

Observations and theories of quantum effects in proton transfer electrode processes

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Abstract

Quantum tunneling effects play an important role in a variety of chemical reactions considerably affecting the reaction rates *via* opening the classically-forbidden paths and emerging as highly efficient or selective processes. However, in the case of electrochemical reactions, quantum tunneling effects are less investigated due to complicated nature of chemical interactions at the

electrified interfaces. In this review, we summarize the experimental/theoretical concept of electrochemical quantum proton tunneling (EQPT), which is a key element in microscopic electrode processes. First, we review the experimental observations of EQPT, and next, we discuss possible theoretical pictures of the process. This review shows that a combination of a wide spectrum of scientific efforts is required to understand microscopic mechanism of EQPT including development of the precise electrochemistry-oriented experimental techniques and methodologies, formulation of the appropriate theoretical models for specific systems and performance of the advanced computational simulations.

Introduction

“Quantum Electrode Process” is a traditional topic in electrochemistry since 1931 when R. W. Gurney described the electron transfer in proton discharge as a tunneling phenomenon [1]. Curiously, the microscopic mechanism of electrochemical quantum proton tunneling (EQPT) was not elucidated at that time. The concept of the applied potential plays a vital role in electrochemistry. Changing the potential one can manipulate electrochemical reactions by altering the activation barrier heights and opening and closing specific reaction channels. Therefore, one can expect a number of very interesting phenomena that can be observed exclusively in electrochemical systems. For example, recently we have demonstrated that it is possible to switch

the mechanism of a proton transfer from a fully quantum tunneling path to a fully classical over-the-barrier path, resulting in appearance of the quantum-to-classical transition (QCT) of proton transfer as a function of the applied potential (Figure 1) [2].

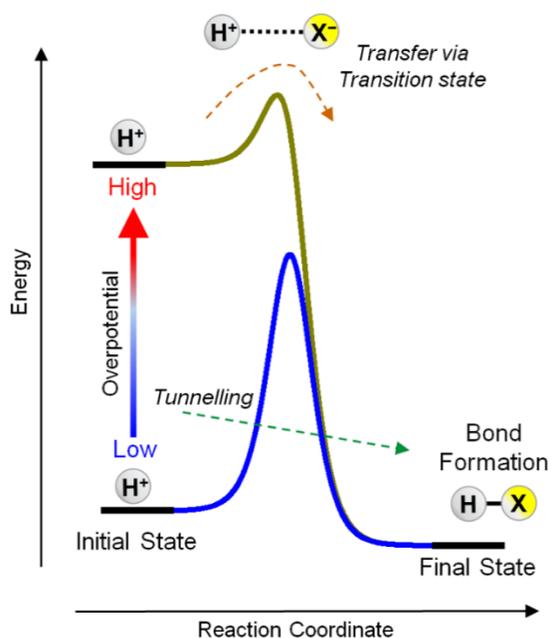


Figure 1. Schematic illustration of the quantum-to-classical transition (QCT). At the low overpotential, a high and narrow activation barrier can emerge for proton tunneling. The height of the activation barrier can be tuned by applying potential resulting in the opening the classical over-the-barrier path. Figure reprinted with permission from [2]. Copyright (2019) by the American Physical Society.

From the point of experiments, efforts to observe EQPT can be traced back to 1930s [3], but a

clear observation of EQPT combined with the theoretical analysis was reported quite recently [2,4]. Furthermore, although theoretical frameworks for proton tunneling in standard chemical reactions were well-established during the last three decades, a systematic theoretical analysis of the EQPT process and quantum-to-classical transition of proton transfer is still lacking. The aim of this review is to summarize recent experimental results on EQPT, and to analyze various theoretical models and approaches in order to shed light on microscopic mechanism of EQPT.

