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ABSTRACT

Hydrogen evolution reaction (HER) by splitting water is a key technology toward a clean energy society, where Pt-based catalysts were long known to have the highest activity under acidic electrochemical conditions but suffer from high cost and poor stability. Here, we overview the current status of Pt-catalyzed HER from a theoretical perspective, focusing on the methodology development of electrochemistry simulation, catalytic mechanism, and catalyst stability. Recent developments in theoretical methods for studying electrochemistry are introduced, elaborating on how they describe solid–liquid interface reactions under electrochemical potentials. The HER mechanism, the reaction kinetics, and the reaction sites on Pt are then summarized, which provides an atomic-level picture of Pt catalyst surface dynamics under reaction conditions. Finally, state-of-the-art experimental solutions to improve catalyst stability are also introduced, which illustrates the significance of fundamental understandings in the new catalyst design.

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I. INTRODUCTION

The past century has witnessed a surge in energy demand, predicted to approach 26 TW in 2040 around the world.¹ Despite many drawbacks of fossils, particularly their huge damage to climate, it is still the main energy source for economic and technical reasons, and the seek for a clean, efficient alternative becomes never been more urgent in recent years. Among the potential energy carriers, hydrogen molecule (H₂) is the one with outstanding advantages attracting much attention for its highest energy density and clean products while combusting.² On the other hand, to date, H₂ is unfortunately mainly produced by the steam reforming process in the industry where the carbon source (CO) still comes from coal-based raw materials.^{2,3} It is therefore highly desirable to realize the massive production of H₂ using the clean route, such as the electrochemical water splitting, in which the half-cell hydrogen evolution reaction (HER, H⁺ + e⁻ $\rightarrow 1/2$ H₂)^{2,4} occurring on the cathode catalysts can generate hydrogen from water in a green way.^{5,6} The key challenge in the field is to find an active, abundant, and stable cathode catalyst that is capable of massive H_2 production.⁷ This Review aims to review the current status of fundamental research on Pt-based HER catalysts.

Pt-based catalysts were long identified as the most efficient catalyst for HER under acidic conditions, achieving the highest exchange current density of ~1 mA cm⁻² at room temperature with normal rotating electrode (RDE) techniques.^{8,9} The exchange current density increases markedly with efficient mass transport.^{10,11} In addition, HER catalyzed by Pt-based catalysts has a diminished onset overpotential, excellent kinetics,¹² and low Tafel slope.¹³ Nevertheless, the high cost, poor earth-abundant, and low stability of Pt catalysts strongly limit the wide applications, in practice.^{6,14} For example, after 1000 cycles of cyclic voltammetry (CV) between +0.4 and -0.15 V vs SHE in an acidic environment, the state-of-the-art commercial Pt/C catalyst has a loss of 19% of the current density at

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the overpotential of 0.05 V and the average particle size increases from 4.2 to 5.5 nm in high-resolution transmission electron microscopy (HRTEM) images.¹⁵ Furthermore, serious aggregation occurs as the potential becomes lower,¹⁶ suggesting that the high H coverage may induce high Pt mobility by weakening Pt–C support interaction. In addition, the direct dissolution of small Pt nanoparticles (<0.4 nm) could also trigger the Ostwald ripening for the growth of Pt nanoparticles and leads to the metal precipitate in the membrane of the proton exchange membrane water electrolyzer.^{17–19} Therefore, it is a must not only to significantly reduce the expensive Pt content in cathode catalysts but also to improve markedly the long-term catalyst stability. To this goal, huge fundamental efforts have been devoted to understanding the HER mechanism and the active site dynamics of Pt catalysts.

It is now clear that HER consists of three elementary reactions.¹³ First, a proton in solution combines with an electron on the cathode to generate an adsorbed H* species on the metal surface, the so-called Volmer reaction (H⁺ + M + e⁻ \rightarrow M-H^{*}). Then, H₂ can be generated via two routes. One is the Heyrovsky reaction where H^* reacts with another H^+ in solution and e^- of the electrode to release H_2 (M-H^{*} + H⁺ + e⁻ \rightarrow M + H₂). The other is the Tafel reaction where two surface H* atoms couple to become H₂ (2M-H* \rightarrow 2M + H₂). According to the Butler-Volmer equation, Tafel slopes should be 120 mV/dec (half-electron transfer), 40 mV/dec (oneand-half electron transfer), and 30 mV/dec (two-electron transfer) if the rate-determining step is the Volmer reaction, Heyrovsky reaction, and Tafel reaction, respectively.²⁰ Since the Tafel plot can be facilely obtained from linear sweep voltammetry (LSV) curves in experiments, the HER on metals has been the model electrochemical reaction extensively studied in history to verify the electrochemical reaction theory. Interestingly, the measured Tafel slope for HER on Pt catalysts varies largely from experiment to experiment, which is often not at the characteristic values (120, 60, 40, and 30 mV/dec), particularly on the single crystal (111) surface where the measured Tafel slope is in a wide range of 37–300 mV/dec.^{9,21–24} Apparently, due to the too-fast kinetics of HER on Pt and the interference of aqueous solution and Pt surface structure variation, it is difficult to measure the accurate kinetics data of HER on Pt by experiment; particularly, the reaction barrier and the pre-exponential factors of elementary steps are generally unknown.

On the other hand, the past two decades have seen the active development of theoretical methods for investigating electrochemical reactions. These methods generally rely on density functional theory (DFT) calculations and further consider the effects due to the solution and the external electrochemical potential at a certain level of approximations.⁷ With these approximations, delicate effects caused by the complex structural dynamics of the aqueous solution and the electrolyte under electrochemical potentials can be quantified properly, and thus, the theory is capable of providing important insights into the HER kinetics, mechanism, and surface reconstructing under electrochemical potentials.²⁵⁻²⁷ The relatively simple reaction network of HER on Pt surfaces is thus an ideal testing ground for accurate and low-cost electrochemistry simulations.

