Quantum Proton Tunneling in Multi-electron/-proton Transfer Electrode Processes

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Quantum proton tunneling (QPT) in the two representative multi-electron/-proton transfer electrode processes, \textit{i.e.} hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), was investigated by using polycrystalline platinum (pcPt) and gold (pcAu) electrodes at 298 kelvin (K). In order to observe quantum effects in the electrode processes, the hydrogen/deuterium kinetic isotope effect constant ratio (\(\equiv K_H/D\)) was measured in a variety of conditions. For the HER in both an acidic and an alkaline conditions, it was concluded that the pcPt shows a negligible QPT evident by a small value of \(K_{H/D}\) (1 < \(K_{H/D}\) < 3), which indicates that the semiclassical transition state theory (sc-TST) scheme dominates the rate-determining step (RDS) and there is a small or negligible contribution of QPT. In case of the pcAu in alkaline condition, the \(K_{H/D}\) was small value showing ca. 1 at a low \(\eta\) region around 0.2 V, however at a high \(\eta\) region
> 0.6 V, a high $K_{H/D}^{\text{HID}}$ ($> 13$) was obtained. This result suggests that there is a transition of the electrode process from sc-TST to a full QTP in the RDS on increasing the overpotential. For the ORR with pcPt, a $K_{H/D}^{\text{HID}}$ higher than the theoretically maximum in sc-TST was observed in the alkaline condition at a low overpotential region. A primitive but robust theoretical analysis suggests that the QPT governs the rate-determining step of ORR in this condition. However this full QPT path transits to the classical in a higher overpotential region. Therefore, on the contrary to the HER on pcAu in alkaline, the electrode process shows a transition from a full QPT to sc-TST on increasing the overpotential. No QPT in ORR on a pcPt electrode was observed in an acidic condition. In this Contribution, it is shown that the QPT in surface electrochemical system is highly affected by a choice of system. Although several systems show a clear manifestation of QPT in the electrode processes and primitive interpretations can be given to these observations, it is still challenge to derive a fine molecular-level picture on the results including several complicated effects. However, based on the observations, a selection of a full QPT path may be strongly affected by the different microscopic proton transfer mechanisms, i.e. proton transfer from hydronium ion or water molecule.
1. Introduction

Tunneling phenomena is one of the most traditional topics in quantum physics.\textsuperscript{1} It can be traced back to the Hund’s seminal reports in 1927,\textsuperscript{2} which introduced an idea of barrier penetration in the framework of quantum mechanics in order to explain the theory of molecular spectra. During the efforts to build a theoretical interpretation of alpha decay, the quantum tunneling theory was developed by a huge number of physicists. Quantum tunneling is also known as a part of chemical and biological systems.\textsuperscript{3-8} Furthermore, the idea of tunneling emerged giant leaps towards advancement of modern technology, such as semiconductor devices or microscopy.\textsuperscript{9,10}

It was in 1931 by R. W. Gurney,\textsuperscript{11} who firstly applied quantum tunneling in electrode process to explain electron transfer from an electrode to a proton in solution as a key step of kinetics in hydrogen evolution reaction. This view was modified in much more realistic form by J. A. V. Butler,\textsuperscript{12} \textit{i.e.} electron transfer \textit{via} radiationless quantum tunneling to a proton to form an adsorbed hydrogen (H\textsuperscript{8}) on an electrode surface, and further developments were made by many other researchers. In addition to electron tunneling, the formulation of quantum proton tunneling (QPT) in electrode process was given in the work of Bawn and Ogden,\textsuperscript{13} and later the detailed theoretical discussion was made by S. G. Christov, and many other researchers.\textsuperscript{14-16} The aforementioned theories put the emphasis on an initial activation process due to anharmonic oscillations and the
quantum distribution of vibrator levels of nuclei, for instance the protons within water or the hydroxonium ion. However, there are other theories to describe QPT in electrode process, which is based continuum electrostatic approach initiated by Libby and Weiss,\(^{17, 18}\) which model was further develop to electrochemical formalizations based on the Marcus-Hush theory,\(^{19-21}\) or the Dogonadze-Kuznetsov-Levich theory.\(^{22-26}\) In addition, recently, first-principle-based or path-integral molecular dynamics approaches have been introduced to investigate QPT in general.\(^{27-32}\) Not only from theoretical contributions but also there is of course an anomalous number of experimental efforts to observe/discuss QPT in electrode process, for example by B. E. Conway, and S. G. Christov.\(^{33-38}\) Therefore, there are a lot of previous efforts in both experimental and theoretical works to unveil quantum effects in electrode processes. However, it is still unclear in which system we can observe QPT in electrode process and why it is emerged. Furthermore, the theoretical framework for the microscopic mechanism of QPT in electrode process is also still under development. This is one of the major reasons why it is challenge to understand mechanism of electrode processes in general, which has a quite long research history since the Faraday’s era.\(^{39}\) And this leads electrochemistry-oriented technology obscure to apply modern quantum principles as its core mechanism to advance its properties in contrast to other energy conversion technology.\(^{40}\)
In this Paper, an investigation of QPT in multi-electron/-proton transfer electrode processes is briefly shown with a present primitive understanding of the mechanism. As the model reactions, hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), were studied by using polycrystalline platinum (pcPt) and gold (pcAu) electrodes at 298 kelvin (K) in acidic and alkaline conditions. It will be presented that the QPT can be observed in several system and will be discussed a possible mechanism.

