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On the optimum binding energy for the hydrogen evolution reaction: How do experiments contribute?

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Abstract

Binding energies of reaction intermediates are largely used to comprehend activity trends in a class of electrode materials. For a two-electron process, such as the hydrogen evolution reaction (HER), it is a well-established paradigm that the optimum electrocatalyst binds adsorbed hydrogen thermoneutrally at zero overpotential. While this picture was challenged recently by means of density functional theory (DFT) calculations and microkinetic considerations, reporting a shift of the optimum binding energy to strong or weak bonding with increasing overpotential, now experiments show further evidence for this theory. This perspective article juxtaposes the different views of the optimum binding energy for the HER by means of the Sabatier principle, microkinetic considerations, DFT calculations, and experiments, and provides an outlook of potential future investigations by the combination of experiments with DFT aiming at sustainable materials development for the hydrogen electrocatalysis.

KEYWORDS

electrocatalysis, hydrogen evolution reaction, optimum binding energy, platinum

The hydrogen evolution reaction (HER) is a simple two-electron process, yet the most frequently studied reaction in electrocatalysis: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})}$ ($U_{\text{HER}}^0 = 0\text{ V}$ versus reversible hydrogen electrode).¹ Platinum (Pt) is considered to be an ideal electrocatalyst for the HER, and despite the identification of material motifs with promising HER activity,² none of these materials can reach the catalytic properties of Pt in acid, the intrinsic activity of which is still underestimated due to mass-transport limitations.³

In the 50th of the last century, Parsons and Gerischer initiated to connect the chemical structure of HER electrocatalysts to catalytic activity by the construction of a

so-called volcano curve,⁴ a strategy that was continued by Parsons in the 70th, rendering the high activity of Pt due to its location at the volcano apex.⁵ With the rise of ab initio theory in the density functional theory (DFT) approximation at the beginning of the 21st century, Nørskov and coworkers established the adsorption free energy of hydrogen ($\Delta G_{\text{H}} = G_{\text{H}} - G_{*}$, in which G_{H} and G_{*} are the free energies of adsorbed hydrogen and the unoccupied active site, respectively), often simply denoted as the hydrogen binding energy, as a descriptor for HER activity.⁶ Based on the Sabatier principle, their model purports the view that the optimum HER catalyst binds

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adsorbed hydrogen thermoneutrally at zero overpotential ($\Delta G_{\text{H}} = 0 \text{ eV}$ @ $\eta = 0 \text{ V}$), considering that this notion may maximize the exchange current density. The simple concept of thermoneutral bonding for the HER caused a steeply increasing amount of materials-screening trend studies to search for electrocatalysts based on earth-abundant elements, and in the last decade this design criterion has also been actively applied to electrocatalytic processes beyond the simple hydrogen electrocatalysis.⁷

Yet, it needs to be emphasized that the concept of thermoneutral bonding at zero overpotential as optimum situation for a two-electron process relies on several tacit assumptions. On the one hand, the binding strength of the reaction intermediate, adsorbed hydrogen, is assumed to universally scale with the overall reaction kinetics in that the thermodynamically most unfavorable reaction step also governs the rate-determining step.⁸ On the other hand, the link between the thermodynamics and kinetics is set at zero overpotential corresponding to electrochemical equilibrium, whereas electrocatalytic turnover can only be observed as soon as a finite overpotential is applied.

Recently, the author introduced “the extended Sabatier principle” for electrocatalytic processes by factoring the applied overpotential and partly kinetic effects relating to the Tafel slope into the analysis of the optimum binding energy (ΔG_{H}).⁹ Incorporating the Tafel slope into the assessment of the optimum ΔG_{H} value results in a catalytic material that binds adsorbed hydrogen weakly rather than thermoneutrally at zero overpotential ($\Delta G_{\text{H}} > 0 \text{ eV}$ @ $\eta = 0 \text{ V}$).¹⁰ This can be explained by the fact that weak bonding at zero overpotential renders thermoneutral bonding of adsorbed hydrogen at the target overpotential of the reaction feasible; this concept was deduced from the analysis of free-energy diagrams as a function of the applied overpotential.⁹ On the contrary, strong bonding of adsorbed hydrogen at zero overpotential can never result in a catalytic material that stabilizes the reactive precursor thermoneutrally under reaction conditions. This is the reason why the author shares the view that the optimum ΔG_{H} value corresponds to weak (ΔG_{H} of about 100 meV) rather than to thermoneutral bonding.¹⁰