This Review serves to summarize the recent theoretical and experimental advances in Pt-catalyzed HER. This Review is organized as follows. Section II describes the key methodology developed to model electrochemistry. This follows the theoretical efforts in the

past decades to clarify the active site of HER on Pt-based catalysts in Sec. III. In Sec. IV, we review the representative experimental means to improve the stability of Pt catalysts. At last, we provide our perspective on the future research of HER on Pt-catalysts.

II. METHODOLOGY FOR MODELING ELECTROCHEMISTRY

Electrochemical reactions occur at the solid–liquid interface where the external potential can be forced to keep constant with the help of a potentiostat device. The intimate coupling between the solid–liquid interface reaction and the electrochemical potential creates profound, complex, potential-dependent phenomena in electrochemical reaction systems. From a fundamental point of view, revealing atomic structures of the interface under electrochemical conditions might be the first step toward understanding electrochemical reactions, which are however difficult to achieve not only in experiments but also in theory.

To properly account for electrochemical reactions, one, therefore, has to consider both the solid-liquid interface and the electrochemical potential accurately in one theoretical framework.²⁸ While quantum mechanics (QM) calculations based on DFT can be routinely utilized for solid surface calculations using a periodic slab model,^{29,30} it is not straightforward to incorporate the solvation effect and the electrochemical potential effect within the current QM calculation framework. In principle, brute-force molecular dynamics calculations based on QM calculations, that is, by adding a number of water and electrolyte molecules on top of solid surfaces, offer a possible solution for describing the dynamic nature of the solid-liquid interface, but the huge computational cost associated with QM calculations prevents such applications in a large-scale, not even mentioning the intrinsic difficulty in MD simulations in capturing reactions, the rare events. Furthermore, the constant potential condition applied in the experiment implies the grand canonical ensemble of the electron in the system, which can flow in and out at a constant chemical potential. The variable number of electrons in QM calculations thus raises another technique challenge, which could introduce huge instability of charge density in the selfconsistent loop and thus greatly slow the energy convergence. In the following, we overview the current methodology to account for electrochemical conditions.

A. Methods to describe solid-solution interface

The solvent not only controls the molecular adsorption/desorption equilibrium but also may directly take part in reactions at the interface, as most encountered in the protoncoupled electron transfer (PCET) reactions. For HER on metals, both the Volmer and Heyrovsky steps involve the PCET, and thus, a reliable description of the electrolyte solution is essential for determining the activation energy and understanding electrochemical reactions.

Before the advent of a more sophisticated solvation approach, a static ice-like hexagonal water bilayer model was adopted to account for the possible solvation effect, which is certainly much more convenient than long-time MD simulations. The ice-bilayer approximation is based on the surface science evidence,^{31–33} which 09 August 2024 07:40:23

shows that the water hexagonal bilayer can form on Pt(111) surface below 150 K in ultrahigh vacuum, a stable configuration also confirmed by DFT calculations.³² In such a bilayer, there are two alternating types of water (one close-packed layer of hexagonal ice), which can interact with the metal surface either using H or using O. The former is known as the H-down bilayer, and the latter is the H-up bilayer, the exact nature of the bilayer depending on the metal surfaces-for Pt(111), the H-down water bilayer is thermodynamically more stable than the H-up water bilayer under moderate acidic HER conditions.^{34,35} In the structure, one type of water molecule is parallel to the Pt(111) surface and bonds to Pt atoms from the ontop sites, and the other type is perpendicular to the metal surface, as depicted in Figs. 1(a) and 1(b). While the bilayer ice model is a rather crude approximation to water on Pt at ambient conditions, it does capture the essential physics of water-metal interaction. For example, the work function of Pt(111) drops markedly from ~5.9 eV in vacuum to ~4.9 eV in solution,³⁶ which can be understood by the strong electrostatic screening of the H-down dipole. A single water bilayer even yields the capacitance of the double layer that is consistent with the experimental data³⁷ (the capacitance is determined by the curvature of the parabolic relation between the integral free energy of the double layer and the electrode potential). The dominance of the H-down configuration also provides a direct picture for how protons transfer from the solution to the surface and react with surface H in the Heyrovsky step (further discussed in Sec. III). However, direct ab initio molecular dynamics (AIMD) simulations at the room temperature by Gross and his co-workers³⁸



FIG. 1. Typical model for the metal–water interfaces (a) and (b) H-down water bilayer. Reprinted with permission from K. Tonigold and A. Gross, J. Comput. Chem. **33**(6), 695 (2012). Copyright 2012, John Wiley and Sons. (c) and (d) Snapshot of the disorder interface in AIMD after 11 ps. Adapted with permission from T. Roman and A. Gross, Catal. Today **202**, 183 (2013). Copyright 2012 Elsevier. (e) The interface of Pt(111)/H₂O at the potential of zero charge. The blue curve shows a charge redistribution along the z coordinate. Reproduced with permission from Le *et al.*, Sci. Adv. **6**(41), eabb1219 (2020). Copyright 2020 with American Association for the Advancement of Science.

demonstrate that the water layers on the Pt surface, in fact, deviate, to a large extent, from the ideal bilayer model with pronounced H-up water molecules. As can be seen in Figs. 1(c) and 1(d), the snapshot of the H₂O/Pt(111) interface after 11 ps shows the disordered H₂O interface layer. A similar picture was then observed by Cheng and his co-workers in their DFT-MD simulations.^{40,41} Therein, a number of H-up waters are found to chemically adsorb on the metal, and the charge moving from the water layer to the metal surface can induce the interface dipole potential [Fig. 1(e)]. It should be mentioned that these MD simulations were performed at the potential of zero charge (PZC), i.e., 0.2-0.3 V vs SHE.⁴¹ Hence, the H-down waters are expected to be dominant at the interface under HER conditions (0 V vs SHE). Li et al.⁴² have recently demonstrated the importance of the H-bond networks of water in HER using AIMD. They found that the less connectivity of H-bond networks in alkaline than acid solution increases H transfer barriers, which is the principal reason for the slow HER kinetics in alkaline conditions.

