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Current oscillatory phenomena based on electrogenerated superoxide ion at the HMDE in dimethylsulfoxide

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Abstract

A study on the current oscillation based on the electrogenerated superoxide ion ($O_2^{\bullet -}$) at a hanging mercury drop electrode (HMDE) in dimethylsulfoxide solution containing tetra-*n*-alkylammonium perchlorate as the electrolyte was carried out. Cyclic voltammetric, potential step chronoamperometric, normal and reverse pulse voltammetric techniques were employed in this study. A bare glassy carbon electrode, a liquid hemispherical mercury (Hg) drop-coated gold (Au) electrode and a Hg film-coated Au electrode were also used as working electrodes to understand the mechanism of the current oscillation. The experimental conditions were optimized for a simple, regular and reproducible current oscillation. The specific adsorption phenomenon of iodide ion and the adsorption of the alkyl chain of the supporting electrolyte on the HMDE surface were also considered to clarify the experimental factors governing the current oscillation phenomenon. It has been concluded that the oscillation is mainly due to the promoted oxidation (dissolution) of the HMDE itself by the adsorption of $O_2^{\bullet -}$, resulting in the formation–destruction of a passive film such as $Hg_2(O_2^{\bullet -})_2$ on the electrode surface. A probable mechanism for the observed current oscillation is discussed.

Keywords: Current oscillation; Hanging mercury drop electrode; Superoxide ion; Cyclic voltammetry; Normal and reverse pulse voltammetry; Potential step chronoamperometry

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1. Introduction

Current oscillatory phenomena are well known to many research groups in the world and much attention has been paid to those systems where the occurrence of oscillation is connected with physical and chemical processes taking place near or at the electrode surface [1–12]. Our group first reported the cyclic voltammetric current oscillation during the molecular oxygen (O_2)/superoxide ion ($O_2^{\bullet -}$) redox reaction at a hanging mercury drop electrode (HMDE) in aprotic media containing tetra-*n*-alkylammonium salts [13–16]. It was found that the oscillation depends on many experimental factors. The occurrence of oscillation was thought to be mainly due to: (i) the streaming phenomena, i.e., the movement of the mercury (Hg) electrode surface and its adjoining solution resulting from an inhomogeneous polarization of the electrode, (ii) the depletion and an inhomogeneous adsorption of electrogenerated $O_2^{\bullet -}$ on the electrode surface and (iii) the formation/destruction of a passive film such as $Hg_2(O_2^{\bullet -})_2$ on the electrode surface: the dissolution of the Hg electrode itself was found to occur during the oscillation [15,16].

However, the current oscillation previously observed was not regular and reproducible. This fact has made it difficult for us to correlate the extent of oscillation clearly with the experimental variables (e.g., concentration of O_2, potential scan rate and potential range in cyclic voltammetry), and consequently the mechanism of oscillation remains obscure still. Thus, the optimiza-

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tion of the experimental conditions for a reproducible oscillation would be a favorable clue to a clear understanding of the oscillation mechanism. Recently, Ortiz et al. [17] have observed similar current oscillations during the redox reaction of the $O_2/O_2^{\bullet -}$ couple in dimethylsulfoxide (DMSO) solution. They have reported that the oscillatory phenomenon diminishes and finally disappears when the O_2 concentration decreases and that, as the potential scan rate increases, the current oscillation disappears. In our previous studies [15,16], unfortunately, this oscillation in DMSO solution has not been observed, while very recently we have optimized the experimental conditions for a simple, regular and reproducible current oscillation.[1]

In the present investigation, the mechanism of the current oscillation at the HMDE during the $O_2/O_2^{\bullet -}$ redox reaction in dried DMSO containing tetra-*n*-alkylammonium perchlorate has been clarified using cyclic voltammetric, potential step chronoamperometric, normal and reverse pulse voltammetric techniques. Furthermore, the effects of specific adsorption of iodide (I^-) ion and the supporting electrolyte on the HMDE surface on the current oscillation are discussed.