Besides the extended Sabatier principle, several studies investigated the location of the volcano apex for the hydrogen electrocatalysis corresponding to the optimum ΔG_{H} value by means of microkinetic considerations. It was reported that the optimum binding energy can be reconciled with either strong bonding ($\Delta G_{\text{H}} < 0 \text{ eV}$ @ $\eta = 0 \text{ V}$) or weak bonding ($\Delta G_{\text{H}} > 0 \text{ eV}$ @ $\eta = 0 \text{ V}$) of adsorbed hydrogen as soon as the HER is analyzed at finite overpotentials rather than at equilibrium.^{11–14} Thus far, it remains elusive whether the displacement of the optimum binding energy to weak or strong bonding of adsorbed hydrogen is more likely. The author elaborated that also the microkinetics

indicates weak bonding of adsorbed hydrogen as the preferred situation (ΔG_{H} of about 200 meV).^{10,13} The reason for this finding is that the concept of thermoneutral bonding of adsorbed hydrogen at the target overpotential, corresponding to the extended Sabatier principle,⁹ was reproduced by a microkinetic approach in conjunction with the steady-state approximation.¹³ Quite in contrast, microkinetic models using the quasi-equilibrium assumption predict either strong or weak bonding of adsorbed hydrogen as the thermodynamic ideal.^{11–14} Yet, quasi-equilibrium is not necessarily a suitable approximation for the description of electrocatalytic processes due to the fact that the quasi-equilibrium assumption holds only true in a single linear Tafel regime, but is violated as soon as a switch in the Tafel slope is observed.^{15–17} Therefore, the analysis of the optimum ΔG_{H} value by means of the steady-state assumption may provide a more reliable picture than the adoption of quasi equilibrium, thus, confirming the conclusion that weak bonding of adsorbed hydrogen is preferential for the hydrogen electrocatalysis.

Initial gas-phase DFT calculations for the HER over Pt(111) revealed that Pt is a nearly thermoneutral material ($\Delta G_{\text{H}} = -0.09 \text{ eV}$).¹⁸ This finding, however, contrasts with the most recent DFT studies for the HER over Pt(111), reporting that the active hydrogen species is bonded weakly when considering the aqueous electrolyte by means of implicit or explicit solvation approaches (ΔG_{H} of about 200 to 400 meV).^{19,20} The author ascribed these differences to a type II error.²¹ The Sabatier principle in its thermodynamic form at zero overpotential purports thermoneutral bonding as the optimum situation for a two-electron process. This notion was approved for Pt(111), which is thought to be an ideal HER catalyst, based on gas-phase DFT.^{5,18} The true volcano apex, however, is located at weak bonding of adsorbed hydrogen based on the extended Sabatier principle including overpotential and kinetic effects,^{9,10} which coincides with the solvation-corrected ΔG_{H} value of Pt(111).^{19,20}

Based on the extended Sabatier principle, microkinetic considerations, and DFT calculations, for Pt(111), it can be fairly concluded that the optimum hydrogen binding energy shifts from thermoneutral to weak bonding with increasing overpotential. Recently, experimental evidence for this theoretical prediction has been reported by Ooka, Wintzer, and Nakamura, who analyzed experimental Tafel measurements for the HER over a polycrystalline Pt electrode in an acidic electrolyte.²² Ooka et al. adopt a mechanistic description that incorporates both the Volmer-Tafel and Volmer-Heyrovsky mechanisms into the analysis. Combining the experimental Tafel measurements with microkinetic modeling and machine-learning techniques, the binding energy of adsorbed hydrogen for the combined Volmer-Tafel-Heyrovsky pathway is extracted

