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Review

Beyond current frontiers of electrocatalysis

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Abstract

One of the key reasons why the transition to renewable energy sources is progressing slowly is the low efficiency of processes at electrified interfaces where electricity is converted and stored as chemical energy. The challenge behind low efficiency is sluggish electrochemical conversion reactions. To resolve low efficiency, it is necessary to comprehend the intrinsic reasons behind the unusually complex phenomena of converting electrical energy into chemical energy, and vice versa, chemical energy into electrical energy. An important example is the electrolysis of water, where, after decades of research, it is not clear how to significantly accelerate the processes of hydrogen and oxygen generation. Of critical importance for the control of the water electrolysis mechanism is understanding the origins of the electrocatalytic activity. If we ask a key question from a conceptual point of view, namely: what are the origins of electrocatalytic activity? The answer will be, in most cases, as it was 70 years ago. Namely, the paradigm of electrocatalysis is the Sabatier principle, which suggests optimal ("not too strong, not too weak") binding of intermediates as the main prerequisite for a high reaction rate. Conventional wisdom suggests that confirmation of this should be a linear relationship between the adsorption energy of the intermediate and the activation energy, known as the Brønsted-Evans-Polanyi relation. However, recent results show that lowering the activation energy is not necessarily beneficial for increasing the reaction rate. In this work, some fundamentally important questions about the nature of electrocatalytic activity will be raised. Identifying and analyzing these issues can be an important trigger and driver towards efficient water electrolysis and a more comprehensive understanding of electrocatalysis as a scientific field of key importance for the conversion, storage and utilization of energy from renewable sources.

Keywords
Activation energy, preexponential factor, barrier, reactant-catalyst collisions, characteristic vibrations, tunneling

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Introduction

Electrocatalysis is the area of electrochemistry that studies the impact of the nature of the electrode material on the rate of the electrochemical reaction [1]. Electrocatalytic reactions involve the formation/cleavage of a chemical bond(s) between the intermediate and the electrode surface (*i.e.,* adsorption of the intermediate), suggesting that the energetics of intermediate formation, including the strength of the chemical bond(s) between the intermediate and the electrode surface, plays an important role in the overall reaction rate. Taking into account the above, it becomes clear why, for more than a century, the paradigm of heterogeneous catalysis, and therefore of electrocatalysis, has been Sabatier's principle [2].

Sabatier's principle postulates that the high rate of the catalytic reaction is due to the optimal binding of intermediates to the electrode surface. Optimal binding of intermediates in qualitative terms implies "not too strong, not too weak" chemical bond. If the chemical bond is too strong, recombination reactions are inhibited, and if the chemical bond is too weak, desorption of reactants/intermediates occurs before products are formed. This qualitative rule is usually manifested graphically through the so-called Balandin-type volcano plots where the kinetics of the reaction is given as a function of the enthalpy of adsorption of intermediates [3,4]. The peak of the volcano plot corresponds to the optimal enthalpy of adsorption. This qualitative consideration received a quantitative interpretation in electrochemistry in the late 1950s, when the exchange current density was expressed mathematically as a function of the standard Gibbs energy of hydrogen adsorption [5]. A graphic illustration of this dependence is the volcano plot, the slope of which depends on the elementary step that determines the overall reaction rate. In other words, the slope of the volcano plot depends on the symmetry factor and intermediate coverage of the elementary step that determines the overall reaction rate. The Balandin-type of volcano plot, as a consequence of Sabatier's principle, was generally accepted in electrocatalysis in the early 1970s, when a sufficient amount of experimental data for d-metals and sp-metals had been accumulated and analyzed, including relatively credible values of the exchange current density for the hydrogen reaction in acidic electrolytes, and relatively problematic values for the energy (*i.e.* enthalpy change) of metal-hydrogen bond formation (ΔH(M-H)) [6]. The values used are problematic because they came from three different environments: 1) "bulk" interactions during hydride formation, 2) interaction of hydrogen with metal atoms on the surface, but in the gas phase, 3) electrochemical adsorption. The first two experimental environments are not relevant for electrochemistry, while the values obtained in the electrochemical experiment represented the differential values of the activation energy of the Volmer reaction on the investigated metal in relation to the activation energy of the Volmer reaction on mercury. A decade after the publication of the hydrogen volcano plot, by re-analyzing the experimental values of the hydrogen adsorption enthalpy in an electrochemical environment used in the construction of the hydrogen volcano curve, a linear dependence between the exchange current density and the adsorption enthalpy was obtained [7]. This contradiction was the trigger for considering in detail an experimental methodology that would give reliable values of the hydrogen adsorption enthalpy at the liquid/solid interface with an established Galvanic potential difference because computational chemistry did not add enough clarity here [8,9]. One of the possible approaches is the methodology to measure with a Kelvin probe the change in the work function of the metal during the adsorption of hydrogen through the water layer at the metal surface [10]. Having the realistic values of hydrogen adsorption enthalpies for various metals of interest, we could answer several key questions and, based on reliable experimental insights, create a more realistic picture of the nature of electrocatalytic activity.

Some of the most important questions that should be answered in the future are the following:

1. whether there is a straightforward relationship between the exchange current density for the hydrogen reaction and the enthalpy of adsorption, and if so, is it a volcano-type relationship or a linear relationship or something else;
2. do the trends in the enthalpy of adsorption coincide with the trends in the Gibbs energy of adsorption, that is, what is the influence of the entropy of adsorption on the trends in activity;
3. if the relationship between the exchange current density and the enthalpy of adsorption is of the volcano-type, is it possible to overcome the volcano-plot apex and how? At the same time, if the relation between exchange current density and adsorption enthalpy is linear, what approach should be applied to overcome the activity of the most active metals;
4. whether the adjustment of the enthalpy of adsorption has a direct effect on the activation energy as predicted by Brönsted-Evans-Polanyi (BEP) relations;
5. what is the contribution of the adsorption to the pre-exponential factor through the coverage of intermediates;
6. what other parameters from the rate law, besides adsorption energies (*i.e.,* adsorption enthalpy, adsorption free energy and adsorption entropy) have a significant influence on the overall reaction rate either through activation energy or through preexponential factor and with what properties of electrified interface they can be related to. Special emphasis here should be on partial orders of reaction in preexponential factor and activation barrier symmetry coefficient in exponential factor (*i.e.,* activation energy), both well-known kinetic parameters in the conventional expression for the rate law, whose physical meaning was never really resolved.
7. if we identify relevant properties of the electrified interface that have a significant impact on the total reaction rate (*i.e.,* through a particular parameter in the rate law), the following question is what material properties are responsible for that and how can they be tuned;
8. is it possible to have a separate impact on activation energy and preexponential factor?

In this work, some of the important questions listed above will be the topic of analysis, with the intention of giving a perspective on how to proceed with the development of electrocatalysis. Currently, experimental data that could resolve the questions listed above are lacking. However, analysis on the conceptual level is very important and represents the first step in achieving in-depth clarification of electrocatalytic mechanisms. The ultimate goal is to gain knowledge on how to sufficiently accelerate key electrocatalytic reactions so they can be utilized efficiently in energy conversion devices and systems.

