ARTICLE

Kinetics Study on O₂ Adsorption and OHad Desorption at Pt(111), Its Implication to Oxygen Reduction Reaction Kinetics

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Kinetics of dissociative O₂ adsorption, OHad desorption, and oxygen reduction reaction (ORR) at Pt(111) electrode in 0.1 mol/L HClO₄ has been investigated. Reversible OHad adsorption/desorption occurs at potentials from 0.6 V to 1.0 V (vs. RHE) with the exchange current density of ca. 50 mA/cm² at 0.8 V, the fast kinetics of OHad desorption indicates that it should not be the rate determining step for ORR. In the kinetic- or kinetic-mass transport limit controlled potential region, ORR current at constant potential displays slight decrease with reaction time. ORR current in the positive-going potential scan is slightly larger than that in the subsequent negative-going scan with electrode rotation speed (>800 r/min) and slow potential scan rate (<100 mV/s). The open circuit potential of Pt/0.1 mol/L HClO₄ interface increases promptly from 0.9 V to 1.0 V after switch from O₂ free- to O₂-saturated solution. The increase of open circuit potential as well as ORR current decays under potential control due to the accumulation of OHad from dissociative adsorption of O₂. It indicates that at Pt(111) the net rate for O₂ decomposition to OHad is slightly faster than that for OHad removal, one cannot simply use the assumption of rate determining step to discuss ORR kinetics. Instead, the ORR kinetics is determined by both the kinetics for O₂ decomposition to OHad as well as the thermo-equilibrium of OHad + H⁺ + e⁻ = H₂O.

Key words: Oxygen reduction reaction, Pt(111) electrode, Rate determining step, Kinetics, Overpotential, Thermodynamic equilibrium

I. INTRODUCTION

Oxygen reduction reaction (ORR) is one of the most important model systems in electrocatalysis. Uncovering factors which limit ORR kinetics is paramount to design better electrocatalysts for fuel cells. Pt and Pt-based materials are the most active ORR electrocatalysts, but even on the best Pt based electrocatalysts large overpotential (η>0.22 V) are still required in order to achieve any appreciable ORR current [1–10]. In acidic solutions, the overall reaction for ORR is:

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad (1) \]

\[ E^0 = 1.23 \text{ V vs. SHE} \]

On Pt-based electrodes, two pathways are suggested for ORR: one major path with 4e reduction of O₂ via a direct or series pathway, and a minor route involving the ‘2e’ pathway to peroxide when there is strongly adsorbed species on Pt electrode [11–13]. On the Pt based electrocatalysts, intermediates such as O₂²⁻, O₂⁻, HO₂⁻, H₂O₂, O, and OH may be produced [10].

Most of these intermediates are hard to be detected by experimental methods due to their short lifetime and their low coverage at the electrode surface. As a result, it will be very difficult to derive the detailed mechanism for ORR. Even, by now there is no consensus on its rate determining step (r.d.s.) at all. Reactions (2) – (5) listed below are all suggested to be the r.d.s. for ORR in acidic electrolyte [2, 3, 5, 6]:

\[ \text{O}_2 + \text{H}^+ + e^- \rightarrow \text{OOH}_{\text{ad}} \quad (2) \]

\[ \text{O}_2 + e^- \rightarrow \text{O}_{\text{ad}}^- \quad (3) \]

\[ \text{O}_{\text{ad}} + \text{H}^+ + e^- \rightarrow \text{OH}_{\text{ad}} \quad (4) \]

\[ \text{OH}_{\text{ad}} + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O} \quad (5) \]

In order to clarify the above discrepancies and to discover the key factors which limit ORR kinetics at Pt, we have studied the kinetics for O₂ adsorption, OHad desorption and ORR at Pt(111) electrode in 0.1 mol/L HClO₄. Kinetic implication for ORR at Pt-based electrocatalysts will be briefly discussed based on present results and density functional theory (DFT) calculations.

II. EXPERIMENTS

Experimental conditions are similar to that described in Ref.[7]. 0.1 or 1.0 mol/L HClO₄ solution was pre-
pared using 70% perchloric acid (Suprapure, Sigma-Aldrich) and ultra-pure water (18.2 MΩ/cm), N₂ and O₂ were of purity 99.999% (Linde China). Most measurements were done under hanging meniscus rotating disk electrode configuration in a conventional three electrodes cell. Bead type Pt(111) was used as a working electrode. A reversible hydrogen electrode (RHE) and a Pt wire were used as reference and counter electrode. All potentials were quoted against the RHE. Reaction kinetics for O₂, OH⁻ adsorption/desorption and ORR were examined using potential step technique at 2000 r/min and fast scan cyclic voltammetry at 3600 r/min after purging the solution with O₂ for 20 min, the high electrode rotation speed was used in order to eliminate the interference of mass transport effect. The change of OCP for Pt when switching from O₂ free to O₂ saturated 0.1 mol/L HClO₄ solution was carried out with a flow cell [14].

