



Electrochemical oxidation of hydrogen peroxide at platinum electrodes. Part II: effect of potential

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Abstract—The electrochemical oxidation of H₂O₂ at a platinum rotating disc electrode was studied at pH 7.26 for the [H₂O₂] range 0–70 mM, rotation rates 630–10000 rpm and anodic potential +264 to +712 mV vs Ag/AgCl using staircase potentiometry. A mechanism is proposed to account for the steady-state current as a function of rotation rate, [H₂O₂] and anodic potential. This mechanism involves reversible binding of H₂O₂ to electrochemically generated Pt(II) surface sites, reduction of the site and inhibiting competitive adsorption of H⁺ and O₂. Potential-invariant values of the constants for H₂O₂, H⁺ and O₂ binding are determined and the rate constants for the reduction and the re-oxidation of the binding site as a function of potential are evaluated. © 1998 Elsevier Science Ltd. All rights reserved.

Key words: platinum, hydrogen peroxide, oxidation, rotating disc electrode, mechanism.

INTRODUCTION

Platinum finds widespread use as an electrochemical catalyst for the oxidation of hydrogen peroxide in amperometric biosensors, where H₂O₂ is generated in an enzyme reaction so that the rate of oxidation is proportional to analyte concentration [1]. Many devices incorporate platinum as a fine dispersion on carbon [2–5]. For such dispersions catalysis of H₂O₂ oxidation is maintained provided the size of the platinum particulates is similar to that of the electric double layer [6].

Relatively few studies have been reported for this reaction on solid planar electrodes and most of these have explored only low [H₂O₂]. Zhang and Wilson [7] found that a pronounced depression of response is evident for [H₂O₂] > 1 mM. These deviations from a linear response were accounted for in terms of the saturation of the electrode surface by H₂O₂ and O₂, a concept proposed earlier by Urbach and Bowen [8] for their potentiometric studies.

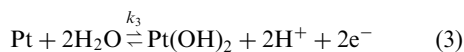
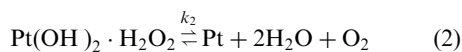
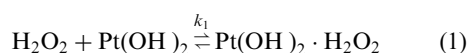
It has also been shown that oxidation of H₂O₂ is favored on oxidized Pt surfaces [9–11] in that H₂O₂

oxidation occurs in the potential region corresponding to platinum oxide film formation [12]. Lingane and Lingane [10] used this as supporting evidence for an earlier proposal by Hickling and Wilson [13] that H₂O₂ acts to reduce these oxide films and that the observed current is due to the re-oxidation of platinum.

Similar behavior is reported for palladium catalyzed oxidation of H₂O₂. Gorton [14] found non-linear steady-state responses for [H₂O₂] > 10 mM on sputtered Pd/Au on carbon and also proposed that the overall reaction was reliant on Pd oxide films. Johnston *et al.* [15] extended this work and showed that the experimental data could be accounted for by the formation of a surface Pd(II)/H₂O₂ complex prior to the rate determining reduction of Pd(II).

Recently, we reported our findings for H₂O₂ oxidation on planar Pt rotating disc electrodes under steady-state conditions [16]. We developed a mechanism, incorporating features of the previous work on both Pt and Pd, that describes the rate of oxidation over a relatively wide range of concentrations (0–80 mM) and rotation rates (630–10000 rpm). The main reaction scheme is summarized as follows:

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H_2O_2 near the electrode surface is in rapid equilibrium with the Pt(II) binding site as described in reaction (1). The binding site could well involve Pt(IV) since Anson and Lingane [12] have detected this oxidation state together with Pt(II) on the surface of platinum. If this were the case in the present study, then reaction (2) would involve the two electron reduction of Pt(IV) to Pt(II). This would not alter the form of the ensuing kinetic analysis. We have chosen to continue to label the binding site as Pt(OH)₂ to maintain consistency with Johnston *et al.* [15] and our earlier work [16]. The adsorption constant K_1 for this process is given by

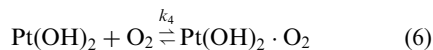
$$K_1 = \frac{\theta_{\text{Pt}(\text{OH})_2 \cdot \text{H}_2\text{O}_2}}{[\text{H}_2\text{O}_2]\theta_{\text{Pt}(\text{OH})_2}} \quad (4)$$

where θ_i refers to the fractional surface coverage of each species i and the concentration is that at the surface of the electrode unless otherwise identified as bulk concentration in this and following expressions.