Results and discussion

Why is a thorough understanding of the hydrogen evolution reaction essential?

Hydrogen evolution reaction (HER) in acidic electrolytes is the simplest electrocatalytic reaction and is naturally a prerequisite for understanding more complex reactions such as oxygen reduction reaction, oxygen evolution reaction, *etc.* The reaction is given together with the indicated redox potential (for pH 0) in relation to the reference scale of the standard hydrogen electrode, Equation (1):

$$2H^+ + 2e^- \leftrightarrow H_2 \quad E^\circ = 0.00 \text{ V } vs. \text{ SHE} \tag{1}$$

HER is a reaction during which are exchanged two electrons and two protons, usually on metal surfaces that do not structurally change significantly during the course of the reaction. Exceptions exist for this, like in the case of Pd, where significant bulk absorption impacts surface adsorption properties and this material requires different, more complex treatment [11]. Today, there is general agreement on the reaction pathway of HER in acidic media. The elementary step in which a proton from the electrolyte reacts on the inner Helmholtz plane with an electron from the Fermi level of the metallic electrocatalyst, forming an intermediate product, is known as the Volmer step (Equation (2)). The Volmer step is followed by an elementary step in which an intermediate recombines with a proton and an electron, forming a hydrogen molecule in one active site and/or an elementary step in which two intermediates recombine, requiring two adjacent active sites. The formation of hydrogen molecules through electrochemical recombination is known as the Heyrovsky step (Reaction 3a), while chemical recombination is known as the Tafel step (Equation (3b)).

$H^+ + e^- \leftrightarrow H_{ad}$ Volmer's degree (2)

$H_{ad} + H^+ + e^- \leftrightarrow H_2$ Heyrovsky stage (3a)

$2H_{ad} \leftrightarrow H_2$ Tafel degree (3b)

Of fundamental importance for catalysis and electrode kinetics is the identification of the elementary step that determines the total reaction rate. It is generally accepted that the elementary step that determines the total reaction rate can be evaluated using the value of the Tafel slope. Conventional wisdom suggests that for weak hydrogen bonding and very low intermediate coverage, the overall rate is determined by the Volmer step, with a Tafel slope of 120 mV/dec. If the Heyrovsky step determines the total reaction rate, which is typical for low to medium coverage with intermediates and the binding is stronger than in the Volmer step, then the Tafel slope is 40 mV/dec. Finally, when the Tafel step determines the overall rate, which is typical for moderately strong binding of intermediates and medium to high coverages, then the slope is typically 30 mV/dec or can reach 120 mV dec^{-1} if the coverage with intermediates approaches a monolayer. The Tafel slope, which determines how easy it is to alter reaction rate with overpotential for the given solvent (*i.e.* water), essentially depends on the nature of the electrode material, where besides the impact of intermediate coverage, of particular importance is shape/steepness of activation barrier that is described by symmetry factor. The symmetry factor, which determines how easy it is to change the height of the barrier with a potential, essentially depends on the nature of the electrode material, but in a way that remains unknown to us for decades. Practically all diagnostic criteria of electrode kinetics (*i.e.* partial orders of reaction, stoichiometric number and charge transfer coefficient for multi-electron reactions) depend on the nature of the electrode material, but in a way that we still cannot comprehend. This was the reason why many kinetic studies did not make any significant contribution to the design of new, superior electrode materials and the reason why, over time, there is a growing interest in a correlative approach where the search for material properties (*i.e.* descriptors) that could relate with reaction rate appears to be much more realistic strategy [12,13]. The correlative approach has been visibly intensified in the last twenty years, which coincides with the rise of computational chemistry [14]. Many descriptors have been investigated, whereas most descriptors lack a show of how exactly they contribute to the activation process and what their direct link to the rate law is. On that road, it was important to introduce and define interfacial descriptors that are essentially different than material descriptors because they are strictly the result of the interaction of electrode with electrolyte [15,16]. A rational approach would imply that the property of the material (*i.e.* material descriptor) is related to the property of the electrified interface (*i.e.* interfacial descriptor), which ultimately should be related to the total reaction rate through some of the parameters in the rate law. At the same time, the descriptors should contribute to understanding the activation process.

Heuristic model of proton adsorption activation process

If we analyze the electrified electrode/electrolyte phase boundary during proton adsorption (Figure 1), using the heuristic model, we can notice that there are four important processes relevant to the formation of intermediate, as discussed previously in detail [10,15,17]:

1. The metallic electrode is treated as an equipotential surface and electron source, where electronic energy is described by the Fermi level or work function of the metal. Water molecules have two non-bonding electron pairs on the oxygen atom, where one of them is energetically less stable and forms a covalent bond with the metal surface (M-OH_2). The consequence of established chemical bond is metal-specific interfacial water structure that can also be described, despite the significant thermal motion of water molecules (*i.e.* vibrations and rotations of chemical bonds and water dipole flip), by preferential water molecule orientation. Preferential water molecule orientation reflects a statistical probability because the water bilayer is in a dynamic state. Water orientation, besides metal-water bond strength, depends on the strength of the electric field in the double layer (*i.e.* interfacial electric field). The electric field strength in the double layer is proportional to the potential difference between the potential of zero charge and the actual/applied potential. The stronger the metal-water bond and the larger the interfacial potential difference (*i.e.* as more positive), the more significant the orientation of water with hydrogen towards the metal surface will be. In other words, the covalent metal-water interaction that primarily dictates the structure of water in the double layer will be modulated by the electrostatic interaction as a secondary interaction that additionally affects the structure and dynamics of water molecules in a double layer;
2. The movement of protons from the outer Helmholtz plane to the inner Helmholtz plane (IHP). In reality, the proton " jumps" from one solvation shell to another in a non-linear motion, where in one instance, it will be positioned close to the metal surface so that electron transfer is likely. In essence, this interaction is a proton-electric field interaction, which depends significantly on the structure of the water in the double layer, which in turn depends significantly on the strength of the metal-water interaction and the strength of the interfacial electric field;
3. When the proton, including its solvation shell, is located at the IHP, then the deformation/reorganization of the solvation shell (including the reorganization of water molecules on the metal surface) is necessary as a prerequisite for electron transfer or proton-electron interaction. Deformation/reorganization of the solvation shell is actually a proton-water interaction that is influenced by the water structure, which is again influenced by the strength of the metal-water bond and the strength of the interfacial electric field;
4. Finally, when the water molecules on the metal surface, as well as the solvation shell around the proton, are reorganized in such a way that the positive charge of the proton is exposed to the negatively charged metal surface, electron transfer will occur, resulting in the formation of a chemical bond (M-H). The formation of the M-H bond is a metal-proton interaction. However, exposure of the positive charge of protons to the negatively charged surface depends on the stability of the solvation shell, which also depends on the structure of interfacial water that is again influenced by the strength of the metal-water bond and the strength of the interfacial electric field. So, in summary, we have three key covalent interactions: metal-water (solvent), metal-proton, and solvent-proton. These three covalent interactions can be modulated by the electrostatic interactions, which originate from the interfacial electric field. When we apply cathodic polarization, the surface of the metal becomes increasingly negatively charged proportionally to the applied potential, the water molecule's orientation with hydrogen towards the surface of the

electrode becomes statistically more probable and importantly the concentration of protons increases in the double layer. Practically, electrostatic interactions add to the above-mentioned existing covalent interactions. The contribution of electrostatic interactions depends on the interfacial electric field strength, which is directly proportional to the difference between the potential of zero charge and the actual/applied potential. Bearing all this in mind, the activation process of intermediate formation depends on the energetics of interactions: metal-water, metal-proton and proton-water, and the potential of zero charge. Individual or combined, these four properties of the phase boundary should be brought, if possible, into a direct relationship with experimentally available measurable physico-chemical quantities and with parameters in the rate law.

