Quantum-to-Classical Transition of Proton-Transfer in Potential-Induced Dioxygen Reduction

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We report an observation of a quantum tunneling effect in a proton-transfer (PT) during potential-induced transformation of dioxygen on a platinum electrode in a low overpotential (η) region at 298 K. However, this quantum process is converted to the classical PT scheme in high η region. Therefore, there is a quantum-to-classical transition of PT (QCT-PT) process as a function of potential, which is confirmed by theoretical analysis. This observation indicates that the quantum-tunneling governs the multistep electron-proton-driven transformation of dioxygen in low η condition.

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Quantum tunneling plays vital roles in a wide spectrum of physical, chemical and biological processes, providing efficient functions to life and modern technology \[1–7\]. The basic principle of quantum tunneling is transmission of particles through an activation barrier due to its non-zero permeability \[1,8\], instead of overcoming the barrier via the transition state \[9\]. Especially, quantum proton tunneling can emerge as various significant effects in key physical phenomena in a wide range of temperature \[10–13\]. Usually in physical or chemical processes the activation barrier is predefined by a combination of the reactant and product of the reaction. Therefore once the initial and final states of the process are fixed and the activation barrier is known one can calculate the permeability of the barrier for each elementary step of the process and predict the probability of the quantum tunneling \[14\]. On the other hand, in the case of potential-induced processes, for instance mutielectron-multiproton transfer in electrochemical reactions \[15,16\], one can alter the energy of the initial or final state by applying the external potential. That means that a height of an activation barrier can be a function of the potential via simple Brønsted-Evans-Polanyi relationship \[17,18\], and hence one can expect the unique phenomena when the ratio of probabilities to overcome the barrier classically via the transition state and quantumly via tunneling through the barrier can be modified by the potential. In other words one can switch on or off quantum-mechanical tunneling by changing the height of the barrier. In spite of simplicity of this idea such a phenomenon has not been observed to the best of our knowledge.

In this Letter, we demonstrate observation of the quantum-to-classical transition of proton transfer (QCT-PT) in the process of potential-induced dioxygen reduction on platinum electrode at 298 K. Our results clearly show appearance of the QCT-PT in electrode process as a function of the potential: at lower overpotential condition (high barrier, when overcoming via transition state becomes difficult), proton prefers to be transferred by quantum-tunneling, while at high overpotentials (small barrier, when overcoming the barrier via transition state becomes favorable) the classical mechanism of overcoming the activation barrier controls the process, as schematically illustrated in Fig. 1.

We show that QCT-PT can be observed in the potential-induced O\(_2\) reduction process on Pt electrode in alkaline solution, when four hydroxide ions are produced by transferring four electrons and four protons supplied from two water molecules into dioxygen: \(\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-\). As a descriptor of quantum tunneling in PT and quantum-to-classical transition effect we have investigated the hydrogen/deuterium kinetic isotopic rate constant
FIG. 1. (color online). Schematic diagram for two possible paths of the proton-transfer reaction: (a) proton transfer via transition state (classical); (b) proton tunneling through the barrier (quantum). In the electrochemical system relative contribution of the two mechanisms can be tuned by the applied potential.

ratio $k_H/k_D (\equiv K^{H/D})$. By measuring $K^{H/D}$, we can clarify the nature of the PT processes because the replacement of hydrogen by deuterium can considerably affect the reaction rates of electrode processes \cite{19,22}. We show that $K^{H/D} = 32$ for O$_2$ reduction on Pt in alkaline condition and this value drops down to 3.7 as a function of the potential. The large value of $K^{H/D} = 32$ considerably exceeds is semiclassical limit indicating manifestation of the tunneling effect \cite{19}. Therefore our results clearly demonstrate appearance of the quantum-to-classical transition in the electrode process as a function of potential, as schematically illustrated in Fig. 1. Thus, it is demonstrated that proton tunneling can play an important role in the microscopic electrode processes of O$_2$ reduction when number of conditions are fulfilled and shows exciting undiscovered insights of a key electrochemical process.

