

Revisiting Trends in the Exchange Current for Hydrogen Evolution

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Computational Details

We use the Vienna Ab Initio Simulation Package (VASP) for the first-principles density functional theory (DFT) calculations. We use the Perdew-Burke-Ernzerhof (PBE) exchange-correlational functional and Revised Perdew-Burke-Ernzerhof (RPBE) to solve the Kohn-Sham equations within periodic boundary conditions, and the PAW pseudopotentials to describe electron-nucleus interactions.¹⁻⁴ The dDsC dispersion correction is used for the Van der Waals (VdW) corrections. The electronic self-consistent loops are terminated within energy-change tolerance of 1×10^{-6} eV. The periodic slab models are 3×3 supercells cleaved using the calculated bulk structures in Table 1 with a thickness of at least 10 Å. We used 15 Å vacuum perpendicular to the surfaces. The relaxations are done by fixing at least two layers in bulk position and relaxing the top three layers for all surfaces. We use the most stable terminations: for the metals in $Fm\bar{3}m$ and $P6_3/mmc$ phase⁵⁻⁶, we use (111) and (001), respectively, (111) for Bi and In surfaces⁷, and (110) for Mo surface.⁸

The calculated free energy (ΔG_H) values in Table 2 corresponds to the hydrogen coverages of 1/9 ML or 1 ML for the surfaces with positive or negative ΔG_H , respectively. A single water layer is added to test the solvation effects. We find that the effects on adsorption energies are less than 0.05 eV for all the metals therefore not included. Comparing all the ΔG_H values for a metal, it is observed that the PBE results are systematically ~ 0.15 eV less than the results obtained from RPBE for the cases with and without VdW corrections. For each functional, the VdW corrections amounts to less than 0.06 eV. In summary, the trends we show in Figure 3 will be similar for the four cases of ΔG_H calculations.

| | K-points | Phase | PBE | RPBE |
|----|----------|--------------|--|--|
| Ag | 12x12x12 | $Fm\bar{3}m$ | a=b=c=2.93 $\alpha=\beta=\gamma=60$ | a=b=c=2.97 $\alpha=\beta=\gamma=60$ |
| Au | 12x12x12 | $Fm\bar{3}m$ | a=b=c=2.94 $\alpha=\beta=\gamma=60$ | a=b=c=2.97 $\alpha=\beta=\gamma=60$ |

| | | | | |
|----|----------|---------------|---|---|
| Bi | 12×12×12 | R $\bar{3}m$ | a=b=c=4.83 $\alpha=\beta=\gamma=56.69$ | a=b=c=4.99 $\alpha=\beta=\gamma=54.98$ |
| Cd | 12×12×12 | P6 $_3$ /mmc | a=b=3.05; c=5.59 $\alpha=\beta=90; \gamma=120$ | a=b=3.10; c=5.67 $\alpha=\beta=90; \gamma=120$ |
| Co | 12×12×12 | Fm $\bar{3}m$ | a=b=c=2.44 $\alpha=\beta=\gamma=60$ | a=b=c=2.46 $\alpha=\beta=\gamma=60$ |
| Co | 12×12×12 | P6 $_3$ /mmc | a=b=2.45; c=3.95 $\alpha=\beta=90; \gamma=120$ | a=b=2.47; c=3.98 $\alpha=\beta=90; \gamma=120$ |
| Cu | 12×12×12 | Fm $\bar{3}m$ | a=b=c=2.57 $\alpha=\beta=\gamma=60$ | a=b=c=2.60 $\alpha=\beta=\gamma=60$ |
| In | 12×12×12 | R $\bar{3}m$ | a=b=c=8.49 $\alpha=\beta=\gamma=23.139$ | a=b=c=8.61 $\alpha=\beta=\gamma=23.134$ |
| Ir | 12×12×12 | Fm $\bar{3}m$ | a=b=c=2.74 $\alpha=\beta=\gamma=60$ | a=b=c=2.75 $\alpha=\beta=\gamma=60$ |
| Mo | 8×8×8 | Im $\bar{3}m$ | a=b=c=2.73 $\alpha=\beta=\gamma=109.471$ | a=b=c=2.74 $\alpha=\beta=\gamma=109.471$ |
| Ni | 12×12×12 | Fm $\bar{3}m$ | a=b=c=2.48 $\alpha=\beta=\gamma=60$ | a=b=c=2.50 $\alpha=\beta=\gamma=60$ |
| Pd | 12×12×12 | Fm $\bar{3}m$ | a=b=c=2.78 $\alpha=\beta=\gamma=60$ | a=b=c=2.81 $\alpha=\beta=\gamma=60$ |
| Pt | 12×12×12 | Fm $\bar{3}m$ | a=b=c=2.81 $\alpha=\beta=\gamma=60$ | a=b=c=2.82 $\alpha=\beta=\gamma=60$ |
| Re | 12×12×12 | P6 $_3$ /mmc | a=b=2.77 c=4.48 $\alpha=\beta=90; \gamma=120$ | a=b=2.78; c=4.50 $\alpha=\beta=90; \gamma=120$ |
| Rh | 12×12×12 | Fm $\bar{3}m$ | a=b=c=2.70 $\alpha=\beta=\gamma=60$ | a=b=c=2.72 $\alpha=\beta=\gamma=60$ |
| Ru | 12×12×12 | P6 $_3$ /mmc | a=b=2.72; c=4.28 $\alpha=\beta=90; \gamma=120$ | a=b=2.73; c=4.30 $\alpha=\beta=90.000; \gamma=120$ |
| Nb | 12×12×12 | Im $\bar{3}m$ | a=b=c=2.88 $\alpha=\beta=\gamma=109.471$ | a=b=c=2.89 $\alpha=\beta=\gamma=109.471$ |
| W | 12×12×12 | Im $\bar{3}m$ | a=b=c=2.75 $\alpha=\beta=\gamma=109.471$ | a=b=c=2.76 $\alpha=\beta=\gamma=109.471$ |