2. Present Understanding on Quantum Proton Tunneling in Electrode Processes

As it was already mentioned above, interests on quantum tunneling began to appear in the early 20th century during the establishment of quantum mechanics. Due to this long history of investigation, we can find a wide spectrum of detailed reports on electrochemistry using the H-D exchange isotope effects up to now. Furthermore, a variety of theoretical models are available. However, QPT is still poorly understood because of several experimental challenges on electrochemical experiments. And, unlike in ordinary water systems, this made challenge to carry out precise electrochemical analysis using deuterated water, which is an essence to study quantum effects. For example, to the best of our knowledge, the first comparison of cyclic voltammograms in a fully deuterated and protonated systems was shown by Yeager and co-workers in 1985. Furthermore, as it is shown in Section 3, it was quite recent to be established
the both experimental procedures and the analytical equations to observe and analyze QPT in electrode processes, respectively.\textsuperscript{48, 49} From this point, we actually know very little about QPT in molecular-level electrode processes, therefore, we have to begin experimental studies on this topic from an embryonic stage. In addition to this, the theoretical description of microscopic activation process on electrode surface is still obscured. Indeed, this is the aim of this contribution to share and discuss the protocol and analytical equations to observe/analyze QPT in electrode process, and develop its present understanding by integrated with modern theories and experimental results from related subjects.

3. Experimental methods and Analytical Equations

3.1. Standard Electrochemical Methods

The Electrochemical measurements were conducted using a RRDE set-up (Dynamic Electrode HR-301, HOKUTO DENKO) with an electrochemical analyzer (HZ-7000, HOKUTO DENKO) based on a custom-made three-compartment electrochemical glass cell at 298 K ± 1. The ring electrode was kept at 1.2 V vs. reversible hydrogen electrode (RHE) or reversible deuterium electrode (RDeE). We denote potential with RHE scale and with RDeE scale as $V_{\text{RHE}}$ and $V_{\text{RDeE}}$, respectively. The cell was firstly cleaned by boiling in a mixture of concentrated sulfuric acid for overnight and then boiling in ultrapure ordinary water (MilliQ water, 18.3 MΩ cm) for overnight.
Before electrochemical measurements, the cells were washed by an ultrapure electrolyte several times, and then were poured the ultrapure electrolyte for measurements. The electrolytes in the cell were bubbled with O$_2$ (purity > 99.999%, Taiyo Nippon Sanso) or Ar (purity > 99.99995%, Taiyo Nippon Sanso) for 30 min before the experiments to prepare the O$_2$-saturated condition or Ar-saturated condition, respectively. Resistance of electrochemical systems was measured prior to each experiment by using impedance measurements, and this value was used to correct $iR$-drop.

In this paper, all potential values are $iR$-corrected. For preparation of ultrapure electrolytes with ordinary water, a high purity KOH (semiconductor grade, 99.99% trace metals basis, Sigma-Aldrich) or H$_2$SO$_4$ (96 %, Ultrapur., Merck) was mixed with ultrapure water (Milli-Q water, 18.3 M$\Omega$ cm). The electrolytes based on the deuterated oxide were prepared by mixing potassium deuteroxide solution (40 wt. % KOD in D$_2$O, Cambridge Isotope) or sulfuric acid-$d_2$ solution 96-98 wt. % in D$_2$O (99.5 at. % D, Sigma-Aldrich), with a high-purity deuterated oxide (“100 %” distilled D$_2$O, Sigma-Aldrich) in order to obtain ultrapure 0.1M KOD or 0.05M D$_2$SO$_4$ in D$_2$O.

In order to prepare the ultrapure deuterated electrolytes, the as-received “100 %” D$_2$O was purified based on the previous method.$^{49}$ We note here that highly clean electrolytes are indispensable to measure KIE.

A three-electrode setup is consisted of a carbon counter electrode, a RHE or RDeE as the reference
electrodes, and a commercial fixed polyAu or polyPt working electrodes (purchased from HOKUTO DENKOU) with a diameter of 0.5 cm (Therefore, the geometrical surface area of electrodes is 0.196 cm$^2$). Typically, we used a scan rate of 50 mV s$^{-1}$ and a rotation rate of 1600 rpm for the ORR experiments, and a scan rate of 1 mV s$^{-1}$ and a rotation rate of 2000 rpm for HER / deuterium evolution reaction (DER). An electrochemically active surface area (ECSA) was measured by the typical method to use CV in order to normalize obtained currents for the reliable comparison.$^{50}$ A charge of 220 μC cm$^{-2}$ is assumed for a charge of full coverage of monolayer proton and deuteron on a smooth polyPt surface. In case of polyAu, a value of 424 μC cm$^{-2}$ is assumed as the charge per unit area due to a reduction of a monolayer of surface oxide.

3.2. Standard Analytical Equations to Study Kinetics of Electrode Processes

The transfer coefficient analysis based on the Eq. 1 can be applied to acquire the introductory information on electrode processes,$^{51}$ especially on rate-determining steps, where $\alpha$, $s$, $\nu$, $\beta$, and $r$ is transfer coefficient, number of transferred electron before the RDS, stoichiometric number, symmetric factor, and number of transferred electron in the RDS (usually $r = 1$), respectively. In order to use Eq. 1, we hypothesized that only a single RDS exists in each system.