Observation of electrochemical quantum proton tunneling at electrode surfaces

In 1934, Bawn and Ogden suggested that a magnitude of proton tunneling in the hydrogen evolution reaction (HER) at metal electrodes can be investigated by measuring the H/D (hydrogen/deuteron) separation factors, $S^{H/D}$, and they reported that EQPT should have a major contribution in the HER [3]. Following this work and other reports on measuring $S^{H/D}$, Conway and his co-workers performed careful experiments in order to obtain $S^{H/D}$ by using a mercury electrode (Hg) [5-9]. Their result on EQPT was negative: There were no clear evidence of quantum effects and they concluded that EQPT in the HER at Hg is not significant. On the other hand, Bockris and Matthews found out that EQPT is significant in the same conditions by comparing not only H/D, but also H/T (hydrogen/tritium) separation factors, $S^{H/T}$ [10]. Thus, the EQPT was an unsolved problem in the electrochemical community. At that time experimental

difficulties were the following: (1) Hg was a major electrode which could satisfy a clean electrochemical condition, therefore there were not so many choices for electrode materials; (2) the major diagnostic method was based on measuring the separation factor S , which needs to use tritium to have a clear evidence of the EQPT by comparing $S^{\text{H/D}}$ and $S^{\text{H/T}}$.

In contrast to measuring S , we have used another experimental approach to detect EQPT, such as measuring of the H/D kinetic isotopic rate constant ratio, $K^{\text{H/D}}$ [2,4,11-15]. The $K^{\text{H/D}}$ is a well-known descriptor to elucidate contribution of a proton transfer in the rate-determining step of standard chemical reactions. The corresponding theoretical models to estimate $K^{\text{H/D}}$ are well established. However, there were no appropriate analytical equations to determine $K^{\text{H/D}}$ in electrochemical experiments although even enormous interests are attracted to understand reaction mechanisms of Pt-free or Pt-less electrocatalysts [16-21]. The main challenge was to account for a difference in thermodynamic constants and parameters in the fully deuterated systems compared to the protonated systems. Therefore, in the series of recent works [2,4,13-15] we have developed the analytical procedure to determine $K^{\text{H/D}}$ in the HER,

$$K^{\text{H/D}}_{\text{HER}}(\eta) = \frac{j_0^{\text{H}}}{j_0^{\text{D}}} \times \frac{[\text{D}^+]}{[\text{H}^+]} \times \exp\left\{\frac{(\alpha^{\text{D}} - \alpha^{\text{H}})F\eta}{RT}\right\}, \quad \text{Eq. 1}$$

and the oxygen reduction reaction (ORR),

$$K^{\text{H/D}}_{\text{ORR}}(\eta) = \frac{j_0^{\text{H}}}{j_0^{\text{D}}} \times \frac{c_0^{\text{D}}}{c_0^{\text{H}}} \times \exp\left\{\frac{(\alpha^{\text{D}} - \alpha^{\text{H}})F\eta}{RT}\right\}. \quad \text{Eq. 2}$$

Here j_0 represents the exchange current density, $[X]$ ($X = D^+, H^+$) is the concentration of the corresponding cations, α is the transfer coefficient, F is the Faraday's constant, R is the gas constant, T is the temperature, C_0 is the concentration of the dissolved oxygen in the corresponding electrolyte, and η is the overpotential. The superscripts H and D indicate the coefficients in the protonated or the deuterated systems, respectively. The transfer coefficient α can be obtained from the experimental value of the Tafel slope, b , using following simple relation: $\alpha = 2.303RT/Fb$.

The HER and ORR are two most representative reactions to study multi-electron/-proton transfer electrode processes. Using Eqs. 1 and 2 in combination with the various theories for electrochemical reaction rates, one can elucidate contributions and possible microscopic mechanisms of EQPT in the HER and ORR.

We note that our concept postulates that (1) there is the Arrhenius relation in overpotential *versus* log kinetic current density plots, (2) there is only a single rate-determining (or potential-determining) step in a reaction, and (3) a symmetry factor, β , is correlated to microscopic quantum effects in electrode processes.

The symmetry factor β controls the transformation of electrical to chemical energy and connected with the transfer coefficient α by simple relation [22]: $\alpha = \frac{s}{\nu} + \beta r$, where s represents the number of transferred electrons before the reaction rate-determining step (RDS), ν as the stoichiometric number, and r as the number of transferred electrons in the RDS. We note here that

this relation postulates the absence of double-layer effects and the low coverage of reactants/products on an electrode. The detailed discussions and the derivation of the above equation is available in the reference [22].