For the investigation of interface chemical reactions, both the bilayer model using static calculations and MD simulations of explicit multiple water layers meet great difficulties to get converged reaction energetics since the results could be highly sensitive to the number of water molecules and their configurations in the model. In particular, first principles MD simulations with a few picoseconds time-scale are generally far not enough for describing the change of solvation shell during reactions. It thus asks for better solvation models to treat the solid–liquid interface.

In fact, implicit solvation models have long been utilized for molecular systems, generally known as the polarizable continuum model (PCM) based on the generalized Born model to describe the long-range electrostatic interaction between solution and solute. PCM models typically have several adjustable parameters, such as the solvation atomic radius and the atomic charge, which can be parameterized using the solvation data of molecules from experiments. However, the quantitative experimental data of solid surface solvation are generally not available, which delays the development of analogous periodic implicit solvation models for the solid-liquid interface. From ~2008, several groups^{21,25,28,43-45} developed their own versions of the periodic implicit solvation model by solving the (modified) Poisson-Boltzmann (MPB) equation where the DFT charge density ρ and the dielectric distribution function $\varepsilon(r)$ are taken as the input following the work of Fattebert and Gygi.46 The CM-MPB version, as shown in Eqs. (1)-(3), developed by our group considers explicitly the counter charge (in electrolytes) to distribute in a manner of MPB equation [the right-hand second term in Eq. (1)]. Importantly, the approach can be utilized to obtain a reasonable electrochemical potential using Eq. (3) via a doublereference approach: first, referencing the Fermi level $(\Psi_{\rm F})$ to the potential level of implicit solution (Ψ_{ref}) and then comparing to the absolute vacuum level of SHE that is 4.44-4.85 V⁴⁷ from experiments (typically, the average value of 4.6 V was used).^{21,25,48,49} It might also be mentioned that the value of 4.44 V⁵⁰ appears to be more accepted recently,²

$$\nabla \cdot (\varepsilon(r)\nabla(\Psi)) = -4\pi\rho + 8\pi zec_b \frac{\sinh\left(\frac{ze\Psi}{kT}\right)}{1 - \nu + \nu \cosh\left(\frac{ze\Psi}{kT}\right)}, \quad (1)$$

$$\varepsilon(\rho(r)) = 1 + \frac{\varepsilon_{\infty} - 1}{2} \left[1 + \frac{1 - (\rho(r)/\rho_0)^{2\beta}}{1 + (\rho(r)/\rho_0)^{2\beta}} \right],$$
(2)

$$U_{cal}^{q} = (\Psi_{ref} - \Psi_{F}) - 4.6.$$
 (3)

In the above equations, v is a parameter related to the electrolyte and satisfies $v = 2a^{3}c_{b}$ (a is the effective ion size and c_{b} is the bulk concentration of electrolyte); the smooth dielectric function $\varepsilon(r)^{46}$ is to provide a solvation environment of the continuum dielectric medium. ρ_0 and β are the two key parameters, where ρ_0 sets the threshold of electron density $\rho(r)$ and, hence, adjusts the cavity size and β adjusts the smoothness of ε when changes from 1 to ε_{∞} (78.36 for water in room temperature). The MPB equation can be solved facilely during the QM self-consistent loop as long as $\varepsilon(r)$ is fixed. The implicit solvation model is known to fail when strong steric and directional polarization occurs (such as reactions with solvation proton), and thus, typically, a few extra explicit water molecules are required to account for the local polarization.⁵² At the present time, many modern periodic DFT packages have the MPB solver (SIESTA, VASPsol, JDFTx, and GPAW), and thus, implicit solvation is routinely utilized in recent literature.

With the advent of machine learning (ML) potentials, explicit solvation via long-time MD simulation becomes feasible in recent years. For example, the free energy barrier of solid-liquid interface reactions can be facilely determined by combining the global neural network (G-NN) potential developed by our group with enhanced MD techniques (such as umbrella sampling).^{53,} ⁴ While such explicit solvation calculations can provide important insights into the effects due to the solvent and electrolytes, there are still severe limitations in ML potential calculations. In particular, the current ML potentials lack electronic structure information, especially the charge density. It is thus not possible to read out readily the electrochemical potential from the calculation and also to polarize the interface under a preset potential. The electrochemical potential can be obtained by post-DFT calculations based on the MD trajectory from ML simulations.

B. Methods to control electrochemical potential

The electrochemical potential is the key variable controlled by the experiment to change the reaction rate. Compared to real experiments where the area of the interface is essentially infinite and a single charge transfer of reaction does not change the potential, theoretical simulations are limited by the small-sized supercells where the occurrence of reaction will inevitably lead to the change of electrochemical potential, no matter with or without the implicit/explicit solvation models. The thus-computed reaction kinetics are not accurate, where the initial (IS), transition (TS), and final states (FSs) correspond to different electrochemical potentials. Therefore, to model electrochemical reactions at a given electrochemical potential on a given structure, a variable surface charge model to keep the potential constant as the structure changes needs to be developed.

