Nature of Highly Active Electrocatalytic Sites for the Hydrogen Evolution Reaction at Pt Electrodes in Acidic Media

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ABSTRACT: The hydrogen evolution reaction (HER) is one of the two processes in electrolytic water splitting. Known for more than two centuries, the HER still receives great attention in fundamental and applied science in view of its apparent simplicity (only two electrons are transferred), fast kinetics in acidic media, and promising technological applications in electrolyzers. However, the exact nature of active catalytic sites for this reaction is often uncertain, especially at nonuniform metal electrodes. Identification of such centers is important, as the HER will probably be central in future energy provision schemes, and it is simultaneously a convenient model reaction to study structure−composition−activity relations in catalysis. In this work, using simple coordination−activity considerations, we outline the location and geometric configuration of the active sites at various model Pt single-crystal electrodes. We show that when the coordination of such surface sites is optimized and their density at the surface is maximized, the experimental-specific HER activities are among the highest reported in the literature for pure platinum with a well-defined surface structure under similar conditions.

■ INTRODUCTION

The hydrogen evolution reaction (HER) is not only one of the pillars of the so-called “hydrogen economy” but also one of the fastest reactions in electrocatalysis. However, relevant modern devices which make use of it, such as polymer electrolyte membrane electrolysers, require significant loadings of costly Pt catalysts on the cathodes to achieve reasonable efficiencies. The loadings can be reduced if the most active sites are first identified and then maximized on the catalysts by suitable synthesis methods. However, the nature of the active catalytic sites for the HER on Pt is still under debate. In this communication, we demonstrate that simple coordination−activity relations can shed light on the nature of the most active catalytic centers on various model stepped surfaces of pure Pt in acidic media. We show that increasing the density of those sites grants high activities without any need for alloying or other modifications with foreign metals. In addition, we explain some typical trends experimentally observable in HER electrocatalysis at Pt surfaces in acidic media.

We start our analysis assuming that during the HER only adsorbed hydrogen species (\(^*\)H) play a dominant role. Besides, following the approach of Nørskov et al. 4,5 we do not consider any prevailing mechanism for this reaction: as a first approximation, we only consider the binding energy of hydrogen at a specific catalytic site as a descriptor and neglect, for instance, the surface diffusion of adsorbed hydrogen species during the reaction, which is necessary for the so-called Tafel step. In this order of ideas, a simplified “roadmap” to reach the HER activity maximum is shown in Figure 1. The figure links the trends in the measured HER activities (y-axis) with the \(^*\)H binding energies for pure metals (x-axis) assessed with density functional theory (DFT) calculations. Although the exact value of the activity optimum likely depends on the surface coverage of hydrogen, in general lines, it can be concluded that the optimal active sites should bind the \(^*\)H intermediates \(\sim 0.1\) eV more weakly than Pt(111).

Figure 1. “Volcano” plot correlating the experimentally measured HER activities for the closely packed metal surfaces and the calculated binding energies of \(^*\)H, according to ref 6. The optimal catalytic sites should bind the \(^*\)H intermediates \(\sim 0.1\) eV more weakly than Pt(111).

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useful predictions of new materials. The advantages of this thermodynamic approach are that it avoids transition-state calculations and does not require knowledge on whether the reaction mechanism is Volmer–Tafel or Volmer–Heyrovsky, paramount to make affordable computational models because the two mechanisms might be operative under HER conditions on Pt.9 Note, however, that Figure 1 gives a trend and provides an adsorption-energy condition for the optimal HER catalyst but does not provide any additional information on how to actually design enhanced active sites.