Using the approach described above, we found a solely EQPT paths, where quantum effects play a main role in proton transfer processes, such as the HER on Au in an alkaline condition and the ORR on Pt in an alkaline condition. We would like to stress that proton transfer in electrochemical reactions is often a combination of the quantum tunneling through-the-barrier and classical over-the-barrier processes. Therefore, a tunneling effect itself can be trivial, but in contrary a full EQPT process, a solely tunneling phenomena in electrochemical environment, is non-trivial.

First we consider the full EQPT in the HER on gold electrode where the first proton coupled electron transfer, $\text{H}_2\text{O} + e^- + * \rightarrow \text{H}^* + \text{OH}^-$, schematically shown in Figure 2A is the rate-determining step [4]. This EQPT demonstrates the following two key features (Figure 2B, C):

(I) There is a large difference in Tafel slopes for protonated and deuterated systems (Figure 2B). As the result, the $K^{\text{H/D}}_{\text{HER}}(\eta)$ value increases with increasing the overpotential η (Figure 2C). This observation is unusual from the point of view of the Brønsted-Evans-Polanyi (BEP) principle.

(II) The $K^{\text{H/D}}_{\text{HER}}(\eta)$ value measured at high overpotentials exceeds 10 and cannot be explained by a semi-classical transition state theory (SC-TST). This observation suggests that a tunneling effect dominates the proton transfer.

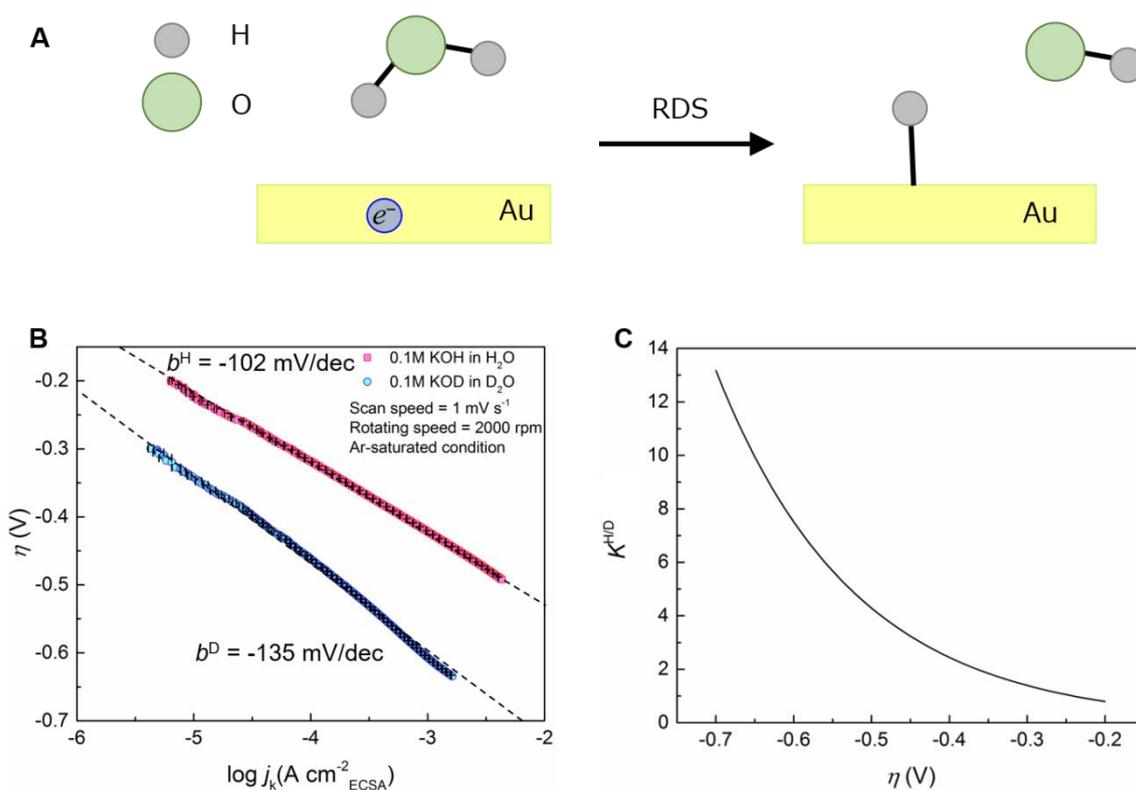


Figure 2. **A.** Schematic representation of the reaction rate-determining step (RDS) for the HER at Pt electrode in alkaline condition ($\text{H}_2\text{O} + e^- + * \rightarrow \text{H}^* + \text{OH}^-$); **B.** Dependence of the overpotential η on logarithm of the kinetic current, j_k for HER/DER to investigate Tafel's law. **C.** The $K^{\text{H/D}}$ vs. η dependence obtained from the Tafel slopes b^{H} and b^{D} in B. Reproduced from [4] with permission of The Royal Society of Chemistry.