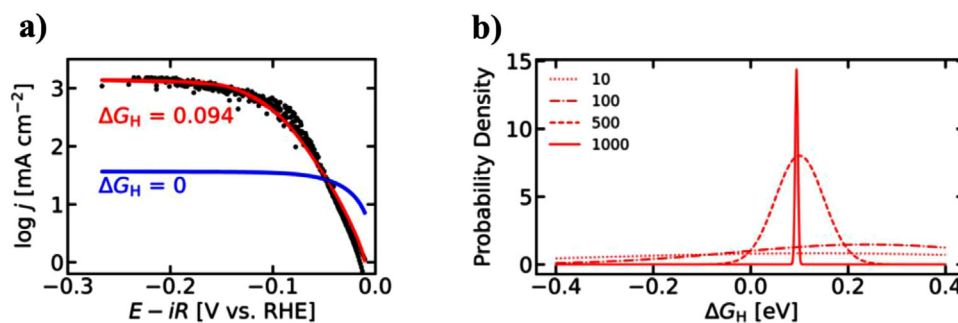


FIGURE 1 (a) Experimental Tafel plot (black dots) for the hydrogen evolution reaction (HER) over a polycrystalline Pt electrode. The red curve corresponds to the best-fit line of the current versus potential relationship, obtained from microkinetic considerations in conjunction with a genetic algorithm to enhance the precision for the determination of the adsorption free energy of hydrogen, ΔG_H . Panel (b) illustrates that the algorithm converges to $\Delta G_H = 0.094$ eV. It is noteworthy that by using the same fitting parameters for the Tafel plot in (a), but using $\Delta G_H = 0$ eV (thermoneutral bonding) instead of $\Delta G_H = 0.094$ eV, the resulting hypothetical electrocatalyst (blue line) is more active than Pt at small overpotentials ($\eta > -0.03$ V) but significantly less active at typical HER conditions ($\eta = -0.10$ V). Reproduced with permission from Ref. [22]. Copyright 2021, American Chemical Society

from the experimental data by joining the Butler-Volmer and Brønsted-Evans-Polanyi relationships to build a bridge between the kinetics (Tafel plot) and thermodynamics (ΔG_H), in which a genetic algorithm, including gradient descent, was used to minimize the error of the fit parameters. Following this procedure, Ooka et al. obtained $\Delta G_H = (0.094 \pm 0.002)$ eV as adsorption free energy of hydrogen at zero overpotential, which clearly deviates from the notion of thermoneutral bonding (cf. Figure 1).²²

Considering that so far, no other electrocatalyst has been reported with a comparable intrinsic activity, such as Pt,³ polycrystalline Pt can be seen as the ideal HER electrocatalyst, and thus, the study of Ooka et al. sheds further light on the definition of the optimum binding energy for a two-electron process. Here, it should be noted that the authors compared the weak-binding Pt catalyst to a hypothetical thermoneutral material, illustrating that thermoneutral bonding of adsorbed hydrogen is indeed favorable close to equilibrium (cf. Figure 1a). This is in agreement with the Nørskov model⁶ but also with the analysis of free-energy diagrams.⁹ Yet, under typical HER conditions, that is, overpotentials of about 100 mV, the weak-binding Pt catalyst is far more active than the hypothetical thermoneutral material. This aspect coincides with the extended Sabatier principle,⁹ microkinetic considerations,^{10,13} and DFT calculations,^{19,20} and thus, renders weak bonding of adsorbed hydrogen as the optimum binding strength, illustrated in Figure 2. In short, the concept of thermoneutral bonding as the optimum for a two-electron process holds only true close to equilibrium but cannot be used for the assessment of electrocatalysts under operational conditions (cf. Figure 2).

The work of Ooka et al.²² opens new doors in the development of electrode materials for the hydrogen electrocatalysis since a powerful bridge between the experimental