2. Experimental

2.1. Reagents

Dimethylsulfoxide (DMSO) of reagent grade was purchased from Kanto Chemical Co. Inc., dried over molecular sieves (4 Å 1/16, Wako Pure Chemicals Industries) and used as a solvent. Tetra-*n*-butylammonium perchlorate (TBAP), tetramethylammonium perchlorate (TMAP) (Tokyo Kasei Kogyo Co. Ltd.), tetraethylammonium perchlorate (TEAP) and tetra-*n*-butylammonium iodide (TBAI) (Kanto Chemical Co. Inc.) were used as supporting electrolytes.

2.2. Apparatus and procedures

Cyclic voltammetric, potential step chronoamperometric, normal and reverse pulse voltammetric experiments were carried out using a computer-controlled electrochemical system (Model 50W, Bioanalytical Systems, Inc. (BAS)). The electrochemical cell was a conventional two-compartment Pyrex glass container with a working electrode, a spiral Pt-wire counter electrode and an Ag|AgCl|NaCl(sat.) reference electrode. A hanging mercury drop electrode (HMDE; model CGME 900, BAS) was used as the working electrode. In order to minimize the *IR* drop across the cell and the diffusion of water into the cell solution, the reference electrode was placed in a glass beaker containing NaCl-saturated aqueous solution and connected to the cell solution via a salt bridge filled with the electrolytic solution used. This arrangement of the reference electrode was applied in all of the electrochemical measurements, except for the potential step chronoamperometric experiments that were carried out by dipping a freshly cleaned silver (Ag) wire into the cell solution as a quasi-reference electrode. In the measurements, air, O_2, N_2 or Ar gases were bubbled directly into the cell in order to obtain their saturated solutions, and during the measurements air, O_2, N_2 or Ar gas were flushed over the cell solutions. All the measurements were carried out at room temperature (20 ± 2 °C).

2.3. Preparation of electrodes used

Mercury (Hg, commercial grade) was washed several times with dilute nitric acid, then with Milli-Q water under fluxing conditions in a column, distilled under reduced pressure and kept in an Ar gas atmosphere. Each experiment was carried out at a freshly formed Hg drop (HMDE, electrode area: 0.018 cm^2) unless otherwise noted. A glassy carbon (GC) electrode of 1.0 mm diameter and a gold (Au) electrode of 1.6 mm diameter were polished with alumina powder and then washed under sonicating conditions for 10 min. The Au electrode was then electrochemically pretreated in N_2-saturated 0.05 M H_2SO_4 solution by repeating the potential scan in the range of −0.2 to 1.5 V vs. Ag|AgCl|NaCl(sat.) at 0.1 V s^{-1} for 10 min or until the CV characteristic of a clean Au electrode was obtained. The Hg hemispherical drop-coated Au electrode was prepared by dipping the Au electrode in pure liquid Hg for 2 min. The coated electrode was then removed and used as a working electrode [13]. This Hg drop-coated Au electrode was also shaken strongly to remove the liquid portion of Hg completely, which resulted in the formation of a mirror film of Hg and used it was then used as a Hg film-coated Au electrode. Prior to use, all the solid electrodes were dried by blowing cold air over them.

Caution! Mercury vapor is a serious human health hazard. Great care should be taken during the distillation process to avoid any contact or exposure due to unexpected circumstances.

3. Results and discussion

3.1. Effects of O_2 and electrogenerated $O_2^{\bullet -}$ concentrations

Recently, Ortiz et al. [17] have reported that the current oscillation is observed during the redox reaction of the $O_2/O_2^{\bullet -}$ couple at the HMDE in DMSO solution,

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[1] In our previous studies [15,16], we could not observe the current oscillation phenomena in DMSO solution. The adsorption of some possible impurities such as mercaptane, dimethylsulfide and dimethylsulfone on the HMDE surface as a surfactant to stop the oscillation like PVC [15] may be considered as a probable reason, but the true reason is not elucidated.