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RRDE experiments with independent potential scans at the ring and disk electrodes — 3D map of intermediates and products of electrode processes

S. Vesztergom, M. Ujvári, G.G. Láng *

Institute of Chemistry, Laboratory of Electrochemistry and Electroanalytical Chemistry, Eötvös Loránd University, Pázmány P. s. 1/A, H-1117 Budapest, Hungary

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ABSTRACT

The dual cyclic voltammetry technique and the electrochemical measuring system with rotating gold disk-gold ring electrodes have been tested in air-saturated and deaerated aqueous sulfuric acid solutions (selected as model systems). The oxygen reduction process has been chosen as model reaction. A new 3D representation of the data has been proposed which can be used to reveal the formation of electroactive species (intermediates or products) at the disk.

1. Introduction

While in conventional rotating ring-disk electrode (RRDE) experiments usually the potential of at least one of the two electrodes is held constant during the measurement [1–6], it has been shown in a recent paper [6] that in some cases the sensitivity of the RRDE technique can be further improved by using dynamic potential control simultaneously at both the disk and the ring electrodes. In the experiments reported in [6], the symmetrical triangular waveforms driving the potentials of the two electrodes were identical (the vertex potentials and the potential sweep rates for the two signals were the same), but the phases were different. An interesting result reported in [6] is that detectable amounts of reducible gold-containing species are leaving the oxidized gold surface during the reduction of the surface oxide layer in H_2SO_4 solutions.

However, the dual cyclic voltammetric technique can also be used to study electrode processes in different ways. For instance, if the "disk electrode" is polarized at a sufficiently low and the "ring electrode" at a sufficiently high scan rate, a 3D map can be constructed using the measured potential and current data, which may reveal the electroactive intermediates or products that are formed in the electrode process(es) taking place on the disk.

The objective of this paper is to demonstrate the applicability of the proposed technique using the Au|0.5 M H_2SO_4(aq.) system (under air-saturated and deaerated conditions) as an illustrative example, i.e. the oxygen reduction process has been chosen as model reaction.

The oxygen reduction reaction (ORR) at gold surfaces has been extensively studied in the literature. Although some details of the reaction mechanism are still unclear, it is known that on gold in acid media the process usually involves the formation of H_2O_2 and the peroxide intermediate is reduced to water only at more negative potentials [5,7–9]. This is a rapidly developing area of electrochemistry. A recent review on the subject (including a section on the use of rotating ring-disk electrodes to determine the mechanism of oxygen reduction) is given in [10]. Whether the $2e^-$ or the $4e^-$ process is more favorable on a polycrystalline gold surface is known to be a function of mainly the electrode potential and the pH [5,7,11,12]. The method proposed in this paper can be used both to identify the potential region where the two-electron pathway is dominant and to estimate the disk potential at which the maximum amount of H_2O_2 is formed.

2. Experimental

In order to carry out the measurements, the multi-channel electrochemical measuring system presented in [6] was used with a bi-potentiostatic setup of XPot devices manufactured and modified specially for our needs by ZAHNER-Elektrik, Kronach, Germany, and with a "PINE AFE7R8" RRDE tip (collection efficiency: 22%). Both the disk (geometric surface area $A_d = 0.1642\ \mathrm{cm}^2$,) and the ring ($A_r = 0.0370\ \mathrm{cm}^2$) were made of polycrystalline gold (gap size between the ring and the disk: 178 μm, roughness factor $R_F \approx 2.1$). The electrode surface was firmly polished with diamond suspensions (Struers) down to a diamond particle size of 0.1 μm. The RRDE tip was

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* Corresponding author. Fax: +36 1 372 2592.
E-mail address: langgyg@chem.elte.hu (G.G. Láng).

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then rinsed with pure ethanol and ultrapure water (Milli-Q), was cleaned ultrasonically for several minutes, and washed extensively with ultrapure water. Every glass parts used in the experiments were immersed in Caro's acid, rinsed in de-ionized water, and cleaned by steam. The thermostated electrochemical cell ($T = 25$ °C) contained a separate reference compartment being connected to the cell by a *Luggin* capillary positioned ~1 mm below the RRDE surface. A gold plate with large surface was used as a counter electrode, and a NaCl-saturated calomel electrode (SSCE) was applied as a reference. The H_2SO_4 solutions were made by dilution of concentrated sulfuric acid (Merck) with ultra-pure water (specific resistance ~18.2 MΩ cm). In some cases, the cell was deaerated by a pure argon flow; while in other cases the O_2 concentration in the solution was maintained constant using an external air pump. Before entering the cell the air passed through a purification system to remove inorganic and organic contaminants.

3. Results and discussion

3.1. Simultaneous dynamic polarization of the disk and the ring electrodes

After the usual cleaning process [6] voltammetric curves were recorded simultaneously at the two electrodes in 0.5 M H_2SO_4 solutions. The applied potential programs are shown in Fig. 1: while the disk electrode was slowly polarized from 600 to −600 mV vs. SSCE (at a sweep rate of 0.25 mV/s), several cyclic voltammograms were recorded at the ring electrode at a sweep rate of 100 mV/s and between the potential limits of 1450 and −550 mV vs. SSCE. The RRDE tip was rotated at $\omega = 1000$ rpm (16.667 Hz) during the experiment.