The double-reference method proposed by Neurock and coworkers^{55,56} with explicit solvation and later utilized in the CM-MPB method as described in Eqs. (1)-(3) is the common approach to determine the electrochemical potential. Basically, this method assumes that the solution level is constant with respect to surface charging, where the counter-charge distribution will strongly affect the solution level in calculations. In periodic slab calculations, the counter-charges due to surface charging are automatically added for charge neutralization in a manner of homogeneous background. The homogeneous background charge may, however, introduce wrong physics occasionally: unrealistic charges will move to the vacuum from the electrode⁵⁷ when the potential in the middle of the vacuum layer is lower than the work function of the metal; the added charge tends to delocalize on the electrode, making the charged defect calculations unlikely.^{58,59} Certainly, it is physically more appropriate to distribute the counter charge following the MPB equation, as implemented by our group using the CM-MPB method and recently in the solvated jellium (SJ) method,^{44,60} where the counter-charge is distributed in implicit solution positions, the same as real anions/cations nearby the surface. The Debye lengths of the electrochemical double layer can be utilized to speed up the distribution of the countercharge with finite supercell sizes.⁶⁰

Knowing the electrochemical potential of a given state, it further demands the alignment of potential between different reaction intermediate states, particularly the IS and the TS, to determine the reaction barrier of an electrochemical reaction. Early calculations using the ice-like bilayer model have shown a rather linear relationship between energy changes and potential changes, which validates simple extrapolation methods either by using differentsized unit cells with the different number of excess hydrogen atoms,^{37,48,61} as seen in Figs. 2(a) and 2(b), or by using the chargeextrapolation method.^{62,63} Figures 2(a) and 2(b) represent, respectively, the reaction energy ΔE and activation energy E_a of some common charge transfer reactions against the potential change $\Delta \Phi$ in different cell sizes and their extrapolation to the infinite cell size where $\Delta \Phi = 0$. A clear linear relation can be seen in Figs. 2(a) and 2(b) except scatter in the situation of the Volmer reaction at 1 ML H*. Such scatter can be attributed to the slightly different H binding environment in different cell sizes.⁶² To avoid repeating calculations at different cell sizes in the cell-extrapolation scheme, the charge-extrapolation method was established by Chan et al.,^{62,63} who assumed that (i) reaction energies between two states at a constant potential Φ_1 can be partitioned into a chemical part and an electrostatic part and (ii) the electrostatic part can be treated as basic capacitor energy, as shown in the following equation:

$$E_{2}(\Phi_{1}) - E_{1}(\Phi_{1}) = E_{2}(\Phi_{2}) - E_{1}(\Phi_{1}) + \frac{(q_{2} - q_{1})(\Phi_{2} - \Phi_{1})}{2}.$$
(4)

In the above equation, E, Φ , and q denote the DFT energy, DFT work function, and interfacial charge, respectively. It should be mentioned that the linearity between ΔE (Φ) = E_2 (Φ) – E_1 (Φ) and Φ in Eq. (4) can be perturbed when the interfacial charge Δq changes nonlinearity that can be caused by many factors, such as water structure variation between the IS and FS (or TS), the lateral interactions of adsorbates and adsorbates, and strong hybridization between atoms.^{63,64} According to the above equation, the energy change at constant potential (work function) Φ_1 can be calculated by the value of the energies, work functions, and interfacial charges of states 1 and 2. The exact number of charges at the interface can be determined from DFT using charge-partition methods, such as Bader method,^{65,66} or, more generally, from the explicitly added charges in the CM-MPB framework. Both approaches can be further utilized to deduce the important kinetics quantity, the



FIG. 2. (a) and (b) Extrapolation scheme applied to the typical proton transfer reactions for both reaction energies and activation energies. Reprinted with permission from K. Chan and J. K. Nørskov, J. Phys. Chem. Lett. **6**(14), 2663 (2015) (part of the data are taken from Refs. 37 and 61). Copyright 2015 American Chemical Society. (c) The fitting plot of the potential (U) and the free energy (G) vs the surface charge density σ changed in the CM-MPB scheme of a 1 ML H covered Pt(111) surface. Adapted with permission from Fang *et al.*, J. Phys. Chem. C **118**(7), 3629 (2014). Copyright 2014 American Chemical Society.

charge transfer coefficient α ($q_2 - q_1$ between states 2 and 1 at a constant potential).

In the CM-MPB framework developed by our group, the added charge to the supercell accumulates on the surface (measured by the surface charge density σ) and thus changes the work function.

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The charge transfer coefficient α can then be computed using the following equation: 67

$$\alpha = \frac{SC_d \Delta \Phi}{\theta F},\tag{5}$$

where θ , *F*, and *S* are the surface coverage, Faraday constant, and unit area of one surface atom, respectively. $\Delta \Phi$ is the relative potential change from state 1 to state 2. The differential capacitance C_d can be obtained by a linear fitting between the charge density σ and the electrode potential U using the following equation:

$$C_{\rm d} = \frac{\partial \sigma}{\partial U}.$$
 (6)

A typical plot of free energy (*G*) and potential (*U*) vs surface charge density is illustrated in Fig. 2(c), Pt(111) covered with 1 ML H^{*}. As shown, both C_d and *G* have a good linear relation to the surface charge density, which validates the accuracy of the charge-extrapolation method for metal surfaces and further leads to the classification of electrochemical reactions.⁶⁷ Recently, Chan *et al.*^{64,68} have developed a force-based method to acquire the electron transfer coefficient α . The charge difference between two states, such as IS and TS, can be converted to the first derivatives of atom-centered forces with respect to the applied field.

While the above conventional canonical DFT calculations with *a posteriori* grand canonical (GC) corrections are the most popular approach, direct GC calculations were also attempted in the past few decades, where the chemical potential of the electrons instead of the number of electrons is fixed during DFT calculations. Melander and his co-workers⁶⁹ and Bonnet *et al.*⁷⁰ developed GC-DFT approaches that can automatically adjust the surface charge to satisfy the constant-potential constraint. Similarly, the continuum description of the solvent and ions using the MPB equation can be applied to accurately control the potential. These methods, while being elegant in methodology, are still less utilized in the community, which could be due to the slower convergence of electronic structure.