$$\alpha = \frac{s}{\nu} + \beta r.$$  

Eq. 1
We note that Eq. 1 assumes the Tafel’s law\(^\text{52}\) and the absence of double-layer effects and a low coverage of reactants/products on an electrode. Furthermore, coverage of proton or oxygen species on surface is well known to give effects to electrode kinetics, and these terms are usually potential dependent and can set as an exponential term together with \(\beta\) for rate expression, for instance,

\[-\frac{1}{b} = \frac{F}{RT}(\beta + \frac{RT\partial(\ln\theta_H)}{F\partial\eta}),\]

for HER\(^\text{53}\) where \(b\), \(R\), \(T\), \(\theta_H\) and \(\eta\) are Tafel slope, the gas constant and temperature, a proton coverage on electrode surface, and overpotential, respectively. From this, here we give the second assumption to treat Eq. 1 that major microscopic effects due to adsorbed species and electrified surface, which affect electrode processes, can be incorporated in \(\beta\):

\[\beta = \beta' + \sum_{x=1}^\infty O(\eta^x)\]

The term \(\beta'\) indicates a symmetry factor in the traditional definition, which is often assumed as 0.5, however this value can be varied if we consider the microscopic effects, such as
anharmonicities of the H* bond vibration. The additional term $\Sigma O(\eta^4)$ represents interactions between adsorbed species, electrified surface, solvent, etc., which can be varied with a selection of theoretical framework. Symmetry factor $\beta$ has a central role in electrode kinetics and it is a fundamental entity to understand microscopic mechanism in both experimental and theoretical approaches. Therefore, due to the second assumption, it is challenge to obtain a detailed view on microscopic mechanism. However, although it is a quite primitive approach, in this study, we focus on the observation of QPT and to extract fingerprints of main effects to emerge quantum phenomena. Towards this aim, the above-mentioned simple framework is enough to pursue this study. Nevertheless, because of the second assumption, transfer coefficient $\alpha$ can be obtained from a simple form of Tafel slope $b$ by using Eq. 2.

$$b = \frac{2.303RT}{aF}$$

Eq. 2

Due to the following equation, we can obtain $j_0$ from a corresponding log $j_k$-$\eta$ diagram:

$$j_k = j_0 \times \exp\left\{ -\frac{aF}{RT} \eta \right\}$$

$\Leftrightarrow \log j_k = \log j_0 - \frac{aF}{2.303RT} \eta$

$\Leftrightarrow \eta = -b (\log j_k + \log j_0)$

Eq. 3
The ORR kinetic currents on Pt electrode can be separated from diffusion limiting current by using a following equation since we can observe clear diffusion-limited currents:

\[ \frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_{lim}} \Leftrightarrow j_k = \frac{(j_{lim} - j)}{(j_{lim} - j_k)}, \]

where \( j \) and \( j_{lim} \) are an experimentally obtained current with RRDE technique and an diffusion limiting current, respectively.

The equilibrium potential for the D\(_2\)O formation (\( E_{D2O}^{0} \)) is \( 1.262 \text{ VRDE} \), therefore the overpotential for the ORR in deuterated system (\( \eta_{DORR}^{D} \)) can be obtain by following the definition of overpotential:

\[ \eta_{DORR}^{D} (V) = \text{An experimentally obtained potential (VRDE)} - 1.262 \text{ (VRDE)}. \]

The overpotential for the ORR in the ordinary system (\( \eta_{HORR}^{H} \)) can be obtain by following:

\[ \eta_{HORR}^{H} (V) = \text{An experimentally obtained potential (VRHE)} - 1.229 \text{ (VRHE)}. \]
3.3. Analytical Equations to Obtain Kinetic Isotope Effect Rate Constant Ratio

In order to investigate kinetic isotope effect (KIE) for HER, a KIE rate constant ratio in HER

\( \frac{k^H(\eta)}{k^D(\eta)} = K^{\text{HD}}_{\text{HER}}(\eta) \)

can be obtained by the following general equation:

\[
K^{\text{HD}}_{\text{HER}}(\eta) = \frac{k^H(\eta)}{k^D(\eta)} = \frac{j^H}{j^D} \times \frac{[D^+]}{[H^+]} \times \exp \left\{ -\frac{\Delta G_{\text{D}-\text{H}}F\eta}{RT} \right\},
\]

Eq. 4

\[ j_0 = nF[X]k_0 \quad (X = H^+ \text{ or } D^+) \]

\[ j_{\text{HER}} = nF[H^+]k_0^H \exp \left\{ -\frac{\Delta G_{\text{D}-\text{H}}F\eta}{RT} \right\}, \]

and \[ j_{\text{DER}} = nF[D^+]k_0^D \exp \left\{ -\frac{\Delta G_{\text{D}-\text{H}}F\eta}{RT} \right\}, \]

where \( j_0, k_0, [H^+], [D^+], \eta, F, R \) and \( T \) are, an exchange current density, a rate constant at \( \eta = 0 \), proton concentration, deuteron concentration, overpotential, the Faraday’s constant, the gas constant and an experimental temperature (298±1 K in this study), respectively. We note here that we have to take into account the different dissociation constant of D2O compared to that of H2O.44 This simple difference is some time underestimated in several studies.42,43,55 However it is a key quantity to analyze KIE in electrode process as shown in the following equations. For example, the 0.1M KOD in D2O solution gives \([D^+] = 10^{-13.87} \text{ mol L}^{-1} \), and therefore, the \( K^{\text{HD}}_{\text{HER}}(\eta) \) for the case comparing the 0.1M KOH in H2O ([H+] = 10\(^{-13}\) mol L\(^{-1}\)) and 0.1M KOD in D2O solutions is
$K_{\text{HER}}^{\text{H/D}}(\eta) = 0.1349 \times \frac{j^H_0}{j^D_0} \times \exp\left\{\frac{(\alpha^D - \alpha^H)F\eta}{RT}\right\}.$