Table S2. The calculated ΔG_H from two functionals with and without VdW correction.

| | PBE | RPBE | PBE with VdW | RPBE with VdW |
|---------------------|--------|--------|--------------|---------------|
| Ag | 0.416 | 0.565 | 0.381 | 0.527 |
| Au | 0.418 | 0.574 | 0.388 | 0.532 |
| Bi | 1.040 | 1.127 | 1.004 | 1.099 |
| Cd | 1.051 | 1.038 | 1.058 | 1.031 |
| Co (Fm $\bar{3}m$) | -0.355 | -0.202 | -0.411 | -0.252 |
| Co (P6 $_3$ /mmc) | -0.352 | -0.201 | -0.407 | -0.250 |
| Cu | 0.040 | 0.188 | -0.002 | 0.147 |
| In | 0.847 | 0.948 | 0.813 | 0.912 |
| Ir | -0.208 | -0.081 | -0.273 | -0.136 |
| Mo | -0.453 | -0.321 | 3.620 | -0.352 |

| | | | | |
|----|--------|--------|--------|--------|
| Ni | -0.388 | -0.231 | -0.445 | -0.280 |
| Pd | -0.286 | -0.123 | -0.359 | -0.176 |
| Pt | -0.192 | -0.038 | -0.232 | -0.082 |
| Re | -0.293 | -0.154 | -0.333 | -0.195 |
| Rh | -0.270 | -0.116 | -0.318 | -0.159 |
| Ru | -0.330 | -0.180 | -0.375 | -0.220 |

Table S3-1. The experimental $\log(j_0/(A \cdot \text{cm}^2))$ from Ref⁹ (Nørskov Data) is compared with the calculated $\log(j_0/(A \cdot \text{cm}^2))$ using Eq. (1) with constant $k_0 = 200 \text{ s}^{-1}$ (Nørskov Model) and with $k_0 = \exp(23.16|\Delta G_{\text{H}}/eV| + 3.17)$ (Present Model).