Since the overpotential-dependent $K^{H/D}$ is defined as the ratio of the isotopic rate con-
stants, one can obtain this value from the following general equations:

\[
K^{\text{H/D}} = \frac{k_0^\text{H}}{k_0^\text{D}} = \frac{j_0^\text{H} C_0^\text{D}}{j_0^\text{D} C_0^\text{H}} \exp \left( \frac{(\alpha^\text{D} - \alpha^\text{H}) F \eta}{RT} \right) \tag{1}
\]

\[
j = j_0 \exp \left( -\frac{\alpha F \eta}{RT} \right) \tag{2}
\]

\[
j_0 = n F k_0 C_0, \tag{3}
\]

where \(j_0, C_0, \alpha, \eta, F, R, \) and \(T\) are exchange current density, oxygen concentration, transfer coefficient, overpotential, Faraday constant, gas constant and temperature (298 ± 1 K in this experiment), respectively. The superscripts H and D indicate the values in H\(_2\)O and D\(_2\)O systems, respectively. For the calculation of the pD in alkaline conditions, we have to mind that the dissociation constant of D\(_2\)O is different from that of H\(_2\)O \[22\]. Furthermore, in order to avoid unknown liquid junction effects due to the use of reference electrodes such as an Ag/AgCl electrode \[23, 24\], we used a reversible hydrogen or deuterium electrodes by following the protocol of Yeager and his coworkers \[25\]. Prior to discuss the dioxygen reduction process, the cyclic voltammogram and linear-sweep voltammetry (LSV) combined with rotating ring-disk electrode (RRDE) technique were applied to check that the experimental H\(_2\)O and D\(_2\)O systems work properly (Supplemental Material Fig. S1). We used \(n = 4\) for both H\(_2\)O and D\(_2\)O systems based on the experimental results (Supplemental Material Fig. S2). All observed currents were normalized by electrochemical active surface area (ECSA). The \(C_0^\text{D}/C_0^\text{H}\) is known to be 1.101. The equilibrium potential for D\(_2\)O formation, \(E_{\text{D}_2\text{O}}^0\), can be calculated by thermophysical values (see, e.g., Ref. \[25\] and references therein) and we obtain \(E_{\text{D}_2\text{O}}^0 = 1.262\) V vs reversible deuterium electrode. Transfer coefficient \(\alpha\) can be obtained from the Tafel slope, \(b\):

\[
\alpha = \frac{2.303RT}{Fb}. \tag{4}
\]

The O\(_2\) reduction kinetics in 0.1M KOH in H\(_2\)O and 0.1M KOD in D\(_2\)O were analyzed by comparing the kinetic currents presented in Fig. 2 and Table I. Detailed method to obtain kinetic values is well described in our previous report \[22\]. Since Pt is known to show the clear diffusion limiting current \(j_{\text{lim}}\), the O\(_2\) reduction kinetic currents can be separated from diffusion limiting current by using a simple following equation:

\[
\frac{1}{j} = \frac{1}{jk} + \frac{1}{j_{\text{lim}}} \Leftrightarrow \frac{1}{jk} = \frac{j_{\text{lim}} \cdot j}{j_{\text{lim}} - j}. \tag{5}
\]
FIG. 2. (color online). Overpotential vs. log $j_k$ diagram of Pt in $O_2$-saturated 0.1M KOD and 0.1M KOH solutions. (a) Three different regions to obtain Tafel slope: low overpotential region (area surrounded by red dotted line), linear region I (middle overpotential) and linear region II (high overpotential). (b) Enlarged overpotential vs. log $j_k$ diagram in the low overpotential region, $-0.2 \text{ V} < \eta < -0.1 \text{ V}$. Detailed method for the fitting of plots is described in the Supplemental Material. The coefficient of determination, $R^2$, for $H_2O$ and $D_2O$ systems are 0.993 and 0.995, respectively.