However, the $K_{\text{HER}}^{\text{H/D}}(\eta)$ for the case comparing the 0.05M H$_2$SO$_4$ in H$_2$O ([H$^+$] = 10$^{-1}$ mol L$^{-1}$) and 0.05M D$_2$SO$_4$ in D$_2$O ([D$^+$] = 10$^{-1}$ mol L$^{-1}$) becomes

$K_{\text{HER}}^{\text{H/D}}(\eta) = \frac{j^H_0}{j^D_0} \times \exp\left\{\frac{(\alpha^D - \alpha^H)F\eta}{RT}\right\},$

which is identical to the equation shown by Krishtalik as the general equation to obtain $K_{\text{HER}}^{\text{H/D}}(\eta).$\(^{55}\)

A KIE rate constant ratio for ORR ($K_{\text{ORR}}^{\text{H/D}}(\eta)$) can be obtained by the following general equation:

$K_{\text{ORR}}^{\text{H/D}}(\eta) = \frac{k^H(\eta)}{k^D(\eta)} = \frac{j^H_0}{j^D_0} \times \frac{c^D_0}{c^H_0} \times \exp\left\{\frac{(\alpha^D - \alpha^H)F\eta}{RT}\right\},$ \hspace{1cm} Eq. 5

$\therefore j^H_{0,\text{ORR}} = n k^H_0 C^H_0 \exp\left\{-\frac{\alpha^H F\eta}{RT}\right\}$ and $j^D_{0,\text{ORR}} = n k^D_0 C^D_0 \exp\left\{-\frac{\alpha^D F\eta}{RT}\right\}$

where $C_0$ is, the oxygen concentration. The $C^D_0/C^H_0$ is known to be 1.101 at 298 K.\(^{42}\)
4. Results and discussion

4.1. Quantum Proton Tunneling in Hydrogen Evolution Electrode Process

First of all, the HER activities and electrode processes of pcPt in 0.05M H₂SO₄ in H₂O/0.05M D₂SO₄ in D₂O are discussed based on the diagrams of the common logarithm of the \( iR \)-corrected kinetic HER current densities (log \( j_k \)) vs. the overpotential (\( \eta \)) (Figure 1a). We used current densities normalized by the electrochemically active surface areas (ECSA) of the electrocatalysts.\(^\text{50}\) In order to discuss the mechanism of HER in acid, we follow the two well-accepted paths:\(^\text{53, 56}\) the primary discharge step (or so-called Volmer step, * indicates adsorbed species or adsorption sites),

\[
\text{H}_3\text{O}^+ + * + e^- \rightarrow \text{H}^* + \text{H}_2\text{O}, \quad \text{(Step I)}
\]

coupled with either the electrochemical-desorption step (Heyrovský step)

\[
\text{H}^* + \text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_2 + \text{H}_2\text{O}, \quad \text{(Step II)}
\]

or the recombination step (Tafel step)

\[
\text{H}^* + \text{H}^* \rightarrow \text{H}_2. \quad \text{(Step III)}
\]

We found that the Tafel slopes (\( b \)) are slightly different for the ordinary and deuterated systems, showing \(-27.4 \pm 0.2 \) mV/dec and \(-29.9 \pm 0.4 \) mV/dec, respectively, which are well agreed with previous reports showing \( b = \text{ca.} \) 30 mV/dec for HER on Pt in acidic conditions (Figure 1a).\(^\text{57, 58}\)
A small difference of $b$ in the deuterated and ordinary systems might be explained by the difference of $H^*$ and $D^*$ bond vibrations, which leads to different anharmonicities and therefore different symmetry factors, or other microscopic effects. From Eq. 2, we obtain transfer coefficients ($\alpha$) = ca. 2 for both the ordinary and deuterated systems. With $\alpha$ and Eq. 1, we can obtain further details on rate-determining step (RDS) and KIE. When $\alpha = 2$, the possible combination of $(s, v, r)$ in Eq. 1 is $(2, 1, 0)$ due to $0 < \beta < 1$ and typically $\beta = 0.5$. This indicates that the possible RDS of HER on pcPt in 0.05M $H_2SO_4$ in $H_2O/0.05$ M $D_2SO_4$ in $D_2O$ is Step III (the recombination of adsorbed protons ($H^*$) /deuteron ($D^*$) on the electrode surface), which is well agreed with a huge number of previous reports for the HER activity of Pt in acidic conditions using the ordinary water.\textsuperscript{53}

Moving on to the analysis of KIE, the pcPt electrode in the acidic condition shows a $K^{HD}_{\text{HER}}(\eta)$ of about 2 in the overpotential range from $-0.005$ to $-0.02$ V, which is corresponding to the linear region in 0.05M $H_2SO_4$ solution (Figure 1a). As we discussed already, the $b$ shows slightly different values in the deuterated and ordinary water systems, therefore this leads to $\alpha^H \neq \alpha^D$ for Eq. 2. In this case, KIE in electrochemistry is obviously a function of potential (Eq. 4). This suggests that KIE can be significantly varied on potential change even small difference between $\alpha^H$ and $\alpha^D$. As shown in Figure 1b, $K^{HD}_{\text{HER}}$ is 1.74 at $\eta = -0.005$ V and increases to 1.93 at $\eta =$
−0.02 V, suggesting 11% increase of \( K^{\text{H/D}}_{\text{HER}} \) with 0.015 V of an overpotential shift. However, although \( K^{\text{H/D}}_{\text{HER}} \) increases with shift of overpotential, the small value of \( K^{\text{H/D}}_{\text{HER}} \) can be explained with the semiclassical transition-state theory (sc-TST), therefore QPT has no or negligible role for this process in this condition.