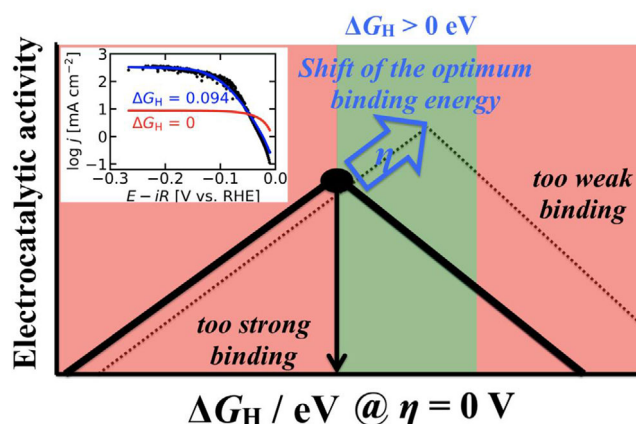


FIGURE 2 Initially, the optimum binding energy of adsorbed hydrogen, corresponding to the apex of the volcano curve, was ascribed to thermoneutral bonding ($\Delta G_H = 0$ eV @ $\eta = 0$ V). This notion, however, is only fulfilled close to equilibrium conditions (red curve in the inset). With increasing overpotential, the optimum binding energy shifts from thermoneutral to weak bonding of adsorbed hydrogen ($\Delta G_H > 0$ eV @ $\eta = 0$ V), represented by a blue arrow. This theoretical prediction based on the extended Sabatier principle and microkinetic considerations^{9,10,13} is experimentally corroborated by the hydrogen evolution reaction (HER) over a polycrystalline Pt electrode (blue curve in the inset).²¹ Adapted with permission from Ref. [10]. Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA

Tafel plot and ΔG_H by microkinetic modeling and machine learning has been established. I would like to emphasize, though, that such a correlation was also reported in the works of the Liu group for the oxygen evolution reaction (OER).^{23,24} Yet, to extract the free-energy changes for the OER from the experimental Tafel plot, Liu and coworkers needed to stipulate the rate-determining reaction step (RDS) a priori, a dangerous assumption considering that

Electrocatalyst I: record experimental Tafel plot

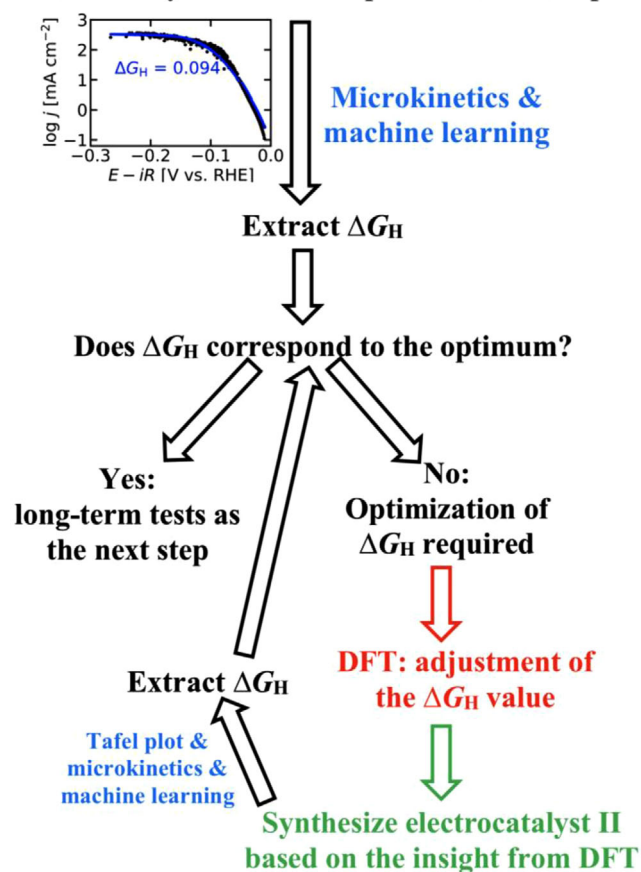


FIGURE 3 Scheme of how to use the extracted ΔG_H value from the experimental Tafel plot for materials development in the hydrogen evolution reaction, thereby combining experiments (green) and density functional theory (DFT) calculations (red) within a self-consistent loop. The determination of the ΔG_H value by conjoining microkinetic modeling and machine learning refers to the approach reported by Ooka et al. (blue).²²

the RDS can change with increasing driving force.¹⁶ The approach of Ooka et al., however, is not relying on an a priori presumption of the RDS, and thus, could be directly transferred from polycrystalline Pt to sustainable materials development, as discussed hereinafter.

Applying the combined framework of Tafel plots, microkinetic modeling, and machine-learning techniques, ΔG_H for the catalytic material under consideration is determined (cf. Figure 3). Thereafter, the location of the ΔG_H value in the volcano curve is inspected, aiming to optimize the ΔG_H value toward the benchmark of slightly weak bonding, that is, ΔG_H of about 100–200 meV (cf. Figure 2). Different tactics are feasible to modify the atomic and electronic structure of the electrocatalyst, which are accompanied with a modulation of the hydrogen binding strength; these approaches may comprise the insertion of foreign metal atoms, the combination of multiple functional components, shape-controlled catalysis, or the rational design of surface site densities, among others.^{25,26} Here, DFT cal-

