Hydrogen Evolution Reaction Activity of Heterogeneous Materials – a Theoretical Model

Supporting document

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Table S1. Symbols used in the manuscript and their descriptions.

Symbol	Description
R1, R2, R3	Elementary reaction steps corresponding to Volmer, Heyrovsky, and Tafel reactions
ΔG_H	Hydrogen adsorption free energy
i_0	Exchange current density
$\theta_{tot}{}^*$	Total equilibrium hydrogen coverage
θ_{tot}	Total hydrogen coverage
$\theta_{totDFT}{}^*$	Total equilibrium hydrogen coverage obtained from the DFT model, used to calculate the ΔG_H.
p_{H_2}	Hydrogen pressure
k	Boltzmann constant
T	Temperature
h	Planck constant
$\theta_i{}^*$	Equilibrium Occupation of adsorption site (*i*)
θ_i	Occupation of adsorption site (*i*)
N_{sites}	Total number of adsorption sites
r	Strength factor of the linear dependence of ΔG_H to the total coverage θ_{tot}
$\overrightarrow{v_i}$	Forward rate of elementary reaction step *i*
$\overleftarrow{v_i}$	Backward rate of elementary reaction step *i*
v_i	Net rate of reaction *i*. $(\overrightarrow{v_i} - \overleftarrow{v_i})$
$\overrightarrow{\Delta G_i^0}$	Standard free energy of activation of elementary reaction step *i*