III. HER ACTIVITY OF PT CATALYST

A. Experimental kinetics data

Although it was long established that Pt catalysts perform the best in HER, there are still many debates on the reaction kinetics and its dependence on the catalyst structure. Because of the ultrafast HER kinetics, early studies concluded that the HER activity is rather insensitive to synthetic methods of Pt catalysts (the surface structure of Pt).^{71–73} However, by making the mass transport rate comparable to the HER kinetics, more recent experiments^{9,74-78} tend to support that HER on Pt is, in fact, a highly structure-sensitive reaction. By measuring the electrochemical curves of Pt(111), Pt(100), and Pt(110), Markovic groups^{9,74,75} and Conway groups⁷⁶⁻⁷⁸ both found that the HER activity is affected by the choice of single-crystal surfaces. Nonetheless, their activity sequences are not exactly the same, where the Markovic group deduced the activity sequence (111) < (100) < (110), with the exchange current density (i_0) being 0.45, 0.60, and 0.98 mA/cm² at 303 K in 0.05M H₂SO₄, respectively,⁹ while Conway group reported a different order (100) < (111) < (110).⁷⁶ Nevertheless, the fact that the ridged (110) surface is the most active is also consistent with the conclusion from the

Hoshi group, who identified a linear relationship between i_0 and the concentration of step sites.^{79–81} These experiments implied that a small fraction of the most active Pt(110) may entirely determine the HER activity, which thus reconciles with the structure insensitivity observed in early experiments. These active sites may further be created dynamically by surface reconstruction during electrochemical HER cycles.

According to the measured Tafel slope, the Markovic group deduced the apparent charge transfer coefficients, 2 for (110) and 1 for (111). As for (100), there are two distinct regions with different charge transfer coefficients, 1.5 for low overpotential and 0.5 for high overpotential. In fact, the measured Tafel slope for the (111) surface varies largely and corresponds to apparent charge transfer coefficients from ~1.6 to ~0.2.^{9,21-24} The Arrhenius plots between the logarithm of i₀ and 1/T from the Markovic group give the apparent activation energy being 0.19, 0.12, and 0.10 eV for (111), (100), and (110), respectively.⁹ However, in a recent experiment by He et al.,²² the apparent activation energy value of Pt(111) is in the range of 0.5 and 0.7 eV, which varies with the potential and is much larger than the result of Markovic. The large differences in the kinetics data between experiments suggest the intrinsic difficulty in measuring accurately the fast HER kinetics, where the entropy effects in proton transfer could play important roles.²

For Pt nanoparticles, the HER activity appears to be even more complex, being sensitive to the size of the particle.^{82,83} Klein *et al.*⁸² prepared a series of Pt nanoparticles with various scales from 25 atoms to 110 atoms and found that the HER activity has a volcano-like shape against the particle size. When the number of atoms is ~38, the HER activity reaches its maximum with the mass-specific current density being ~5.27 A mg_{Pt}⁻¹, while it is ~0.14 A and ~0.11 A mg_{Pt}⁻¹ for Pt₂₅ and Pt₁₁₀, respectively. By monitoring the HER kinetics of Pt nanoparticles increasing the size from 1 atom to ~8 nm, Zhou *et al.*⁸³ observed a limiting plateau of non-normalized HER kinetics at ~4 nm, which supports that HER occurs on metallic Pt and the defected sites at corners or after surface reconstruction are the key active sites.

The surface dependence and the size dependence of HER kinetics on Pt pose challenges for theoreticians to understand the structure-activity relationship of HER on Pt. The key questions are (*i*) why Pt(110) or, more generally, the defected sites have the higher HER activity and (*ii*) which elementary reaction, Volmer, Tafel, or Heyrovski step, is the rate-determining step of HER.

B. Mechanism and kinetics from theory

The most popular explanation of why Pt is the most active is the thermodynamics argument first proposed by Parsons in 1958. It was found that the exchange current density (i₀) against the adsorption free energy of hydrogen ($\Delta G_{\rm H}$) shows a volcano-like shape.⁸⁴ Furthermore, in 1972, Trasatti claimed another version of the volcano curve between i₀ and the metal-H bond strength.⁸⁵ The Nørskov group introduced DFT calculations to such picture and made such a thermodynamic method popular from 2006.^{8,86} $\Delta G_{\rm H}$ at the equilibrium potential is taken as the descriptor to evaluate the catalytic performance of catalysts for HER. This is because the free energy of an adsorbed H atom can be referenced to half of a hydrogen molecule by DFT and further related to a single proton together with a single electron at a certain electrochemical potential by using a computational hydrogen electrode (CHE) approach. The HER activity of catalysts (represented by i₀) from the experiment against the computed $\Delta G_{\rm H}$ does reproduce the volcano-like shape, as illustrated in Fig. 3(a). As can be seen, Pt locates at the peak of the volcano with its $\Delta G_{\rm H}$ approaching 0.⁸⁶ The closer $\Delta G_{\rm H}$ approaches 0, the more efficient the catalyst is, which is a thermodynamics consequence of the Sabatier principle and the Brønsted-Evans-Polanyi (BEP) relation.⁸⁷ The too large $\Delta G_{\rm H}$ value (poor H adsorption) hinders the electrochemical adsorption of the proton, while the too low $\Delta G_{\rm H}$ goes against the release of hydrogen. A typical application of the CHE approach can be seen in Fig. 3(b) as an experimental example. In this example, the single Pt atom anchored on an onion-like carbon (OLC) nanosphere was synthesized, which has the ability to adsorb 3 H atoms, and the adsorption free energy of the third H atom is -0.01 eV.⁸⁸ This explains why the catalyst has a high HER activity.