**Figure 1.** (a) log \( j_k \) vs \( \eta \) diagrams and (b) \( K^{\text{H/D}}_{\text{HER}} \) vs \( \eta \) diagram of the pcPt in 0.05 M H\(_2\)SO\(_4\) in H\(_2\)O/0.05 M D\(_2\)SO\(_4\) in D\(_2\)O. Kinetic current densities (\( j_k \)) are normalized by ECSA (A cm\(^{-2}\)ECSA). All data are corrected for Ohmic drops (\( iR \) correction). The measurements were performed with a scan rate of 1 mV s\(^{-1}\) and a rotation rate of 2000 rpm. Error bars are shown for every 3\(^{rd}\) data point.

Next, the HER activities and electrode processes of pcPt in 0.1M KOH in H\(_2\)O/0.1M KOD in D\(_2\)O are discussed based on the log \( j_k \) vs. \( \eta \) (Figure 2a). In alkaline, water molecule becomes the proton source:
\[
\text{H}_2\text{O} + * + e^- \rightarrow \text{H}^* + \text{OH}^- , \\
\text{H}^* + \text{H}_2\text{O} + e^- \rightarrow \text{H}_2 + \text{OH}^- , \\
\text{H}^* + \text{H}^* \rightarrow \text{H}_2 .
\]

(Step I')

(Step II')

(Step III)

There is a clear line in both the ordinary and deuterated systems (Figure 2a), and the Tafel slopes (b) are identical, showing \(-69.2 \pm 0.1 \text{ mV/dec} \) and \(-69.1 \pm 0.2 \text{ mV/dec} \), respectively. This result is also well agreed with the previous reports shown the b in alkaline condition between 50 to 75 \text{ mV/dec}.\textsuperscript{59, 60} From Eq. 2, we obtain the transfer coefficient (\(\alpha\)) = 0.86. When \(\alpha = 0.86\), the possible combinations of (\(s, v, r\)) in Eq. 1 are (0, 2, 1) or (1, 1, 1), which gives \(\alpha = \beta\) and \(\alpha = 1 + \beta\), respectively, as we hypothesized that there is only a single RDS in the total process (section 3.2.). In the case of \(\alpha = \beta\), the limiting step is Step I' with \(\beta = 0.86\). On the other hand, in the case of \(\alpha = 1 + \beta\), the limiting step is Step II' with \(\beta = 0.36\). From previous report, we can expect that the Step I' is quasi-equilibrium, therefore Step II' can be the possible RDS.

In order to analyze the further details of the electrode process in this system, KIE was checked. The KIE of the pcPt electrode in the alkaline condition shows a hydrogen/deuterium kinetic isotopic rate constant ratio (\(K_{\text{HER}}^{\text{HD}}(\eta)\)) close to 1. Because the b shows the identical value of \(-69\) \text{ mV/dec} in the deuterated and ordinary systems, we obtained potential independent \(K_{\text{HER}}^{\text{HD}}\) due
to $\alpha^H = \alpha^D$ for Eq. 4 (Figure 2b). Since in case of $K_{HD} = 1$, it is the sign for no involvement of proton transfer in the RDS. Therefore, combined with above discussion based on Eq. 1, the RDS in this system could be an electron transfer process related to Step II'. Nevertheless, there is no QPT therefore we don’t discuss the detailed mechanism in this condition further.

Figure 2. (a) log $j_k$ vs $\eta$ diagrams and (b) $K_{HD,HER}$ vs $\eta$ diagram of the pcPt in 0.1M KOH in D$_2$O/0.1M KOD in D$_2$O. Kinetic current densities ($j_k$) are normalized by ECSA ($A \text{ cm}^{-2}_{\text{ECSA}}$). All data are corrected for Ohmic drops ($iR$ correction). The measurements were performed with a scan rate of 1 mV s$^{-1}$ and a rotation rate of 2000 rpm. Error bars are shown for every 3rd data point.

Next we move to the system with a pcAu electrode. In the Figure 3, it is shown the HER activities and electrode processes of pcAu in 0.05M H$_2$SO$_4$ in H$_2$O/0.05M D$_2$SO$_4$ in D$_2$O. In this condition, there is a clear line in the both systems, and the Tafel slopes ($b$) are identical, showing $-82.2 \pm$
0.7 mV/dec and −81.8 ± 0.2 mV/dec, in 0.05M H₂SO₄ in H₂O and 0.05M D₂SO₄ in D₂O, respectively. From Eq. 2, we obtain the transfer coefficients (α) = 0.72, which gives the possible combinations of (s, v, r) in Eq. 1 as (0, 2, 1) or (1, 1, 1) leading to \( α = β \) and \( α = 1 + β \), respectively.

