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A rotating tungsten disc electrode in concentrated strong alkaline solutions: An electroanalytical aspect

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ABSTRACT

Electrochemical behavior of tungsten in concentrated strong alkaline solutions (10^{-3}–10^{-1} M KOH, $11 < pH < 13$) was studied by means of rotating disc electrode technique. Contrary to the case of less concentrated alkaline solutions, the formation of solid anodic passive film was not evidenced. Chronoamperometric measurements evidenced a fast establishment of steady state conditions in the surface region. In spite of the complexity of overall surface electrochemistry, a linear relationship between the limiting anodic currents and the concentration of OH^- ions was evidenced, which may be used for easy and accurate determination of OH^- ion concentration at high pH values where the glass electrode loses its high reliability.

1. Introduction

Glass electrode presents a commonly used sensor for the determination of acidity and basicity of solutions. However, its significant “alkaline error” in the solutions of high pH is an always present disadvantage [1].

In the last two decades voltammetric and amperometric approaches under steady state conditions have been studied in order to develop the methods of non-potentiometric determination of concentration of OH^- ions [2–22]. A series of papers by Daniele and co-workers [13–17] was devoted to the voltammetric determination of hydroxide ions in aqueous solution using both gold microelectrode [13–16] and rotating disk electrode [15]. Their measurements involved the oxidation of OH^- ions under diffusion limiting conditions. A relatively narrow potential window, of about 0.2 V, of diffusion control of OH^- ion oxidation on gold electrode, being limited on the high potential side by H_2O oxidation, presents an aggravating factor of this procedure. Abu-Rabi et al. [18] published recently that the current of OH^- ions oxidation may be shifted to the cathodic side by intense cathodic electrode pretreatment. Hence, a reliable measurement of OH^- concentration using gold electrode requires a careful control of the state of the surface, relating particularly to the surface coverage by gold oxide.

The Compton group [19] proposed gold ultra-microelectrode arrays consisting of hundreds and thousands electrochemically active electrodes for sensing hydroxyl ions. The reproducible voltammetric waves were observed, and the linearity of peak height vs. hydroxide concentration was proven in the concentration range 50 mM up to 1 mM.

Trough a series of investigations, Banks et al. [20–22] developed a nickel oxide screen printed electrodes for the electroanalytical sensing of OH^- ions. The sensor allows the detection of OH^- ions over the low micro-molar to millimolar range with a detection limit of 23 mM.

According to the available data related to the electrochemical behavior of tungsten at pH values close to 7, its anodic oxidation proceeds in a manner similar to the oxidation of valve metals, namely, obeys the high-filed mechanism of the formation of passive oxide layer [23–27]. As demonstrated by Ortiz et al. [27] for a pH range 7–10, when the cyclic voltammetry (CV) experiments were performed in a quiescent solution, the oxide formation was terminated immediately upon reversing polarization direction. If, in a series of CV experiments, vertex anodic potential was enlarged with respect to the previous one, the oxide formation started at slightly lower potential with respect to the vertex potential of the previous polarization cycle. This indicated a chemical dissolution of WO_3 at a measurable rate. The dissolution rate increased with the increase in pH, and the passivation almost disappeared at pH 12 [24–27]. Such an behavior is not specific for true valve metal oxides, e.g. titanium dioxide, which is quite insoluble under similar conditions [28]. As regards to the anodic dissolution of

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tungsten in highly alkaline media, it is worth mentioning that, at sufficiently high potentials, the current passes into a plateau, which is sensitive towards the rotation rate and extends to a surprisingly large potentials, up to about 8 V [27].

Davydov et al. [29–31] considered theoretically the ion fluxes accompanying the anodic dissolution of tungsten in alkaline solution, and derived the equations of limiting current under both steady state [29] and pulsed [30] conditions. Some other examples of anodic dissolution of metals, e.g. iron, copper and nickel dissolution in acidic media, leading to a mass transfer control too, were studied by Barcia et al. [32].

Although in several published papers [24,29,30] the rate of anodic dissolution of tungsten in alkaline solutions was found to depend on the base concentration, none of them did consider the question whether this behavior may be used for amperometric determination of OH^- ion concentration. Therefore, the subject of the present study is analytical determination of OH^- ion concentration in a high concentration region, above 10^{-3} M, by means of anodic dissolution of tungsten. The applicability of rotating disk (RDE) technique in both supported (K_2SO_4) and unsupported electrolyte solutions was studied.

2. Materials and methods

A tungsten rod (Alfa Aesar, 99,99%) 3.17 mm in diameter, was mounted in a cylindrical Teflon holder of a rotating electrode. The cross section surface (0.079 cm^2) of tungsten rod was exposed to the electrolyte. It was polished by dry corundum particles (1 μm) before the first use. The three-electrode cell (effective volume 20 ml) with a Pt foil as a counter electrode and a saturated calomel electrode (SCE) as the reference one were used. The solutions were purged by bubbling N_2 (5 N) through the cell. All the experiments were conducted at room temperature (25 ± 1)°C. The electrochemical measurements were carried out by means of the device Gamry PC14-750 equipped with Pine Rotator.