While the CHE approach provides a convenient and quick way to compare the catalytic activity between materials in a wide range without searching for the detailed reaction pathway, one must recognize that the thermodynamics approach is a crude approximation by neglecting a number of key issues to reaction kinetics, such as the surface H coverage effects, the solution effect, and the surface structure reconstruction. Indeed, none of the questions raised above, Pt(110) being more active and the rate-determining step of HER, can be answered by the $\Delta G_{\rm H}$ thermodynamics. These questions are certainly the key to searching for the best catalyst at the peak of the volcano plot.



FIG. 3. (a) HER volcano plot for a series of metal and metal overlayer. Reprinted with permission from Greeley *et al.*, Nat. Mater. 5(11), 909 (2006). Copyright 2006 Nature Publishing Group. (b) The free energy profile of 3 H atoms consecutively adsorbed on the Pt₁/OLC with the condition of pH 0 and equilibrium potential. Adapted with permission from Liu *et al.*, Nat. Energy 4(6), 512 (2019). Copyright 2019 Springer Nature.

As for the kinetics, the activation energy of the Tafel step $(H^* + H^*)$ on the Pt(111) surface was most computed in the literature, which yields the value from 0.40 to 1.00 eV.^{21,37} Computational models (e.g., H coverage and the H2O numbers) and computational methods, e.g., the choice of exchange-correlation functional [Perdew-Burke-Ernzerhof (PBE) or revised Perdew-Burke-Ernzerhof (RPBE)], and solvation approaches appear to strongly affect the computed kinetics data. No consensus is achieved for the rate-determining step, although the Volmer-Tafel mechanism dominating the HER on the (111) surface appears to be more accepted. By the combination of the cell-extrapolation, explicit water bilayer model, and DFT-nudged elastic band (NEB) methods, Skúlason et al.37 found that on the Pt(111) surface, free energy barriers around the equilibrium potential are 0.69, 0.85, and 1.40 eV with the RPBE functional for the Volmer, Tafel, and Heyrovsky reaction, respectively, with the H coverage being ~1 ML from the thermodynamic analysis. Their results suggest that the Volmer-Tafel pathway is the main mechanism of Pt(111) and the Tafel reaction is the rate-determining step. At 303 K, the exchange rate calculated by the Tafel barrier of 0.85 eV is 5.1×10^{-5} A/cm², which approaches the experimental value 4.5×10^{-5} A/cm² by Markovic.⁹ By using the DFT-NEB method, Marcus theory, and microkinetic simulation, Lindgren⁴⁴ found that free energy barriers are ~0.27 eV for the Volmer reaction and ~0.40 eV for the Tafel reaction at 0 V vs SHE in the SJ method. Their microkinetic simulation suggested that the coupling of two adjacent overpotential-deposited H on top sites leads to a Tafel slope of 30 mV/dec. On the other hand, Fang et al.²¹ applied the CM-MPB model to describe the interface and constrained-Broyden minimization (CBD) scheme to determine the TS, which found that the free energy barrier of the Volmer reaction at 0 V vs SHE on Pt(111) is lower than 0.2 eV, while the values of the Heyrovsky reaction and Tafel reaction are both ~0.92 eV with the H coverage of ~1 ML at the PBE level. The Tafel slope is deduced to be 83 mV/dec for (111) from microkinetics, suggesting a mixed mechanism of Volmer and Tafel and Volmer and Heyrovsky on the (111) surface. By contrast, Tang et al.⁵¹ used the charge-extrapolation method to determine the HER kinetic barriers with explicit water. The barriers of Volmer, Tafel, and Heyrovsky steps at Pt(111), with H coverage being around 1 ML, are 0.61, 0.77-0.83, and 0.62-0.74 eV in the BEEF-vdW functional, respectively. Their calculated Tafel slopes deduced from the mean-field microkinetic simulation are ~120 mV/dec for Pt(111), suggesting that the Volmer-Heyrovsky pathway is the controlling mechanism.

Beyond the static TS search approaches using DFT calculations, enhanced MD methods have also been utilized to evaluate the barrier

of elementary steps. Using a model of 180 Pt atoms and 160 explicit water molecules, thermodynamic integration simulation at the equilibrium electrode potential by Kronberg and Laasonen⁵⁸ yields the free energy barriers of 0.69 eV (1 ML H coverage) and 0.67 eV (0.66 ML H coverage) for the Volmer reaction and 0.53 eV (1 ML H coverage) and 0.80 eV (0.66 ML H coverage) for the Tafel reaction at Pt(111), respectively. After the charge-extrapolation method to correct the potential dependence of the barrier of the Volmer reaction (hydrogen adsorption is endergonic), the rate-determining step is still the Tafel step, although the Heyrovsky reaction is not considered in their work. Recently, Rice et al.53 have employed the global neural network (G-NN) potential to speed up umbrella sampling MD simulations, which extends greatly the simulation time to ~400 ps. Their model is a 202-atom unit cell with 44 H₂O molecules and two solvated Cl atoms. Importantly, at equilibrium, the total equilibrium coverage of H_{ads} and H₂O_{ads} is found to be 0.56 ML with vdW (D3) correction, as depicted in Fig. 4(a), which is different from the commonly utilized ~1 ML from thermodynamics analysis. As can be seen in Fig. 4(b), in the structure at the equilibrium, the H_{ads} atoms prefer the three-fold fcc-hollow sites, while H₂O_{ads} molecules tend to locate on the top site. The total coverage is in good accordance with the experimental result of 0.66 ML from Markovic.9 They further showed that the Tafel barrier is 0.83 eV, while the Heyrovsky barrier varies from 0.89 eV at 0.56 ML to 0.82 eV at 0.33 ML. They concluded that the Volmer-Tafel mechanism is preferred at high H coverage and the Volmer-Heyrovsky channel opens at low H coverages, suggesting a mixed mechanism on Pt(111).