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α, β, γ	Charge transfer coefficients
ϕ	Inner potential (potential between material and solution)
ϕ^*	Equilibrium inner potential
η	Overpotential
e_0	Electron charge
a_H	Activity of protons in the solution
G1, G2, G3	"Magnitude" of the exchange current of the three elementary reaction steps
N_{nb}	Number of neighboring sites to site i
J_{tot}	Total electrical current density
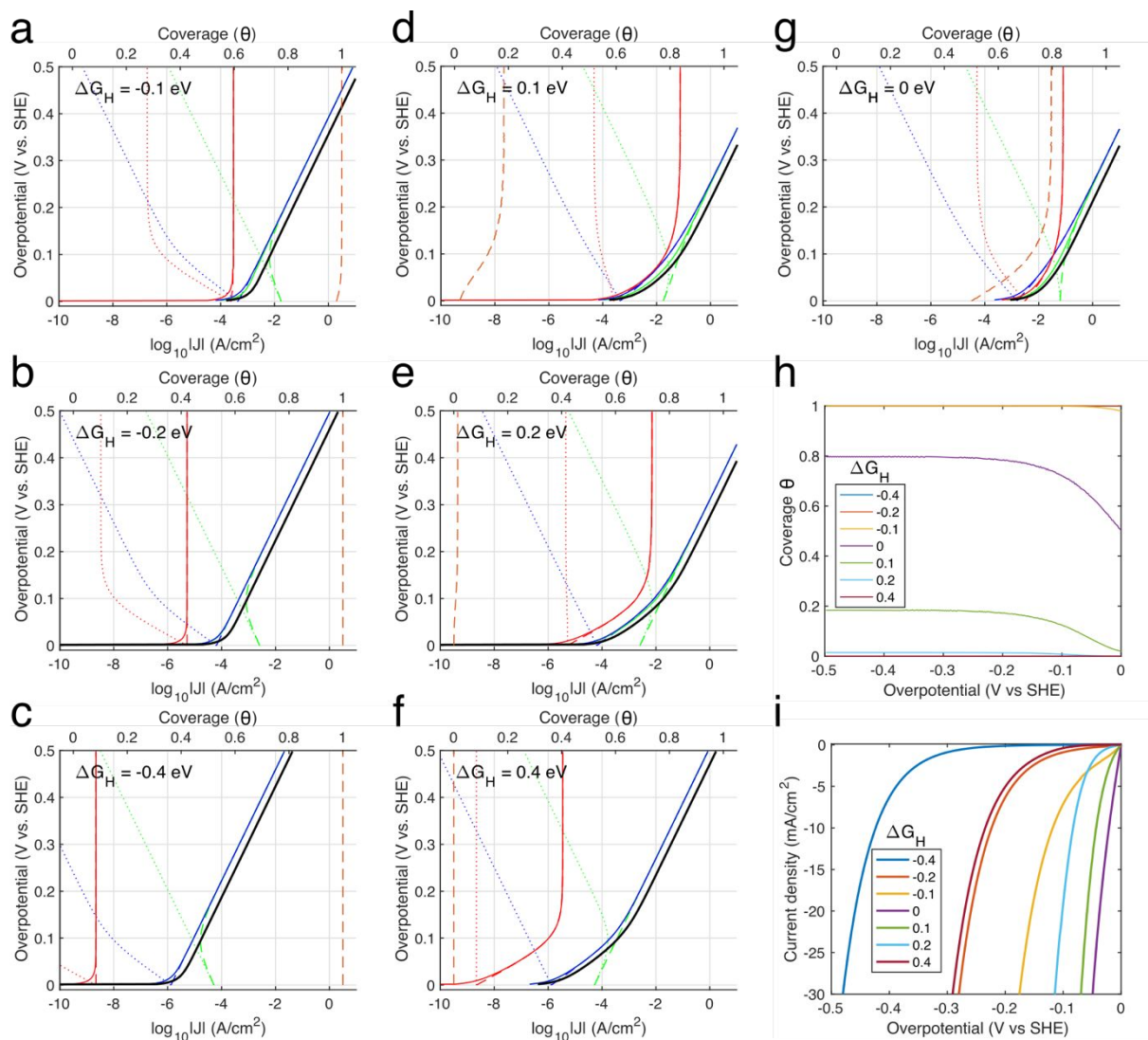
Figure S1. (a-g) Theoretical Tafel plots of homogeneous materials considering different values of ΔG_H. The ΔG_H is varied from -0.4 to 0.4 eV as displayed in each figure. **(h)** The hydrogen coverage against overpotential and **(i)** a voltammetry curves for the same systems are also shown.
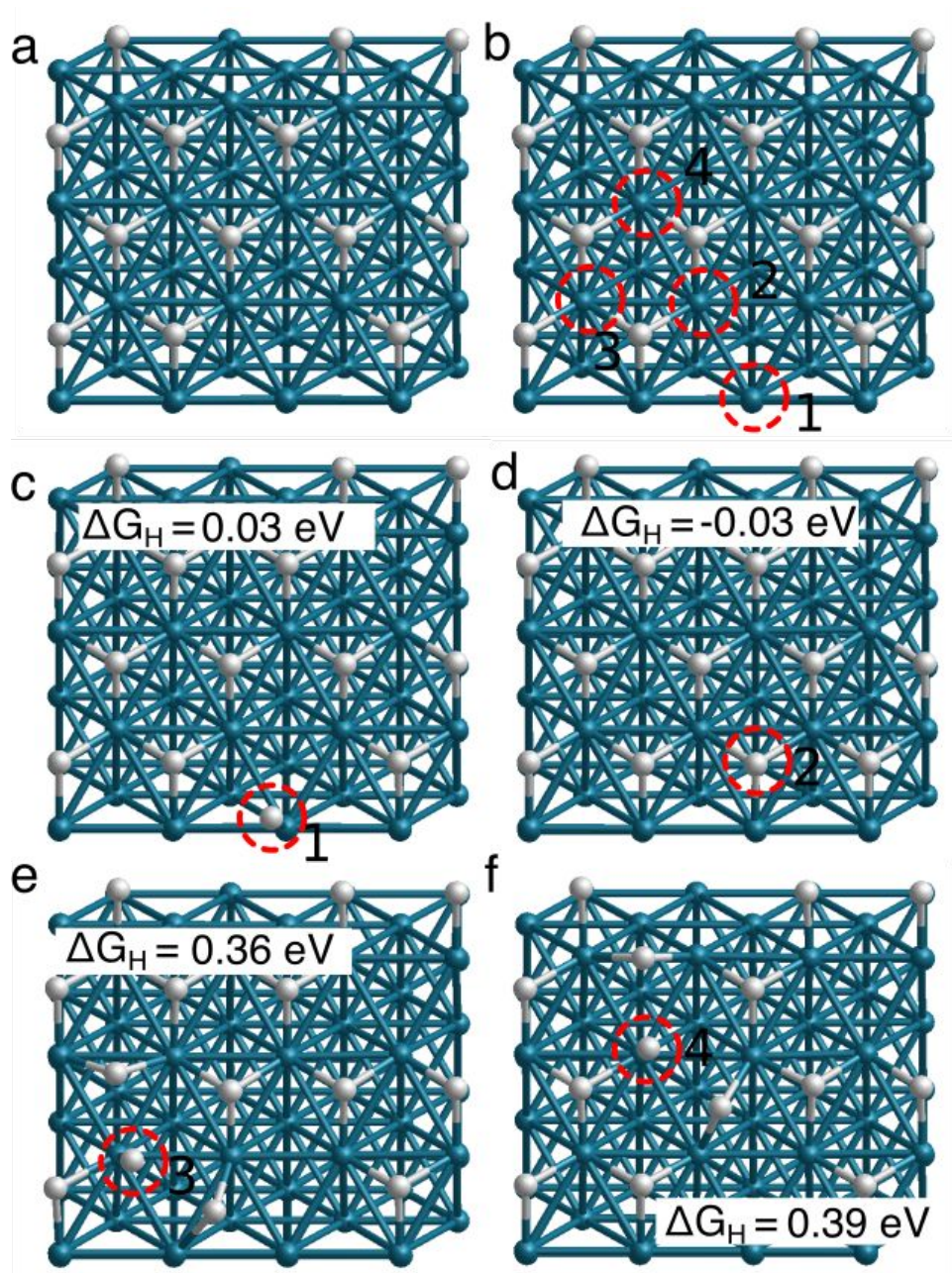
Figure S2. (a) Equilibrium H-coverage structure of Pt_{111} with a coverage of 0.81 ML with only fcc adsorption sites occupied. **(b)** Non-equilibrium ontop adsorption sites tested and the final relaxed structures of these are shown in **(c-f)**.