| | Nørskov Data | Nørskov Model | Present Model |
|----|--------------|---------------|---------------|
| Pt | -3.1 | -1.95 | -2.58 |
| Pt | -2.63 | -1.95 | -2.58 |
| Pt | -3.34 | -1.95 | -2.58 |
| Ir | -3.7 | -1.93 | -2.55 |
| Ir | -3.46 | -1.93 | -2.55 |
| Pd | -3 | -2.85 | -2.87 |
| Pd | -3 | -2.85 | -2.87 |
| Rh | -3.6 | -2.35 | -2.67 |
| Rh | -3.22 | -2.35 | -2.67 |
| Ni | -5.21 | -5.09 | -3.70 |
| Ni | -5.2 | -5.09 | -3.70 |
| Co | -5.32 | -5.41 | -3.82 |
| W | -5.9 | -11.26 | -6.25 |
| W | -5.9 | -11.26 | -6.25 |
| Cu | -5.37 | -5.41 | -4.42 |
| Mo | -7.07 | -10.25 | -5.84 |
| Re | -2.87 | -4.85 | -3.66 |
| Nb | -6.8 | -10.80 | -6.09 |
| Au | -6.6 | -9.89 | -6.29 |
| Au | -6.8 | -9.89 | -6.29 |
| Au | -5.4 | -9.89 | -6.29 |
| Ag | -5 | -10.90 | -6.69 |
| Ag | -7.85 | -10.90 | -6.69 |

Table S3-2. The experimental $\log(j_0/(A \cdot \text{cm}^2))$ from Table 5 (Present Data) is compared with the calculated $\log(j_0/(A \cdot \text{cm}^2))$ with $k_0 = \exp(23.16|\Delta G_{\text{H}}/eV| + 3.17)$ (Present Model). The first column label reflects experimental setup. The “Present Model” utilize slabs of well-defined terminations as described before.

| | Present Data | Present Model |
|----------|--------------|---------------|
| Pt (111) | -3.35 | -2.83 |
| Pt/C | -1.80 | -2.83 |

| | | |
|----------|--------|--------|
| Pt/C | -0.92 | -2.83 |
| Ir | -1.44 | -3.15 |
| Ir | -1.89 | -3.15 |
| Pd | -3.72 | -3.44 |
| Pd | -2.52 | -3.44 |
| Pd | -3.08 | -3.44 |
| Rh/C | -2.28 | -3.30 |
| Rh/C | -2.17 | -3.30 |
| Ru | -2.35 | -3.71 |
| Cu | -6.84 | -4.13 |
| Co | -5.44 | -3.84 |
| Ni | -5.59 | -4.04 |
| Au (111) | -6.60 | -6.84 |
| Au (111) | -6.47 | -6.84 |
| Poly Au | -6.85 | -6.84 |
| Re | -5.90 | -3.56 |
| Re | -6.00 | -3.56 |
| Bi | -9.10 | -11.05 |
| Cd | -10.77 | -10.24 |
| In | -10.82 | -9.54 |

Table S4. The data used in Figure 3 in the main paper. The experimental j_0 s are collected from reliable literatures listed in Table S4. The calculated $\ln(k_0)$ and ΔG_H are obtained using Eq. (1) and Eq. (2), respectively, in the main document. The area is determined from the structures obtained using RPBE functional listed in Table S1.

| | ΔG_H | Exp. j_0 | $\log j_0$ | $\ln(k_0)$ | Area (cm ²) | # sites in Area | Ref. |
|----------|--------------|-----------------------|------------|------------|-------------------------|-----------------|------|
| Pt (111) | -0.082 | 4.50×10^{-4} | -3.35 | 3.87 | 6.20×10^{-15} | 9 | 10 |
| Pt/C | -0.082 | 1.60×10^{-2} | -1.80 | 7.43 | 6.20×10^{-15} | 9 | 11 |
| Pt/C | -0.082 | 1.20×10^{-1} | -0.92 | 9.46 | 6.20×10^{-15} | 9 | 12 |
| Ir | -0.136 | 3.60×10^{-2} | -1.44 | 10.27 | 5.89×10^{-15} | 9 | 12 |
| Ir | -0.136 | 1.28×10^{-2} | -1.89 | 9.23 | 5.89×10^{-15} | 9 | 11 |
| Pd | -0.176 | 1.90×10^{-4} | -3.72 | 6.60 | 6.16×10^{-15} | 9 | 13 |
| Pd | -0.176 | 3.00×10^{-3} | -2.52 | 9.37 | 6.16×10^{-15} | 9 | 14 |
| Pd | -0.176 | 8.4×10^{-4} | -3.08 | 8.08 | 6.16×10^{-15} | 9 | 11 |
| Rh/C | -0.159 | 5.20×10^{-3} | -2.28 | 9.20 | 5.77×10^{-15} | 9 | 12 |
| Rh/C | -0.159 | 6.70×10^{-3} | -2.17 | 9.45 | 5.77×10^{-15} | 9 | 11 |
| Ru | -0.220 | 4.50×10^{-3} | -2.35 | 11.40 | 5.81×10^{-15} | 9 | 15 |
| Cu | 0.147 | 1.45×10^{-7} | -6.84 | 0.34 | 5.25×10^{-15} | 1 | 16 |
| Co | -0.252 | 3.60×10^{-6} | -5.44 | 5.31 | 4.70×10^{-15} | 9 | 17 |
| Ni | -0.280 | 2.60×10^{-6} | -5.59 | 6.09 | 4.89×10^{-15} | 9 | 18 |
| Au (111) | 0.532 | 2.50×10^{-7} | -6.60 | 16.05 | 6.86×10^{-15} | 1 | 19 |