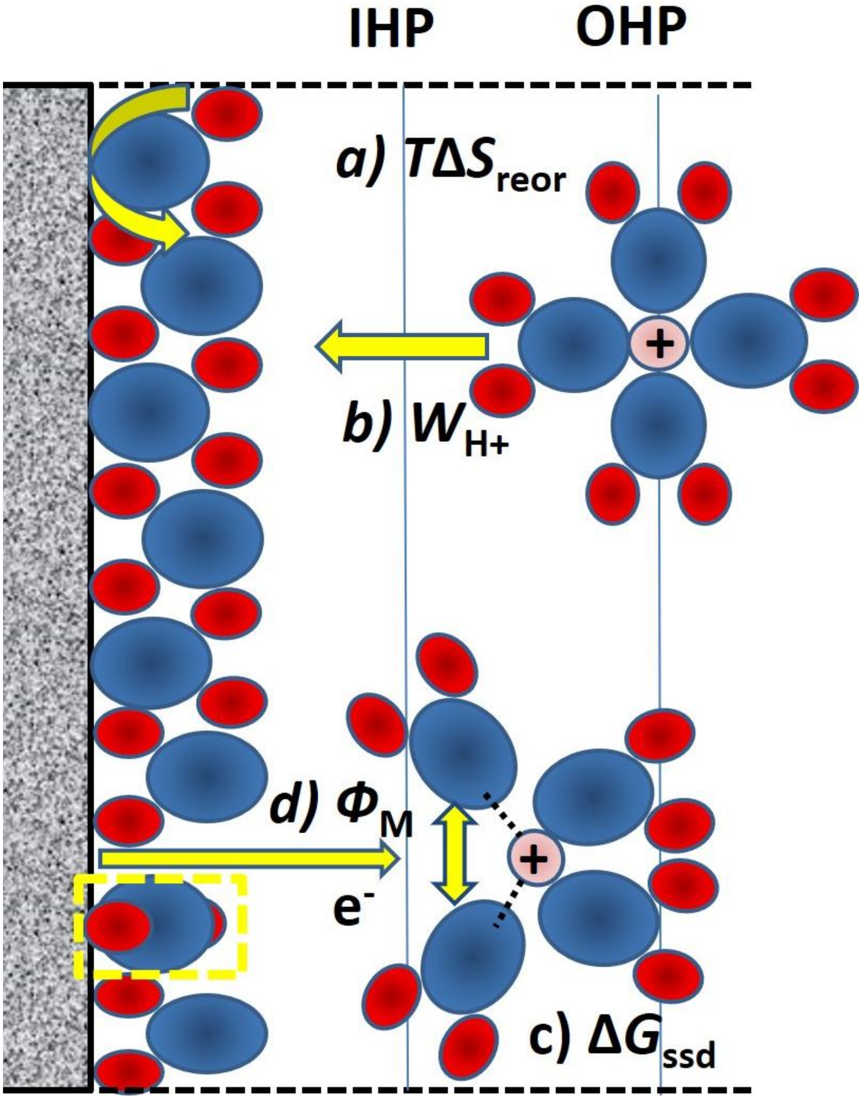

Figure 1. *Structural changes of the electric double layer during proton adsorption at the solid/liquid phase boundary including: (a) reorganization of water molecules in the electric double layer under the influence of covalent metal-water interaction and the strength of the interfacial electric field , given as the average change in the entropy of the reorganization of water in proximity of the solvation shell (ΔS_{reor}), (b) average work invested on transferring proton (W_{H+}) from the outer Helmholtz plane (OHP) to the inner Helmholtz plane (IHP), (c) the average free energy of deformation/reorganization of the solvation shell in the inner Helmholtz plane (ΔG_{ssd}) in combination with further reorganization of water in the double layer in the proximity of the solvation shell, and (d) electron transfer from the Fermi level of the metal to a proton with a partially deformed solvation shell with partially exposed positive charge, driven by work function of the metal (Φ_m). Color code: metal surface—grey, oxygen—blue, hydrogen from water—red, proton and adsorbed proton—pale red. The space between the first and second layers of water in the double layer is intentionally left for clarity. Yellow dashed rectangular indicates that besides water dipole flip important is water molecule rotation*

Three out of four mentioned interactions (*i.e.* metal-water, metal-proton and potential of zero charge) are strongly electrode material dependent, while proton-water interaction is strongly electrolyte dependent. If we utilize the same electrolyte to investigate different metals (*i.e.* electrode materials), then proton-water interaction is irrelevant to the investigation. However, we can alter the properties of solvent [18], use different counterions [19], use additives and/or impurities [20], so proton-water interaction can be a very relevant parameter for HER kinetics.

Phase boundary dynamics during hydrogen evolution reaction through the prism of the pre-exponential frequency factor

In electrocatalysis, the activation process is generally much better understood than the collision process. Therefore, the pre-exponential frequency factor is a much bigger unknown than the processes contributing to the activation energy. For electrocatalytic reactions like HER reaction rate is usually defined with the following expression (Equation (4)) [17]:

$$j_0 = nFc_{\mathrm{H^+}}{}^{p}(1-\theta)^{q}k_{\mathrm{et}}\exp\left(\frac{-\beta FE_{\mathrm{rev}}}{RT}\right)\exp\left(\frac{-\gamma\left(\left(\Delta G_{H_{\mathrm{ad}}}\right)_{\theta=0}+r\theta\right)}{RT}\right) \tag{4}$$

