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Interaction of hydrogen peroxide with a Pt(111) electrode

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ABSTRACT

Hydrogen peroxide is recognized as one of the most probable intermediate species during oxygen reduction reaction (ORR) on various metals. In this work, H_2O_2 reduction and oxidation on Pt(111) have been studied in a non-adsorbing electrolyte by cyclic voltammetry and online electrochemical mass spectrometry. H_2O_2 is oxidized and reduced into two different, but interrelated electron transfer processes. As the potential increases, the reduction of H_2O_2 switches rapidly to its oxidation at ~$E > 0.9$ V. The whole process exhibits a marked hysteresis in the mixed charge transfer–diffusion controlled potential region, together with current overshoots at $E > 0.85$ V and $E < 0.27$ V in quiescent solutions. At high potentials, Pt(111) oxides and O_2 evolution explain the current–potential characteristics, while at low potentials, hydrogen adsorption is at the origin of the current response.

1. Introduction

Among fuel cell cathodic processes, oxygen reduction reaction (ORR) is undoubtedly the most important. According to mechanistic proposals in the literature, O_2 is reduced to water either via a 'direct' path, or in a 'two-step' or serial, process through hydrogen peroxide formation as intermediate species [1,2]. Of course, both reaction schemes may occur also concomitantly [2]. Tafel slope measurements suggest that the first electron transfer is the rate determining step (RDS) and thus leaves considerable freedom to speculate about the sequence of the following, comparatively fast, steps of the mechanism.

However, the nature of the initial step is not fully understood. Is O_2 adsorbed at Pt/solution interfaces? If so, the oxygen bond could be split at ambient temperature as occurs at the solid/gas interface. If O_2 is not molecularly adsorbed, however, intermediate species would still adsorb, as required by the electrocatalytic character of the reaction, but the oxygen bond would not necessarily split immediately and the reaction would lead to possible peroxide intermediates that could eventually react further [3]. Recent studies with nano-structured model Pt electrodes have suggested that ORR proceeds at least partly by the serial pathway [2].

In this respect, it is surprising that comparatively few reports have been devoted to the study of the interaction of H_2O_2 on well-defined Pt electrodes [4–6]. Early studies on Pt(poly) highlighted a very complex, interrelated dynamics of the near-reversible oxygen–H_2O_2 and H_2O_2–water couples on platinum [7–9], a situation we will refer to as a multi-couple system [7,9]. It has also been suggested that electro-reduction of O_2 induces the reduction of H_2O_2 and vice-versa [10]. In the work reported here, we study the reactivity of H_2O_2 on a single-crystal Pt(111) electrode, with particular emphasis on product formation, and its possible implications for the ORR.

2. Experimental

Electrodes with (111) surface orientation were prepared [11] and all the experiments were carried out in a two-compartment, three electrode all-glass cell, following an experimental protocol detailed elsewhere [12]. Suprapure perchloric acid (Merck) and H_2O_2 (TraceSelect® Ultra) were used to prepare aqueous solutions in ultrapure water (Purelab Ultra, Elga—Vivendi). Online Electrochemical Mass Spectrometry (OLEMS) was used to detect the gaseous products formed during the reaction [13].

3. Results and discussion

Fig. 1 shows the cyclic voltammograms (CVs) of 2 mM $H_2O_2 + 0.1$ M perchloric acid on Pt(111) electrode between 0.06 and 1.15 V. Results are shown for a quiescent solution (Fig. 1A) and for a rotated electrode at 500 r.p.m. (Fig. 1B), using the hanging meniscus rotating disk electrode (HMRDE) configuration [14]. For the latter case, the Tafel curve is also shown as an inset to Fig. 1B.

During the positive-going scan, the stationary reduction current observed between 0.3 and 0.9 V is followed by a transition to the H_2O_2 oxidation at higher potentials. The potentials at which the current crosses zero are slightly different for both positive-and negative-going scans, and they depend on the scan and rotation rates (ν and ω), upper potential limit (E_{up}) of the sweep, as well as on the H_2O_2 concentration in the solution (Fig. 2), as was found on