| | | | | | | | |
|----------|--------|------------------------|--------|-------|------------------------|---|----|
| Au (111) | 0.532 | 3.38×10^{-7} | -6.47 | 16.35 | 6.86×10^{-15} | 1 | 20 |
| Poly Au | 0.532 | 1.40×10^{-7} | -6.85 | 15.47 | 6.86×10^{-15} | 1 | 19 |
| Re | -0.195 | 1.25×10^{-6} | -5.90 | 2.30 | 6.04×10^{-15} | 9 | 21 |
| Re | -0.195 | 1.00×10^{-6} | -6.00 | 2.07 | 6.04×10^{-15} | 9 | 22 |
| Bi | 1.099 | 8.00×10^{-10} | -9.10 | 33.10 | 1.65×10^{-14} | 1 | 23 |
| Cd | 1.031 | 1.7×10^{-11} | -10.77 | 25.83 | 7.49×10^{-15} | 1 | 24 |
| In | 0.912 | 1.5×10^{-11} | -10.82 | 21.33 | 9.30×10^{-15} | 1 | 25 |

Selection of HER Exchange Current Densities from the Research Literature

Experimental exchange current densities (Table 4) were collected from prior literature reports that showed evidence for a high level of analytical rigor. Each of the following were treated as exclusion criteria by incrementally decreasing a “rigor score” for the associated report:

- Electrolytes were not pre-purified or noted to be of highest available commercial purity
- Counter electrodes comprised materials with higher HER activity than the working electrode; these can dissolve and re-deposit on the working electrode and significantly modify its catalytic activity
- Electrode cleaning protocols (if used) involved exclusions to potentials outside the stability limits for the noted pure metal in strong acid conditions
- Evidence that the working electrode was not completely flat (e.g., roughness factor ≥ 2) and the surface roughness was not taken into consideration in the reported exchange current density
- Tafel plots used for kinetic analysis did not give rise to clearly linear behavior over at least 1 order of magnitude in current density
- Mass transfer limitations convoluted kinetic analysis; note this is especially important for high-performing catalysts like Pt, whose HER activity is so high that conventional hydrodynamic methods like RDE cannot achieve a pure kinetic limit
- Control measurements using comparatively well understood HER catalysts (usually Pt) exhibited excessively low or inconsistent catalytic activity

HER measurements exhibiting one of the deficiencies listed above very often suffered from several, which resulted in a subset of measurements with high rigor and another subset with relatively low rigor. Reports with high rigor are shown in the table, and these were used for the regression analyses in the main text. Notes have also been included in Table 4 summarizing the associated experimental protocols, where the bold text notes relatively minor experimental concerns or incomplete information. Mo and W entries are included in Table 4, but these metals were not included in our analysis because neither is thermodynamically stable as a zerovalent metal under HER conditions in acid; accordingly, DFT-calculated H-binding energies are not directly comparable to experimental results, which most likely involve HER on partially oxidized Mo and W sites.

Several other metals (e.g., Ni and Co) are also only stable in an oxidized form at applied potentials near 0 V vs RHE in strong acid solution, but the oxidation products are soluble (and therefore do not irreversibly modify the electrode surface) and rigorous measurements can be executed over sufficiently negative applied potentials to maintain a metallic composition.