where: j_0 - exchange current, n - number of exchanged electrons, F - Faraday's constant, $c_{\mathrm{H^+}}$ - concentration of protons, p - partial order with respect to proton concentration, q - partial order with respect to number of available active sites, θ - total coverage including intermediates and eventual blocking species, β - symmetry factor, E_{rev} - reversible potential, R - universal gas constant, T – temperature, $(\Delta G_{\mathrm{Had}})_{\theta=0}$ - the change in free-energy of adsorption at zero coverage, r - the interaction parameter. The interaction parameter originates in lateral interactions of intermediates (assisted with surrounding water molecules/dipoles) and can be positive (for repulsive interactions) or negative (for attractive interactions) and can have a great impact on the overall value of the free-energy of adsorption (*i.e.* $(\Delta G_{\mathrm{Had}})_{\theta\neq0} = (\Delta G_{\mathrm{Had}})_{\theta=0} + r\theta$ - the change in free-energy of adsorption at defined coverage), γ - Bronsted-Evans-Polanyi (BEP) coefficient. Conventional wisdom suggests that electrocatalytic activity is a result of a balance established by $(\Delta G_{\mathrm{Had}})_{\theta\neq0}$ *vs.* $(1-\theta)$, where for very exergonic adsorption, the resulting activation energy should be very low while the coverage should be very high and consequently, preexponential factor should be low. Conversely, for very endergonic adsorption, the resulting activation energy should be high while coverage should be low and consequently, the preexponential factor should be high. This is in accordance with the Sabatier principle. The HER exchange current has its highest value when $\mathrm{H_{ad}}$ formation is thermoneutral and entropy-driven ($(\Delta G_{\mathrm{Had}})_{\theta\neq0} = 0$). Activity trends based on this assumption are nowadays widely accepted. Some authors introduce in the exponential factor two additional parameters: the potential at the outer Helmholtz plane in reference to the potential of the electrolyte bulk, (what can be brought into correlation with the potential of zero charge) as well as the reorganization energy of the solvent, what according to discussion linked to Figure 1 seems to be justified [21]. In the preexponential factor, the same authors also include the density of states at the Fermi level, the distance between the inner and outer Helmholtz plane as well as the overlapping integral between wave functions of reactant and atoms of the electrocatalysts, suggesting a role of quantum mechanics in electrocatalysis [21]. Quantum mechanics was introduced to electrochemistry approximately a century ago [22]. Developments included both, electron transfer studies [23] and proton transfer studies [24], as well as studies on electrocatalytic reactions like HER [25], nevertheless, works were predominantly based on theoretical and/or computational chemistry. Importantly, the mentioned works did not focus on the preexponential frequency factor of electrocatalytic reactions, which is essential for understanding interfacial dynamics intermediate/product formation.

From Equation (4), it seems that the preexponential factor, besides partial orders of the reaction and the coverage by intermediates, which are understood as classical chemical effects, depends on the electron transfer rate constant. The electron transfer rate constant, for outer sphere reactions according to the semi-classical treatment of electron transfer, is defined as following (Equation (5)) [26,27]:

$$k_{\mathrm{et}} = \kappa_{\mathrm{el}} \Gamma_{\mathrm{n}} \nu_{\mathrm{n}} \exp\left(\frac{-\Delta G^*}{RT}\right) \tag{5}$$

where k_{et} - the electron transfer rate constant, ΔG^* - the standard free energy of activation when Galvani's potential difference is zero and, according to Marcus theory is only solvent dependent; κ_{el} - electron transfer coefficient ($\kappa_{\mathrm{el}} \leq 1$) refers to the probability of electron tunneling, which depends on the strength of the interaction between the reactant and the electrode; Γ_{n} - the nuclear tunneling factor ($\Gamma_{\mathrm{n}} \geq 1$) which corrects the electron transfer rate for reactants (protons) that react without completely overcoming the classical barrier; ν_{n} - the nuclear frequency factor that represents the frequency of energy barrier attempts and is generally associated with bond vibrations and solvent motions, which are relevant for the transformation of the reactant into the activated complex and the transformation of the activated complex into the product. As mentioned above, the model given by Equation (5) was initially proposed for outer sphere reactions, not for electrocatalytic reactions. However, it introduces a very interesting platform for understanding interfacial dynamics. The preexponential factor generally in electrochemistry was discussed in more detail relatively recently [28]. On the one hand, it is understood that if the interaction between the metal valence band and frontier orbital of adsorbate species is strong, then the electron transfer coefficient that refers to the probability of electron tunneling is equal one, and that should be the case for the most of relevant d-metals that are used as HER electrocatalysts. On the other hand, the nuclear tunneling factor is a parameter that can significantly differ amongst different d-metals. Proton tunneling has been discussed relatively thoroughly in the past. However, it was never considered essential for HER electrode kinetics or generally essential for rates of electrocatalytic reaction [29-32]. Rare are authors in the past that had intuition and understanding that preexponential factor should be investigated thoroughly [33] and that it can be related to the nature of electrode material, potential and reaction mechanism [34]. Some initial experimental results illustrated substantially divergent values for activation energies and preexponential factor in a case of HER on Pt when comparing the results of different research groups [35,36]. Interestingly, the results of high-temperature kinetic experiments in the case of oxygen reduction reaction (ORR) were very similar between the two leading research groups at that time, but the interpretation was essentially different. Namely, the enhancement of ORR at Pt alloyed by 3d-metals was coupled with an unexpected increase in activation energy [37]. One research group interpreted that as a consequence of reduced total coverage by adsorbed intermediate and/or blocking species [38], like in heterogeneous gas-phase catalysis [39]. In contrast, the other group interpreted that obtained coverage by adsorbed intermediate and/or blocking species becomes even higher [40,41]. Latter interpretation implicitly suggested the rate of ORR strongly depends on the preexponential frequency factor, however, due to some other contributor to the preexponential factor than the coverage with intermediates and/or blocking species. Based on this experimental results it was proposed that the eventual role of the preexponential factor is equally important as activation energy or even more important for electrocatalytic rates [42,43]. Finally, taking all this into consideration, systematic HER high-temperature electrochemistry experiments were conducted on a series of d-metals in acidic and alkaline media for the first time recently [44,45]. Results showed very interesting tendencies (Figure 2a): a) preexponential frequency factor strongly depends on the nature of the electrocatalytic material, b) for the most active metals for HER, activation energies have intermediate to high values and at the same time intermediate to high values of preexponential frequency factor c) preexponential frequency factors span over ten orders of magnitude suggesting that divergent behavior of metals should not be due to difference in coverage, d) slope of dependence E_{act} *vs*. log *A* has almost identical value in acidic and alkaline media and it is around 5.6-5.8 kJ mol^{-1}. Exact physical meaning for this slope remains unknown, but it seems that represents some kind of universal limitation, like compensation effect in heterogenous gas-phase catalysis [39]. Dependence shown in Figure 2a is first straightforward illustration of compensation effect in electrocatalysis and proof that preexponential frequency factor has to be considered very thoroughly to understand the nature of electrocatalytic activity.

