Quantifying Confidence in Density Functional Theory Predicted Surface Pourbaix Diagrams at Solid-Liquid Interfaces and its Implications for Electrochemical Processes

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Abstract
Density Functional Theory (DFT) calculations have been widely used to identify active catalysts by constructing free energy diagrams incorporating the electrochemically stable surface structure. Surface Pourbaix diagrams are required to determine the state of the surface under reaction conditions. The adsorption energetics of reaction intermediates are determined self-consistently based on the state of the surface at the reaction conditions. The close energetics of oxygen intermediates determine the rich surface phase diagram on transition metal surfaces at oxidizing conditions. In this work, we utilize error-estimation capabilities within the BEEF-vdW exchange correlation functional to propagate the uncertainty associated with the energetics for the construction of Pourbaix diagrams. As a result, within this approach, the surface-transition phase boundaries are no longer sharp and have a finite width. We determine the surface phase diagram for several transition metals under reaction conditions and electrode potentials relevant for oxygen reduction reaction. We compare against linear sweep voltammetry experiments and observe the most predominant species are in good agreement with our predictions for Pt(111), Pt(100), Pd(111), and Ir(111) when compared to previous cyclic voltammetry experiments and DFT-based predictions. We argue that the probabilistic approach enables a more accurate determination of the surface structure, and can readily be incorporated in computational studies for better understanding the catalyst surface under operating conditions.

Introduction
Electrochemical processes are at the heart of many routes towards sustainable energy storage in the form of chemical bonds.\textsuperscript{1} The storage routes involve hydrogen and oxygen electrochemistry occurring at solid-liquid interfaces.\textsuperscript{2} Determining the activity of electrode materials
active for these processes requires a thorough understanding of the surface dynamics at the electrode-electrolyte interfaces. Probing the electrode-electrolyte interface directly is an extremely challenging problem. There has been substantial development towards the coupling of X-ray spectroscopy directly with electrochemical cells. This can be complemented by electrochemical impedance spectroscopy (EIS) to deconvolute the signals and assign them to surface adsorbed species. Theoretically, density functional theory calculations have been used to construct surface phase diagrams based on probing many different possible surface configurations. However, a major challenge associated with this approach is that the choice of the exchange-correlation functional often plays a key role in determining the dominant surface phases.

Recently, the use of Bayesian error estimation techniques has brought capabilities to estimate uncertainty associated with DFT simulations. In this work, we develop a systematic method to determine the confidence value (c-value) associated with the stable surface phases at a given electrode potential and pH. Armed with this method, we probe the surface Pourbaix diagram of three important fcc metals, Pt, Pd and Ir. Based on our method, we identify that on Pt(111) at an electrode potential of 0.7 V, we find that the surface could be a combination of OH* or O* covered. Our method reproduces the well-known uncertainty associated with OH* to O* phase transition on Pt(111) at the GGA level. On Pt(100), we note that the predicted stable phases of $\frac{1}{3}$OH* and $\frac{1}{2}$OH* are consistent with the suggested structural transitions by Han et al. On Pd(111), we observe with high confidence that OH* adsorption ($\frac{1}{3}$OH*) occurs at a potential $\sim$0.7 V, close to that reported experimentally. Our results indicate that at higher potentials starting $\sim$0.75 V, the surface is O* covered, consistent with that attributed to the current peak corresponding to oxidation. On Ir(111), we find voltage regimes where our prediction confidence is limited relative to that other surfaces explored in this work. We observe the onset of OH adsorption at a low potential of 0.2 V consistent with prior DFT predictions that Ir is more oxophilic than Pt.

Our analysis suggests that oxygen covered surface dominates between 0.7 V and 0.9 V. Given the important of the stable state of the surface in determining electrochemical reaction mechanisms, we believe this method will be extremely crucial in constructing free energy diagrams on the appropriate surface and will play an important role in determining the subsequent (expected) limiting potential.