III. RESULTS AND DISCUSSION

CVs for Pt(111) electrode in 0.1 mol/L HClO₄ solution are given in Fig.1. From Fig.1(a), it is noticed that there is symmetric butterfly feature in the potential region from 0.4 V to 0.85 V with a sharp peak at 0.8 V. It is followed by a current plateau in the potential region from 0.85 V to 1.0 V, which is obviously higher than that in the double layer potential region. The “butterfly” feature in the potential region of 0.5 V < E < 0.85 V together with the small plateau from 0.85 V to 1.0 V is associated with the adsorption of OH⁻ from water and its desorption [15].

\[ \text{OH}^- + \text{H}^+ + e^{-} \xrightarrow{k_a} \text{H}_2\text{O} \]  

(6)

Irreversible Pt-O₂ formation/reduction only occurs when the upper potential limit used for the cyclic voltammetry is higher than 1.0 V (Fig.1(b)). A typical polarization curve for ORR recorded in O₂ saturated 0.1 mol/L HClO₄ solution at 2000 r/min is given in Fig.1(d). By comparing the base CV recorded in O₂-free solution, it is noticed that ORR only occurs at potentials negative of the upper limit (ca. 0.98 V) where reversible OH⁻ adsorption/desorption occurs [7]. The kinetic and kinetic-mass transport mixed-controlled potential regions for ORR at Pt(111) just locate in the same potential region where OH⁻ adsorption/desorption is reversible in O₂-free solution. Systematic studies on ORR at Pt(111) in solutions with other pH reveal that such phenomenon applies for all solutions with pH within the range of 1≤pH≤13 and ORR kinetics at Pt(111) is pH independent [7]. The equilibrium potential \( E_{\text{eq}}^{\text{ad}} \) for Eq.(6) is:

\[ E_{\text{eq}}^{\text{ad}} = E_{\text{ad}}^0 + \frac{RT}{F} \ln \frac{a_{\text{OH}^-}a_{\text{H}^+}}{a_{\text{H}_2\text{O}}} \]  

(7)

where \( a \) is the activity of respective species specified in the subscript, \( E_{\text{ad}}^0 \) is standard potential of reaction (6), \( R \) is molar gas constant, \( T \) is temperature, \( F \) is Faraday constant. The superimposition of the onset potential for ORR with that of OH⁻ adsorption/desorption indicates that the high value of the overpotential at the onset for ORR at Pt(111) is determined by \( E_{\text{eq}}^{\text{ad}} \). This can also be understood by the fact that since reaction (5) (i.e., the forward reaction in reaction (6)) is the last step for ORR, hence ORR only occurs when \( E < E_{\text{eq}}^{\text{ad}} \). This conclusion agrees well with recent predictions based on DFT calculation, i.e., among all possible elementary steps for ORR at Pt(111), OH⁻ adsorption has the most positive Gibbs free energy change \( (\Delta G) \), which renders the onset potential for ORR ca. 0.25 V negative of 1.23 V [6]. Reaction (5) is called the potential determining step (p.d.s.) for ORR at Pt(111) [6, 9].

To clarify whether OH⁻ adsorption or the dissociative adsorption of O₂ is the r.d.s for ORR at Pt(111), fast scan voltammetry and potential step experiments were carried out to derive the kinetics of the respective processes. Figure 2 displays the current transients for OH⁻ formation and the reductive removal of OH⁻ at Pt(111) in 0.1 mol/L HClO₄ after stepping from 0.5 V to 0.8 V.
FIG. 2 Current transients for (a) OH\text{ad} formation and (b) OH\text{ad} desorption at Pt(111) in 0.1 mol/L HClO\textsubscript{4} after potential step to the respective potentials. (c) Capacitance \(C_F\) vs. \(E\) curves for Pt(111) in 0.1 mol/L HClO\textsubscript{4} at various potential scan rates. (d) The change of open circuit potential for Pt/0.1 mol/L HClO\textsubscript{4} interface after switching from a O\textsubscript{2}-free to O\textsubscript{2}-saturated solution.