Model Pt(111) is a rather active surface for the HER, but there are affordable ways to increase its activity. For example, the activity can be increased by alloying Pt with other (mainly transition) metals or by positioning monolayer amounts of those metals on the surface.10–13 Another approach would be to optimize the active catalytic centers by introducing certain defects, which can be, for instance, identified using the so-called generalized coordination numbers (CN).14 In simple terms, CN is a weighted average (see the Experimental Section) of the conventional coordination numbers that links adsorption energies of the intermediate to the geometric environment of the active sites where they adsorb.15 Consequently, general information about the geometry of the sites can be obtained if activity plots are made based on CN. In this context, coordination–activity plots provide a means to connect two of the pillars of modern heterogeneous catalysis, namely, the Sabatier principle (optimality is found when adsorption and desorption processes are equally fast) and the Taylor hypothesis of active centers.16 While the connection between HER activity and hydrogen binding strength through the Sabatier principle is well-accepted,5,6,9,30 the systematic connection between the HER activity and surface morphology is much less common. This is probably because most of the theoretical approaches in catalysis37 are based on energetic descriptors, namely, adsorption energies, band centers, work functions, and so forth, which do not contain any structural information per se. In this work, we identify the geometric nature and location of the most probable HER active sites at some model Pt electrodes and, based on that, experimentally demonstrate one of the highest HER activities for pure platinum well-defined surfaces reported in the literature under similar conditions.

## RESULTS AND DISCUSSION

Figure 2A displays the coordination–activity plot for a series of sites at Pt surfaces, namely, Pt(hkl) surfaces and Pt adatoms located on Pt(111). In the following, Pt(hkl) is also represented as Pt[n(h1k1l1) × (h2k2l2)]. In this notation, (h1k1l1) is the terrace type, n is the atomic length of such terrace, and (h2k2l2) are the step types that separate consecutive terraces. Note that only the threefold hollow sites and the bridge sites are considered here as the most probable active centers (see examples in Figure 2B–F) because *H does not occupy “on-top” positions at low and moderate coverages, according to DFT calculations (see, e.g., ref 7).

In particular, the inset in Figure 2A demonstrates how the *H adsorption energies change with the generalized coordination number at different sites on various Pt surfaces compared to Pt(111), as indicated in the plot by $\Delta \Delta G_{\text{H*}}$. For comparison, note that the face-centered cubic (fcc)-threefold hollow sites on Pt(111) have the generalized coordination number 6.95 (Figure 2B), hexagonal close-packed (hcp)-threefold hollow sites—7.5, whereas the optimal sites are predicted to have a generalized coordination number 7.7.

The above-mentioned optimal Pt sites can be constructed without any introduction of atoms of foreign metals. Probably, the most straightforward way is to introduce concave Pt defects, as shown in Figure 2, in which the most active sites are always located at the bottom of the steps. Taking the case of Pt(331), which can also be denoted by Pt[3(111) × (111)], where n = 3 is the atomic width of the terraces. For instance, the bridge sites at the step bottoms (Figure 2C right) have a generalized coordination number 7.33, which is closer to the optimum (7.7) in terms of *H binding energies compared to pure Pt(111). Sites with larger coordination, such as the step bottoms of Pt(553) (the generalized coordination of which is identical to those at the step bottoms in Pt(221) and Pt(775), the only difference being the terrace length) should also enhance the HER activity with respect to Pt(111).

By contrast, the undercoordinated bridge sites at the step edges schematically shown in Figure 2C (left) have low generalized coordination numbers (5.44) and consequently bind *H too strongly to consider them as active centers (see Figures 1 and 2A). Lowering the generalized coordination
numbers even further (e.g., by having adatoms of Pt on Pt(111), nAD@Pt(111)) in Figure 2A, with \( n = 2, 3 \) (see the *H adsorption sites in Figure 2D–F) should not enhance the activity either.

Regarding the accuracy of the analysis in Figure 2A, note that the maximum/mean absolute errors (MAX and MAE) in the correlation between \( \Delta G_{\text{H}} \) and \( \Delta \) are as low as 0.05/0.02 eV. Such small errors make it fair to attribute activity differences to sites for which \( \Delta G_{\text{H}} \) differs by \( \sim 0.10 \) eV. As all calculations were made only for Pt, using the same calculation settings and proportional \( k \)-point samplings according to the cell size, most DFT-associated errors should cancel out when subtracting adsorption energies, which justifies the choice of \( \Delta \Delta G_{\text{H}} \) in Figure 2A (i.e., the differential hydrogen adsorption energy vs Pt(111)). Figure 2A includes error bars as well, showing the error propagation from correlations between \( \Delta G_{\text{H}} \) and \( \Delta \) to log \( \beta \).