These two features (I) and (II) are unusual because the BEP principle predicts the decrease in the corresponding activation barrier of the rate-determining step with increasing overpotential. Therefore the probability of an over the barrier SC-TST path should increase and one can expect that the classical proton transfer mechanism dominates. With this standard view, the maximum value of $K^{\text{H/D}}_{\text{HER}}(\eta)$ should not exceed ~ 10 as follows from the Kiefer-Hynes' model for an adiabatic proton transfer [23].

Although the exact microscopic mechanism of this EQPT on Au is still not fully understood, it is clear that the quantum effects can be noticeable due to the large difference in the values of the transfer coefficients α^{H} and α^{D} as follows from Eq. 1. The large difference $\alpha^{\text{D}} - \alpha^{\text{H}}$ was observed in another system (triethylammonium in acetonitrile) by a different group, and they also showed an increase of $K^{\text{H/D}}_{\text{HER}}(\eta)$ with increasing the overpotential [24]. These results suggest that there is a large difference in changing activation barrier heights, i.e. evolution of the reaction coordinates, on increasing overpotential between the protonated and deuterated systems.

In [4] authors suggested that if the RDS in the protonated and deuterated systems is the same, a large difference between α^{H} and α^{D} appears as a result of the difference in the corresponding

symmetry factors β^H and β^D . A difference between β obtained for the protonated and deuterated systems indicates that there is a difference in decrease of the corresponding activation barrier height with increasing the overpotential. In addition, the surface-enhanced infrared spectrometric observations by Osawa and his coworkers suggested that a distance between Au surface and hydrogen atoms of water molecules at the Au/water interface becomes smaller with increasing the overpotential [25]. This effect results in the narrowing of the width of the activation barrier of the proton discharge to the surface with increasing the overpotential. Therefore, one can suggest that probability of the proton tunneling increasing in the high overpotential region due to decrease in the width of the potential barrier.

Let us now consider manifestation of the quantum effects in proton transfer reactions in ORR. Recently, a full EQPT path in ORR has been observed on platinum electrodes (Pt) in an alkaline condition at 298 K [2]. In this condition, manifestation of the EQPT was confirmed only in a low overpotential region showing $K^{H/D}_{\text{ORR}} = 32$ considerably exceeding the semiclassical limit (Figure 3). However, in the high overpotential region $K^{H/D}_{\text{ORR}}$ dropped down to the value of 3.7 indicating the classical over-the-barrier scheme. Therefore, a quantum-to-classical transition of proton transfer in ORR was observed as a function of the potential. Indeed, a large $K^{H/D}_{\text{ORR}}$ is a strong evidence of EQPT because the maximum value of $K^{H/D}$ for the O–H bond breaking in

semiclassical framework is ca. 13 [26]. Furthermore, other general proton-transfer models, such as Westheimer-Melander or Kiefer–Hynes models [23,27] predict lower values of the maximum $K^{H/D}$ for proton-transfer without tunneling. Therefore again, the high value of $K^{H/D}$ exceeding the semiclassical limit is the strong criterion for manifestation of the EQPT paths. The details of theoretical analysis on this system will be discussed in the next section.

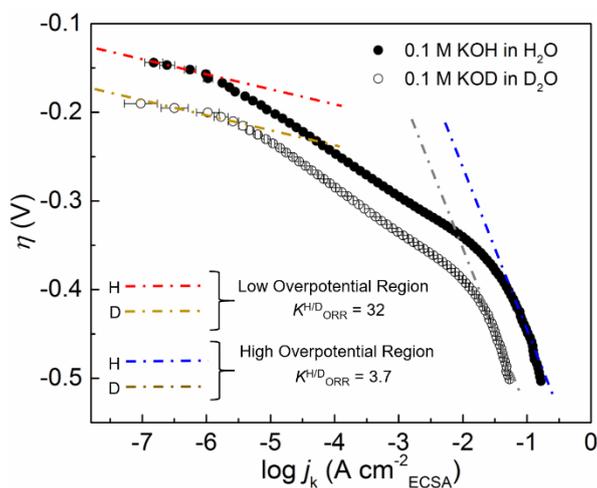


Figure 3. The η vs. $\log j_k$ plots for ORR at Pt electrode in the alkaline conditions. Figure reprinted and modified with permission from [2]. Copyright (2019) by the American Physical Society.