Methods

Construction of Surface Pourbaix Diagrams

The surface Pourbaix diagram represents the stable state of the surface in aqueous electrochemical systems as a function of the pH and electrostatic potential. Let us consider the set $S$ of all possible states of the surface, $S = \{s_0, s_1, ..., s_n\}$ at all possible conditions of pH and potential. Also let $s_0$ be the initial reference state of the surface. We will define the free energy change $\Delta G_{s_i}$ for all other states from the reference state as a function of potential $U$ and pH. Now consider a reaction involving a phase transition from the surface state $s_0$ to
another surface state belonging to $S$, $s_i$ involving water, protons and electrons.

$$s_0 + ne^- + mH^+ \rightleftharpoons s_i + H_2O$$  \hspace{1cm} (1)

Here, a state includes the dissolving species in solution such that the reaction is charge balanced. The free energy change associated with the reaction as a function of potential $U$ and pH can be given by:

$$\Delta G_{s_i}(U, pH) = G_{s_i} - G_{s_0} + G_{H_2O} + nG_{e^-} + mG_{H^+}$$ \hspace{1cm} (2)

where $G_{s_i}$ and $G_{s_0}$ are the free energy of states which includes the substrate, adsorbates on the substrate and dissolved species and are independent of pH and potential $U$, $G_{e^-}$ is the free energy of the electrons determined by the potential and $G_{H^+}$ is the free energy of protons dependent on pH and $G_{H_2O}$ is the free energy of water. The free energy of protons can be determined from the computational hydrogen electrode using the equilibrium of reaction: $H^+ + e^- \rightleftharpoons \frac{1}{2}H_2$. This gives us that $G_{H^+} = \frac{1}{2}G_{H_2} + U_{SHE} + k_BT(ln[H^+])$, where $U_{SHE}$ is the potential $U$ of the standard hydrogen electrode. Thus now we can write the free energy change for converting state $s_0$ to state $s_i$ as a function of given pH and potential as:

$$\Delta G_{s_i}(U, pH) = G_{s_i} - G_{s_0} + G_{H_2O} - nU + \frac{m}{2}G_{H_2} + mU_{SHE} - m(2.303k_BT(pH))$$ \hspace{1cm} (3)

The potential can be referenced to standard hydrogen electrode only when one also references the free energy of the dissolved species to SHE as well. Using the equation 3, we can derive the free energy change associated for all possible states $s_i$ in reference to the free energy of water and state $s_0$ under standard conditions as a function of given pH and potential $U$. Note that $\Delta G_{s_0}(U, pH) = 0$. We can now plot all these free energies changes for all phases as a function of potential $U$ and pH. From the second law of thermodynamics, the most stable state at a given condition is the state with minimum free energy. Thus to determine the Pourbaix diagram, we will choose the state with minimum $\Delta G_{s_i}$ for all potentials $U$ and pH.

**Bayesian Error Estimation**

Recently, Bayesian Ensemble Error Functional with van der Waals correlations (BEEF-vdW)$^{11}$ has provided a way to systematically estimate the uncertainty of a DFT calculation. BEEF-vdW is a semi-empirical exchange correlation functional including non local contributions, developed by using training data sets for molecular formation energies, molecular reaction energies, molecular reaction barriers, noncovalent interactions, solid state properties, and chemisorption on solid surfaces.

The exchange correlation energy in BEEF-vdW is expressed as a sum of the GGA exchange energy expanded using Legendre polynomials, the LDA and PBE$^{17}$ correlation energies and the non local correlation energy from vdW-DF2$^{18}$.

$$E_{xc} = \sum_m a_m E_{m}^{GGA} - x + \alpha_c E_{c}^{LDA} - c + (1 - \alpha_c) E_{c}^{PBE} - c + E_{c}^{nl} - c$$ \hspace{1cm} (4)

The parameters $a_m$ and $\alpha_c$ are optimized with respect to the above mentioned data sets.
The error estimation functionality is enabled by deriving an ensemble of energies from an ensemble of exchange correlation functionals non-self-consistently. The ensemble of exchange correlation functionals is generated using a probability distribution function for the parameters $a_m$ and $\alpha_c$ such that the standard deviation of the ensemble of energies reproduces the standard deviation for the training properties calculated using BEEF-vdW self consistently.