The cyclic voltammetry experiments (RDE–CV) were performed at a scan rate 20 mV s^{-1}, under simultaneous electrode rotation. The cyclovoltammograms were recorded in the potential range between −1.3 and 1.2 V vs. SCE in the solutions containing K_2SO_4, and in the potential range between −1.3 and 1.7 V vs. SCE, in the unsupported electrolyte solutions.

The rotating disk chronoamperometry was performed at fixed potentials corresponding to the limiting current of W dissolution, namely at 1.2 V vs. SCE, in the solutions containing the supporting electrolyte (K_2SO_4), and at 1.5 V vs. SCE, in the unsupported solutions. The starting solution was 10 ml of 0.01 M of KOH. The analyte, 0.1 M KOH, was injected in equal portions, and the transient current was registered during roughly 60 s.

3. Results and discussion

According to the RDE–CV curves, presented in Figs. 1 and 2, in 0.08 M KOH solution, extensive current of tungsten electrooxidation onsets at the potential −0.4 V vs. SCE. With the progress of anodic polarization, the oxidation current makes several maxima and then passes into a flat plateau.

The wavy form of current–voltage curve in the potential region that precedes the occurrence of the current plateau agrees with the well accepted multi-step mechanism of *W* dissolution in alkaline solutions elaborated by Kelsey [33]:

$$W + 2OH^- \rightarrow WO_{2(s)} + 2H^+ + 4e^- \quad (1a)$$

$$WO_{2(s)} + OH^- \rightarrow WO_3H_{(s)} + e^- \text{ (RDS)} \quad (1b)$$

$$WO_3H_{(s)} + OH^- \rightarrow WO_3(s) + H_2O + e^- \quad (1c)$$

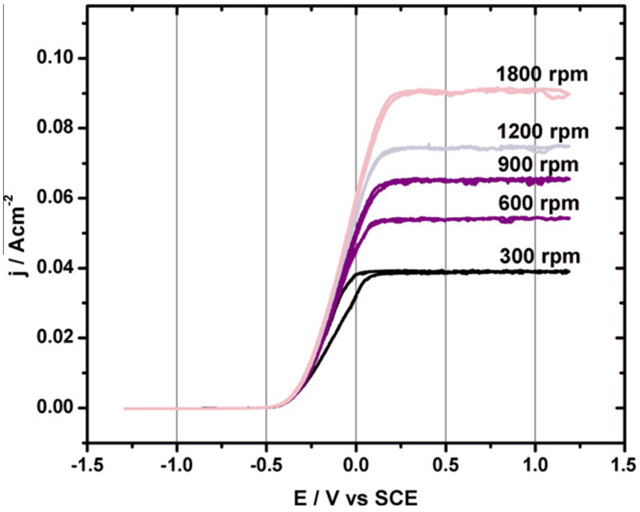

Fig. 1. Cyclic voltammograms of tungsten rotating disc electrode in 0.08 M KOH solution supported by 0.25 M K_2SO_4. Polarization rate was 50 mV s^{-1}.

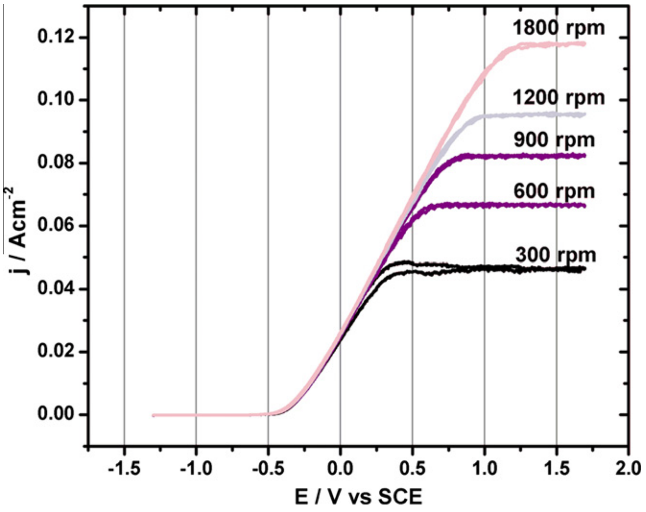

Fig. 2. Cyclic voltammograms of tungsten rotating disc electrode in unsupported 0.08 M KOH solution. Polarization rate was 50 mV s^{-1}.

$$WO_{3(s)} + OH^- \rightarrow HWO_4^- \quad (1d)$$

$$HWO_4^- + OH^- \rightarrow WO_4^{2-} + H_2O \quad (1e)$$

General dissolution reaction may be written as [33]:

$$W + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^- \quad (1)$$

The current oscillations corresponding to these processes are more pronounced in diluted solutions, however, their amplitude does not change with the change in concentration, and consequently, they become negligible at high hydroxide concentrations.

As Figs. 1 and 2 show, upon several initial oscillations, current passes into plateau. According to the literature data [27], the potential region of the current plateau extends up to even 8.5 V vs. SCE before than a visible current of oxygen evolution appears.

Contrary to the case of diluted base solutions, where passivation may occur [23,27], in the case of concentrated base solutions, the dissolution of tungsten proceeds without any passivation, which is evidenced in Figs. 1 and 2 by the fact that, at any rotation rate, almost overlapping currents are registered during anodic and cathodic scans.