Theoretical pictures of the electrochemical quantum proton tunneling

From the theoretical point of view investigation of electrode processes requires description of the transfer of electrons and protons. The development of theories of electron transfer (ET) in

solutions goes back to the early works of Libby [28], Weiss [29], Marcus [30,31], Hush [32], Levich and Dogonadze [33] in the second half of 50s of the last century; while the related theory for the proton transfer (PT) accounting for the change in solvent polarization has been proposed by Dogonadze and his co-workers [34-36] and later Borgis and Hynes [37-39]. Since then the theoretical understanding of electrochemical ET and PT has been extensively developed. In this short review it is not possible to describe all related works and variety of methods; therefore we confine ourselves only to the most recent studies related to the focus of this review. A detailed survey on the development of PT theories is available in the recent paper [4].

A number of works have been devoted to improvements of the original Marcus theory [40-42] focusing on the evaluation of the rate constant of the heterogeneous non-adiabatic ET accounting for quantum-mechanical effects [43-47]. Of course, numerical calculations of the rate constants are not a problem, but there is an interest to develop more accurate approximate analytical expressions to elucidate the physics of ET and use such models for practical applications [47,48]. Alternatively, a number of works account for the molecular nature of the solvent using the classical or *ab initio* Molecular Dynamics or statistical theory of liquids [49-52]. Yet another method to reformulate the molecular ET theory has recently been proposed by Salanne et al who have elegantly applied a molecular density functional theory approach to ET reactions [53].

It has been recognized that coupling between electrons and protons plays a vital role in chemical and electrochemical processes, see, e.g. [54] and references therein. In general proton-coupled electron transfer (PCET) reactions can be either sequential, where the electron transfer is followed by the proton transfer or *vice versa*, or concerted, where the electron and proton transfers occur simultaneously. This difference is not strictly defined but nevertheless can be used as a useful guide to understand the mechanism of the process [55]. It is important to keep in mind that in

PCET processes the relative timescales of the electrons, protons, solute and solvent as well as coupling between these subsystems can vary considerably. Therefore, a large variety of different theoretical approaches has been used to describe PCET. A very clear classification scheme of the PCET reactions in terms of these timescales and couplings reflecting the electronic, vibrational and vibronic nonadiabaticity is presented in a review by Hammes-Schiffer [56].

The theory of PCET has been strongly influenced by developments of theory of ET in solutions. Thus, the theoretical description of a PCET process can be derived as an extension of Marcus theory for ET where the PT coordinate is treated as an inner-sphere solute mode [57,58]. In this case the resulting reaction rate includes an overlap of the proton wave functions for the reactant and product states [54]. This approximation was generalized in the works by Hammes-Schiffer and Soudackov by introducing two collective solvent coordinates for ET and PT [59-63], where the reaction was described as nonadiabatic transitions between electron-proton vibronic states. In this formalism the solvent environment has been represented by a dielectric continuum, while later forms of theory include explicit molecular solvents in a full accord with the developments of the similar models for ET.

An alternative approach based on the use of a model Hamiltonian for combined electrochemical electron and proton transfer, containing terms for ET and PT steps and their coupling to solvent and vibrational modes has been proposed by Schmickler and his co-workers [64,65]. Development of such models is especially important for an understanding of fundamental mechanisms of ET and PT reactions. In the last decade theory of PCET has been considerably developed [55], and applied to different electrochemical processes including investigation of the molecular electrocatalysis with nanoparticles [66], development of the electronically adiabatic

model of proton discharge on metal surfaces, where the nuclear quantum effects for the moving proton were included by quantization along the proton coordinate, while the solvent interactions were treated within dielectric continuum model in the linear response regime [67], as well as modelling the potential-dependent kinetic isotope effects for proton discharge on electrode surfaces [68]. Recently a quasi-diabatic propagation scheme for direct simulation of PCET reaction based on a partial linearized path-integral approach and symmetrical quasi-classical approach has been proposed [69]. Such approximation can provide accurate vibronic dynamics of PCET reactions and predict the reaction mechanism without any a priori assumptions. A comprehensive review on recent advances on nonadiabatic mixed quantum-classical dynamics methods for description of the time evolution of a wide class of nonadiabatic phenomena in molecular systems has been recently given by Crespo-Otero and Barbatti [70]. This review gives a general guidance to select an adequate method for each application.