**Prediction Confidence of Surface Pourbaix Diagrams**

Pourbaix diagrams (Fig. 1a) typically depict only the most stable state of the surface, with sharp phase boundaries. We utilize error estimation capabilities within the BEEF-vdW exchange correlation functional to determine the ensemble of free energies for all states at given potential and pH. We will assume for tractability of computations, that the zero point energies do not vary significantly across the ensemble of functionals. Each functional from the ensemble will give a unique $\Delta G_{s_i}$ for a particular state $s_i$ at a particular pH and potential. For each of the functionals, this allows us to determine the most stable molecular state of the surfaces at a particular condition, represented by the minimum $\Delta G_{s_i}$. We observe that in general, different functionals will predict different stable states at a particular condition, especially near phase boundaries. From the ensemble of free energies, we are interested in identifying the confidence or prediction efficiency in determining whether a certain state of the surface, $s_i$, is the most energetically favourable state of the surface at a given pH and potential, out of all the considered states of the surface, $S = \{s_0,..s_n\}$. We quantify the confidence by defining a confidence value (c-value), in a similar manner to the definition in a recent work on predicting magnetic ground states\(^\text{19}\), for a given surface molecular state that quantifies the agreement between the ensemble of BEEF functionals that it is the most stable surface state. The c-value, $c_{s_i}(U,pH)$, of a specific state of the surface, $s_i$, is defined as the fraction of functionals that predict $s_i$ to have the lowest Gibbs’ free energy, given by

$$c_{s_i}(U,pH) = \frac{1}{N_{\text{ens}}} \sum_{n=1}^{N_{\text{ens}}} \prod_{j \neq i} \Theta(\Delta G_{s_j}^n(U,pH) - \Delta G_{s_i}^n(U,pH))$$

where, the summation is over the $N_{\text{ens}}$ ensembles, and the product is over all the remaining surface molecular states. $\Theta(x)$ denotes the Heaviside step function. We use Pt-group transition metals in the context of ORR as an example case to demonstrate that c-value($pH,U$) provides a computationally efficient approach to identifying regimes of pH and potential where the state of the surface is likely a mixed phase of the the considered states of the surface. We show that the methodology can be used to identify specific regimes where simulating coexistence of multiple states of the surfaces can lead to more accurate determination of catalytic activity through precise energetics.
Results and Discussion

Pt(111)

The Pourbaix diagram for Pt(111) previously investigated\(^8,20\) has now been reproduced using the BEEF-vdW exchange correlation functional, shown in Fig. 1a. We consider the following oxygenated adsorbate states of Pt(111): clean surface, 1/3 OH*, 1/4 O*, 1/3 O*, 1/2 O*, 2/3 O*, 3/4 O*, and 1 O*. While modeling OH* with water stabilization effects we ignore potential dependent water orientation effects\(^21\) and we neglect water stabilization for O*\(^22\) states. Mixed phases are expected to be energetically unfavorable and are not considered since surface O* repels water unlike adsorbed OH* where a hexagonal water stabilizing layer occurs due to hydrogen bonding\(^22\). In addition, mixed phases are complex to simulate\(^20\) incorporating long range disorder\(^23\), which is undoubtedly present. We neglect configurational entropy of adsorbed oxygen intermediates, since the effect is expected to be small\(^24\).

The state of the surface is governed by the reactions:

\[
\begin{align*}
\text{OH}^+ + e^- + H^+ & \rightleftharpoons H_2O \\
\text{O}^* + 2e^- + 2H^+ & \rightleftharpoons H_2O
\end{align*}
\]

where * refers to an adsorption site on a metal catalyst surface.