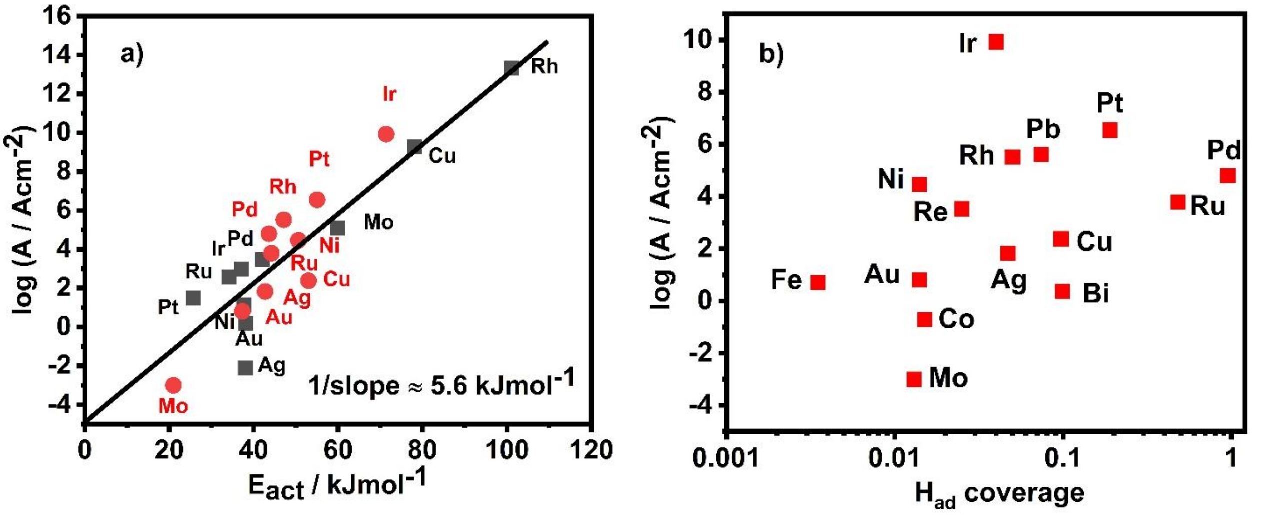

Figure 2. *Relation between preexponential frequency factor and some important inerfacial kinetic parameters, including: (a) activation energy in acidic electrolyte (0.1 M $HClO_4$) and alkaline electrolyte (0.1 M KOH). Data related to acidic electrolyte (red circles) are extracted from [44] under the terms and conditions of the Creative Commons Attribution 4.0 International License. Published by American Chemical Society (2022). Data related to the alkaline electrolyte (black rectangular) are extracted from [45] under the terms and conditions of the Creative Commons Attribution 4.0 International License. Published by Wiley (2021). (b) intermediate coverage in acidic electrolyte. Data are extracted from [46] under the terms and conditions of the Creative Commons Attribution 4.0 International License. Published by Wiley (2024).*

When comparing HER in acidic and alkaline media, Au, Ag, Ru and Pd are at approximately similar positions for both electrolytes, while the other six metals are distributed differently, which indicates that HER in alkaline media follows a completely different kind of mechanism, as discussed recently in more detail [46]. At the same time, when analyzing the relation between preexponential frequency factor and H_{ad} intermediate coverage (Figure 2b), we could say there is a certain relation between them, but it is not straightforward to be explanatory why preexponential frequency factor for different metals span over ten orders of magnitude, because H_{ad} intermediate coverage for the same metals span in the best case three orders of magnitude. The partial order of reaction also has a role (Equation (4), however, partial order of reaction is practically never greater than three because the effective collision of ions or molecules of the reactant with the electrocatalyst surface has to happen with specific orientation and specific frequency. Even if partial order of reaction would be three, still if concentrated electrolytes are utilized, the contribution of partial order of reaction to the total value of preexponential frequency factor or to the total value of exchange current suggests enhancement by order of magnitude or maximum two orders of magnitude, what cannot explain divergent behavior of various metals.

From Equation (5), it seems that the focus has to be on proton tunneling and on the nuclear frequency factor. The precondition for tunneling is that the vibrational quantum is much larger than the thermal quantum (*i.e.,* $h\nu_b >> k_bT$, where h -Planck constant, k_b - Boltzmann constant, T – temperature and ν_b - vibrational frequency). When we talk about proton tunneling, important to stress is that the probability of tunneling increases if a wave function of the initial state of proton significantly overlaps with a wave function of the final state of proton and that is the case for metals that are weakly binding hydrogen [47]. Interestingly, previously, it was predicted by the microkinetic analysis that to uplift the apex of the HER "volcano"-plot, M-H bond formation should be endergonic in reference to thermoneutral conditions $(\Delta G_{\mathrm{Had}})_{\theta=0}$ [7]. In that scenario, the tunneling distance is rather large and would require long-range polarization effects, including cooperative orientational displacements of solvent dipoles. On that basis, the general expectation is that metals with weak M-H bond will have large wave function overlap (Figure 3a), a high probability of tunneling and, therefore, a high preexponential frequency factor, but also, according to the compensation effect plot (Figure 2a), high activation energy. At the same time, if we observe potential energy curves (Figure 3b), it is possible that the metal that binds hydrogen more strongly, despite the downshift of the potential energy curve, has an equal or even higher activation barrier than the metal that binds hydrogen weakly, due to more emphasized curvature (*i.e.* more emphasized steepness) of the potential energy curve. This is an important observation because it provides a qualitative framework for decoupling activation energy and preexponential frequency factors. The exact nature of the compensation effect is not resolved; however, what links the collision process and activated complex is the shape of the potential barrier that depends on the shape of potential energy curves. Potential energy curves can be more or less steep, can be of a parabolic shape or Morse-type potential curve, *etc*. The essential question is: what controllable interfacial properties determine or impact the shape of potential curves and potential barrier? In the rate law, the symmetry factor is the parameter related to the shape and steepness of the potential barrier, although how to alter or tune the symmetry factor remains unknown. In other words, it remains unknown what interfacial descriptors and material descriptors are dictating the value of the symmetry factor.

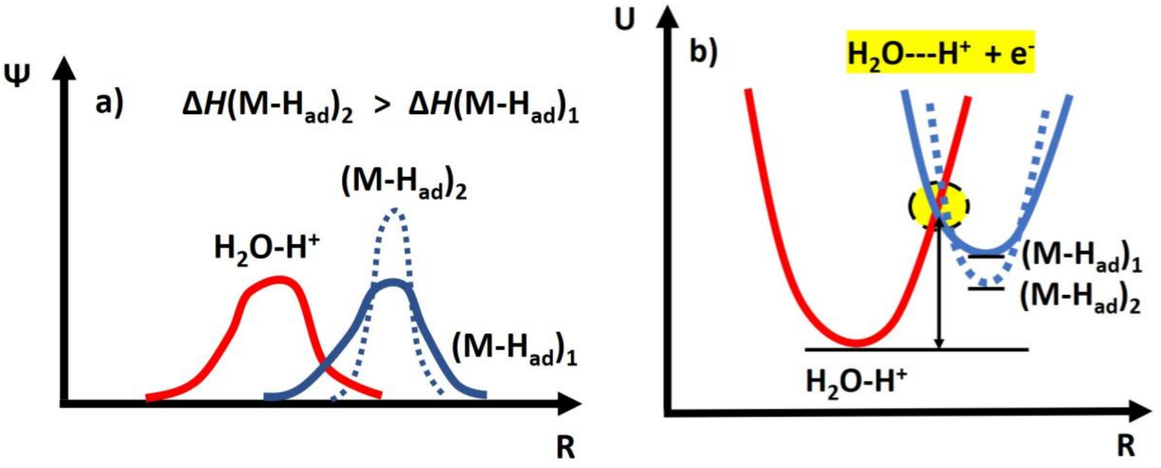

Figure 3. *Schematic representation of the overlap between wave function of proton in the electrolyte (*i.e. *proton bonded to water molecule) and wave functions for the two metals with different metal-hydrogen bond strength and coresponding potential energy diagram: (a) illustration of more significant overlap of wave function in case of metal that adsorbs hydrogen weakly (*i.e. *lower enthalpy change of M-H bond formation) (b) possible up-lifting of intersection point (*i.e. *barrier height) in a case of stronger M-H bonding, because of more emphasized curvature (*i.e. *more emphasized steepness) of potential energy curve*