to the respective reaction potentials or stepping from higher potential to lower ones. From Fig.2 it is seen that in O\textsubscript{2} free solution OH\text{ad} establishes its equilibrium coverage within ca. 5 ms to 30 ms after potential step from either higher or lower potentials to the desired ones. This reveals that the kinetics for both OH\text{ad} adsorption and desorption are very fast, which is in well agreement with literature report [16–18]. The \(j\)-\(t\) curves recorded during the potential step experiment can be described as [19]:

\[
\begin{align*}
    j_{\text{ad}}(t) &= F \frac{d\theta_{\text{OH} \text{ad}}(t)}{dt} \\
                     &= F[k_{-6}a_{\text{H}_2\text{O}}[1 - \theta_{\text{OH}}(t)] - \theta_{\text{OH}}(t)] \\
    \theta_{\text{OH} \text{ad}}(t) &= \frac{1}{Q_C} \int_{0}^{t} j_{\text{ad}}(t) dt \\
                              &= \frac{1}{240} \int_{0}^{t} j_{\text{ad}}(t) dt
\end{align*}
\]

where \(\theta_{\text{OH} \text{ad}}\) is coverage of OH species. From the current transients and Eq.(8) and Eq.(9) the rate constant for OH\text{ad} adsorption/desorption \((k_{6}, k_{-6})\) can be derived (note only data recorded after ca. 0.3 ms have been taken into estimation, cell time constant is \(\tau=90\ \mu\text{s}\). By defining the state with \(\theta_{\text{OH} \text{ad}}=0.3\ \text{ML}\) at 0.8 V as the standard state, exchange current density \(j_0\) for reaction (6) is estimated as follows:

\[
    j_0 = -Fk_{6}(E)\theta_{\text{OH}}(E)a_{\text{H}^+} = Fk_{-6}(E)a_{\text{H}_2\text{O}}[1 - \theta_{\text{OH}}(E)]
\]

At 0.8 V, \(j_0\) is estimated to be ca. 50 mA/cm\textsuperscript{2}. The current density for OH\text{ad} desorption (the forward reaction in reaction (6)) are estimated to be \(-2.7\) and \(-7.1\) mA/cm\textsuperscript{2} at 0.95 and 0.9 V by assuming a symmetric factor of 0.5. The fast kinetics for OH\text{ad} adsorption/desorption is further supported by the good symmetry for OH\text{ad} adsorption/desorption under fast potential scan rate (Fig.2(c)). On the other hand, the kinetic current densities \((j_{k,\text{ORR}})\) for ORR after elimination of the mass transport effect are \(-0.35\) and \(-1.8\) mA/cm\textsuperscript{2} at 0.95 and 0.90 V, respectively, as derived from the Koutecky-Levich equation [8]. Obviously, \(j_{k,\text{ORR}}\) is smaller than the rate for OH\text{ad} desorption under otherwise identical condition, indicating that the kinetics for ORR is not limited by the "slow" kinetics for OH\text{ad} desorption. In addition, reaction (4) should also not be the r.d.s. for ORR based on the Brønsted-Evans-Polanyi relationship and it has similar Gibbs free energy change as that for reaction (5) [6].

On the other hand, the Tafel slope for \(E\) vs. \(\lg j_0\) is ca. \(-70\ \text{mV/dec}\) in the potential region from 0.95 V to...
When normalized to the active surface sites by taking into account that OH$_{ad}$ coverage is the same as that in O$_2$ free solution (which can be determined from the OH$_{ad}$ adsorption charge in the potential region from 0.6 V to 1.0 V based on the CV given in Fig.1(a)), the Tafel slope is just ca. $-78$ mV/dec (Fig.1(e)). This indicates that the OH coverage does not affect the Tafel slope significantly. Assuming that OH$_{ad}$/O$_{ad}$ coverage under ORR condition is higher than that in O$_2$-free solution under otherwise identical condition and the discrepancies for OH$_{ad}$ coverage in these two cases increase with increase in electrode potential, the Tafel slope after being normalized with the free active sites should be within the range of $-70$ mV/dec to $-78$ mV/dec. This value is significantly smaller than $-120$ mV/dec, which indicates that the first charge transfer step (either reactions (2) or (3)) is probably not the r.d.s for ORR on Pt(111) at $E>0.85$ V.

