

ARTICLE

Kinetics Study on O₂ Adsorption and OH_{ad} Desorption at Pt(111), Its Implication to Oxygen Reduction Reaction Kinetics

Fan Yang, Ling-wen Liao, Ming-fang Li, Dong Mei, Yan-xia Chen*

Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

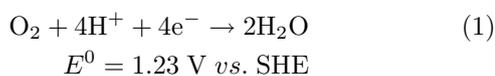
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Kinetics of dissociative O₂ adsorption, OH_{ad} desorption, and oxygen reduction reaction (ORR) at Pt(111) electrode in 0.1 mol/L HClO₄ has been investigated. Reversible OH_{ad} adsorption/desorption occurs at potentials from 0.6 V to 1.0 V (*vs.* RHE) with the exchange current density of ca. 50 mA/cm² at 0.8 V, the fast kinetics of OH_{ad} desorption indicates that it should not be the rate determining step for ORR. In the kinetic- or kinetic-mass transport mix 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 OH_{ad} from dissociative adsorption of O₂. It indicates that at Pt(111) the net rate for O₂ decomposition to OH_{ad} is slightly faster than that for OH_{ad} 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 OH_{ad} as well as the thermo-equilibrium of OH_{ad}+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 ($\eta > 0.22$ V) are still required in order to achieve any appreciable ORR current [1–10]. In acidic solutions, the overall reaction for ORR is:



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 have all been suggested to be the r.d.s. for ORR in acidic electrolyte [2, 3, 5, 6]:



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, OH_{ad} 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

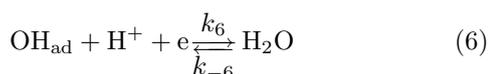
Experimental conditions are similar to that described in Ref.[7]. 0.1 or 1.0 mol/L HClO₄ solution was pre-

* Author to whom correspondence should be addressed. E-mail: yachen@ustc.edu.cn Tel./FAX: +86-551-63600035

pared using 70% perchloric acid (Suprapure, Sigma-Aldrich) and ultra-pure water (18.2 M Ω /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_{ad} 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_{ad} from water and its desorption [15].



Irreversible Pt-O_x 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_{ad} 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_{ad} 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 E₆^{eq} for Eq.(6) is:

$$E_6^{\text{eq}} = E_6^0 + \frac{RT}{F} \ln \frac{a_{\text{OH}_{\text{ad}}} a_{\text{H}^+}}{a_{\text{H}_2\text{O}}} \quad (7)$$

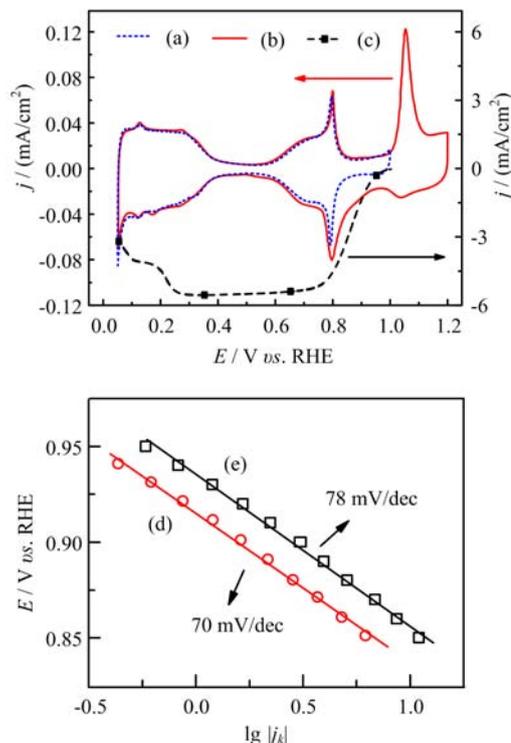


FIG. 1 (a, b) Base CVs and (c) polarization curves for ORR at Pt(111) in N₂- (a, b) or O₂- (c) saturated of 0.1 mol/L HClO₄ in positive-going scan. Potential scan rate of 50 mV/s. Electrode rotation speed of 2000 r/min. The tafel plot of E vs. lg|j_k| for ORR before (d) and after (e) normalizing to the active surface sites (by taking OH_{ad} coverage under ORR as the same as that in O₂ free solution).

where *a* is the activity of respective species specified in the subscript, E₆⁰ 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_{ad} desorption indicates that the high value of the overpotential at the onset for ORR at Pt(111) is determined by E₆^{eq}. 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 < E₆^{eq}. This conclusion agrees well with recent predictions based on DFT calculation, *i.e.*, among all possible elementary steps for ORR at Pt(111), OH_{ad} desorption has the most positive Gibbs free energy change (Δ*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_{ad} desorption 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_{ad} formation and the reductive removal of OH_{ad} at Pt(111) in 0.1 mol/L HClO₄ after stepping from 0.5 V