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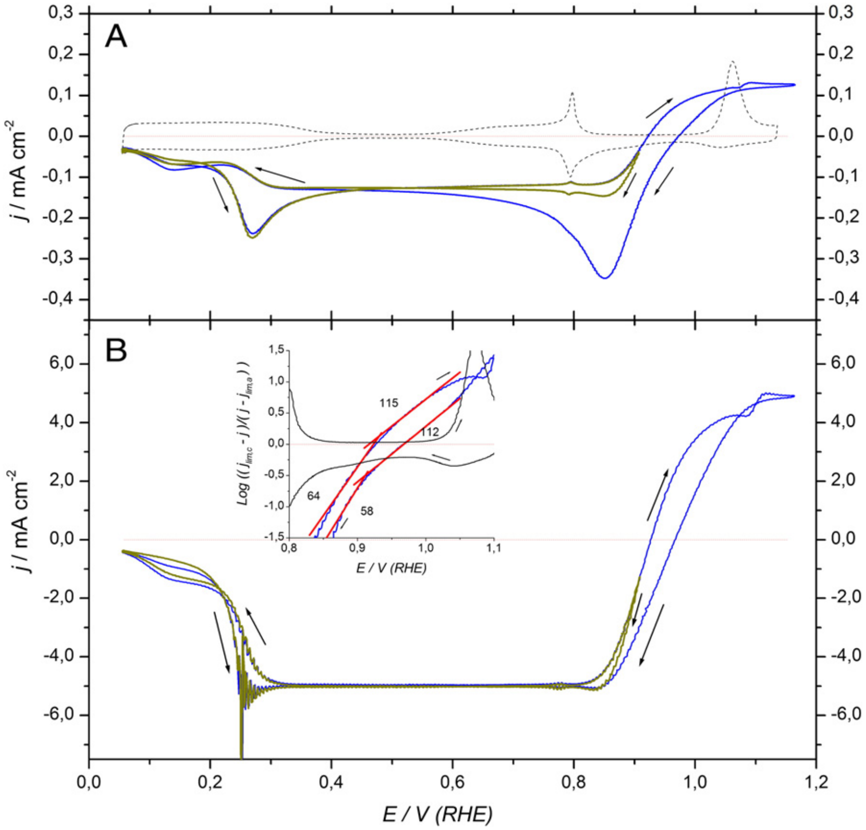

Fig. 1. Stable voltammetric profile of Pt(111) in 2 mM H_2O_2 in 0.1 M $HClO_4$ solution at 50 mV s^{-1}, at two upper potential limits: 0.9 V (—) and 1.15 V (—). A: Quiescent solution. The blank voltammogram is also given (– –). B: The electrode is rotated at 500 r.p.m. Inset: Tafel plot for the H_2O_2 oxidation and reduction. Note that y-axis is not the same in both figures.

Pt(poly) [7,8,17]. Interestingly, the open-circuit potential (OCP) measured under static conditions changes with the time. Initially, it is ~0.945 V and after 12 min it reaches a value close to ~0.926 V. In the case of Pt(poly), variations of as much 20 mV, or more, between different measurements of the OCP have been found for similar concentrations as the employed in this study [9].

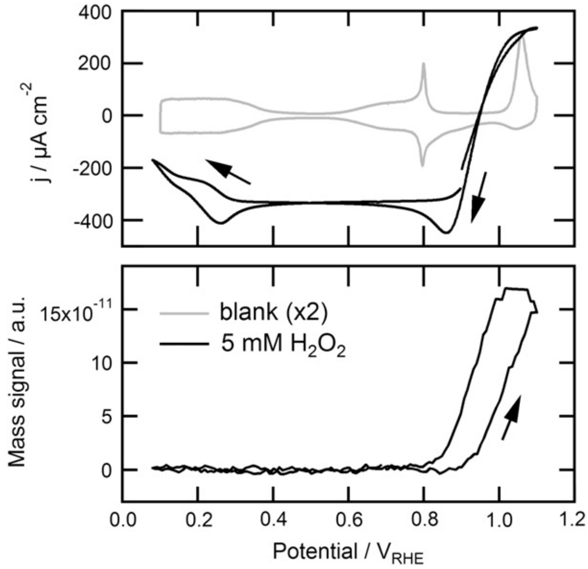

Fig. 2. Top: cyclic voltammogram of Pt(111) in 0.1 M $HClO_4$ + 5 mM H_2O_2 at 2 mV s^{-1}, together with the blank CV in 0.1 M $HClO_4$ at 50 mV s^{-1}. Bottom: associated oxygen formation measured as m/z = 32 with OLEMS.

At high enough overpotentials, the current reaches a constant value corresponding to two electron (2e^{-}) processes controlled by diffusion for both H_2O_2 oxidation and reduction. The current–voltage curve shown in Fig. 1 can be interpreted in terms of a multi-couple system involving the oxygen–H_2O_2 and H_2O_2–water couples. The reactions taking place would be the oxidation of H_2O_2 to O_2 in the positive-going sweep:

$$H_2O_2 \rightleftarrows O_2 + 2H^+ + 2e^- \quad E_1{}^0 = 0.695\,V \tag{1}$$

and the reduction of H_2O_2 to water in the negative-going sweep:

$$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O \quad E_2{}^0 = 1.763\,V \tag{2}$$

From the cited equilibrium potentials, we must conclude that the potential at which the current crosses zero in Fig. 1 must be a mixed potential. Mixed potential systems may be sensitive to changes in the mass transport of the species involved. In addition, complications arise when intermediate species play a role in a multi-couple system, because these species are simultaneously product and reactant in separate couples [7].

Additionally, between 1.0 < E < 1.15 V, where O_{ads} is formed on Pt(111) [15], a complex dynamic is seen; during the positive scan a small current step is observed in both curves (Fig. 1A and B). Besides, in the quiescent solution an overshoot of current is observed during the negative-going scan (Fig. 1A), which depends on E_{up} and v (Fig. 2). These results suggest that Pt(111) oxides play a role during H_2O_2 oxidation. In the positive-going sweep, the zero current is crossed in the region in which only the "butterfly" process has taken place and thus the surface is only covered by adsorbed hydroxide (OH_{ads}) [15], while in the negative-going scan, the surface would also contain adsorbed oxygen (O_{ads}), at a coverage