

Short Communication

The influence of cathodic pretreatment on the kinetics of hydroxide ion oxidation on polycrystalline gold electrode

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Abstract

The electrochemical oxidation of the hydroxide ion was studied on a gold rotating disc electrode (RDE), in aqueous NaOH solutions in the presence of lithium perchlorate as a supporting electrolyte. By potentiodynamic polarization within the limits -1.6 V and $+1.6$ V vs. SCE, it was demonstrated that the overvoltage of the OH^- ion oxidation reaction may be significantly reduced with a 5 min long delay at the vertex cathodic potential of -1.6 V. This finding was explained in terms of the type of gold oxide formed on the gold surface under different experimental conditions.

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1. Introduction

In any aqueous alkaline solution, the oxygen evolution reaction commences on the basis of the hydroxide ion oxidation reaction:



having standard electrode potential $E^0 = 0.401$ V vs. standard hydrogen electrode (SHE).

For a reasonably small concentration of hydroxide ions, in the presence of the supporting electrolyte, the reaction (I) shows a clear diffusion limitation [1–6]. In enlarged anodic polarizations, the current of hydroxide ion oxidation, must pass into the current of oxygen evolution based on direct water oxidation:



having standard electrode potential $E^0 = 1.229$ V vs. SHE. The reaction (II) may not reach the diffusion limitation in aqueous solutions, where water represents a dominant component.

A series of papers by Daniele et al. [2–6] was devoted to the voltammetric determination of hydroxide ions in aqueous solutions. The concentration of the hydroxide ion in both strong [2–4] and weak [5,6] alkaline solutions has been measured by means of both a gold microelectrode [2–5], and a gold rotating disc electrode [4]. For the same purpose, the gold microelectrode was also used in total absence of a supporting electrolyte [3]. The influence of the nature of the microelectrode material, being gold [3], nickel [3] and platinum [3,6], on the shape of voltammograms were investigated too, and a well pronounced voltammetric wave, attributed to the oxidation of OH^- ions, has always been registered [3,6]. The best reproducibility of voltammograms was attained by using the gold microelectrode [3]. Thus, for analytical determination of the OH^- ion concentration, voltammetry with a gold microelectrode was suggested as an alternative to potentiometry

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[2], particularly at high alkaline concentrations beyond the limit of applicability of the glass electrode.

As published in the above mentioned papers [2–6], the current of OH^- ion oxidation commenced to a measurable extent always at potentials higher than 1.1 V vs. SCE, and the diffusion plateau was always observed in the voltage region 1.3–1.6 V vs. SCE (≈ 2.4 – 2.7 V vs. RHE). However, among the studies of anodic processes on the gold electrode in media of various pH values [7–12], that relating to gold oxide formation in concentrated alkaline solutions [10, Fig. 1B] showed that oxygen evolution commenced at 1.60 V vs. RHE (which is approximately 0.53 V relative to SCE), which corresponds to AuO monolayer completion. Therefore, one may expect that hydroxide ion oxidation attains diffusion limitation at potentials close to 0.8 V vs. SCE, i.e., far more negative than those reported in the literature [2–6].

The present work offers an explanation why thus far diffusion limitation of hydroxide ion oxidation on gold electrode was always attained at unexpectedly high over-voltages [2–6].

2. Experimental

757 VA Computrace (Metrohm) was used to perform the voltammetric investigations. All experiments were performed in a thermostated three electrode electrolytic cell at 25 °C. Commercial Metrohm polycrystalline gold disc (2 mm in diameter) electrode, was used as a working electrode. Pt foil served as an auxiliary electrode, while the saturated calomel electrode (SCE) was used as the reference. In order to suppress electrolyte contamination by chloride ions, the reference electrode was bridged by a Luggin capillary filled with the investigated electrolyte. After each set of measurements, the working electrode was polished with dry α -alumina powder ($\sim 1 \mu\text{m}$) applied to a polishing cloth.

Unless otherwise stated, the solutions, prepared from analytical grade reagents and twice distilled water, were deoxygenated by bubbling with oxygen-free nitrogen (99.9995%) during the experiments.