As it was mentioned by Hammes-Schiffer and Stuchebrukhov that the variety of methods describing PCET is in their great diversity and “*there is no one magic formula for the reaction rate constant as in the pure ET case*” [63]. The quantum-mechanical effects for electrons and protons can play an important role for PCET reactions. Therefore the electrochemical PCET processes can demonstrate large kinetic isotope effects and unusual behavior of the reaction rate on temperature, pH and applied potential. In this connection the use of simple and physically clear models can considerably enhance our understanding of the complicated mechanisms of the electrode processes. For example, for electronically nonadiabatic processes classical or semiclassical trajectory methods of molecular dynamics is a reasonable approach. It can be made more realistic by including tunneling effects as it was proposed by Truhlar and his co-workers [71,72]. Even more simple approach to account for quantum tunneling effects in a proton-transfer

during the potential induced reduction of dioxygen on a platinum electrode has been proposed by the authors [2], considering the following expression for the rate constant $k(T)$:

$$k(T) = \frac{A}{k_B T} \int_0^\infty P(E) e^{-E/k_B T} dE, \quad \text{Eq. 3}$$

where A is a rate constant frequency factor, k_B is Boltzmann's constant, and $P(E)$ is the barrier permeability at energy E . In order to analyze the experimental observations it was suggested to approximate the barrier for proton transfer by the asymmetric Eckart's one-dimensional potential energy function,

$$V(r) = \left[(V_1)^{\frac{1}{2}} + (V_1 + \Delta V)^{\frac{1}{2}} \right]^2 / 4 \cosh^2 \left(\frac{r}{a} \right) - \Delta V e^{\frac{r}{a}} / 2 \cosh \left(\frac{r}{a} \right), \quad \text{Eq. 4}$$

where V_1 is the barrier height, ΔV is reaction exothermicity, and a is the barrier width parameter. In the case of the Eckart potential of Eq. 4, the barrier permeability $P(E)$ can be evaluated analytically/numerically by solving the corresponding Schrödinger's equation [73,74]. This simple and robust model provides a clear physical picture of the corresponding process. In the case of the PT in electrode processes, parameters of the reaction barrier height and exothermicity can be changed on applied potentials and the simple BEP principle was used to describe variations in the barrier height on changing potentials, i.e.

$$V_1 = -C\Delta V + B, \quad \text{Eq. 5}$$

where C characterizes the position of the transition state along the reaction coordinate, herein taken to be 0.5, and B is the barrier height at the equilibrium. The barrier width was selected as 0.3 Å because the widths corresponding to hydrogen bonds between intermediate species of ORR, for instance adsorbed dioxygen or adsorbed atomic oxygen, are 0.25–0.35 Å, and the barrier height can be used as a parameter. It was confirmed that the initial barrier height of 0.8 eV can well reproduce the experimental observation. This barrier height is very close to the values reported by other theoretical groups as an activation barrier at the RDS of ORR [75]. With this quite simple model, EQPT can be analyzed and also a quantum-to-classical transition can be confirmed on increasing the overpotential (Figure 4).