Using the process described in the methods section, we represent these reactions in terms of pH and electrostatic potential at equilibrium as shown in the following relations.

\[
\Delta G = (G_{OH^*} + \frac{1}{2}G_{H_2} - G_{H_2O}) + k_B T \ln[H^+] - eU \tag{6}
\]

\[
\Delta G = (G_{O^*} + G_{H_2} - G_{H_2O}) + k_B T \ln[H^+] - eU \tag{7}
\]

Using eqns. (6) and (7) we construct a surface Pourbaix diagram in reference to Pt(111) clean surface shown in Fig. 1a. A free-energy vs potential diagram (Fig. 1b) determines the surface phase boundaries from the optimal BEEF-vdW functional and therefore identifies the most stable state of the surface at given conditions of potential and pH. At an activity of \(a_{H^+}=1\), we observe that below 0.63 V vs. SHE (all potentials reported vs. SHE unless otherwise specified), clean Pt(111) surface is the most stable, and at higher potentials water gets oxidized starting with 1/4 monolayer O* and increases monotonically to 1/2 monolayer O* until Pt dissolution occurs at 1.18 V\(^25\). Since the dissolution potential is pH independent, at higher pH values we observe higher O* coverages below the dissolution potential. This trend is largely in accordance with those reported by Hansen et al\(^8\). However, our predictions suggest that 1/3 OH* does not occur on the surface before the onset of O* adsorption with is consistent with prior calculations\(^15\). In the free-energy vs potential diagram in Fig. 1b it is evident that the 1/4 O* surface is slightly more stable than 1/3 OH* between 0.63 V and 0.91 V.

We then construct a modified surface Pourbaix diagram (Fig. 2) in accordance with the confidence prediction methodology described earlier. We observe that the new surface Pourbaix representation captures crucial computational details not evident in Fig. 1a by
assigning c-value($U, p\text{H}$) to coverage phases otherwise not visualized. Wang et al\(^{26}\), Koper\(^{27}\),
and Garcia-Araez et al\(^{28,29}\) attribute the butterfly region between 0.6 V and 0.85 V in linear
sweep voltammetry experiments to OH*, which is also supported by Wakasika et al\(^{5}\) in ex situ XPS experiments. According to our model in Fig. 2, we predict OH* to adsorb
starting at 0.6 V. At $U_{SHE} < 0.6$, the confidence of clean Pt(111) surface is much higher
and more likely to occur than the 1/3 OH* surface phase. The uncertainty in the transition
between OH* and O* in the potential range $\sim 0.6$ V- $\sim 0.8$ V has also been reported using
ambient pressure XPS spectra\(^{6}\) and has been attributed to different degrees of hydration of
the hydroxyl species.

At higher potentials from 0.6 V to 0.8 V we see an area with low degree of confidence
to distinguish between clean Pt(111), 1/3 OH*, and 1/4 O* implying that prediction
uncertainty is high. From 0.8 V until the dissociation potential for Pt, O* surface state gradually
increases to greater coverage fractions and to higher c-values. Wakasaka et al\(^{5}\) report that
oxygen formation begins at 0.85 V which is within reasonable bounds of our prediction. We
note that our findings of a monotonic increase in the oxygen coverage compare well with
reported blank voltammetry\(^{7}\) of Pt(111) in 0.1 M HClO\(_4\), to avoid encountering the specific
adsorption of sulfate as occurs in sulfuric acid electrolyte. We note that Fig. 2 can be
extended for determining the most stable state of the surface for any proton concentration.

Figure 1: (a) For Pt(111) the surface Pourbaix diagram shows regions of stability for different
coverages of OH* and O* at conditions of pH and electrostatic potential relative to the
standard hydrogen electrode (SHE). Dissolution of Pt is expected to occur at a potential of
1.18 V irrespective of pH. We see that 1/4 O adsorption begins at 0.63 V and 1/2 O* at 0.91
V at pH=0. We regard the most stable surface phase to minimize Gibbs free energy. The
plot in (b) shows that 1/4 O* is slightly more stable than 1/3 OH* in the range from 0.63
V to 0.91 V which explains why 1/3 OH* is not evident in (a).

