a rather small barrier of 0.21 eV, which means that hydrogen adsorption is very easy. The Heyrovsky reaction occurs when a proton in the water layer combines with a hydrogen atom adsorbed on the surface to form a H<sub>2</sub> molecule. The barrier is as large as 1.05 eV, indicating that hydrogen desorption is probably the RDS. By calculating the Tafel barriers

at several different potentials, we obtain a linear  $\Delta G^{\ddagger} \sim U_{\text{SHE}}$  dependence. By extrapolating the

dependence to the zero potential, we obtain a large Tafel barrier of 1.20 eV under the SHE condition, which is much larger than Heyrovsky barrier. This indicates that the Heyrovsky step is the RDS. The detailed analysis of the reaction mechanism could be found in Ref. 18.

Fig. S2 shows the HER reaction pathway at the interface of  $1T-MoS_2/H_2O$ . We calculate the minimum energy pathways around  $U_{SHE} = 0$  V for the Volmer and the Tafel reactions. For the Heyrovsky reaction, we only give a result at  $U_{SHE} = -0.63$  V because no hydroniums are available for supercells of the current size around the zero potential. We find that both the Heyrovsky and the Tafel steps are preceded by a hydrogen atom diffusion from a surface low-S site to a neighboring high-S site. This is because H adsorption on the high-S site is relatively weaker. Diffusion to a high-S site can decrease the overall desorption barrier. Fig. S2 (b) and (c) show that the barriers for both the diffusion steps are smaller than those of the desorption steps. Therefore, the overall Tafel barrier is determined to be 0.95 eV, whereas the overall Heyrovsky barrier is 1.20 eV. By calculating the Heyrovsky barriers at several different potentials, one can obtain the barrier at the zero potential by a linear extrapolation (Fig. S2 (d)). This generates a Heyrovsky barrier of 1.28 eV, much larger than the Tafel barrier. This means that the Tafel reaction is the RDS. The detailed analysis of the reaction mechanism could be found in Ref. 24.

Fig. S3 shows the HER reaction pathway at a potential of  $U_{\text{SHE}} = -0.20$  V at the interface of 2H-MoS<sub>2</sub>-V<sub>S</sub>/H<sub>2</sub>O. First, the initial structure (Fig. 2 (c)) undergoes a low-barrier (0.15 eV) reversed Volmer reaction, in which a hydrogen atom transfers from the surface O site to the water layer (Fig. S3 (a)). This provides a hydronium ion in water and facilitates the subsequent reactions. Second, hydrogen desorption could take place through two pathways, as shown in Fig. S3 (b) and (c). The first one is a two-step process consisting of a Volmer step and Tafel step. In this pathway, a proton in water is transferred to a S vacancy which has already adsorbed a hydrogen atom. This step takes a large barrier of 1.14 eV. Then the two hydrogen atoms in the S vacancy combine into a H<sub>2</sub> molecule via a Tafel manner with a small barrier of 0.55 eV. The overall reaction barrier for this pathway is 1.14 eV. The second pathway is single-step Heyrovsky process, in which a proton in water combines with a hydrogen atom adsorbed on a S vacancy to form a H<sub>2</sub> molecule. This process has a reaction barrier of 0.80 eV, much smaller than that of the first one. Consequently, one can conclude that the Heyrovsky route is the RDS. The detailed analysis of the reaction mechanism could be found in Ref. 25.

Previous theoretical studies have demonstrated that hydrogen coverage on Pt(111) is 100% under the SHE condition.<sup>32, 33</sup> Besides, hydrogen atoms prefer to adsorb on top sites at HER potentials.<sup>32</sup> Based on these characteristics, we constructed the interfacial model and calculated the free energy barriers of the Tafel and the Heyrovsky reactions at  $U_{\text{SHE}} = 0$  V, as shown in Fig. S4. The calculated Tafel barrier is 0.67 eV, in reasonable agreement with the 0.70 eV estimated from the experimental  $j_0$  of 2.344 mA cm<sup>-2</sup>.<sup>10</sup> In contrast, the Heyrovsky barrier is calculated to be 1.37 eV, which is too large for the reaction to occur. Because surface H atoms are underpotentially adsorbed, we only calculate the desorption barrier.

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