Table S2. The hydrogen adsorption free energies for metals at and above the equilibrium hydrogen coverage. Both ontop and 3-fold adsorption sites are tested above the equilibrium coverage. If fcc sites are filled, the 3-fold sites are hcp and vice versa.

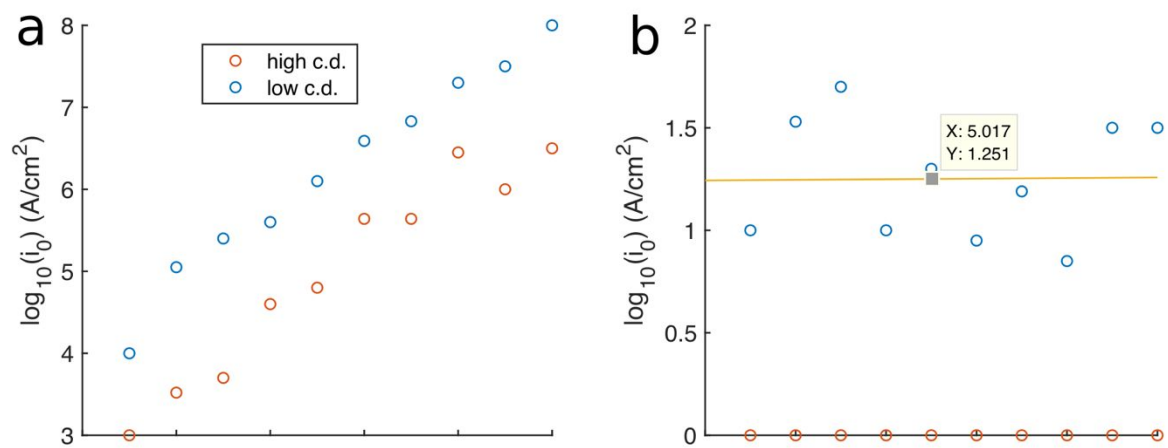| Metal	ΔG_H, θ = eq. (eV)	ΔG_H OT, θ > 1 ML (eV)	ΔG_H 3-fold, θ > 1 ML (eV)
Pd111	-0.26	0.87	0.57
Pt111	-0.04	~ 0.39 eV. 2 NB-H moves to bridges.	H moves to bridge. 3 NB-H moves to bridge/OT
Ir111	-0.05	-	0.11
Fe111	-0.39	0.75	0.86
Ni111	-0.38	1.03	0.88
Co111	-0.47	0.72	0.76
Rh111	-0.16	0.49	0.64

Figure S3. (a) Absolute values of experimental exchange current densities obtained from high current density regions (orange) and low current density regions (blue) for several different elements including, Mo, Pt, Au, Ag, Pd, W. **(b)** Here the i_0 are subtracted for each data point showing the difference between high and low obtained i_0. The mean difference is calculated to 1.25 ($\log_{10}$ |A/cm^2|). Experimental data are taken from ref[1-5].

Table S3. Theoretical exchange current densities and overpotentials needed for 10 mA/cm^2 for different MoS$_2$ configurations with different relative amounts of edge-atoms.

Percentage of edge-atoms (%)	Exchange current density $\log_{10}(A/cm^2)$	Overpotential at 10 mA/cm² (V)
0	-17.41	1.64
1	-5.34	0.26
3	-4.86	0.21
5	-4.64	0.18
10	-4.34	0.15
25	-3.94	0.11
50	-3.64	0.09
100	-3.34	0.07

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