Table S5. The collected exchange current densities from experiments with comments.

| Electrode | Reported j_0 (A/cm ²) | Electrolyte | Temperature | Reference |
|--|-------------------------------------|---------------------------------------|-------------|-----------|
| Pt (111) | 4.5×10^{-4} | 0.05 M H ₂ SO ₄ | 303 K | 10 |
| Pt (100) | 6.0×10^{-4} | | | |
| Pt (110) | 9.8×10^{-4} | | | |
| <ul style="list-style-type: none"> • Studied different crystal facets of Pt at different temperatures • Single crystal electrodes tested, RDE measurement • Low electrolyte concentration chosen to be able to clearly distinguish hydrogen activity • Electrode surface protected by a drop of water, luggin capillary for reference electrode to avoid Cl⁻ contamination • HUPD characterization correlated to the theoretical charge to determine adsorption layers • Tafel plots determined from the kinetically limited region • Exchange current densities obtained from micropolarization region • j_0 might still contain contribution from diffusion | | | | |
| Pt/C | 1.6×10^{-2} | 0.2 M H ₃ PO ₄ | 293 K | 11 |
| <ul style="list-style-type: none"> • Studied precious metal catalysts at different pHs • Commercial powders tested, RDE measurement • Luggin capillary, Pt counter • Performed CVs in 0.1 M KOH prior to testing at different electrolytes (contamination risk) • ECSA determined from HUPD peaks in 0.1 M KOH • ECSA obtained from HUPD is 1.6 times lower than that obtained by CO-stripping • Exchange current densities obtained from Butler Volmer, are consistent with the measurements from H₂-pump; may still be transport limited | | | | |
| Pt/C | 1.2×10^{-1} | 0.1 M HClO ₄ | 313 K | 12 |
| <ul style="list-style-type: none"> • Studied precious metal catalysts at different temperatures • Commercial powders were tested in H₂ pump configuration (speeds up mass transfer) • Pt/C counter/reference electrode, scrupulous cell cleaning • ECSA calculated by CO-stripping at 293 K are consistent with TEM analysis • j_0 values were calculated by Butler Volmer and micro-polarization region, and was within 10 % error | | | | |
| Ir/C | 3.6×10^{-2} | 0.1 M HClO ₄ | 313 K | 12 |
| <ul style="list-style-type: none"> • Studied precious metal catalysts at different temperatures • Commercial powders were tested in H₂ pump configuration • Pt/C counter/reference electrode, rigorous cell cleaning | | | | |

| | | | | |
|--|-----------------------|--------------------------------------|---------------|----|
| <ul style="list-style-type: none"> • ECSA calculated by CO-stripping at 293 K are consistent with TEM analysis • j_0 values were calculated by Butler Volmer and the micro-polarization region and were nearly same. Oxide covering did not have a huge influence. | | | | |
| Ir/C | 1.28×10^{-2} | 0.2 M H ₂ SO ₄ | 293 K | 11 |
| <ul style="list-style-type: none"> • Commercial powders tested, RDE measurement • Luggin capillary, Pt counter • Performed CVs in 0.1 M KOH prior to testing at different electrolytes • ECSA determined from HUPD peaks in 0.1 M KOH • ECSA obtained from HUPD is almost same as that obtained by CO-stripping • Exchange current density values obtained from Butler Volmer, are consistent with the measurements from H₂-pump; may still be transport limited | | | | |
| Pd | 1.9×10^{-4} | 0.5 M H ₂ SO ₄ | Not mentioned | 13 |
| <ul style="list-style-type: none"> • Studied nanoporous Pd (powder) • Carbon counter, nitrogen purge, RDE measurement • Current normalization not mentioned, appears to be from electrode area • ECSA calculated from C_{dl} • Linear Tafel fitting | | | | |
| Pd/C | 3.0×10^{-3} | 0.1 M HClO ₄ | 313 K | 12 |
| <ul style="list-style-type: none"> • Commercial powders were tested in H₂ pump configuration • Pt/C counter/reference electrode, rigorous cell cleaning • ECSA calculated by CO-stripping at 293 K are consistent with TEM analysis • j_0 values were calculated by Butler Volmer and the micropolarization region and were nearly same. Hydride covering did not have a significant influence. | | | | |
| Pd/C | 8.4×10^{-4} | 0.1 M HClO ₄ | 293 K | 11 |
| <ul style="list-style-type: none"> • Commercial powders tested, RDE measurement • Luggin capillary, Pt counter • Performed CVs in 0.1 M KOH prior to testing at different electrolytes • ECSA determined from PdO peaks in 0.1 M KOH • ECSA obtained from HUPD is slightly lower (by 1.2 times) than that obtained by CO-stripping • j_0 values obtained from Butler Volmer, consistent with the measurements from H₂-pump | | | | |
| Rh/C | 5.2×10^{-3} | 0.1 M HClO ₄ | 313 K | 12 |
| <ul style="list-style-type: none"> • Commercial powders were tested in H₂ pump configuration • Pt/C counter/reference electrode, rigorous cell cleaning • ECSA calculated by CO-stripping at 293 K are consistent with TEM analysis • j_0 values were calculated by Butler Volmer and the micropolarization region and were nearly same. Oxide covering did not have a significant influence. | | | | |
| Rh/C | 6.7×10^{-3} | 0.1 M HClO ₄ | 293 K | 11 |
| <ul style="list-style-type: none"> • Commercial powder tested, RDE measurement • Luggin capillary, Pt counter • Performed CVs in 0.1 M KOH prior to testing at different electrolytes | | | | |