In contrast to Pt electrode, we observe negligible UPD-/OPD-H in case of Au electrode, therefore, the quasi-equilibrium for Step I is not a reasonable, therefore the case of (s, v, r) = (1, 1, 1), i.e. Step II as the RDS, is unlikely at least in a low \( η \) region for this system. In order to consider the RDS in this system, we follow the previous reports, which used a first-principle-based calculation in order to consider the proton adoption and HER on metal electrodes. These reports suggested that the proton adsorption on the Au(111) surface is endergonic at the equilibrium potential (i.e. \( η = 0 \)) for the HER. This result indicates that Step I determines the rate of the overall reaction as the potential-determining step. The \( K_{HER}^{D/\text{HER}}(η) \) of this system can be calculated to 3.0 ± 0.3 with no potential-dependency due to \( α^H = α^D \). Although even for a primitive estimation of a tunneling magnitude to an overall reaction is required a detailed information on H* bond length and an activation barrier height and width at a RDS, \( K_{HER}^{D} = 3 \) indicates that the electrode kinetics can be affected by the QPT, however is a minor effect.
Figure 3. (a) log $j_k$ vs $\eta$ diagrams and (b) $K^{\text{H/D\_HER}}$ vs $\eta$ diagram of the pcAu in 0.05M H$_2$SO$_4$ in D$_2$O/0.05M D$_2$SO$_4$ in D$_2$O. Kinetic current densities ($j_k$) are normalized by ECSA (A cm$^{-2}$). All data are corrected for Ohmic drops ($iR$ correction). The measurements were performed with a scan rate of 1 mV s$^{-1}$ and a rotation rate of 2000 rpm. Error bars are shown for every 3rd data point.

Finally, in the Figure 4, it is shown that the HER activities and the electrode processes of the pcAu electrode in 0.1M KOH in H$_2$O/0.1M KOD in D$_2$O. In this condition, we can observe a clear line in each system for a wide range of overpotential. The values of the Tafel slopes are quite different in the two systems. In the fully protonated and the fully deuterated systems, the Tafel slopes ($b$) are 101.7 $\pm$ 0.2 mV/dec and 135.2 $\pm$ 0.6 mV/dec, respectively (Figure 4a). From Eq. 2, we obtain the transfer coefficients in the ordinary hydrogen system and the fully deuterated system as $\alpha^H = 0.58$ and $\alpha^D = 0.44$, respectively. From these results, we assigned ($s$, $v$, $r$) in Eq. 1 as (0, 0, 1), and obtain $a = \beta$, therefore the RDS is Step I’. The $K^{\text{H/D\_HER}}(\eta)$ in this system shows an anomalous
behavior. The $K^{\text{HD}_{\text{HER}}}(\eta)$ is close to 1 at $\eta = -0.2$ V, suggesting there is no contribution of proton transfer or proton transfer with sc-TST in the RDS. However, the $K^{\text{HD}_{\text{HER}}}(\eta)$ drastically increases to $> 13$ at $\eta = -0.7$ V, which can be possible to attributed to the sign of the full quantum process (Figure 4b), therefore in this system, the electrode process can be transited from the (semi)classical process to the quantum process associated on overpotential increase.

![Figure 4. (a) log $j_b$ vs $\eta$ diagrams and (b) $K^{\text{HD}_{\text{HER}}}$ vs $\eta$ diagram of the pcAu in 0.1M KOH in D$_2$O/0.1M KOD in D$_2$O. Kinetic current densities ($j_b$) are normalized by ECSA (A cm$^{-2}_{\text{ECSA}}$). All data are corrected for Ohmic drops ($iR$ correction). The measurements were performed with a scan rate of 1 mV s$^{-1}$ and a rotation rate of 2000 rpm. Error bars are shown for every 3rd data point.](image)

4.2. Summary of Quantum Proton Tunneling in Hydrogen Evolution Electrode Process

The key results in hydrogen evolution electrode processes are summarized in Table 1. We can
find that, beside the pcPt electrode in the alkaline condition, the $K^{H/D}$ values suggest there are the fingerprints of quantum effects in proton transfer in other three systems. Especially, the most interesting system out of three is the pcAu electrode in the alkaline condition due to the observation of classical-to-quantum transition of proton transfer on increasing overpotential: in this system initially proton transfer is negligible or is participated with very weak quantum correction because $K^{H/D}$ is close to 1 at $\eta = -0.2$ V, however its value drastically increases to > 13 at $\eta = -0.7$ V, suggesting a domination of QPT, *i.e.* a full QPT path.

| Electrode | Condition          | $\alpha$ | RDS   | $-\log j_0$ (A cm$^{-2}$) | $K^{H/D}$           |
|-----------|--------------------|----------|-------|-------------------------|---------------------|
| pcPt      | 0.05M H$_2$SO$_4$ in H$_2$O | 2        | Step III | 2.66                  | ca. 1.8 $\eta$ dependent weak QPT |
| pcPt      | 0.05M D$_2$SO$_4$ in D$_2$O | 2        | Step III | 2.88                   | 1 $\eta$ independent no QPT |
| pcPt      | 0.1M KOH in H$_2$O    | 0.86     | Step II$^*$ | 3.24                  | 3 $\eta$ independent weak QPT |
| pcPt      | 0.1M KOD in D$_2$O    | 0.86     | Step II$^*$ | 4.07                 | 1 to > 13 $\eta$ dependent classical-to-quantum transition |
| pcAu      | 0.05M H$_2$SO$_4$ in H$_2$O | 0.72     | Step I  | 5.73                  | 1 to > 13 $\eta$ dependent classical-to-quantum transition |
| pcAu      | 0.05M D$_2$SO$_4$ in D$_2$O | 0.72     | Step I  | 6.21                  | 1 to > 13 $\eta$ dependent classical-to-quantum transition |
| pcAu      | 0.1M KOH in H$_2$O    | 0.58     | Step I$'$ | 7.15               | 1 to > 13 $\eta$ dependent classical-to-quantum transition |
| pcAu      | 0.1M KOD in D$_2$O    | 0.44     | Step I$'$ | 7.55               | 1 to > 13 $\eta$ dependent classical-to-quantum transition |