The surface complex undergoes internal electron transfer in reaction (2) with the formation of the reduced site and release of the products H_2O and O_2 . The binding site is subsequently reformed electrochemically in reaction (3). It was assumed that a sufficiently anodic potential was applied (+600 mV vs Ag/AgCl) so that $k_3 \gg k_2$ and reaction (2) became rate limiting and the overall reaction was given by

$$j = k_2 N \theta_{\text{Pt}(\text{OH})_2 \cdot \text{H}_2\text{O}_2} \quad (5)$$

where N is the number of binding sites per m^2 . Saturation and a maximum current is exhibited as $\theta_{\text{Pt}(\text{OH})_2 \cdot \text{H}_2\text{O}_2} \rightarrow 1$. Two inhibiting binding modes were identified. The first involves competitive binding of O_2 to the Pt(II) site so that reaction (1) is inhibited

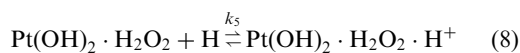


where the competitive inhibition binding constant K_4 is given by

$$K_4 = \frac{\theta_{\text{Pt}(\text{OH})_2 \cdot \text{O}_2}}{[\text{O}_2]\theta_{\text{Pt}(\text{OH})_2}} \quad (7)$$

The second involves reversible protonation of the

surface Pt(II)/ H_2O_2 complex where the protons are the product of reaction (3)



The protonation constant K_5 is given by

$$K_5 = \frac{\theta_{\text{Pt}(\text{OH})_2 \cdot \text{H}_2\text{O}_2 \cdot \text{H}^+}}{[\text{H}^+]\theta_{\text{Pt}(\text{OH})_2 \cdot \text{H}_2\text{O}_2}} \quad (9)$$

Given that $\theta_{\text{Pt}} \rightarrow 0$ under these conditions, applying the steady-state approximation and solving for j yielded the product-inhibited rate equation in terms of the surface concentration of each solution species.

$$j = \frac{k_2 N K_1 [\text{H}_2\text{O}_2]}{1 + K_4 [\text{O}_2] + K_1 [\text{H}_2\text{O}_2] (1 + K_5 [\text{H}^+])} \quad (10)$$

Since steady-state conditions prevailed, the surface concentrations were related to bulk concentrations through use of Fick's First Law and the Nernst diffusion layer thickness controlled by the rotation rate. Substitution of these rate-dependent expressions into equation (10) resulted in a third-order polynomial in terms of bulk concentrations and electrode rotation rates. The validity of the mechanism was tested, and evaluation of kinetic and equilibrium parameters achieved, using a Simplex [17–20] optimization of the most positive root of this polynomial calculated directly using Viète's method*.

In addition to determining the applicability of our new mechanism, we evaluated a new value of the diffusion coefficient for H_2O_2 ($D_{\text{H}_2\text{O}_2} = 0.66 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$). This is substantially lower than values reported by other workers [22–25]. These earlier values were all determined using electrochemical methods reliant on the assumption that simple mass-transport conditions prevail. Our work showed that this is inappropriate and, thus, these values for $D_{\text{H}_2\text{O}_2}$ were likely to be erroneous.

In this paper we test the validity of our mechanism to steady-state measurements obtained over a range of potentials. We also investigate the possibility that the electrochemical re-oxidation of surface sites described by reaction (3) may become rate limiting at less anodic potentials than explored in our previous work.

EXPERIMENTAL

All chemicals used were from Univar and all solutions were prepared in Millipore water. Hydrogen peroxide (30% w/w) was standardized by titration against acidified solutions of KMnO_4 which were prepared immediately prior to use and standardized against anhydrous disodium oxalate.

All electrochemical measurements were made in 250 ml of pH 7.26 phosphate buffer (0.1 M) in a water-jacketed cell maintained at $20 \pm 0.05^\circ\text{C}$ with

*First appears in Francois Viète's treatise *De emendatione* published 1615. Quoted by Ref. [21].

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