New Oscillatory Phenomena in the Redox Reaction of O_2/O_2^- Couple on a Hanging Mercury Drop Electrode in Acetone Media

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(Received October 6, 1997; CL-970771)

A new electrochemical oscillation is found in the redox reaction of O_2/ O_2^- (superoxide ion) couple on a hanging mercury drop electrode (HMDE) in acetone media. Both electrogeneration of O_2^- on HMDE and its dissolution (i.e., anodic oxidation) are indispensable for the present oscillation. A probable mechanism is proposed based on related previous studies.

Electrochemical oscillatory behavior was observed as early as 1828,[1] and has been the subject of numerous investigations since then. Excellent reviews[2-4] have summarized the earlier and recent developments in the field of the electrochemical oscillatory systems. In the present paper, we report on new oscillation phenomena observed in the redox reaction of O_2/O_2^- couple on HMDE in acetone media. To the best of our knowledge, this is the first observation of current oscillations which are associated with in situ electrogenerated O_2^-.

Measurements were performed at laboratory temperature (20±2 °C) by using a standard three-electrode, one-compartment configuration with an HMDE (Model 303A, EG&G Princeton Applied Research, area: 0.011 cm^2)[5] as the working electrode, a spiral platinum counter electrode and an Ag-wire quasi-reference electrode. Cyclic voltammetry and potential-step chronoamperometry were carried out using computer-controlled electrochemical systems (Cypress System CS-1090 and BAS 100B/W).[6] All chemicals were of reagent grade. Doubly distilled mercury was used, although high purity is not a prerequisite for the present oscillation.

Figure 1 shows a series of cyclic voltammograms obtained with the HMDE in O_2-saturated acetone solution containing 0.1 M tetra(n-butyl)ammonium perchlorate (TBAP). During the cathodic potential scan from -0.2 to -1.0 V, the usual cathodic peak for the reduction of O_2 to O_2^- could be seen around -0.75 V, and in the subsequent anodic scan strong current oscillation, superposed to the reoxidation current of O_2^-, was observed in the potential range of ca. -0.7 to -0.4 V. The amplitude and the period of oscillations changed irregularly during the anodic potential scan. The oscillation patterns obtained at a fresh HMDE each time were also irregular. The oscillation behavior could be also observed in other electrolyte solutions (e.g., tetraethylammonium perchlorate and tetra(n-butyl)ammonium bromide) where the (quasi) reversible redox reaction of O_2/O_2^- couple could be actually established.[7] However, no oscillation was, of course, observed in the electrolyte solutions containing no O_2.

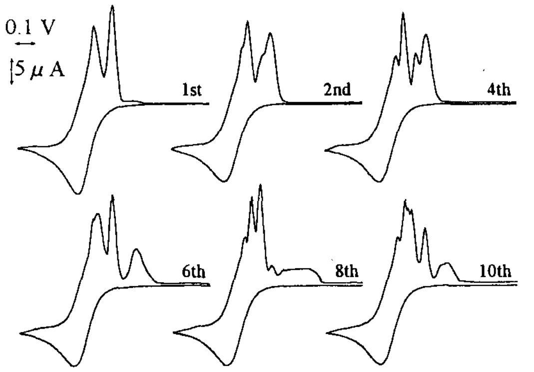

Figure 1. A series of cyclic voltammograms obtained with HMDE at v = 100 mVs^{-1} in O_2-saturated acetone solution containing 0.1M TBAP. Potential sweep direction: -0.2 V → -1.0 V → -0.2 V vs. Ag.

The oscillation was found to depend on the potential scan rate (v), as typically shown in Figure 2. The most remarkable point is that no oscillation was actually observed at high scan rates (in this case, $v \geq 30$ Vs^{-1}). This implies that the overall anodic electrode process is not simply diffusion-controlled one, and at the same time that the oscillation results from complicated chemical /physical phenomena occurring on the HMDE surface (*vide infra*).

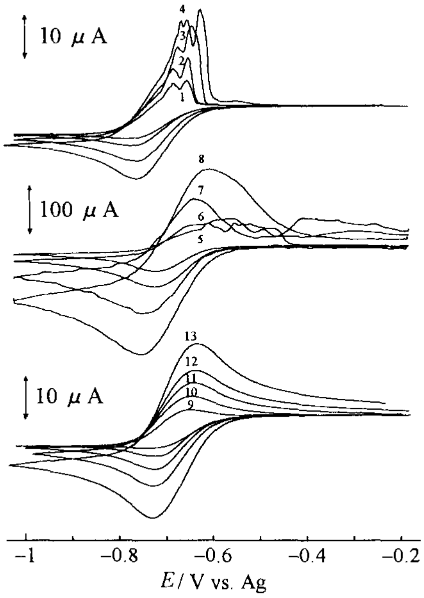

Figure 2. Cyclic voltammograms obtained with HMDE(1-8) and Hg(Au) electrode(9-13) in the same solution as in Fig.1 at various v's: (1) 0.01, (2,9) 0.02, (3,10) 0.05, (4,11) 0.1, (12) 0.2, (13) 0.5, (5) 1, (6) 3, (7) 10 and (8) 30 Vs^{-1}. Area of Hg(Au) electrode: 0.008 cm^2.