As for the most active Pt(110), the unreconstructed (1×1) surface is found to have a barrier of ~0.75 eV for the Tafel step.² Recently, by simulating the cyclic voltammetry response, Fang et al.²⁵ have suggested that the high activity of Pt(110) may arise from the surface reconstruction, where single Pt atoms migrate away from the ridge, forming special five-coordinated Pt ([PtH₅], Pt_{5c}) sites locating at the trough. The stochastic surface walking-neural network (SSW-NN) invented by our group was utilized to explore the probable reconstruction pathways for the Pt(110) facet at different electrochemical potentials and identified several types of surface sites [types I, II, and III in Fig. 5(a)]. Among those, the Pt_{5c} sites [type-I site in Figs. 5(a)-5(c)] are the most active, yielding the free energy barrier of the Tafel reaction of 0.52 eV at the equilibrium potential. The barrier is not only much lower than the HER free energy barrier of ~0.9 eV on Pt(111) and Pt(100) in their previous work but also lower than that on the bulk-truncated Pt(110) ones of ~0.75 eV.



FIG. 4. (a) Surface coverage evolution of H_{ads} and H_2O_{ads} during a 400 ps high-dimensional neural network potential (HDNN)-MD with D3 correction. (b) Snapshots after 300 ps with a total H coverage being 0.56 ML. Reprinted with permission from Rice *et al.*, J. Phys. Chem. Lett. 12(43), 10637 (2021). Copyright 2021 American Chemical Society.



FIG. 5. Reconstruction of Pt surfaces in H-abundant environment. (a) Free energy profile of the Tafel reaction on three different types of Pt(110) surfaces at equilibrium potential. The IS and TS on the type-I surface are shown in (b) and (c). Reprinted with permission from Fang *et al.*, J. Phys. Chem. C **125**(20), 10955 (2021). Copyright 2021 American Chemical Society. (d)–(f) Structure evolution of Pt₄₄ clusters with increasing H adatoms. (d) A polyhedron demonstration of the evolution of Pt₄₄ anaoparticles from octahedron to tetradecahedron. (e) The typical structures of Pt₄₄H₅₀ showing the reconstruction from (111) to (100). (f) The global minimum structures of Pt₄₄H₆₁, Pt₄₄H₇₄, and Pt₄₄H₈₀. Adapted with permission from G.-F. Wei and Z.-P. Liu, Chem. Sci. **6**(2), 1485 (2015). Copyright 2014 Royal Society of Chemistry.

The surface reconstruction of Pt nanoparticles was, in fact, observed earlier by SSW-DFT simulations. Wei and Liu²⁶ investigated the structure evolution of a Pt44 nanoparticle starting from the high-symmetry octahedron Pt44H50 (at 1 ML H coverage), and the results are shown in Figs. 5(d)-5(f). Under the electrochemical potential, more H can adsorb on the nanoparticle surface, which induces the surface reconstruction toward exposing more (100) facets. This is caused by the higher H adsorption capacity of (100) than (111). In addition, the Tafel mechanism via H-H coupling at the apex site, Pt_{5c} sites, of Pt₄₄H₈₀ is found to have the lowest free energy barrier in the range of 0.47-0.71 eV among all the sites considered, which validates that the high HER activity of Pt should come from the defected sites, which can be created by surface reconstruction. It might be mentioned that Tan et al.⁸⁹ also studied the configuration evolution of a Pt₅₅ nanoparticle with adsorbed H* atoms by using Monte Carlo (MC) simulations. However, because they did not consider the surface reconstruction and thus the Pt_{5c} site is not present in their model, the most active site is found to be at the (100) terrace site with a barrier of 0.62 eV.

IV. METAL-SUPPORT INTERACTION AND STRATEGIES TO IMPROVE PT CATALYST STABILITY

Since H adsorption induces significant reconstruction of Pt surfaces and nanoparticles that occurs under HER conditions, a strong metal-support interaction is highly desirable to prevent the detachment of metal nanoparticles from the support. On the other hand, with the massive production of H_2 , the type of support must have a good enough electronic conduction ability in the first place, which led to the graphite-based material as the practical choice. In fact, various other supports, such as MOS_2 ,⁹⁰ WC,⁹¹ Nafion,⁹² and nanopore stainless steel,⁹³ have been tested as the support in the literature, but the decay of the activity in the long-term remains obvious.

The weak interaction between Pt and graphite may be the reason for the low durability of the Pt/C catalyst. By using DFT calculations, Esposito et al.94 showed that the binding energy of monolayer Pt-graphite C(0001) is ~24% lower than that of Pt-Pt in DFT calculations, which indicates that the agglomeration of Pt is inevitable in defect-free graphite. In addition, the electron transfer between Pt and graphite-based support is quite low. Nakada and Ishii applied the Bader analysis to research the charge transfer between single atoms of different elements and the graphene monolayer. Among the first 83 elements on the Periodic Table, Pt and Au are the only two metallic elements where the direction of charge transfer is from the graphene to single metal atoms and the transferred electrons are almost zero for Pt.95 Low charge transfers (less than 0.1 e⁻ per Pt atom) were also reported for Pt clusters with around 40 atoms on the defect-free graphene, while the direction of charge transfer is in debate. Apparently, due to the low interaction between Pt and pristine graphite-based materials, the key to improving the stability of Pt/C catalyst is to introduce defects to carbon materials. Combined HRTEM with DFT calculations, Poidevin et al.¹⁰⁰ showed that Pt clusters do have a strong interaction with the zigzag edge of a basal plane of carbon black-a Pt37 nanocluster is

found to move to a zig-zag edge of the $C_{126}H_{30}$ support in DFT optimization with the interaction energy of -6.54~eV and 0.89 electron transfer from the support to Pt. In the meantime, two planar carbon atoms with sp^2 hybridization convert to the ones with sp^3 hybridization. The distortion of both the cluster and support is observed in HRTEM images.