The value of the Tafel slope $b$ was confirmed to be around 0.05 V/dec in the linear region I (middle $\eta$ region, $-0.35 \text{ V} < \eta < -0.2 \text{ V}$) and shifted to 0.2 V/dec at the linear region II (high $\eta$ region, $-0.5 \text{ V} < \eta < -0.4 \text{ V}$), see Fig. 2(a) for details. These regions are selected by following the procedure reported in Ref. [26]. In the lower overpotential region, $-0.2 \text{ V} < \eta < -0.1 \text{ V}$, there is no linear dependence of $\eta$ on log $j_k$, as it is seen from Fig. 2(b),
TABLE I. Summary of $O_2$ reduction kinetics and $K_{H/D}$.

| Region | Tafel slope $(V/\text{dec})$ | $\alpha$ | $-\log j_0^H$ (A/cm$^2_{\text{ECSA}}$) | $-\log j_0^D$ (A/cm$^2_{\text{ECSA}}$) | $K_{H/D}$ |
|--------|-----------------------------|---------|---------------------------------|---------------------------------|---------|
| Low $\eta$ | 0.031 ± 0.003 | 1.91 ± 0.17 | 11 ± 0 | 12 ± 1 | 32 ± 4 |
| Middle $\eta$ | 0.047 ± 0.002 | 1.26 ± 0.05 | 9.1 ± 0.1 | 9.8 ± 0.0 | 5.5 ± 0.2 |
| High $\eta$ | 0.22 ± 0.01 | 0.27 ± 0.01 | 3.0 ± 0.0 | 3.6 ± 0.2 | 3.7 ± 0.2 |

Therefore, the Tafel slope $b = 0.03$ V/dec was taken as a representative value to calculate $K_{H/D}$ in the low overpotential region, as shown in Table I [27]. For the detailed analysis, the plots in the low overpotential region (Fig. 2(b)) were fitted to obtain the Tafel relation (see Supplemental Material), and this relation was used to calculate $K_{H/D}$. From this fact, as shown above, $\alpha$ was obtained in different overpotentials and overpotential-dependence of $K_{H/D}$ was checked by using these values.

As the results, from the Eqs. 1-4 and Table I, $K_{H/D}$ of Pt in three different regions (low, middle and high overpotential regions) can be obtained as $32 \pm 4$, $5.5 \pm 0.2$ and $3.7 \pm 0.2$, respectively. Our results indicate that the rate-determining step (RDS) of $O_2$ reduction in alkaline condition contains proton transfer. An anomalously large values of $K_{H/D} > 13$ in the low overpotential region indicates manifestation of the quantum-proton-tunneling, which is a classically forbidden proton-transfer mechanism. This is because the maximum KIE for the O-H bond breaking is $\sim 13$ at 298 K based on the semiclassical theory accounting for the change in the reaction barrier due to the differences in zero-point energies associated with the stretching and bending vibrations in O-H and O-D (see, e.g., Ref. [19] and references therein). Furthermore, it is known that the adsorption energies of OH and OD on Pt surface can be different due to the differences in zero-point energies [28]. In addition to this, it has been suggested that the ORR rate on Pt is governed by OH adsorption [29]. However, we found that the difference in OH/OD adsorption energies in our system is $1.2$ kJ/mol, which is similar to values reported in Ref. [28], and this difference should not affect our conclusion (see Supplemental Material Figs. S4 and S5 for the detailed discussion. In order to obtain the OH/OD adsorption energies we have followed the method described in Ref. [30]). By combining previous reports [31, 32], and our experimental observations [22], it can be concluded that the proton-transfer process is related to the rate-determining step of $O_2$.
reduction in alkaline conditions. Furthermore, we have demonstrated manifestation of the quantum tunneling process for the proton transfer in the low overpotential region, which is vanishing in the high overpotentials, showing quantum-to-classical transition, i.e. QCT-PT.