With the computational predictions in mind, we carried out HER experiments with various stepped Pt(111) single-crystal surfaces, namely, Pt(331), Pt(221), and Pt(775). These have 111-like steps and (111) terraces, which are 3-, 4-, and 7-atom wide (in other words, \( n = 3, 4, \) and 7 in Pt(111) \( \times (111) \)). We excluded the experiments on Pt(110) \( (n = 2) \) in this case, as it reconstructs in a missing-row fashion during electrochemical experiments, resulting in longer terraces than expected.\(^{18-21}\) Conversely, Pt(331) \( (n = 3) \) has been shown to be stable against surface reconstruction.\(^{22}\)

To confirm the quality of Pt(kkl) electrodes, cyclic voltammograms were taken in Ar-saturated 0.1 M HClO\(_4\) electrolytes. Figure 3A shows cyclic voltammograms of the investigated surfaces within the electrode potential areas of their electrochemical "fingerprints."\(^{23}\)

In Figure 3A, all of the surfaces exhibit the typical voltammetric behavior of stepped Pt single crystals in 0.1 M HClO\(_4\) revealing different characteristic features in the so-called hydrogen underpotential deposition (H-UPD) region (between \( \sim 0.4 \) and 0.1 V) and the OH adsorption region (more positive than \( \sim 0.5 \) V) and confirming the quality of the electrode surfaces.

Figure 3B shows the integrated cathodic parts of the voltammograms in the H-UPD region. Owing to the availability of different adsorption sites,\(^{23}\) their number is greater than that of Pt(111) by \( \sim 14\% \) for Pt(221), by \( \sim 28\% \) for Pt(331), and by \( \sim 45\% \) for Pt(775). It should also be emphasized here that the sharp features in the hydrogen UPD region, responsible for such an increase, are due to *H/*OH replacement at step edges and similar undercoordinated sites.\(^{24}\) Thus, in the cathodic scan, all *OH species are likely replaced by *H. The importance of these differences will be emphasized later on.

Another important aspect of the *H adsorption at different Pt\([n(111) \times (111)]\) surfaces is that the isotherms are shifted (Figure 3B) toward more negative potentials compared to Pt(111). If one selects a reference point where the adsorbate coverage is half of the maximal for Pt(111),\(^{25,26}\) the differences between the isotherms at this point reflect the average differences in the adsorbate binding energies.\(^{26}\) The shift is \( \sim 0.04 \text{ V} \) for Pt\([3(111) \times (111)]\), it is maximal \( \sim 0.06 \text{ V} \) for Pt\([4(111) \times (111)]\), and it decreases down to \( \sim 0.02 \text{ V} \) for Pt\([7(111) \times (111)]\), in agreement with the general trends and models presented in Figure 2.

Notably, Pt(221) demonstrates an average shift \( \sim 0.06 \text{ V} \) in the binding potential that is very close to the optimum \( \sim 0.09 \text{ V} \). However, note that the experimental isotherms represent not only the contribution of the optimal catalytic sites but also terrace sites with binding energies close to those of Pt(111).

Summarizing, Figure 3B reveals the existence of a significant number of adsorption sites at Pt\([n(111) \times (111)]\) electrodes that bind *H more weakly than Pt(111) and should be, therefore, more active toward the HER in accordance with the theoretical expectations described in Figure 2.

We complement these observations with Figure 4, which contains the activity of Pt(111) and stepped Pt\([n(111) \times (111)]\) electrodes toward the HER in an Ar-saturated HClO\(_4\) under the hanging meniscus configuration. We selected this simplified protocol to ensure the minimal influence of undesired experimental factors\(^{27}\) and to be able to compare the results to the literature, where reports of the activity trends for the state-of-the-art materials in \( \text{H}_2 \)-free electrolytes are abundant (see, e.g., refs 28–2930). Moreover, the results are not corrected for the iR-drop to avoid additional errors in this particular case and to be able to compare the model surfaces under exactly the same conditions.\(^{28}\) Thus, rather than operating with the real exchange current densities, which are extremely difficult to measure in acidic media,\(^{2} \) we compare the activities at the reference points under exactly the same conditions and cell geometries. Cu–Pt(111) near-surface alloy (NSA) was used as an intrinsic probe to additionally benchmark the activities against a highly HER-active surface under similar conditions.\(^{2} \) DOI: 10.1021/acsomega.7b01126