As stated above, besides proton tunneling, it is important to address the nuclear frequency factor. The nuclear frequency factor is introduced for outer sphere reactions, meaning that it is related to bond vibrations and solvent motions. If we make an analogy with electrocatalytic reactions, the bond vibrations of adsorbed intermediates, besides solvent motions, are important. For example, an interesting observation is that characteristic vibrations of adsorbed intermediates and products in the case of chlorine evolution reaction are in the same narrow region like characteristic vibrations/phonons of many transition metal oxides that are investigated as electrocatalysts [48]. An analogy can be drawn for the metals, for which we cannot estimate characteristic lattice vibrations using vibrational spectroscopies, but they exist and could probably be accessed via inelastic neutron scattering. The question is, what are the consequences when oxide phonon or characteristic metal lattice vibrations, individual or collective, interact with characteristic vibration of electrocatalyst-intermediate bond (*i.e.,* M-H bond). If we observe the electrocatalyst surface (*i.e.,* M-M bond) and adsorbed intermediate/reactant (*i.e.,* M-H bond) as two interacting harmonic oscillators, question is rising: is it possible to reach certain resonance state that can contribute to bond cleavage/formation? Based on these premises and experimental insights, including characteristic vibrational frequency-based “volcano”-plot, it was proposed more than a decade ago that electrocatalysis is a resonance phenomenon [48]. Interestingly, while this point of view in electrocatalysis is practically completely disregarded, in heterogeneous thermal catalysis, several orders of magnitude reaction rate enhancement was relatively recently shown at externally imposed “resonance frequencies”[49]. Continuous variation of the catalyst binding energy over varying frequencies ($10^{-6} < f < 10^{11}$ s^{-1}) reveals a band of resonance frequencies [50]. It was postulated that catalytic surface resonance occurs when the frequency of the applied surface state switching waveform matches the natural frequency of the catalytic kinetics [49]. In the electrocatalysis, in the case of chlorine evolution reaction, it was shown that the characteristic vibrational frequency (*i.e.* phonon with highest Raman shift) of the best electrocatalyst (*i.e.* RuO_2) is almost identical to bond vibration of adsorbed intermediate in rate determining step (*i.e.* Cl-O) [48]. The difference between resonance phenomena observed in electrocatalysis [48] and resonance phenomena in thermal heterogeneous catalysis [50] is that enhancement of reaction rate by resonance in heterogeneous thermal catalysis is based on the application of external excitation fields, while enhancement of reaction rate by resonance, in electrocatalysis, should be a consequence of the design of electrocatalyst bulk structure and surface structure. Besides this, the enhancement of reaction rate by resonance in heterogeneous thermal catalysis was related mostly to minimizing activation energy, while the enhancement of reaction rate by resonance in electrocatalysis should be related to preexponential frequency factor [42] or the tuning of the interplay between preexponential frequency factor and activation energy [7].

On this trace, search for the answer on how to identify and what dictates nuclear frequency factor for electrocatalytic reactions (or what characteristic vibrations of intermediates, solvent and electrocatalyst surface are relevant for reaction rate control) should be one of the central research directions. In Figure 4 a schematic illustration of how different vibrations impact different elementary steps of HER is given. For the Volmer step, relevant are $H_2O\text{-}H^+$ vibrations in the solvation shell and lattice vibrations (Figure 4a); for the Heyrovsky step, relevant are $H_2O\text{-}H^+$ vibrations in solvation shell and M-H bond vibrations (Figure 4b); for Tafel step relevant are two neighboring M-H bond vibrations (Figure 4c). As we already can conclude from the values of Tafel slopes of elementary steps that activation energies of elementary steps have diverse values, similar can be concluded for the preexponential factors of elementary steps. The usual approach to electrode kinetics is to search for a rate-determining step (RDS) and then try to accelerate RDS. However, despite one of the elementary steps having the lowest rate, it is possible that some other step, especially one that precedes RDS, has a much lower preexponential frequency factor or much higher activation energy than RDS and that for significant acceleration of total electrocatalytic rate, it is necessary to optimize reaction mechanism beyond just accelerating RDS. Here, it would be very useful to analyze the temperature dependence of elementary steps of HER and, for every elementary step, to obtain preexponential frequency factor and activation energy. This kind of analysis cannot be found today in electrochemistry and electrocatalysis literature.

Resolving concepts analyzed above would generate important knowledge to fully understand how to enhance the preexponential frequency factor without necessarily increasing activation energy. That would be essential in further enhancing HER kinetics and minimizing or even circumventing the compensation effect [7,51]. Of course, it would be ideal if it is possible to simultaneously enlarge the preexponential frequency factor and reduce activation energy. Understanding the mechanism of destabilizing the solvation shell on that pathway would be important. If two reactants are within the distance of the van der Waals radius, then a relatively small expenditure of energy to overcome the repulsive forces would lead to a significant increase in the tunneling probability. That essentially requires a very high concertation of protons in the double layer, if possibly already at HER reversible potential.