When the HMDE was replaced by Hg-coated Au (Hg(Au)) electrode, the cyclic voltammogram possessed a "normal" shape (see Figure 2). Moreover, the oscillation could not be also observed with solid electrodes such as Pt, Au, glassy carbon and pyrolytic graphite. Therefore, the observed oscillation seems to be characteristic of the HMDE. This fact, together with previous studies[8,9] concerning electrochemical oscillations on HMDE and dropping mercury electrode(DME), may suggest that the observed oscillations are associated with the movement of the mercury surface and adjoining solution which may be triggered by a change in the interfacial surface tension caused by an inhomogeneous polarization of HMDE[10] (probably with an intervention of adsorption of O_2^-). Recently, Olexova and Treindl[12-14] have observed current oscillations during the reduction of bromate ions in H_2SO_4 solution over a DME in the presence of phenol and over a stationary Hg electrode in H_2SO_4 and HNO_3 solution in the presence of bromine. The oscillations were attributed to the formation and destruction of passive films (such as $Hg(BrO_3)_2$ and Hg_2Br_2) on the Hg surface. Further, they also have pointed out that the anodic oxidation of Hg plays an important role in their oscillatory phenomena.[15]

In the ICP measurements of the solution electrolyzed under the oscillatory conditions the ICP spectra characteristic of Hg compounds were observed at 194.2, 253.6 and 296.7 nm, suggesting the formation of soluble mercury compound (i.e., dissolution of mercury) during the oscillation.

Figure 3 show a series of the current-time curves obtained under the potential-step electrolysis, where the electrode potential was initially held at -1.0 V for different electrolysis time (t_0 = 1~90 s) and then stepped to -0.5 V. At -1.0 V O_2^- is electrogenerated, and its reoxidation occurs at -0.5 V. The oscillation was found to depend on t_0 and especially its amplitude tended to gradually increase with t_0 (although the period was irregular), and reach an almost constant value. This indicates an increase in O_2^- concentration in the electrode vicinity causes the increased amplitude of the oscillation, namely, O_2^- is essential in the oscillation under study.

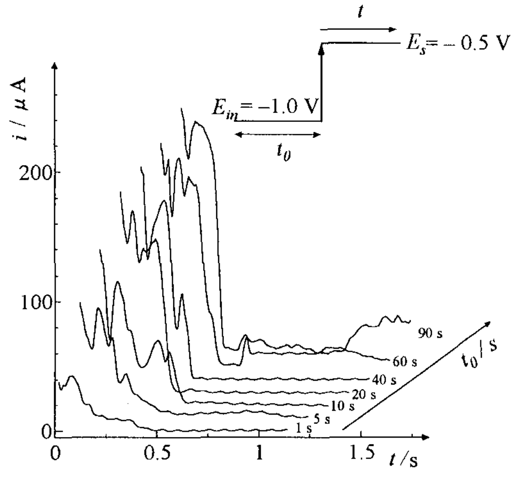

Figure 3. Typical current-time curves obtained in the same solution as in Fig.1. The electrode potential was initially held at -1.0 V for different electrolysis times (t_0) and then stepped to -0.5 V.

On the basis of the present results and previous ones[2-4,8,9,12,13,15,16] concerning electrochemical oscillations on Hg electrodes, it is thought that both electrogeneration of O_2^- on HMDE and its dissolution (anodic oxidation) are indispensable factors for the present oscillation and that the observed oscillation phenomena are caused by the movement of a mercury electrode surface and adjoining solution due to an inhomogeneous polarization of HMDE together with, probably, the formation-destruction of a passive film (e.g., $Hg_2(O_2^-)_2$) on the HMDE surface. A detailed characterization of Hg compounds resulting from the oscillation, which play an essential role in it, would make the oscillation mechanism clear.

The present work was financially supported by Grant-in-Aids for Scientific Research in Priority Areas of "New Polymer and Their Nano-Organized Systems" (No. 277/09232221) and "Exploratory Research" (No.09875207) from the Ministry of Education, Science, Sports and Culture, Japan, and the Katoh Science Foundation, Japan.

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7 The oscillation seems to be solvent-dependent, i.e., it was also observed in N,N-dimethylformamide and pyridine, but not in dimethyl sulfoxide and acetonitrile.

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