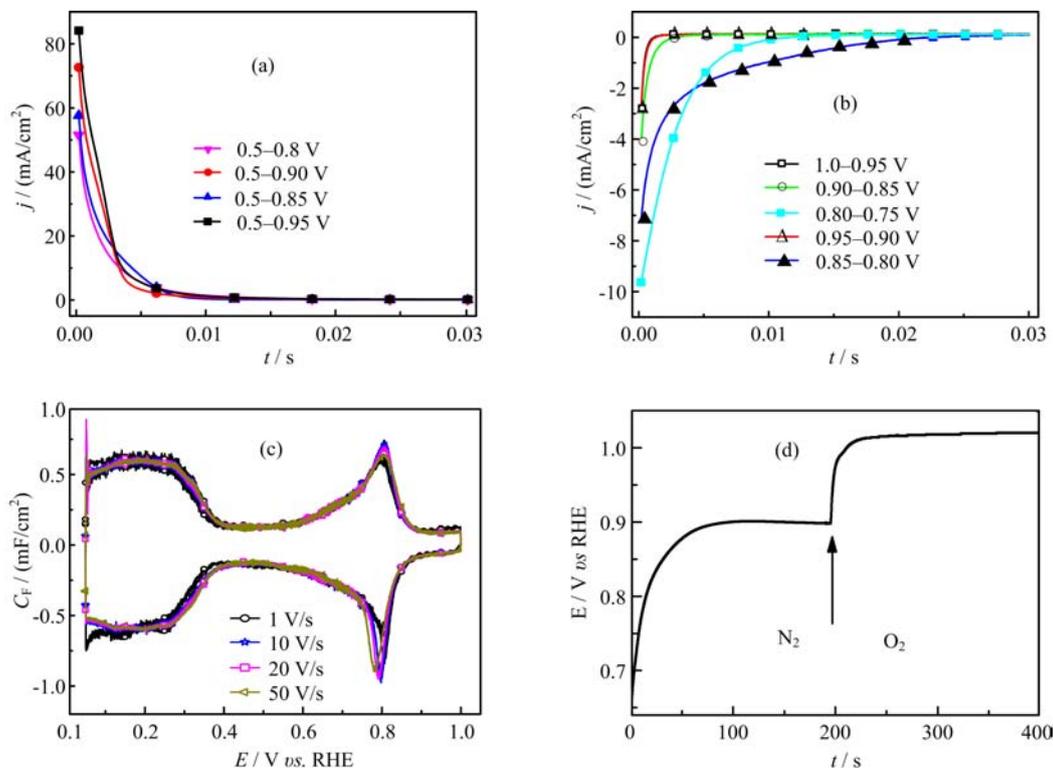


FIG. 2 Current transients for (a) OH_{ad} formation and (b) OH_{ad} desorption at Pt(111) in 0.1 mol/L HClO₄ after potential step to the respective potentials. (c) Capacitance C_F vs. E curves for Pt(111) in 0.1 mol/L HClO₄ at various potential scan rates. (d) The change of open circuit potential for Pt/0.1 mol/L HClO₄ interface after switching from a O₂-free to O₂-saturated solution.

to the respective reaction potentials or stepping from higher potential to lower ones. From Fig.2 it is seen that in O₂ free solution OH_{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_{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]:

$$j_{\text{ad}}(t) = F \frac{d\theta_{\text{OH}_{\text{ad}}}(t)}{dt} = F \{ k_{-6} a_{\text{H}_2\text{O}} [1 - \theta_{\text{OH}}(t)] - k_6 \theta_{\text{OH}}(t) a_{\text{H}^+} \} \quad (8)$$

$$\theta_{\text{OH}_{\text{ad}}}(t) = \frac{1}{Q_c} \int_0^t j_{\text{ad}}(t) dt = \frac{1}{240} \int_0^t j_{\text{ad}}(t) dt \quad (9)$$

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_{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 $\theta_{\text{OH}_{\text{ad}}}=0.3$ ML at

0.8 V as the standard state, exchange current density j_0 for reaction (6) is estimated as follows:

$$j_0 = -Fk_6(E)\theta_{\text{OH}}(E)a_{\text{H}^+} = Fk_{-6}(E)a_{\text{H}_2\text{O}}[1 - \theta_{\text{OH}}(E)] \quad (10)$$

At 0.8 V, j_0 is estimated to be ca. 50 mA/cm². The current density for OH_{ad} desorption (the forward reaction in reaction (6)) are estimated to be -2.7 and -7.1 mA/cm² at 0.95 and 0.9 V by assuming a symmetric factor of 0.5. The fast kinetics for OH_{ad} adsorption/desorption is further supported by the good symmetry for OH_{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/cm² 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_{ad} desorption under otherwise identical condition, indicating that the kinetics for ORR is not limited by the “slow” kinetics for OH_{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. $\lg j_k$ is ca. -70 mV/dec in the potential region from 0.95 V to