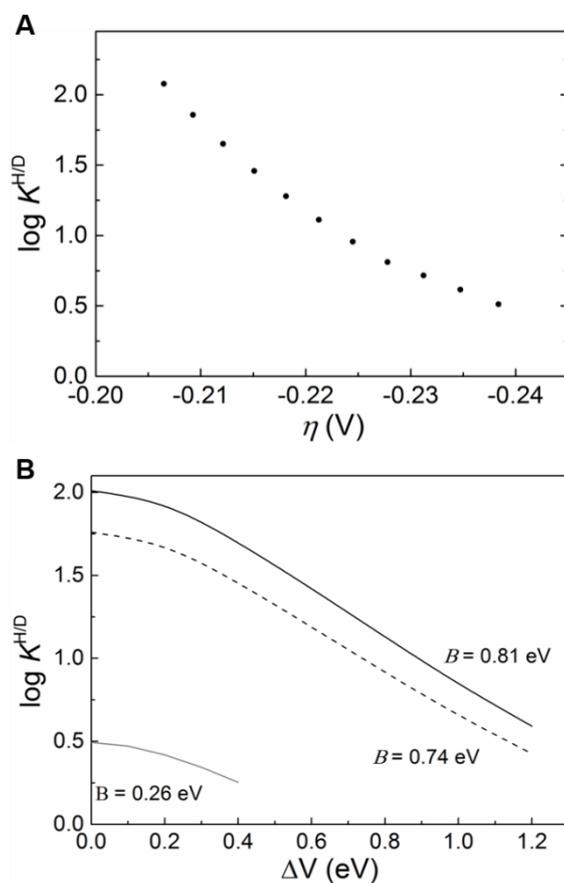


Figure 4. A. Experimentally observed $\log K^{H/D}$ vs. η plots for ORR at Pt in the alkaline condition at 298 K. **B.** Theoretical $\log K^{H/D}$ vs. ΔV plots for different barrier heights. We note that ΔV is a function of the coverage of OH^* (θ_{OH}), but the θ_{OH} is a function of η , and therefore ΔV is a function of η as well (see, [2,76] for details). Figures reprinted with permission from [2]. Copyright (2019) by the American Physical Society.

Conclusion

This review provides a brief outline of the history and recent progress on observations and theories of quantum effects in proton transfer electrode processes:

- (1) It is demonstrated that the electrochemical quantum proton tunneling effects can be observed with appropriate experimental techniques and can dominate the proton transfer process under specific conditions. Furthermore, from the experimental observations suggested fingerprints of solely EQPT paths. However, their microscopic mechanism to trigger a proton transfer purely based on tunneling is still unclear. The complexity of the electrochemical proton transfer processes leads to appearance of many factors affecting the balance between the classical over the barrier path and the quantum tunneling through the barrier path of the reaction.
- (2) From the theoretical point of view there is large diversity of theoretical methods and approaches to describe EQPT processes and it is confirmed that quantum tunneling effects can

play an important role in electrochemical proton transfer reactions. On the other hand, complexity of the methods often hinders their use to describe real processes which strongly depend on many experimental parameters and conditions. Therefore simplified model approaches to account tunneling effects in electrochemical proton transfer reactions in a qualitative and physically clear manner play an important role.

(3) We have shown that a simple and robust model which parametrizes the proton transfer barrier by the asymmetric Eckart's one-dimensional potential helps to elucidate the complicated mechanism of the experimentally observed quantum-to-classical transition in proton transfer in ORR on Pt electrode in alkaline condition.

In summary, we hope that this short review will provide the general picture of quantum effects in electrochemical proton transfer reactions and will stimulate further developments of the theoretical models and experimental techniques [77], in this fascinating area of research.

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Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest

** of outstanding interest

** [2] This article describes the quantum-to-classical transition of the proton transfer process as a function of the potential.

** [4] This article shows a detailed experimental study on EQPT in HER and ORR using Pt and Au electrodes in alkaline and acidic conditions.

** [13] This article describes a detailed experimental methodology for detection of the kinetic isotope effect in electrochemical reactions using carbon-based electrocatalysts.

** [15] This article describes an experimental methodology to measure reliable KIE in electrocatalysis.

* [53] This article presents development of the robust theoretical method to study electron transfer

reactions in solution based on liquid-state theory.

** [55] This comprehensive review represents recent developments and analysis of current challenges for PCET in solution, proteins and electrochemistry.

** [67] This paper presents theoretical description of the Volmer reaction accounting for nuclear quantum effects.

* [68] This paper presents analysis of the potential-dependent kinetic isotope effect for proton discharge on a gold electrode.

** [70] This review gives comprehensive description of nonadiabatic mixed quantum-classical dynamics methods in quantum chemistry to investigate the time evolution of nonadiabatic phenomena in molecular systems.

* [72] This paper describes how to include tunneling effects in real time classical molecular dynamics simulations.

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