Pt(100)

We extend the methodology to Pt(100), which has been well studied\(^{30-32}\) since commercial
state-of-the-art Pt catalysts are comprised largely of the (111) and (100) facets. We consider
the following states of the Pt(100) surface\(^{12}\): clean surface, $\frac{1}{3}$ OH*, $\frac{1}{2}$ OH*, $\frac{1}{3}$ O*, $\frac{1}{2}$ O*, $\frac{3}{4}$
Figure 2: We derive a representation of the surface Pourbaix diagram where we map each surface state with our prediction confidence (c-value). We see that at \( U < 0.64 \text{ V} \), the c-value for clean Pt(111) is significantly greater than for \( 1/3 \text{ OH}^* \). There is a region of large uncertainty between 0.6 V and 0.75 V where there is similar confidence of clean Pt(111), \( 1/3 \text{ OH}^* \), and \( 1/4 \text{ O}^* \) occurring. At \( U > 0.8 \text{ V} \) we observe a monotonic increase in oxygen coverage. The lower x-axis is for mapping the c-value at \( \text{pH}=0 \). We extend this figure for c-value at \( \text{pH}=7 \) since there is a linear relationship between pH and potential. The red line on the lower x-axis marks the region for Pt\(^{2+}\) dissolution beyond 1.18 V.
O* and 1 O*.

Through the constructed Pourbaix diagram, shown in Fig. 3a, we observe that at $a_{H^+} = 1$ the surface exists as clean Pt(100) at potentials below $0.63 \text{V}_{SHE}$. At higher potentials, onset of OH adsorption occurs with $1/3 \text{OH}^*$ at 0.63 V followed by first the $1/2 \text{OH}^*$ surface and then the $3/4 \text{O}^*$ surface, before dissolution at $1.18 \text{V}^{25}$. The identified stable molecular states of the surface are in agreement with the phases identified in the literature through ab-initio DFT calculations and Monte Carlo simulations$^{12}$, and experiments through voltammetry$^{33}$.

We use $c$-value to quantify the confidence in our predictions by constructing the confidence diagram as shown in Fig. 3b. We observe that Pt(100) exists as clean surface up to $U = 0.78 \text{V}$ with the highest prediction confidence. We observe that at $a_{H^+} = 1$, the $c$-value of $1/3 \text{OH}^*$ peaks at around 0.7 V, followed by $1/2 \text{OH}^*$ occurring with the highest prediction confidence between $\sim 0.75 \text{V}$ to $\sim 0.85 \text{V}$. Note that there is low prediction confidence to determine the state of the surface at around 0.7 V since the $c$-values for clean Pt(100), $1/3\text{OH}^*$ and $1/2\text{OH}^*$ are close. There likely exists a small potential window starting from $\sim 0.6 \text{V}$ where $1/3\text{OH}^*$ is most stable followed by a phase transition to the $1/2\text{OH}^*$ phase. It is worth noting that the predicted stable $\text{OH}^*$ phases and the corresponding voltage regimes of stability are in good agreement with the likely surface phase transitions identified by Han et al.$^{12}$ for the structural transition into an OH covered structure. At higher potentials, we notice that with a high prediction confidence the stable state of the surface is $3/4 \text{O}^*$.

**Figure 3:** (a) This plot shows the surface Pourbaix diagram for Pt(100) where the onset of $1/3 \text{OH}^*$ is at 0.63 V. A free-energy vs potential figure is presented in Fig. S1. (b) This plot shows the $c$-value based surface Pourbaix diagram. We observe a gradual transition from $1/3 \text{OH}^*$ to $1/2 \text{OH}^*$ from 0.6 V to 0.9 V. At $U > 0.9 \text{V}$ there is greater likelihood of observing $3/4 \text{O}^*$. The region on the x-axis shaded in red represents the dissolution potential occurring at 1.18 V for Pt.