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Figure 4A shows that, in line with Figures 2 and 3, introducing specific surface defects indeed increases the HER activity of Pt[n(111) × (111)] electrodes. Pt(331), Pt(221), and Pt(775) show HER activities that are similar to those reported for one of the most active alloy surfaces of Cu–Pt(111) NSAs. Figure 4B shows a bar chart comparing the activity at the reference point of ~0.036 V (vs RHE) for the Pt(hkl) and polycrystalline Pt samples normalized to the geometric surface area. It can be seen that the stepped surfaces can display more than twofold activity enhancements with respect to Pt(111). However, taking into account that the experiments (Figure 3B) reveal a noticeable increase in the amount of *H adsorption sites for the stepped Pt single crystals, the corresponding activities should be corrected. The results of this correction are shown in Figure 4C. It can be seen that the maximal corrected activity is observed for Pt[4(111) × (111)] electrodes.

They demonstrate an ~1.8-fold activity improvement over Pt(111) and an ~1.5-fold improvement over polycrystalline Pt. Figure 4D presents the data obtained as an additional reference for the HER: this reaction is likely intrinsically not diffusion-limited at low current densities at pH = 1. Even at a current density of 0.5 A/cm², the diffusion-limited current is not reached. However, some contributions of the diffusion are not excluded at such high current densities.

On the basis of our theoretical modeling and experimental data, we suggest that the active sites which govern the catalytic activity of pure Pt electrodes are located at concave sites with slightly increased coordination, similar to the optimal active sites for the oxygen reduction reaction on Pt surfaces,15,22 and slightly increased coordination, similar to the optimal active sites for the oxygen reduction reaction on Pt surfaces,15,22 and in contrast to those for CO oxidation.31 These HER sites bind *H more weakly than Pt(111) terraces, similar to that of CuPt(111) NSAs.3

Although it has been suggested (see, e.g., ref 32) that the HER activity on Pt is not particularly structure-sensitive (though with some exceptions related to Pt(110) and Pt(100)33), our data suggest that such an idea is probably oversimplified. The latter opinion was supported by measurements using Pt[n(100) × (111)] or other families of stepped surfaces.33 For the sake of discussion, it is interesting to compare our results on Pt[n(111) × (111)] and those reported in the literature for Pt[n(111) × (100)] (Figure 5),33 where only the type of steps is changed [(111) vs (100)]. For Pt[n(111) × (100)] electrodes, the activity improvement is also present, but it is less than 20% (see Figure 5). Interestingly, the same ref 33 reports almost no improvement over Pt(111) when using Pt[n(100) × (hkl)] surfaces.

This suggests that while surface coordination is a primary factor to enhance the activity, it might not be the only one in aqueous solution, where step symmetry is also important to define water solvation.34,35 Note in passing that also for the oxygen reduction reaction it has been observed that Pt(111) terraces in aqueous solution, where step symmetry is also important to define water solvation.34,35 Note in passing that also for the oxygen reduction reaction it has been observed that Pt(111) surfaces with (111)-like steps are more active than those with.
(100)-like steps.27 Thus, only specific types of surface defects with “just right” coordination and beneficial adsorbate–solvent interactions enable high HER activities at nonuniform Pt surfaces.

**SUMMARY AND CONCLUSIONS**

In this work, we offer the following new findings related to the electrocatalytic HER at Pt surfaces in acidic media:

(i) The HER is a structure-sensitive electrocatalytic reaction. The sensitivity is, however, limited to only certain concave defects, found in large quantities at, for example, Pt\(\{n(111) \times (111)\}\) electrodes.

(ii) The most active catalytic sites at pure Pt surfaces should have generalized coordination numbers close to 7.7. Examples of such sites are the threefold hollow or bridge sites at the step bottoms of Pt\(\{n(111) \times (111)\}\), with \(n = 3\) or 4.

(iii) The most active pure platinum surface in 0.1 M HClO\(_4\), namely, Pt\(\{4(111) \times (111)\}\), has an HER activity that is slightly lower (~10–20%) than that measured for the most active alloy [Cu–Pt(111) NSA] under similar conditions.