*Due to $K^{H/D} = 1$, the RDS is the electron transfer step in Step II$'$. 
One of the key factors for a full QPT path in the system is large difference of $\alpha^H$ and $\alpha^D$ due to Eq. 4. Since there is still no enough data about H* bond and the activation barrier for Step I’ in the corresponding system, it is difficult to make an quantitative analysis, however, qualitatively, the difference of $\alpha (= \frac{g}{v} + \beta)$ in the H and D systems suggests that the harmonic approximation and/or ignorance of microscopic interactions (i.e. the interaction term $\Sigma O(\eta')$ in the section 3.2.) would not be suitable approaches anymore to consider electrochemical systems showing significant quantum effects on proton transfer. In classical framework, we assume that the symmetry factor is $\beta = 0.5$ because of the harmonic approximation and no microscopic interactions (i.e. $\Sigma O(\eta') = 0$). On the other hand, there is a wide spectrum of interactions between electrified surface effects, adsorbed species and solvents. Therefore the present results indicates that the theoretical framework to consider the QPT in electrode process should be constructed with a careful selection of interactions and an addition of anharmonicities in reaction scheme (Figure 5). Recent results of surface enhanced infrared spectrometry (SEIRAS) on Au electrode surfaces give a primitive picture on microscopic view of Step I’. Potential below the potential of zero charge, the orientation of water molecules is suggested to be organized with the two hydrogen atoms slightly closer to the electrode surface than the oxygen atom (Figure 5a). Furthermore, we have to take into account of the surface reconstruction in case of Au electrodes. As it is shown by previous works, the first monolayer of Au surface will be developed
associated with potential change. For example, in case of an application of negative potential to the most thermodynamically stable Au (111) surface, the Au(111)-(1×1) phase transits to the Au(111)-(23 × √3) uniaxial striped phase. This fact indicates that the surface phase of Au electrode will be developed on changing the electrode potential. The recent reports suggest that a lattice-strain can give a huge effects on electrocatalytic activity, therefore not only anharmonicities and microscopic interactions but also the surface structure development might be important to take into account, and of course these different effects interact each other to change activation barrier on applying potential (Figures 5b,c). Not last but least, a recent report using Au electrode shows a large difference of the transfer coefficients between the protonated and deuterated systems. These authors indicated that the RDS corresponding to this system is a proton-coupled electron transfer, and this experimental results was well fitted with their model taking into account contributions from excited electron–proton vibronic states, which is affected by isotopes and on changing potential. Although HER is the simplest multi-electron/-proton transfer electrode process, the complexity of the system enormously increases if we try to unveil the quantum effects in its microscopic mechanism.
Figure 5. (a) Schematic illustration for the Step I’ ($\text{H}_2\text{O} + e^- + * \rightarrow \text{H}^* + \text{OH}^-$) on Au electrode with a possible microscopic mechanism. Water in alkaline condition is assumed to be adsorbed on Au electrode with the configuration as same as acidic condition obtained by SEIRAS.$^{64, 66}$ Since the proton source of HER in alkaline condition is water, the adsorbed water is assumed to contribute to the Step I’. Hypothetical reaction coordinates (b) at low $\eta$ and (c) at high $\eta$ based on the KIE results. The different peak position in the protonated and deuterated systems are due to different symmetry factors ($\beta_H = 0.58$ and $\beta_D = 0.44$). The Brønsted-Evans-Polanyi relationship with these symmetry factors predicts that the barrier height in the protonated system should be largely decreased from low to high $\eta$ compared to the one of the deuterated system. Therefore, in order to emerge a full QPT path and a large $K_{\text{H/D}}$ at a high $\eta$, the barrier width in the protonated system is predicted to become enough thinner on increasing $\eta$ to increase the permeability of proton due to microscopic effects such as electrified surface or surface reconstruction.
4.3. Quantum Proton Tunneling in Oxygen Reduction Electrode Process