culations for model systems, reminiscent of the investigated catalytic material, may allow gaining insight into the usage of additives, other functional components, or the catalysis on different surface facets to help adjusting the binding energy of adsorbed hydrogen for the catalytically active phase in a proper fashion. The obtained knowledge is transferred back to experimentalists in that adapted catalytic materials are synthesized, and the experimental Tafel plot is recorded to inspect ΔG_H . Thus, the outlined approach gives rise to a self-consistent loop that is finalized as soon as a sufficiently active electrode material has been developed, which should be subjected to long-term tests in the next step to investigate its potential use for large-scale applications. Figure 3 summarizes the discussion.

The suggested procedure to apply ΔG_H for materials development goes beyond previous theoretical considerations in the DFT approximation,¹⁸ and particularly does not need to evaluate the adsorbate-electrolyte interaction, which appears to be the bottleneck for correct determination of ΔG_H by DFT.^{19,20} Comparing the gas-phase and solvation-corrected ΔG_H values for Pt(111), differences of up to 500 meV manifest; this is even far beyond the error bars of exchange correlation functionals within the DFT approximation, which are in the order of about 200 meV.¹⁸ Consequently, a systematic search of promising electrocatalysts for the HER by DFT becomes tedious if not even impossible, considering that the correct description of the adsorbate-electrolyte interaction requires distinctly more computational efforts than simple gas-phase DFT, and thus, is not suitable for the high-throughput screening of electrocatalysts.²⁷ It shall also be noted that additionally the value of ΔG_H strictly depends on the chosen level of theory for the adsorbate-electrolyte interaction (implicit vs. explicit solvation).²⁰

In contrast, a different situation is encountered with the approach by Ooka et al., where the error bars of ΔG_H are two orders of magnitude smaller compared to DFT,²² thanks to the usage of a genetic algorithm. Evaluating ΔG_H directly from the experimental Tafel plot is an efficient strategy to circumvent the shortcoming of DFT relating to a clear-cut absolute determination of ΔG_H values, while DFT calculations are a valuable supplement to steer the rational design of electrocatalysts based on ΔG_H from experiments. It should be noted that the level of theory within the self-consistent loop (cf. Figure 3) is variable, and high-level DFT calculations are not necessarily required. This is related to the fact that already gas-phase DFT is a powerful method to comprehend trends, but not absolute values, relating to a change in the binding energy when the chemical environment around the active site is systematically altered.¹⁸ Yet, high-level DFT calculations, considering the electrode/electrolyte interface, the applied electrode potential as well as electric field effects and electrolyte ions, may enhance the accuracy of the theoretical

predictions, and the obtained ΔG_{H} values can also be directly compared to the experimentally determined ones. This strategy enables validation of the approximations within the DFT approach, and thus, may contribute to advance the scientific discipline of electrocatalysis.

While the optimization scheme in Figure 3 relies on the adoption of the Sabatier principle, I would like to emphasize that the application of the Sabatier principle for heuristic materials discovery of electrocatalytic processes is controversially discussed in the literature.^{11,28–30} Zeradjanin et al. concluded that the Sabatier principle cannot be transferred from heterogeneous gas-phase catalysis to electrocatalysis in a straightforward manner due to the presence of the complex electrode/electrolyte interface.¹¹ This has initiated the search of descriptors beyond adsorption or binding energies for the HER, purporting the view that properties of the electrified solid-liquid interfaces as well as the reaction kinetics need to be taken into consideration to understand and predict the hydrogen electrocatalysis.^{28–30} A detailed discussion of descriptors beyond adsorption energies goes beyond the scope of the present perspective article, and thus, the reader is referred to a recent overview article dealing with this aspect.²⁹ Yet, I would like to emphasize that the extended Sabatier principle,⁹ albeit analyzing binding energies, considers the reaction kinetics in the analysis, which may indicate that the two different disciplines of descriptors based on binding energies and descriptors beyond binding energies approach each other.

In conclusion, the proposed scheme (cf. Figure 3) may initiate an intimate interplay between experimentalists and theoreticians, may validate the notion of a slightly positive ΔG_{H} value as the optimum situation for other highly active HER materials, and in the optimum case may guide the identification of next-generation HER catalysts consisting of earth-abundant elements within the framework of a sustainable energy economy.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

Not applicable.

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