Another evidence which supports fast decomposition of O$_2$ to OH$_{ad}$/O$_{ad}$ is that when switching from O$_2$ free solution to O$_2$ containing solution, the OCP of Pt/0.1 mol/L HClO$_4$ interface shifts promptly from 0.9 V to 1.0 V (Fig.2(d)) and from the cyclic voltammetric study with relative fast electrode rotation speed (>800 r/min) and slow potential scan rate (<100 mV/s), it is always observed that the $j$-$E$ curve for ORR in the negative-going potential scan is smaller than that in the positive-going scan (Fig.3). Our systematic studies also reveal that the faster the electrode rotation speed or the slower the potential scan rate, the larger such difference is. Furthermore, from chronocoulometric transients measured during ORR in the kinetic and kinetic-mass transport mixed-controlled potential region, it is seen that ORR currents decay with reaction time (Fig.4). Although trace contaminants cannot be fully avoided, the difference of ORR current in the positive-going scan and that in the negative-going potential scan as well as the decay of chronocoulometric transients for ORR do not originate from contaminants. The reasons are the following: in both O$_2$ free and O$_2$ containing solution, the cyclic voltammograms are well reproducible when continuously scanning in the potential region from 0.05 V to 1.0 V within 2 h, if there is contaminants accumulation, characteristic current peaks for the redox of the contaminants or continuous decay of the current waves for H-UPD and OH$_{ad}$ adsorption/desorption should appear [7]; poisoning of the surface with the trace contaminants (such as halides) usually are mass transport controlled, hence its effect on the current decay of ORR under potentiostatic conditions should not depend on the applied electrode potential, i.e., the current at each reaction potential should be simply reduced by a factor $(1-\theta_{contaminant})$. However, the slope for the current decay is maximum at 0.85 V, and it is smaller at 0.9 and 0.8 V (Fig.4), suggesting that the rate for poison formation is potential dependent (or complete or partially kinetic controlled in nature).

Based on the above experiment facts, we think during ORR there is additional accumulation of OH$_{ad}$/O$_{ad}$ at Pt(111) surface from O$_2$ dissociation, the poisoning effect of such accumulated OH$_{ad}$ species leads to smaller
ORR current in the subsequent negative-going potential scan or at elongated reaction time under potentiostatic conditions in the kinetic and kinetic-mass transport mix controlled potential region. The faster the electrode rotation speed, the faster the rate for OH$_{ad}$ built up from O$_2$ dissociation, this leads to larger difference in the ORR current between the negative-going and positive-going potential scan (Fig.3). It should be noticed that the smaller ORR current in the positive-going scan than that for the negative-going ones at electrode rotation speed below 800 r/min is due to the change relative rate of mass transport of O$_2$ to the electrode surface and that of ORR kinetics. When scanning into the kinetic controlled region, the slower ORR kinetics will lead to accumulation of O$_2$ near electrode surface, which leads to the higher ORR current the mix-controlled region in the subsequent negative-going potential scan. The fast kinetics for the decomposition of O$_2$ to OH$_{ad}$/O$_{ad}$ at H$_2$O+OH$_{ad}$ covered Pt(111) is also supported by DFT calculation, which reveals that activation barrier for this process is just 0.48 eV, it is ca. 0.35 eV lower than that for O$_2$ decomposition at clean Pt [6]. And at H$_2$O+OH$_{ad}$ covered Pt(111), the activation energy for the dissociation of O=O bond in OOH$_{ad}$ is only 0.37 eV [6]. All the above facts support that the kinetics of first few steps for ORR involving O$_2$ adsorption and subsequent decomposition of O$_{2,ad}$ to OH$_{ad}$ or O$_{ad}$ (reactions (2) and (3)) are faster than the net rate for OH$_{ad}$ reduction to H$_2$O [10].

As estimated from Fig.1 and Fig.2, the current density for OH$_{ad}$ desorption are -7.1 and -2.7 mA/cm$^2$ at 0.9 and 0.95 V, which are only 4-7 times higher than that for $j_{k,ORR}$ (-1.8 and -0.35 mA/cm$^2$). Since the difference of the rates for both dissociative adsorption of O$_2$ to OH$_{ad}$ and that for OH$_{ad}$ adsorption/desorption are within ten times, one should not simply take the first step as r.d.s and the last step as under fast equilibrium, this is also supported by the significantly smaller Tafel slope (-78 mV/dec) than the value of -120 mV/dec. Instead, the kinetics of the current transients can be analyzed according to the simplified reaction scheme given below:

$$\text{O}_2 + 2\text{H}^+ + 2e^{-} \rightarrow 2\text{OH}_{ad} \quad (11)$$

It is followed by reaction (6).