In order to understand the observed phenomenon we carried out a theoretical analysis of the KIE in the proton transfer accounting for the probability of tunneling in O₂ reduction. Recent theoretical work has clearly demonstrated that the O₂ reduction on Pt in alkaline solution mainly occurs via the (H₂O)ₐds-mediated mechanism, where protons transfer from the water molecules adsorbed on the surface in an organized network structure in a series of reactions [33]:

\[
\begin{align*}
(O₂)ₜₜ + * & \rightarrow (O₂)ₐds, \quad (6a) \\
(O₂)ₐds + (H₂O)ₐds & \rightarrow (OOH)ₐds + (OH)ₐds, \quad (6b) \\
(O)ₐds + (H₂O)ₐds & \rightarrow 2(OH)ₐds, \quad (6c) \\
(OOH)ₐds & \rightarrow (O)ₐds + (OH)ₐds, \quad (6d) \\
(OH)ₐds + e^- & \rightarrow * + (OH)_sol, \quad (6e)
\end{align*}
\]

where asterisk denotes the surface, while subscript indices "ads" and "sol" correspond to the adsorbed and solution species, respectively. In the first step 6a dioxygen is adsorbed on the Pt surface, followed by the proton transfer from the adsorbed (H₂O)ₐds to (O₂)ₐds and (O)ₐds intermediates as well as (OOH)ₐds dissociation in steps 6b, 6c, and 6d, respectively. In the final step 6e, (OH)ₐds dissolves to (OH)ₐds as a result of the one electron reduction. The above mechanism proposed by Liu et al. [33] is different from the well known associative and dissociative mechanisms of reduction by (H₂O)ₜₜ, typically considered for the ORR in acid solution [29]. It should be noted that the steps 6b - 6d involve no electron transfer, and therefore are potential-independent explicitly, however the adsorption energy of ORR intermediates depends on the (OH)ₐds coverage, which is the potential-dependent. Further details can be found in Ref. [33]. The (H₂O)ₐds-mediated mechanism of the dioxygen reduction leads to the formation of (OOH)ₐds, (O)ₐds, and (OH)ₐds intermediates. Such processes consist of bond breaking/-formation with proton, which is O-H bond breaking of H₂O and then formation of O-H bond with one of the intermediates. Based on the above considerations, we analyzed our experimental results by using a theoretical approach.

A simple estimation of the reaction rate constants accounting for the tunneling probability of the proton through the potential barrier can be performed by approximating the barrier
by the asymmetric Eckart’s one-dimensional potential energy function of the barrier height $V_1$, reaction exothermicity parameter $\Delta V$, and the width $a$ (see Supplemental Material for details) [19, 34, 35]. Such a simple but robust approach gives a clear physical picture of the process and has been successfully used in a number of tunneling model analysis of experimental data [36], and able to accurately reproduce the experimentally obtained reaction rates and isotopic rate constant ratios in a large range of temperatures except low ($T < 50$ K) temperatures where it is necessary to take into account zero point energy effects [35]. Note, that more consistent description of tunneling process should take into account reorganization of many degrees of freedom [37–39].

In the case of the potential-induced process, parameters of the barrier height and exothermicity can be altered via applied potentials. In the present work the Brønsted-Evans-Polanyi (BEP) relationship was used to describe linear variations in the barrier height with the reaction energy,

$$V_1 = -A\Delta V + B,$$  \hspace{1cm} (7)

where $A$ 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, i.e. when $\Delta V=0$ [40]. Alternatively, more realistic form of the potential barrier for the proton transfer at electrode/water interface can be evaluated by first-principles atomic-scale simulations under bias potential [41].