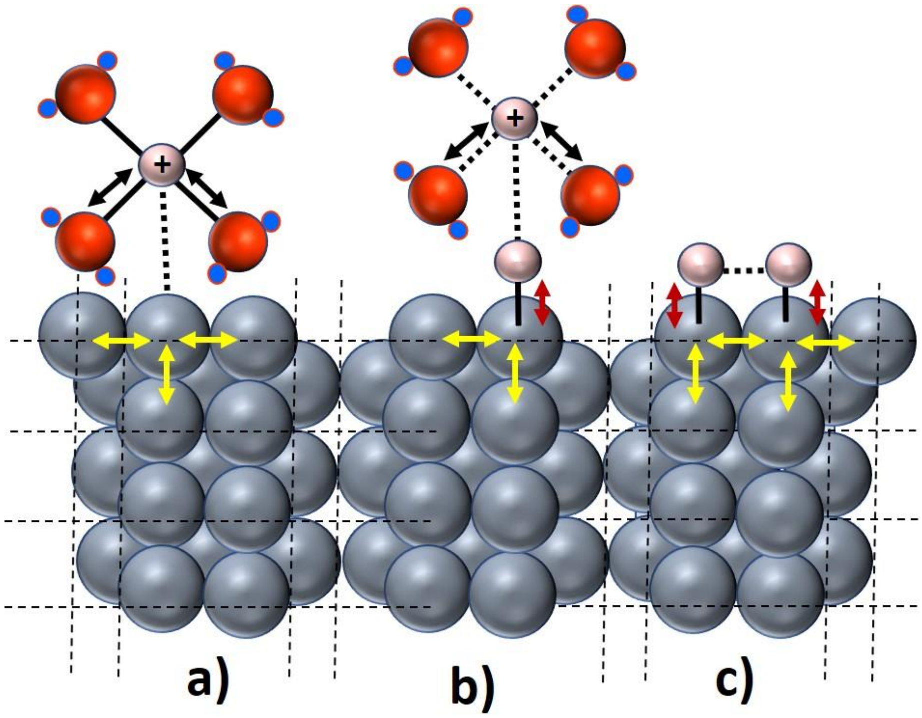

Figure 4. *Schematic illustration how different vibrations impact different elementary steps of HER (a) for Volmer step relevant are* H_2O*-*H^+ *vibrations in solvation shell (black arrows) and lattice vibrations (yellow arrows) (b) for Heyrovsky step relevant are* H_2O*-*H^+ *vibrations in solvation shell (black arrows) and M-H bond vibrations (red arrows) (c) for Tafel step relevant are two neighboring M-H bond vibrations (red arrows). Color code: metal surface—grey, oxygen—red, hydrogen from blue—red, proton and adsorbed proton—pale red*

Besides high concentration of protons in the double layer, probably there is preferential interfacial water ice-like structure that will make the destabilization of the solvation shell more probable [52]. Behavior and the exact role of water in dynamic processes at electrocatalytic interfaces remains elusive. However, there is no doubt that it contributes to both the activation and collision processes or, in other words, to activation energy and to preexponential frequency factors, respectively. Nevertheless, it seems that for the enhancement of HER kinetics, it is required to have: 1) M-H bonding weaker than the apex of a conventional "volcano", 2) a high concentration of protons in the double layer so that the solvation shells around protons are getting destabilized. This can assure that although M-H bonding is not strong, coverage with adsorbed intermediates at the electrocatalyst surface will be high, facilitating a recombination reaction. This strategy requires further understanding of preexponential frequency factor or activation entropy for electrocatalytic reactions, and despite some new insights being offered [7,17,28,42,51] and some new important data being generated [15,36,44-46,52-55], it is still an almost completely unexplored area.

Relevant structure-activity relations as a cornerstone of rational electrocatalyst design

As indicated above, the mechanistic analysis could not appear sufficiently practical from the point of view of material science. Therefore, appropriate structure-activity relations are essential for rational catalyst design as the ultimate tool to sufficiently accelerate key electrocatalytic reactions to be utilized efficiently in energy conversion devices and systems. The fact is that experimental data that could resolve essential questions listed in the introduction section are lacking, but they could be generated in the next 5-7 years systematically. Despite this, analysis on a conceptual level is the essential initial step toward in-depth comprehension of electrocatalytic mechanisms. Being aware that some of the concepts are challenging to be fully absorbed by the targeted reader (*e.g.,* links between electrode kinetics and quantum mechanics), in this sub-section, an effort is made to expand the discussion on how future experimental studies could validate the proposed models and concepts as well as to provide more explicit connections between the proposed theoretical insights and their practical implications for electrocatalytic performance. To simplify the analysis, for the purpose of better clarity, a table summarizing the key unresolved questions, expectations and proposed experimental technique/methodology is shown (Table 1).

Most of the essential issues mentioned in Table 1 are already discussed and are all related to intrinsic electrocatalytic properties of materials and/or electrified interface. Questions 1-7 are related to activation energy; questions 8-14 are related to preexponential frequency factor; questions 15 and 16 are related to the interplay between activation energy and preexponential factor. The one that we did not mention in the text, which has been routinely avoided for years, is the challenge of the effective surface area [57,58]. Namely, when we analyze the intrinsic activity of gas-evolving reactions like HER, it is not relevant total number of active sites at open circuit conditions but the number of available active sites at working conditions (*i.e.,* total number of active sites minus an average number of active sites covered with gas-bubbles at defined overpotential). Methodologies for the effective surface area were proposed more than a decade ago [57,58], and some were relatively recent [59]. By disregarding effective surface area, we obtain "intrinsic activity" that is inaccurate, and we are actually underestimating the activity of electrocatalytic material. So, if we attend to establish relevant structure-activity relations, the essential step is to adequately estimate intrinsic electrocatalytic activity. Further, it is essential to identify interfacial properties/descriptors that can be analogue to the properties used to describe heuristic model (*e.g.* quantities in scheme of activation process in Figure 1). Identified interfacial descriptors should be: 1) measurable, 2) if possible related to some parameter in the rate law and 3) related to some material property/descriptor (*i.e.,* property of electrode or electrolyte) that can be tuned. Considering that material descriptors is what material scientist can tune it would be very important that electrocatalytic investigations are done on single crystals, because majority of kinetic parameters listed in the Table 1 (or in the rate law) will be well defined on single crystal facets, including those properties that are responsible for interfacial dynamics. In this context, it is worth to mention that spatio-temporal oscillations with characteristic visual patterns recorded by photoemission electron microscopy (PEEM) were only visible on single crystal facets [60]. Of course, this should not exclude studies on polycrystalline materials and/or real high-surface-area catalysts because intrinsic kinetic properties of polycrystalline materials (*e.g.,* Tafel slope) can be not only different but also superior in comparison to any single crystal constituent [61].

***Table. 1** Summary of the key unresolved questions, expectations and proposed experimental techniques/ /methodologies . Used abreviations for quantitites and techniques are explained in the text related to the rate law (see Eqs (4) and (5)), except those that are well known in physico-chemical and electrochemistry literature. Questions 1-7 are related to activation energy; questions 8-14 are related to preexponential frequency factor; questions 15 and 16 are related to interplay between activation energy and preexponential factor and quesiton 17 is related to methodological approach relevant for evaluation of intrinsic electrocatalytic activity*

	Question	Expectation	Experimental approach
1	Shape of relation log j_0 *vs.* ΔH_{Had}	“Volcano”-type or linear or…	Kelvin probe (KP) [10]
2	ΔH_{Had} *vs.* ΔG_{Had} or role of ΔS_{ad}	Significant impact of ΔS_{Had} on activity trends	High temperature hydrodynamic LSV [44,46]
3	BEP relative (ΔH_{Had} *vs.* E_{act}) valid or no	If not, that suggests role of solvent for E_{act}	KP [10] and high T hydrodynamic LSV [44]
4	$\Delta H_{\mathrm{H_2Oad}}$ trends for various metals	Strongly metal-dependent, strongly impacts E_{act}	KP [10] and DFT [56]
5	Values and nature of β	Strongly metal-dependent	Hydrodynamic LSV
6	Values and nature of γ	Should be the same for different metals?	KP [10] and high *T* hydrodynamic LSV [44]
7	Values and nature of r	Strongly metal-dependent	Hydrodynamic LSV
8	Nature of partial orders f	Strongly metal-dependent	Hydrodynamic LSV
9	Potential dependent θ_{Had}	Strongly metal-dependent	Hydrodynamic LSV
10	Intermediate vibrations	Metal dependent	Vibrational spectroscopy (*e.g.* Raman)
11	Lattice vibrations	Strongly metal/oxide-dependent	Vib. spectr. or inelastic neutron scattering (INS)
12	Solvent vibrations	Probably metal-dependent	THz vibrational spectroscopy
13	Nuclear tunneling factor	metal-dependent	kinetic isotope separation factor
14	Nuclear frequency factor	metal-dependent	?
15	Log *A* and E_{act} of elementary steps	strongly metal-dependent	High *T* hydrodynamic LSV
16	How to overcome “volcano”-apex	possible *via* interplay of elementary rate constants	hydrodynamic LSV [7,46]
17	Effective surface area	material and morphology-dependent	CV + SECM, [57] or EIS ?