**Pd(111)**

Palladium or an inexpensive Pd-non-noble-metal alloy have been identified to be promising alternative to Pt for the oxygen reduction reaction$^{34-37}$ to enable the widespread adoption of fuel cells. We construct the Pourbaix diagram for Pd(111) by considering the following states of the surface for Pd(111)$^{38}$ similar to that considered for Pt(111): clean surface, $1/3$
OH*, 1/4 O*, 1/3 O*, 1/2 O*, 2/3 O*, 3/4 O*, and 1 O*. We observe from the constructed Pourbaix diagram, shown in Fig. 3a, that at $a_{H^+} = 1$ the surface is dominated by clean Pd(111) until a potential of 0.63 V which is marked by the onset of 1/4 O* coverage surface state. With increasing potential, O* adsorption increases monotonically starting with 1/4O*, followed sequentially by 1/4O* and 1/3O* before dissolution at 0.95 V. Since the dissolution potential is independent of pH, at higher pH values we observe higher O* coverages before dissolution occurs.

We observe in the constructed prediction confidence diagram, shown in Fig. 3b, that the c-value for 1/3 OH* adsorption peak occurs close to 0.7 V$_{SHE}$, which is consistent with the potential at which the broad anodic and cathodic current peaks are ascribed to the OH*-species reported by Hara et al. We notice, however, that at potentials close to 0.75 V that the similar level of confidence in the predictions for the state of the surface being Pd(111), 1/3 OH*, 1/3 O* and 1/3 O*. At higher potentials we observe the presence of 1/3 O* with a high c-value between potentials ~ 0.85 V and ~ 0.95 V. Similarly, we see the presence of 1/2 O* with high confidence in between potentials ~ 1.1 V and ~ 1.2 V. At the reported potential of 1.020 V for the current peak representing the surface oxidation of terrace sites, the confidence diagram indicates a favorable 1/3 O* adsorption or 1/2 O* (equal confidence) close to 1 V.

Figure 4: (a) The plot shows the surface Pourbaix diagram for Pd(111), where at pH=0 we observe oxidation to begin at 0.63 V with 1/4 O* from clean Pd(111). A free-energy vs potential figure is available in Fig. S2. (b) shows the c-value for each surface state at a certain pH=0 where it is evident that strong oxidation to O* covered surfaces is dominant at U > 0.7 V. The shaded red x-axis represents the onset of dissolution at 0.95 V.

**Ir(111)**

Iridium is a highly corrosion resistant platinum group metal and is similar to Pt although relatively less extensively studied. We plot the surface Pourbaix diagram in Fig. 5a to map the adsorption characteristics of the oxygenated surface for Ir(111). Our predictions show that 1/3 OH* surface state occurs at a low potential of 0.2 V and is present until 0.55 V at $a_{H^+} = 1$, consistent with prior DFT predictions that Ir is more oxophilic than Pt. Our Fig. 5b also shows strong confidence in this prediction. Wan et al. through cyclic voltammetry
experiment in 0.1 M HClO₄ has attributed the region between 0.05 V and 0.35 V to hydrogen adsorption. Other voltammetry studies performed by Ganassin et al.¹¹ and Pajkossy et al.¹² show similar voltammetry peaks. Koper²⁷ suggests that the surface is covered by hydrogen in this range, but the peak could also represent a transition between OH and H covered surface. Thus in the absence of more detailed calculations, our interpretation remains speculative. We observe that between 0.55 V and 0.7 V on Fig. 5 there occurs a region of low confidence where we predict an almost equal likelihood of encountering 1/3 OH*, 1/3 O*, 1/2 O*, and 2/3 O*. At potentials U > 0.7 V, we see the c-value for O* increase until the dissolution potential at 1.16 V²⁵. In comparison to experiments²⁷,⁴⁰–⁴² there exists variability regarding the consensus of assignment of the cyclic voltammetry peak at 0.9 V. We suggest that oxygen covered surface dominates at 0.9 V, but that remains speculative when considering experimental work.