| | | | | |
|--|-----------------------|--------------------------------------|---------------|----|
| <ul style="list-style-type: none"> • Currents normalized by ECSA measured in 0.1 M KOH • ECSA obtained from HUPD is 1.8 times lower than that obtained by CO-stripping • Exchange current density values obtained from Butler Volmer, are consistent with the measurements from H₂-pump | | | | |
| Ru | 4.5×10 ⁻³ | 1M HCl + NaCl | 298 K | 15 |
| <ul style="list-style-type: none"> • Studied Ru cylinder, mounted on ptfе cup • Pt counter, separated from working electrode using frit • Pre-electrolysis performed but conditions are unclear (pre-electrolysis implies rigorous purification) • After pre-electrolysis potential sequence of +1 V vs RHE for 10 s followed by -1 V for 10 mins was repeated 6 times with final cathodic pulse for 10 minutes. Rest potential was observed to be -1 V vs RHE. | | | | |
| Cu | 1.45×10 ⁻⁷ | 0.1 N HCl | Not mentioned | 16 |
| <ul style="list-style-type: none"> • Wire working electrode • Graphite counter • Pre-electrolysis was performed for several hours; HCl electrolyte may allow for some Cu dissolution • Statistical analysis included | | | | |
| Co | 3.6×10 ⁻⁶ | 1 M H ₂ SO ₄ | 293 K | 26 |
| <ul style="list-style-type: none"> • Studied rod electrode, electrolytically polished in H₃PO₄ • Detailed cleaning procedure followed • Cathodically pre-polarized starting from low current density • Overpotential increased by applying cathodic current or with several hours of electrolyte contact • Also calculated Tafel slope for the dissolution process, consistent with prior literature | | | | |
| Ni | 2.6×10 ⁻⁶ | 0.5 M H ₂ SO ₄ | 295 K | 18 |
| <ul style="list-style-type: none"> • Studied electrodeposited Ni as control, Ni could be coated with Ni²⁺ compounds • Pt counter separated from main cell using glass frit, argon purge • Electrode was polarized at HER potentials to remove surface oxides • Tafel plot measured in kinetically controlled regime • Tafel slope is higher than theoretical value; attributed to Ni oxidation • <i>j</i>₀ obtained from tafel plot | | | | |
| Au (111) | 2.5×10 ⁻⁷ | 0.1 M HClO ₄ | Not mentioned | 19 |
| Au (100) | 0.5×10 ⁻⁷ | | | |
| Au (110) | 0.3×10 ⁻⁷ | | | |
| <ul style="list-style-type: none"> • Studied single crystals with different crystal facets • Hanging meniscus rotating disc technique, nitrogen purge, Au counter electrode • Surface of electrode protected with electrolyte drop • HER activity was independent of the potential history (scanning even to oxidation potentials), contrary to literature, owing to cleaner surfaces and solutions • Did not document detailed cell cleaning protocols | | | | |