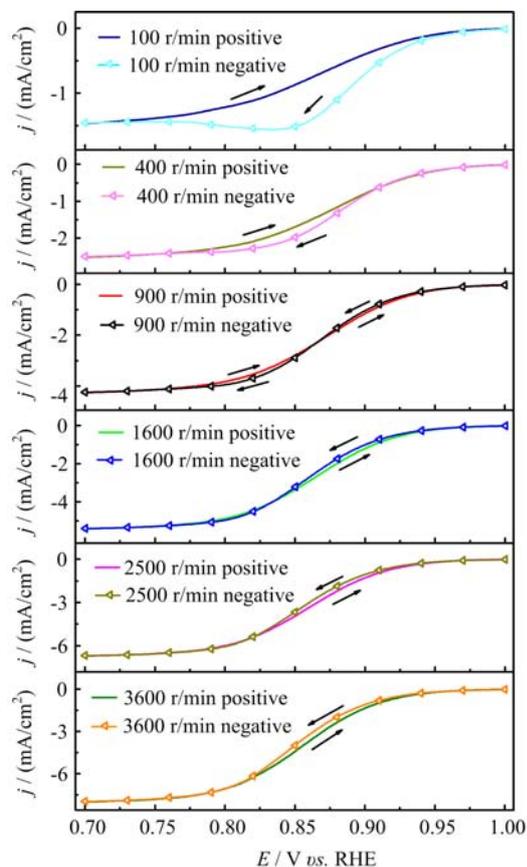


FIG. 3 Positive- and negative-going scan polarization curves for ORR at Pt(111) in O_2 saturated 0.1 mol/L $HClO_4$ with different electrode rotation speed, potential scan rate of 50 mV/s.

0.85 V (Fig.1(d)) [7]. 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

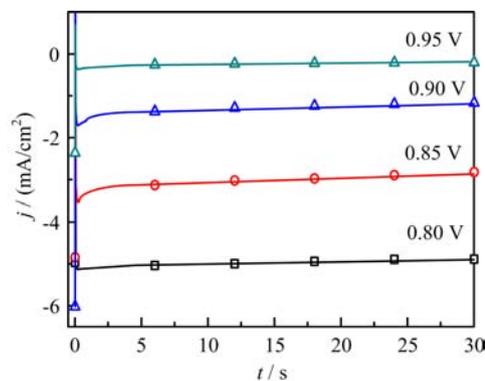


FIG. 4 Current transients for ORR at Pt(111) in 0.1 mol/L $HClO_4$ after stepping from 0.5 V to the respective reaction potentials as indicated, electrode rotation speed is 2000 r/min.

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 chronoamperometric transients measured during ORR in the kinetic and kinetic-mass transport mix-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 chronoamperometric 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 $(1 - \theta_{contaminants})$. 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 O₂ 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 O₂ 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 O₂ 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 O₂ to OH_{ad}/O_{ad} at H₂O+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 O₂ decomposition at clean Pt [6]. And at H₂O+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 O₂ 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 H₂O [10].

As estimated from Fig.1 and Fig.2, the current density for OH_{ad} desorption are -7.1 and -2.7 mA/cm² 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/cm²). Since the difference of the rates for both dissociative adsorption of O₂ to OH_{ad} and that for OH_{ad} adsorption/desorption are within 10 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:



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 HClO₄, 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 O₂ competes with the dissociation of H₂O for the active sites. Ignoring the double layer charging current, the current recorded during linear potential sweeping equals

$$j_{ORR}(E) = 2Fk_1(E)c_{O_2}^s a_{H^+}^2 [1 - \theta_{OH}(E)]^2 + 2Fk_6(E)\theta_{OH}(E)a_{H^+} - 2Fk_{-6}(E)a_{H_2O}[1 - \theta_{OH}(E)] \quad (12)$$

where $c_{O_2}^s$ is the concentration of oxygen near electrode surface. And under potentiostatic condition the ORR current density equals

$$j_{ORR}(t) = 2Fk_1c_{O_2}^s(t)a_{H^+}^2(t)[1 - \theta_{OH}(t)]^2 + 2Fk_6\theta_{OH}(t)a_{H^+}(t) - 2Fk_{-6}a_{H_2O}[1 - \theta_{OH}(t)] \quad (13)$$

These equations clearly express that ORR current is controlled by both the rate for OH_{ad} formation from O₂ 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_6^{eq} 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_6^{eq} changes sensitively with the surface coverage of OH_{ad}. From Eq.(7), it is easily seen that when θ_{OH} increases, E_6^{eq} shifts to positive potentials, and when θ_{OH} decreases, E_6^{eq} shifts to negative potentials. Hence E_6^{eq} 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 O₂ dissociation to OH_{ad} and for OH_{ad} desorption to water equals. It should be mentioned that, for ORR with dissolved O₂ 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 mix 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_6^{eq} . 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 O₂ to the electrode surface.

IV. CONCLUSION

The kinetics for O₂ and OH_{ad} adsorption/desorption and ORR at Pt(111) electrode in 0.1 mol/L HClO₄ have been investigated in order to find the key factors which limit ORR kinetics at Pt. It was found that: (i) E_6^{eq} 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 O₂ 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_6^{eq} as well as the slow mass transport of O₂ 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_6^{eq} to positive direction and improve the mass transport of O_2 , should be key to improve ORR activity for Pt based electrocatalysts.

V. ACKNOWLEDGMENTS

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