An important example is given schematically in Figure 5, where activation energy is “dissected” into four interfacial descriptors related to known material properties. From the heuristic model (see Figure 1 and Eqs. (4) and (5), we concluded that for efficient HER activation, it is essential to have optimal M-H bond strength (*i.e.,* weaker than at thermoneutral binding conditions) and high interfacial concentration of protons with destabilized solvation shells. This suggests four interfacial descriptors: M-H bond strength, M-H_2O bond strength, H^+-OH_2 bond strength and E_{pzc}. While M-H bond strength can be related to d-band center (ε_d) and E_{pzc} can be related to work function (Φ_m), the other two interfacial descriptors (*i.e.,* M-H_2O bond strength and H^+-OH_2 bond strength) cannot be in a straightforward manner related to some material properties.

Even in the case of the d-band center, it can be questioned is it really a reliable material descriptor for M-H bond strength. According to the Newns-Anderson model [62], M-H adsorption energy is related to a minimum of three parameters: the bandwidth, the coupling strength between the electrocatalyst surface and the adsorbed proton, and the energy difference between the d-band center and the protons valence orbital. Only when the first two parameters are constant for various metals inside a homologous group of metals (*e.g.,* 3d-metals) does the d-band center correlate approximately to the adsorption energy in a linear fashion. So, for the HER activation process, we could say that we identified relevant interfacial descriptors, but we still need to dedicate substantial time to discovering relevant material descriptors. This is a good illustration that, despite some widely accepted views that are oversimplifying reality, we have to make a thorough effort to understand the nature of electrocatalytic activity.

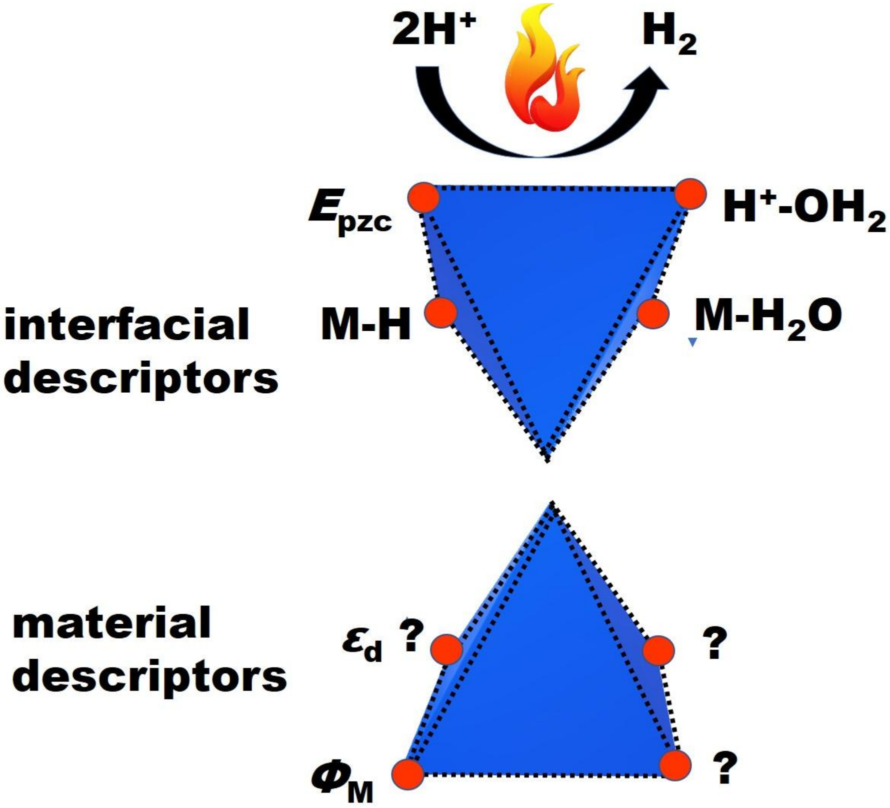

Figure 5. *Relation between interfacial descriptors and material descriptors for the case of HER activation process. While M-H bond strength can be related to d-band center (*ε_d*) and* E_{pzc} *can be related to work function (*Φ_m*), the other two interfacial descriptors (*i.e. *M-*H_2O *bond strength and* H^+*-*OH_2 *bond strength) cannot be in straightforward manner related to some material properties*

In the end, it can be said that some of the listed important scientific questions (see Table 1) are close to being answered, while some will require several years. For example, close to realization during 2025 will be systematic experimental measurements of M-H bond strengths for various relevant metals using Kelvin probe, as well as systematic trends for partial orders extracted from electrochemical measurements. At the same time, some other scientific questions listed in Table 1 will require new specific experiments in the design process. Proper, straightforward and sufficiently convincing experimental proofs will require time because systematic datasets with electrochemical or spectro-electrochemical data, which are the building block for relevant analysis after all these years, are practically not available in the existing literature.

Conclusions

Today, electrocatalysis research has almost entirely gone toward materials science, looking for new, more active and stable electrocatalysts, but in most cases, without clear guidelines, design principles and new mechanical insights or conceptual improvements. In this work, an important discussion was conducted on achieving a breakthrough in electrocatalysis of water splitting and electrocatalysis in general. The complexity of electrocatalysis was pointed out and why hydrogen evolution in acidic electrolytes was identified as a necessary model reaction. Furthermore, the analysis focused on catalytic descriptors and how to connect them with the rate law and the activation process to establish a new, more relevant type of structure-activity relationship. It is recognized that the dynamic aspects of the electrode/electrolyte phase boundary are of special importance, which requires an in-depth understanding of the activation process and an in-depth comprehension of collision processes between reactants, intermediates and active sites at the catalyst surface. Understanding contributors to the activation energy, contributors to the preexponential frequency factor and their mutual interaction was of special importance. It is important to emphasize that fundamentally important unknowns in the understanding of electrocatalysis have been identified, and aspects that need to be investigated in the future have been highlighted in order to obtain a comprehensive dynamic picture of electrocatalytic processes. In the long run, this appears to be the only reasonable path towards rational electrocatalyst design.

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