Figure 5: (a) The plot shows the surface Pourbaix diagram for Ir(111), where we observe oxidation to begin with 1/3 OH* in the range from 0.2 V to 0.55 V. We then see increase in oxidation until the dissolution potential at 1.16 V. A free-energy vs potential figure is available in Fig. S3. (b) shows the c-value representation of the surface Pourbaix for each surface state at pH=0 where we see a region with low confidence between 0.55 V and 0.7 V. Here the surface may covered by 1/3 OH*, 1/3 O*, 1/2 O*, or 2/3 O*. At U > 0.7 V the c-value for oxidation of the surface as 2/3 O* is higher. The shaded red region on the x-axis represents dissolution into Ir³⁺.

Conclusions

Surface Pourbaix diagrams are crucial in determining electrocatalytic reaction mechanisms. In this work, we have developed a method to quantify uncertainty in density functional theory calculated surface Pourbaix diagrams. Based on this method, we define a confidence value (c-value) associated with each possible surface configuration at a given electrode potential, U and pH. Using this method, we have constructed surface Pourbaix diagrams for each of Pt(111), Pt(100), Pd(111), and Ir(111) and the associated confidence values for these surface phases. On Pt(111), our method captures the well-known uncertainty in the phase transition from OH* to O*. We find good agreement between our predicted phase diagrams on Pt(100)
and Pd(111) compared to cyclic voltammetry experiments for the onset of OH* and O*.
On Ir(111), we find that 1/3 OH* peaks at 0.4 V and 2/3 O* peaks at 0.9 V, and a direct link
of this phase diagram to cyclic voltammetry measurements requires further attention. An
important implication from this work is the need to incorporate multiple surface phases in
determining electrochemical reactions mechanisms and the associated activity due to finite
uncertainty associated with predicting the stable state of the surface.

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Supporting Information:
Quantifying Confidence in Density Functional Theory Predicted Surface Pourbaix Diagrams at Solid-Liquid Interfaces and its Implications for Electrochemical Processes

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Calculation Details

All calculations were performed using the projector augmented-wave (PAW)\textsuperscript{1,2} method as implemented in GPAW\textsuperscript{3,4} with the ASE interface\textsuperscript{5}. The Bayesian Error Estimation Functional with Van der Waals corrections (BEEF-vdW)\textsuperscript{6} exchange-correlation functional was employed, which has built-in error estimation capabilities and is calibrated to reproduce the error as mapped to experimental training data. This error estimation capability has been used to quantify uncertainty in heterogeneous catalysis\textsuperscript{7}, electrocatalytic activity\textsuperscript{8,9}, magnetic ground states\textsuperscript{10} and mechanical properties of solid electrolytes\textsuperscript{11}.

For (111) facet surfaces, OH* adsorption is modeled on a \((\sqrt{3} \times \sqrt{3})R30^\circ\) unit cell and O* is modeled on a \((2 \times 2)\) unit cell each consisting of 4 layers of metal atoms. The k-point grids are \(4 \times 4 \times 1\) and \(6 \times 6 \times 1\) respectively. For (100) facet, 4 layer unit cells of \((2 \times 2)\) and \((2 \times 3)\) were used with \(4 \times 4 \times 1\) and \(6 \times 4 \times 1\) k-point grids. A real space grid discretization of 0.18Å was used for all calculations. All DFT calculations were converged with respect to k-point and grid spacing. Each unit cell was periodic in the x and y directions only with 5Å layer of vacuum in z direction above and below the layers. The bottom two layers were fixed and the top two layers including any adsorbates were relaxed to a net force less than 0.05eV/Å. A Fermi smearing of 0.05 eV was used to ensure self consistency in calculation of electron occupations. Calculations were performed with BEEF-vdW optimized lattice constants of 4.02Å, 4.02Å, and 3.90Å for Pt, Pd, and Ir respectively.
Supplementary Figures

Figure 1: The most stable surface state may be determined for Pt(100) by the minimum free energy at each potential.
Figure 2: The most stable surface state may be determined for Pd(111) by the minimum free energy at each potential.
Figure 3: The most stable surface state may be determined for Ir(111) by the minimum free energy at each potential.
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