In this scheme, reaction (5) is not only the last step for ORR at Pt in 0.1 mol/L HClO$_4$, but both forward and backward reaction in reaction (6) are also individual reactions which occur fast and in parallel with ORR. Obviously, the dissociative adsorption of O$_2$ competes with the dissociation of H$_2$O for the active sites. Ignoring the double layer charging current, the current recorded during linear potential sweeping equals

$$j_{\text{ORR}}(E) = 2Fk_1(E)c_{\text{O}}^2 \left[ \frac{1}{2} - \theta_{\text{OH}}(E) \right] + 2Fk_2(E)\theta_{\text{OH}}(E) \left[ \frac{1}{2} - \theta_{\text{OH}}(E) \right] - 2Fk_{\theta} \theta_{\text{OH}}(E) \left[ \frac{1}{2} - \theta_{\text{OH}}(E) \right]$$

where $c_{\text{O}}^2$ is the concentration of oxygen near electrode surface. And under potentiostatic condition the ORR current density equals

$$j_{\text{ORR}}(t) = 2Fk_1 c_{\text{O}}^2 \left[ \frac{1}{2} - \theta_{\text{OH}}(t) \right]^2 + 2Fk_2 \theta_{\text{OH}}(t) \left[ \frac{1}{2} - \theta_{\text{OH}}(t) \right] - 2Fk_{\theta} \theta_{\text{OH}}(t) \left[ \frac{1}{2} - \theta_{\text{OH}}(t) \right]$$

These equations clearly express that ORR current is controlled by both the rate for OH$_{ad}$ formation from O$_2$ dissociation and the OH$_{ad}$ removal governed by the reactions given reaction (6). This is in contrast to what previously suggested where the first step is r.d.s, and the OH$_{ad}$ only limits free sites available for ORR [2]. It should be mentioned that, a significant difference for $E_{\text{eq}}^6$ of reaction (6) from that of other redox pairs with fixed ratio of reactants concentration to that of products in bulk solution is that $E_{\text{eq}}^6$ changes sensitively with the surface coverage of OH$_{ad}$. From Eq.(7), it is easily seen that when $\theta_{\text{OH}}$ increases, $E_{\text{eq}}^6$ shifts to positive potentials, and when $\theta_{\text{OH}}$ decreases, $E_{\text{eq}}^6$ shifts to negative potentials. Hence $E_{\text{eq}}^6$ has a broad range (i.e., 0.6 V to 1.0 V, Fig.1) rather than just has a single value as usual for other redox pairs dissolved in electrolyte.

If mass transport is fast enough, the fast kinetics of reactions (11) and (6) in both directions soon establish a steady state under which the net rate for O$_2$ dissociation to OH$_{ad}$ and for OH$_{ad}$ desorption to water equals. It should be mentioned that, for ORR with dissolved O$_2$ in electrolyte solution as reactants as usually met in the cases using rotating disk electrode system, the actual current is small since the reaction can easily run into mass transport and kinetic mixed controlled mode even with the fastest applicable electrode rotation speed (e.g, 5000 r/min). This renders the applied potential in the kinetic- or mix-controlled potential region for ORR is always just slightly negative of the value for $E_{\text{eq}}^6$. Hence, in most RDE studies the net rate for ORR at Pt based electrode is limited by both the thermo-equilibrium of reaction (6) and the slow mass transport for O$_2$ to the electrode surface.

IV. CONCLUSION

The kinetics for O$_2$ and OH$_{ad}$ adsorption/desorption and ORR at Pt(111) electrode in 0.1 mol/L HClO$_4$ have been investigated in order to find the key factors which limit ORR kinetics at Pt. It was found that: (i) $E_{\text{eq}}^6$ at Pt(111) has a broad range from 0.6 V to 1.0 V, its upper limit determines the onset potential for ORR at Pt(111). (ii) The kinetics for both OH$_{ad}$/O$_{ad}$ formation from O$_2$ dissociation and for OH$_{ad}$ adsorption from water dissociation and its desorption are very fast, a quasi-steady state will be established very fast. (iii) In the potential range from 0.8 V to 1.0 V, the small deviation of the applied potential to $E_{\text{eq}}^6$ as well as the slow mass transport of O$_2$ to the electrode surface renders the net ORR kinetics slow, although the kinetics...
for the elementary steps in both forward and backward direction are fast. Our study reveal that adjusting the catalysts properties or reaction conditions, which shift $E_{eq}$ to positive direction and improve the mass transport of O$_2$, should be key to improve ORR activity for Pt based electrocatalysts.

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