(iv) To maximize the specific and mass HER activity of nanostructured pure Pt electrocatalysts, it is important to modify the shape of the nanoparticles to create “concave catalytic centers” with the values of the generalized coordination numbers close to those of the step bottoms at Pt\(\{n(111) \times (111)\}\) surfaces.

(v) The predictive power of the coordination–activity plots is sufficient to rationalize the trends in HER activities.

**EXPERIMENTAL SECTION**

**Generalized Coordination Numbers.** The generalized coordination number of a site \(i\) is estimated arithmetically from the sum of the conventional coordination numbers \(c_n\) of its \(n\) nearest neighbors and normalized by the maximum number of neighbors found in the bulk of the crystal \(c_{n\text{max}}\)\(^{16}\)

\[
CN = \frac{\sum_{j=1}^{n} c_n}{cn_{\text{max}}}
\]  

(1)

Note that \(cn_{\text{max}}\) is different for each crystal system and also differs per site so that for an fcc metal such as Pt, top sites have a maximum of 12 neighbors, whereas bridge and threefold hollow sites can have up to 18 and 22 neighbors, respectively. Detailed examples on the assessment of generalized coordination numbers can be found in Figure 6 for Pt(111) and elsewhere for stepped surfaces and nanoparticles.\(^3,15,16,36\)

**Computational Methods.** The DFT calculations were carried out with the Vienna Ab Initio Simulation Package,\(^37\) using the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional\(^38\) and the projector augmented-wave method.\(^39\) The slabs contained four metal layers: the topmost two and the adsorbates were completely free to relax, whereas the atoms at the two bottommost layers were immobile and the interatomic distance between them was 2.81 Å. The geometry optimizations were made with the conjugate-gradient scheme using 450 eV as plane-wave cutoff, until the maximum force on any free atom was below 0.01 eV Å\(^{-1}\). The vertical layer of the vacuum between periodic images was larger than 14 Å, and dipole corrections were also incorporated. We used \(k_BT = 0.2\) eV, and the energies were extrapolated to \(T = 0\) K. Given that the differences in \(^\text{H}\) adsorption energies are typically small among Pt active sites, we used dense \(k\)-point meshes for the slabs in Figure 2B–\(F\), namely, 10 × 10 × 1 for Pt(111), 10 × 5 × 1 for Pt(553), 10 × 9 × 1 for Pt(331), and 7 × 7 × 1 for Pt(111) with 2 and 3 adatoms.

The computational hydrogen electrode approach\(^40\) permits the use of the chemical potential of \(\text{H}_2\) instead of that of \((\text{H}^+ + e^-)\) in solution, following the equilibrium

\[
\frac{1}{2}\text{H}_2 \leftrightarrow \text{H}^+ + e^-
\]  

(2)

\(\text{H}_2\) was simulated in a cubic box of 15 Å × 15 Å × 15 Å using a \(\Gamma\)-point distribution and \(k_BT = 0.001\) eV. Thus, the \(^\text{H}\) Adsorption energies are given as

\[
\Delta G^\text{H}_i = G^\text{H}_i - G^\text{H}_0 - \frac{1}{2}G^\text{H}_2
\]  

(3)

where \(0\) is a free surface site. The free energies of the adsorbates are taken as

\[G = E_{\text{DFT}} + ZPE - TS\]

(4)

\(E_{\text{DFT}}\) and ZPE are the DFT-calculated total energy and zero-point energy. ZPE\(_{\text{H}_2}\) on Pt is 0.15 eV, whereas ZPE\(_{\text{H}_2}\) is 0.27 eV. TS\(_{\text{H}_2}\) is 0.01 eV at 300 K and TS\(_{\text{H}_2}\) is 0.40 eV.