| | | | | |
|---|------------------------|--------------------------------------|---------------|----|
| <ul style="list-style-type: none"> • Tafel slope in the low potential region is reported (< 150 mV) | | | | |
| Au (111) | 3.38×10^{-7} | 0.5 M H ₂ SO ₄ | Not mentioned | 20 |
| <ul style="list-style-type: none"> • Studied single crystal as control • Pt counter, nitrogen purge, hanging meniscus • Current normalized to geometric area; no ECSA | | | | |
| Poly Au | 1.40×10^{-7} | 0.1 M HClO ₄ | Not mentioned | 19 |
| <ul style="list-style-type: none"> • Hanging meniscus rotating disc technique, nitrogen purge, Au counter electrode • Surface of electrode protected with electrolyte drop • HER activity was independent of the potential history (scanning even to oxidation potentials) owing to cleaner surfaces and solutions • Did not document detailed cell cleaning protocols • Tafel slope in the low potential region is reported (< 150 mV) | | | | |
| Re | 1.25×10^{-6} | 0.5 M H ₂ SO ₄ | 298 K | 21 |
| <ul style="list-style-type: none"> • Polished wire working electrode • Pt counter, hydrogen purge • Native surface oxide formation was minimized by polarizing at -0.4 V vs NHE • Tafel fit included narrow range at low overpotential (-0.11 to -0.2 V vs NHE) | | | | |
| Re | 1×10^{-6} | 0.5 M H ₂ SO ₄ | 298 K | 22 |
| <ul style="list-style-type: none"> • Polished wire working electrode • Pt counter, hydrogen purge • Polarized at -0.1 V vs RHE, claim to have metallic Re • Current normalized to geometric area; no ECSA • | | | | |
| Cd | 1.7×10^{-11} | 0.5 N H ₂ SO ₄ | Not mentioned | 24 |
| <ul style="list-style-type: none"> • Metal wire working electrode • Heated electrode in hydrogen • Detailed cleaning procedure followed • Electrolyte was purged with pre-purified nitrogen to remove excess oxygen and then purged with hydrogen • Electrolyte was further purified by pre-electrolysis at 1 mA/cm² for 15 – 20 hours | | | | |
| Bi | 8×10^{-10} | 4.8 M H ₂ SO ₄ | Not mentioned | 23 |
| <ul style="list-style-type: none"> • Polished metal wire working electrode • Pt counter electrode • Held the potential at HER potential for 10 mins prior to analysis • Tafel plot measured in kinetically controlled regime | | | | |
| In | 1.51×10^{-11} | 0.1 M HClO ₄ | 303 K | 25 |
| <ul style="list-style-type: none"> • Cylindrical working electrode • Electropolished at negative potential to remove oxide layer before analysis • Pt counter and reference electrode, Luggin capillary used | | | | |

- Varied electrode treatment conditions and electrolyte concentration

Table S6. Ten best models identified by SISO. Primary features used are atomic radius (R), atomic number (N), atomic mass (M) period in Periodic Table (P), metal density (ρ), work function (ϕ), electron affinity (E_A), ionization energy (I), Pauling electronegativity (χ), and hydrogen adsorption energy (ΔG_H).

| SISO Model | r^2 |
|---|--------|
| $((\chi+(\Delta G_H+\chi))+((P\Delta G_H)(\Delta G_H/\chi)))$ | 0.9795 |
| $((N\chi)(\chi/M))+((\Delta G_H E_A)(\Delta G_H/\chi))$ | 0.9789 |
| $((PR)(P/M))((PR)(\Delta G_H+\chi))$ | 0.9782 |
| $((M+N)(\chi/M))+((P\Delta G_H)(\Delta G_H/\chi))$ | 0.9775 |
| $((\chi(R\chi))+((R\Delta G_H)(\Delta G_H+E_A)))$ | 0.9768 |
| $((\Delta G_H+\chi)(\Delta G_H/\chi))((\Delta G_H/\chi)+(\chi/\Delta G_H))$ | 0.9766 |
| $((R(\Delta G_H+\chi))+((R\Delta G_H)(\Delta G_H/\chi))$ | 0.9762 |
| $((\Delta G_H+\phi)(\chi/\phi))/((\chi/\phi)+(\phi/\chi))$ | 0.9759 |
| $((R\Delta G_H)(\Delta G_H+E_A))+((R\chi)(\Delta G_H+\chi))$ | 0.9753 |
| $((\Delta G_H(\Delta G_H+\chi))((EA/\chi)+(\chi/\Delta G_H)))$ | 0.9751 |

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