Using Eckart barrier with the height defined by the BEP relationship we have calculated the $K^{H/D}$ for the proton transfer from the water molecule adsorbed on the surface to the possible intermediates of $O_2$ reduction reported by Liu et al. [33], with the use of computer code described by Le Roy [34]. It should be noted that the tunneling probability is strongly affected by the barrier width as shown in Fig. S3 in the Supplemental Material. We estimated the barrier width parameter $a$ to be equal 0.3 Å using theoretical data on the optimized structures for the adsorption of the reaction intermediates covered by a bilayer of water on Pt surface [33]. The consistent theoretical analysis of the tunneling effect in electrocatalytic oxygen reduction would require direct calculation of the energy barrier profile for proton transfer which goes far beyond the scope of the present work. It has been shown that in the optimized configuration the length of the hydrogen bond between the chemisorbed water molecule and $(O)_{ads}$ intermediate is 1.96 Å [33], which should correspond to the linear reaction path length of 0.99 Å, as the length of the O-H bond in the reaction
product is 0.97 Å. In the case of (O$_2$)$_{ads}$ intermediate two hydrogen bonds with water bilayer are formed with the bond length of 1.74 Å and 1.90 Å, which would correspond to the linear reaction path length for proton transfer of 0.77 Å and 0.93 Å, respectively. For (OH)$_{ads}$ intermediate the hydrogen bond between (OH)$_{ads}$ and (H$_2$O)$_{ads}$ is 1.62 Å. These reaction path lengths correspond to the values of the barrier width lying in the range of $a = 0.25 - 0.35$ Å. Therefore, we selected $a = 0.3$ Å as a typical value for the width of the Eckart’s barrier used in this study and also investigated how KIE depends on the barrier width $a$ (see Fig. S3 of the Supplemental Material).

The value of the barrier height $B$ for the proton-transfer for the steps at the equilibrium is open to debate, and the reported values vary from 0.26 to 0.81 eV \cite{40,42,43}. Therefore, we have calculated the dependence of log $K^{H/D}$ on exothermicity $\Delta V$ for several available values of the proton transfer barrier at equilibrium, see Fig. 3(a). Results of our theoretical analysis demonstrate that for the small values of $\Delta V$, the tunneling effect dominates in the proton transfer in a good agreement with the experimental observation of the log $K^{H/D} - \eta$ relation in the low overpotential region, see Fig. 3(b). For further details of mathematical models and procedures, see the Supplemental Material. It is interesting that for $B = 0.74$ eV reported by Sugino et al. \cite{42}, and for $B = 0.81$ eV reported by Janik et al. \cite{43}, the maximum log $K^{H/D}$ is equal to 1.76 and 2.01, respectively, which are very close to the experimentally observed value of log $K^{H/D} = 2.1$ at $\eta = -0.208$, where $K^{H/D}$ value was obtained at the minimum
overpotential to be observable in our experiment, therefore probably this $K^{H/D}$ value is close to the maximum and can be the limit to be verified by our mathematical models. Nevertheless, both theoretical and experimental results demonstrate that tunneling can be observed in the low overpotential regime while the proton transfer process becomes classical at higher overpotentials. Our combined-theoretical/experimental study clearly demonstrates the manifestation of the potential-dependent KIE in electrochemical systems. The observed QCT-PT phenomenon in the proton-transfer mechanism as a function of potential shows that the tunneling can dominate in the proton transfer in the low $\eta$ region because in this case it has higher probability than overcoming the activation barrier classically via transition state. However, in higher $\eta$ region, the barrier becomes low enough and therefore the classical proton-transfer mechanism controls the overall process.

In conclusion, we have shown that there is a quantum-to-classical transition in potential-induced oxygen reduction on platinum electrode in alkaline solution where proton tunneling can play an important role in the low overpotential regime. Likewise unexpected strong effects of adsorbed ions or crystal structures can alter the kinetics of electrochemical reactions [31], this study indicates the non-trivial importance of proton-transfer in microscopic electrode process of dioxygen reduction and can affect its kinetics. We believe that understanding of quantum proton-transfer mechanism described in the present work is key to clarify the fundamental physical principles in complicated electrode processes. The quantum tunneling effect and the analytical approach based on KIE shown here can be an additional powerful tool to obtain new insights to this process. These could help to build more accurate theoretical models and combine them to experimental systems in order to unveil the complicated proton-transfer reactions at electrodes.

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