We used Nørskov et al.’s microkinetic model to estimate the HER exchange current densities \(i_0\).\(^7\) In this approach, \(i_0\) for \(\Delta G^\text{H}_i < 0\) (left leg of the volcano plot) is estimated as

\[
i_0 = \frac{-ec_k}{1 + e^{-\Delta G^\text{H}_i/k_BT}}
\]  

(5)

In eq 4, \(T = 300\) K, \(-ec = 1.602 \times 10^{-19}\) C is the charge of an electron, \(k_B = 8.617 \times 10^{-5}\) eV K\(^{-1}\) is the Boltzmann constant, and \(k_0\) is a free parameter in the model set to provide exchange current densities on the same order of magnitude of the experimental ones but has no influence on the activity trends (we used a value of \(2 \times 10^{17}\) s\(^{-1}\) cm\(^{-2}\)). On the other hand, when \(\Delta G^\text{H}_i > 0\) (right leg of the volcano plot), \(i_0\) is given as

![Figure 6. Evaluation of the generalized coordination numbers on the four different adsorption sites on Pt(111): (A) top, (B) bridge, (C) hcp hollow, and (D) fcc hollow sites. In each case, the sites for which the assessment is made appear in red, their surface nearest neighbors appear in blue, and their subsurface nearest neighbors appear in green.](Image 354x540 to 534x749)
\[ i_0 = \frac{-e \cdot c \cdot k_0 \cdot e^{-\Delta G_{H}/k_BT}}{1 + e^{-\Delta G_{H}/k_BT}} \]  

(6)

Although eqs 5 and 6 describe correctly the HER activity trends, there are some fair criticisms to Figure 1.\(^{4,5,6}\) One of them is that all DFT data were calculated on the closest-packed surface of each metal disregarding two important facts: (1) elements such as Nb, Mo, W, and Co on the strong binding side of the plot are oxides under HER conditions and deviate largely from the trends. As oxides typically bind adsorbates more weakly than metals,\(^{3,7}\) the actual deviations would be smaller if oxidized phases were considered. Besides, Pt is metallic and stable under HER conditions. (2) The model assumes the same prefactor for all metals. As all sites in Figure 2A are made of Pt, the assumption of an identical prefactor is more justifiable.

As shown in Figure 2B, our calculations were made at low *H coverage for three reasons: (1) we use the PBE exchange–correlation functional, unlike Nørskov et al., who used RPBE. Thus, our hydrogen adsorption energies are stronger than those reported by Nørskov et al. However, the differential adsorption energies should be similar for the two functionals, and increasing the *H coverage would weaken ΔG_H to a point in which they will probably match those of Nørskov et al., whereas the ΔG_H would remain relatively constant. (2) The prediction that ideal HER sites for the HER must have ΔG_H = 0 is functional-independent.\(^{3,7}\) Pt alloys known to bind hydrogen more weakly than Pt(111) have higher HER activity.\(^{3,30}\) These three facts altogether suggest that Pt(111) binds *H slightly stronger than desired, a weakening of its adsorption strength is provided with sites of larger coordination, as Figure 2A shows clear distinctions between step edges (strong binding), (111) terraces (intermediate binding), and step bottoms (weak binding).

**Activity Measurements.** The electrochemical setup used for the measurements is described elsewhere.\(^{41}\) Prior to the measurements, the setup was cleaned with a 3:1 mixture of H_2SO_4 and H_2O_2 (both Suprapur, Merck, Germany) followed by multiple-time boiling in ultrapure water (Evoqua, Germany).

The bare working electrode Pt(331) (Icryst, Jülich, Germany), Pt(221), Pt(775) (both obtained from Prof. Juan Feliú, University of Alicante, Spain), and Pt(111) (Mateck, Jülich, Germany) single crystals were flame-annealed in an isobutane flame and cooled down in a 1000 ppm CO (4.7, Air Liquide, Germany) mixture with Ar (5.0, Air Liquide, Germany). The quality of the surface was confirmed by measuring the characteristic voltammograms of the electrode in the hanging meniscus configuration in an Ar-saturated HClO_4 (Suprapur, Merck, Germany) and comparing the results to that of the literature.\(^{24}\)

Before the activity measurements, the Pt(hkl) electrodes were characterized in the range of potentials between ca. −0.04 and −0.086 V versus RHE, commonly used in the literature, with a scanning rate of 50 mV/s in an Ar-saturated HClO_4.

A polycrystalline Pt microelectrode (CH Instruments, USA) with a diameter of 25 μm was cleaned by scanning (scan rate 50 mV/s) the potential between 1.52 and −0.13 V versus RHE in 0.1 M Ar-saturated HClO_4. Afterward, the HER activity was measured in this electrolyte while scanning between 0.82 and −0.17 V with a scan rate of 50 mV/s.