Recent experiments have made encouraging progress in stabilizing Pt nanoparticles or single atoms via modified carbon materials.^{15,88,101-104} For example, Cheng et al.¹⁵ used the atomic layer deposition (ALD) method to anchor Pt single atoms and small clusters on nitrogen-doped graphene nanosheets (NGNs). The sample (ALD50Pt/NGNs) treated by 50 ALD cycles in 523 K has an overpotential (η_{10}) of ~50 mV when the current density is 10 mA $\rm cm^{-2}$ and shows only a 4% loss of the current density at 0.05 V overpotential after 1000 CV cycles from +0.4 to -0.15 V vs SHE with 100 mV/s. Their DFT calculations show that the single Pt atom has an adsorption energy of -5.171 eV on NGNs, and the normalized x-ray absorption near edge structure (XANES) indicates that ALD50Pt/NGNs have more unoccupied Pt 5d density of states than the commercial Pt/C catalyst. The high activity and durability of subnano-Pt particles (less than 10 Pt atoms) on single-walled carbon nanotubes (SWNTs) were reported by Tavakkoli et al.,¹⁰¹ in which η_{10} is 27 mV and maintains largely after 5000 stability cycles. The adsorption energy of an isolated Pt on the SWNT axial site is -2.38 eV from their DFT results, which is 0.4-0.5 eV more exothermic than that on graphene. Yin et al.¹⁰³ synthesized a single Pt atom catalyst on graphdiyne supports, featuring four-coordinated C2-Pt-Cl2 species (Pt-GDY2). From their XPS and XANES analyses, the valence state of Pt in Pt-GDY2 is between 0 and +2. DFT calculations on the Pt-GDY2 indicate that the H adsorption free energy is close to zero (+0.092 eV), supporting the good HER activity of the single-atom catalyst with η_{10} being ~50 mV. The stability of Pt-GYD2 is also high since the LSV curve after 1000 cycles resembles the initial one, and the current density is almost constant at -95 mV for 10 000 s.

In addition, cage materials were also found to improve the stability of Pt-based HER catalysts via the confinement effect. Wang *et al.*¹⁰⁵ used trigonal prismatic coordination cages {Ni₂₄(TC4A-SO₂)₆(TDC)₁₂(H₂O)₆} (CIAC-121) to imprison Pt clusters. The



FIG. 6. (a) The structure of Pt NCs@CIAC-121. (b) Linear sweep curves of Pt NCs@CIAC-121 and Pt/C for HER in 0.5M H_2SO_4 at a scan rate of 50 mV/s. Reprinted with permission from Wang *et al.*, J. Am. Chem. Soc. **138**(50), 16236 (2016). Copyright 2016 American Chemical Society.

structure of as-synthesized Pt NCs@CIAC-121 is illustrated in Fig. 6(a). The TEM images and mass spectra indicate that the Pt nanocluster is successfully encapsulated in CIAC-121 without changing the morphology of CIAC-121 dramatically. Such a Pt NPs@CIAC-121 catalyst has η_{10} of 26 mV in 0.5M H_2SO4, as shown in Fig. 6(b), and the activity remains over 75% after 5000 cycles of CV from 0 to -0.6~V.

V. PERSPECTIVE

This Review overviews the current status of Pt-catalyzed HER from a theoretical point of view. We emphasize the importance of theoretical methodology developments in the past few decades, which bypass the CHE thermodynamics analysis and lead to a better description of the solid-liquid interface and more accurate control of the electrochemical potential. Theory can now provide potential-dependent reaction profiles for solid-liquid electrochemical reactions, which was not possible 20 years ago. We note that newly emerged methods have already shown great potentials for the future research. In particular, machine-learning potential techniques facilitate the global reaction search and long-time MD simulations. They are thus able to provide deep insights into proton-coupled electron transfer reactions that are unique to solid-liquid interface reactions. On the other hand, grand-canonical constant-potential simulations based on the first principles calculation framework appear to be a general and simple framework that facilitates to reach a consensus on the kinetics data in the community. While the direct combination of the above two machine-learning potential and constant-potential simulations is still a huge challenge, the CM-MPB model with constant-potential calculations is a practical solution.

By joint experiments and theoretical efforts, stepped Pt surfaces are recognized as the active site of Pt-based catalysts. The five-coordinated Pt atom ($[PtH_5]$ under reaction conditions) being present at both the Pt(110) trough and the apex site of Pt nanoparticles is the key surface site responsible for the activity, where the Tafel step for the H–H coupling between top-H and bridging H has a barrier as low as 0.5 eV. The less active but dominant Pt(111) surfaces remain controversial on the reaction mechanism, but a mixed Volmer–Tafel and Volmer–Heyrovsky mechanism is likely to reconcile existing literature, where the switch between pathways depends on the potential and H coverages.

It is generally accepted on the high H coverage of Pt surfaces and nanoparticles under reaction conditions, and the H-induced Pt surface reconstruction revealed from theoretical simulations complements the experimental data from CV curves. The low-stability Pt catalysts can now be understood by the H-induced detachment of Pt nanoparticles from support. Among various experimental means to improve Pt-support interaction, the anchoring of single Pt atoms and the confinement of subnano-Pt particles are the most promising frontiers demonstrated in recent experimental advances. On the other hand, more and more research focused on non-Pt catalysts, aiming to reduce the cost of HER catalysts. The semiconducting twodimensional MoS₂, ¹⁰⁶⁻¹¹⁰ Ni-based catalysts, ¹¹¹⁻¹¹⁴ and Co-based catalysts¹¹⁵⁻¹¹⁷ were reported, although their activities are generally less satisfactory compared to Pt.⁶ Nevertheless, it is encouraging that the advance in electrochemical simulations also greatly benefits these non-Pt HER studies and promotes a new catalyst design therein.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Ke-Xiang Zhang: Writing – original draft (equal); Writing – review & editing (equal). **Zhi-Pan Liu**: Conceptualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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