At the beginning of the slow scan, at electrode potentials more positive than the negative potential limit of the double-layer region ($E_{\mathrm{disk}} > 70$ mV vs. SSCE), cyclic voltammograms characteristic for a clean polycrystalline Au electrode were obtained at the ring (Fig. 2). However, as the disk potential became more and more negative, significant changes of the ring CVs could be observed:

(i) the absolute value of cathodic ring current at negative ring potentials decreased continuously in the disk potential range from $E_{\mathrm{disk}} = 70$ mV to $E_{\mathrm{disk}} = -600$ mV;
(ii) the ring current at positive ring potentials (arising from the oxidation of H_2O_2 formed on the disk) first increased (at disk potentials between about $70\text{ mV} > E_{\mathrm{disk}} > -310$ mV), then decreased again at disk potentials between about $-310\text{ mV} > E_{\mathrm{disk}} > -600$ mV (see Fig. 2).

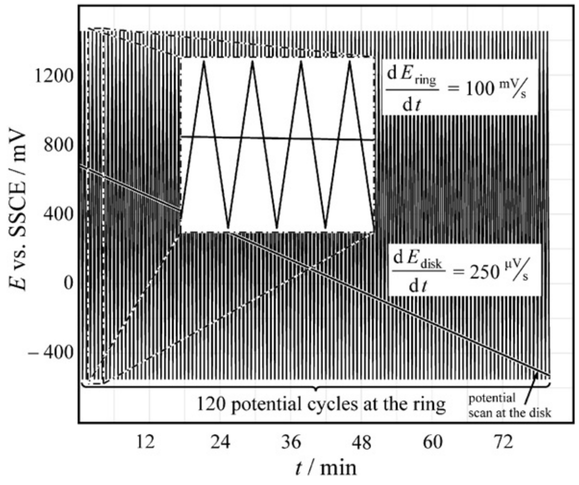

Fig. 1. Controlling waveforms of the disk and the ring electrodes: while the disk electrode is slowly swept towards cathodic potentials, several high-speed cyclic voltammograms can be obtained from the ring.

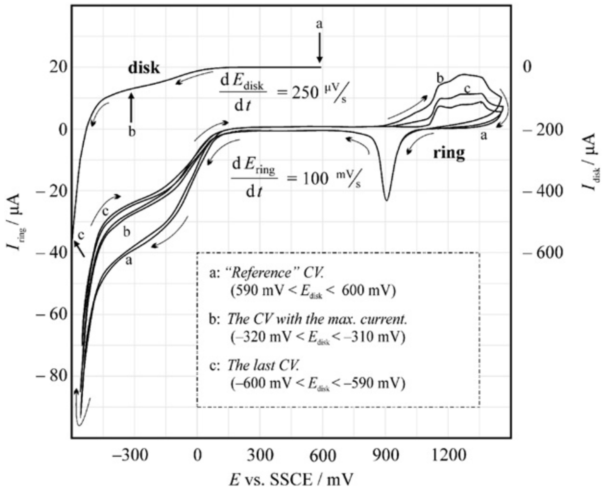

Fig. 2. Ring CVs when oxygen reduction occurs on the disk electrode in air saturated 0.5 M H_2SO_4 solution (the polarization curve obtained from the disk and a few ring CVs are shown together). Rotation rate: 1000 rpm.

Since in strongly acidic solutions the H_2O_2 reduction currents are very small in comparison to the reduction of O_2 [5,7,9], the observed cathodic currents should contain only minor contributions from the further reduction of H_2O_2. It can be therefore concluded that (i) is a typical example of the shielding effect [1]: the flow of bulk electroactive species to the ring is perturbed because of the electrode reaction at the disk. As the disk electrode is polarized towards more negative potentials increasing amount of oxygen gets reduced on the disk and the solution reaching the ring surface is more and more depleted in oxygen, resulting in lower current at the ring electrode. The increase of the ring current at positive ring potentials (see point (ii) above) is most probably due to the oxidation of H_2O_2 produced at the disk. This has been verified by direct H_2O_2 addition experiments (lack of space prevents us from presenting these results). The interesting feature of this effect is that the ring current is not monotonically increasing when the disk potential is swept towards negative values: the current goes through a maximum, and the effect tends to vanish as the ORR at the disk electrode (which is a $2e^-$ process at not too negative potentials) turns to a four-electron process. It is an advantage of the method that the ring electrode surface is kept clean throughout the experiment by the continuous potential cycling; therefore the sensitivity of the collector electrode does not decrease with time.

3.2. Representation of the measured data in three dimensions

In order to represent our measured data, a 10 mV × 10 mV grid was created from the disk and the ring potentials, with $-600\text{ mV} \leq E_{\mathrm{disk}} \leq 600$ mV and $-550\text{ mV} \leq E_{\mathrm{ring}} \leq 1450$ mV. From the measurement records, all such i entries were removed for which $E^{i}_{\mathrm{ring}} > E^{i+1}_{\mathrm{ring}}$; thus, only the measurements made for positively going ring sweeps were left in the dataset. The dataset (practically I_{ring} as a function of E_{disk} and E_{ring}) was then made subject to a (Lánczos-type) resampling process in two dimensions using a kernel with three lobes [13], resulting in a surface of I_{ring} values, defined over the E_{disk}–E_{ring} grid. Next, the values corresponding to the surface for which $E_{\mathrm{disk}} = 600$ mV have been subtracted, in order to obtain the "surface of changes" in the ring currents (ΔI), shown in Fig. 3. Of course, by using appropriate software the resulting diagram can be rotated, zoomed, rescaled, individual data points can be selected, checked, colored, etc. The method described above can be used to detect electroactive species which are generated at the disk electrode with an increased efficiency compared to the traditional "steady ring potential" techniques and the plot shown in Fig. 3(a and b) can be interpreted as a "three dimensional map" of the intermediates or products of electrode processes. In the present case