3. Results and discussion

The voltammograms recorded in the solution 0.0025 M NaOH + 0.1 M KClO_4 using a gold rotating disk electrode (RDE) are presented in Fig. 1. The potential range presented in Fig. 1, encompasses (a) the range of hydrogen evolution ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + 1/2 \text{H}_2$) at potentials lower than -1 V [13], (b) the range of OH^- ion adsorption [14] and surface oxide reduction between -1.07 and 0.17 V [10–12], and (c) the range of surface oxide formation, above 0.17 V, accompanied by gaseous oxygen evolution above 0.75 V, according to the reaction (I) [10–12]. These voltammograms, recorded at the anodic polarization direction, show a plateau between 1 and 1.4 V, which passes into massive oxygen evolution according to reaction (II). In

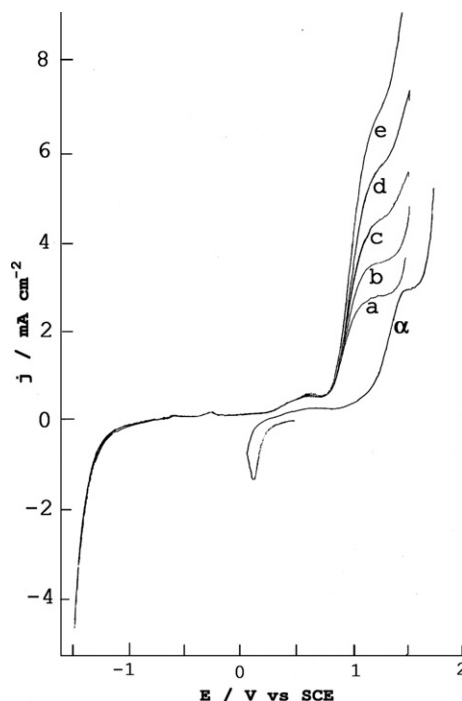


Fig. 1. The voltammograms of the rotating gold disc electrode in a 2.5 mM NaOH + 0.1 M LiClO_4 solution. The series of voltammograms *a*, *b*, *c*, *d* and *e* was recorded at various rotation rates: 5, 10, 15, 20 and 30 cps, respectively, holding before each run, the electrode 5 min at -1.6 V with the cell on, while the curve α is a part of steady state cyclic voltammogram for a potential interval 0.0– 1.7 V vs. SCE, recorded without any hold at the rotation rate of 5 cps. Scanning rate was always 50 mV s^{-1} .

order to maintain the clarity of presentation, the parts of the voltammograms corresponding to the reversed, cathodic polarization direction, were omitted. Having in mind the literature data, that gold oxide as a new phase may appear on gold surface at potentials higher than 0.17 V vs. SCE (i.e., above 1.25 V vs. RHE [10,11]), and being aware of the fact that surface oxides may be completely removed after cathodic polarization extending to -1 V vs. SCE [10–18], we recorded the cyclic voltammograms using potential delay at the vertex potential of -1.6 V vs. SCE 5 min long. Using consecutively ascending rotation rates, a series of voltammograms labeled *a–e* in Fig. 1 was recorded. These voltammograms show an abrupt current rise at nearly 0.75 V, passing into plateaus at potentials between 1 and 1.3 V. According to the literature [10,11], in an alkaline solution, the gold electrode covers itself with an AuO layer in the potential interval 0.17 – 0.9 V vs. SCE (≈ 1.25 and 1.9 V vs. RHE). The charge consumed to complete the monolayer, amounting to 0.386 mC cm^{-2} [7], was used to calculate real surface area and surface roughness of the gold electrode [7]. Thus, we attributed the current waves in Fig. 1 appearing beyond 0.75 V (referred to as I wave in this text), to OH^- ion oxidation on gold covered by the AuO monolayer. If cathodic polarization is limited to 0.0 V only, by recording several consecutive cyclic voltammograms at unchanged polarization and rotation rates, a shift of OH^- oxidation waves

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