So far, the QPT in ORR was observed in case of pcPt in an alkaline condition (Figure 6).\textsuperscript{48} In this case, the QPT was confirmed in a low overpotential region due to $K^{\text{H/D}} = 32$, but the QPT transits to sc-TST scheme ($K^{\text{H/D}} = 3.7$), therefore, there is a quantum-to-classical transition of proton transfer in ORR (Figure 6a) and this was confirmed by a theoretical analysis (Figure 6b). The fingerprint of the QPT was indicated by a large $K^{\text{H/D}} > 13$ in the low overpotential region: the maximum $K^{\text{H/D}}$ for the O-H bond breaking in semiclassical frameworks is ca. 13 at 298 K accounting for the change in the activation barriers because of the differences in zero-point energies due to different vibrations in O-H and O-D.\textsuperscript{75} In addition to this, we note that, although different adsorption energies of OH/OD species on Pt surface could arise the differences in zero-point energies or another reaction path,\textsuperscript{76, 77} the difference of the OH/OD adsorption energies in the system is 1.2 kJ mol$^{-1}$, which is too small to affect to the reaction. In this study, a primitive however robust model was applied to analyze this observation by approximating the barrier by an asymmetric Eckart’s one-dimensional potential energy function.\textsuperscript{78, 79} Furthermore, the Brønsted-Evans-Polanyi relationship was used to describe linear variations in the height of the activation barrier with the reaction energy on potential changing.\textsuperscript{80-82} Since the barrier height for the corresponding reaction is under debate so far, however, as we show later, the values from several reports showing around 0.7 to 0.8 eV fits well to our observation.\textsuperscript{83, 84} Furthermore, the width of
the barrier was selected to be 0.3 Å because the widths, corresponding to hydrogen bond between intermediate species, such O₂* and O*, are ranging in 0.25–0.35 Å. Even though, with such quite primitive model, it was shown that QPT can be possible and also there is a quantum-to-classical transition on increasing the overpotential (Figures 6b, c).
Figure 6. (a) $\eta$ vs log $K^{\text{H/D-ORR}}$ diagram of the pcPt in 0.1M KOH in D$_2$O/0.1M KOD in D$_2$O, and (b) theoretical log $K^{\text{H/D-ORR}}$ vs reaction exothermicity parameter ($\Delta V$) diagram. The proton transfer barriers at equilibrium ($B$) were taken from the previous reports. (c) Schematic diagram for two possible schemes of the proton-transfer reaction: proton transfer via sc-TST and QPT. The relative contribution of the two mechanisms can be tuned on changing electrode potential. Reprinted figures with permission from [Phys. Rev. Lett., 121, 236001, (2018)] Copyright (2019) by the American Physical Society.
In case of pcPt in an acidic condition (Figure 7), no QPT was observed. Our experimental result on $K^{HD}$ was almost identical to the result of Yeager and his co-workers, who carried out the same measurement and analysis for pcPt in a different acid (85 % H$_3$PO$_4$). In our case, it was found that $K^{HD} = 1.5$, and $K^{HD} = 1.4$ for the Yeager’s case, which was concluded that the contribution of proton transfer is negligible therefore the RDS is the electron transfer process even the result was $K^{HD} > 1$. This previous report reached to this conclusion because they carried out their experiments for the protonated system at 298 K but for the deuterated system at 303 K, and this report claims that $K^{HD} = 1.4$ is the result of the 5 K difference, which leads to increase the rate constant in the deuterated system about 30 % compared to the protonated system. It should be emphasized that this Yeager’s report measured the ORR in the 85 % H$_3$PO$_4$/D$_3$PO$_4$ systems, therefore it is a different acidic system compared to the one in the present study, and also, they did not take into account the different solubility of O$_2$ in the protonated/deuterated systems in different temperatures. From the points of a huge number of experimental ORR studies, it is believed that the RDS of ORR on Pt surface in acidic condition is related to the first electron transfer to dioxygen, which leads to $K^{HD} = 1$ if there is no association of proton transfer. However, from several experimental point of view, the RDS of ORR on Pt in acidic condition is the first proton-coupled electron transfer, i.e. a proton transfer is included in the RDS.
Therefore, the present result showing $K_{\text{H/D}} = 1.5$ could confirm these previous observations. Although many efforts are continuously exposing to understand the microscopic mechanism of ORR and there is always updates in the field, there are still demands for both experimental and computational approaches to clarify the microscopic electrode process of this reaction.

![Figure 7. Log $j_k$ vs $\eta$ diagrams of the pcPt in 0.05M H$_2$SO$_4$ in D$_2$O/0.05M D$_2$SO$_4$ in D$_2$O. Kinetic current densities ($j_k$) are normalized by ECSA (A cm$^{-2}$ECSA). All data are corrected for Ohmic drops ($iR$ correction). The measurements were performed with a scan rate of 50 mV s$^{-1}$ and a rotation rate of 2000 rpm. Error bars are shown for every 3rd data point.](image)

5. Conclusions

In order to observe QPT in multi-electron/proton transfer electrode processes and to give fundamental interpretations to these observations in microscopic level, we have established the
basic analytical equations and prepared the detailed experimental procedures to investigate quantum effects in electrode processes with the aid of kinetic isotope effects. Based on these approaches, we studied QPT in HER and ORR as the model processes. This leads to the following main conclusions:

(1) With the appropriate experimental procedures and equations, we can observe and analyze quantum effects in electrode processes. The results in this study indicated that QPT in electrode processes is not a rare phenomenon and this process can be often combined with a TST path, however a full QPT process seems to be non-trivial.

(2) In our study, a full QPT in HER can be only observed in one condition, i.e. pcAu electrode in the alkaline condition at a high overpotential. Other conditions can be shown QPT but it is combined with the TST path or some conditions no QPT.

(3) The strong quantum effect in HER with pcAu electrode in the alkaline condition is due to a huge difference of the symmetry factors between the fully deuterated and protonated systems. The RDS is suggested to the first proton-coupled electron transfer for the both systems. The reason for the different symmetry factors may be due to a sum of several microscopic effects at
the electrode/electrolyte interface, such as anharmonicities in potential energy surface and/or changing adsorption energies of reaction intermediates due to the surface reconstruction.

(4) The ORR using pcPt electrode in the alkaline condition shows a full QPT in a low overpotential region but no QPT in acidic condition at least in the overpotential range in the present study.

(5) There are many different forms of QPT in electrode processes, such as the classical (sc-TST) to a full quantum schemes associate with an increase of overpotential (the HER on pcAu in the 0.1M KOH condition), and a full quantum to the classical scheme (the ORR on pcPt in the 0.1M KOH condition). In this stage, it is a challenge to give molecular-level interpretations to these QPT electrode processes due to participation of many complicated effects. However, the different microscopic proton transfer mechanisms, *i.e.* proton transfer from hydronium ion or water molecule, may be a key for a full QPT path.

Overall, the experimental methods and equations shown here enables to observe and analyze QPT in two model electrode processes, and provide primitive microscopic views on its mechanism on electrolyte/electrode surface associated with quantum effects. So far, it is difficult to give fine
molecular-level interpretations to observed results since it is unclear which effects act the key role to emerge QPT in electrode processes. In order to understand the microscopic picture of these complicated systems, it is still necessary to keep on integrating experimental and theoretical works to understand these systems with state-of-the-art knowledge from physics and chemistry.

Conflicts of interests

There are no conflicts to declare.

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