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On the electrochemical behaviour of the anodic oxide film on tungsten in HCOOH and CH_3COOH solutions

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The electrochemical behaviour of the anodic oxide film on tungsten during, or after, interruption of current flow was studied in HCOOH and CH_3COOH solutions by galvanostatic and capacitance techniques. The results show the conditions under which enhancement of film growth occurs as revealed from its formation and dissolution characteristics. The results also show the possibility of the electrochemical oxidation of formic acid by the thick oxide film on tungsten. The importance of this electrocatalytic process is the occurrence of the oxidation process without appreciable oxygen evolution. The galvanostatic oxidation of tungsten in HCOOH as a reducing agent can be considered as a novel method for the preparation of a class of oxides; oxidation with simultaneous partial reduction.

1. Introduction

Surface oxide films are of interest in many applications such as electrocatalysis, electrochromic displays and charge storage. A decisive factor in their application is their chemical stability, which depends upon their chemical composition and microstructure as well as the composition of the working solution [1, 2].

The formation and dissolution of the anodic oxide film on tungsten has been studied earlier in inert electrolytes [3-5]. The present investigation deals with the possible interactions between tungsten oxide and HCOOH under circumstances resembling those encountered when tungsten oxide is used as an electrocatalyst for the oxidation of a simple organic molecule such as HCOOH. On the other hand, this investigation will show the influence of the reducing agent HCOOH on the chemical dissolution of tungsten oxide. It is worth mentioning that the rate of dissolution of some oxides increases in the presence of an oxidizing agent [6] whereas for others the rate of dissolution increases in the presence of reducing agents [7]. This factor is important with regard to the selective dissolution of a mixture of oxides in an ore material.

The present investigation, *viz.* the anodization of tungsten in the presence of a reducing agent can give rise to a temporary and/or partial reduction of the oxide; then further anodic oxidation of the reduced species occurs and so on. Thus a repetitive process occurs which activates the surface layer by a mechanism similar to that employed for the preparation of the class of oxides known as hydrated oxide films [8]. In this mechanism the reduction process is accomplished electrochemically by reversing the scan (repetitive potentiodynamic cycling) [8]. The oxides obtained by this technique are active materials [9]. Schlotter and Pickelmann [10] have described the active oxide material as a dried gel or colloid in which hydroxylated oxide clusters are randomly linked with W-O-W chains; they emphasized the fact that voids in this material are not to be confused with the regular voids and tunnels found in crystalline tungstic oxides. They also demonstrated that the active oxide exhibited both acidic and cation-ion exchange behaviour.

2. Experimental details

The tungsten electrode was made from spec. pure tungsten rod The electrode was fixed in a glass tube with Araldite resin, leaving a surface area of $0.125\,cm^2$ in contact with the test solution. The electrolytic solutions were prepared from analytical grade reagents and triply distilled water. Naturally aerated solutions were used.

The electrode was abraded with 4/0 emery paper and then immersed in the anodizing solution. The anodic charging curves were measured by the galvanostatic technique. For study of the currentless dissolution of the anodic oxide film, the latter was formed at a constant current density. The current was then interrupted and the electrode was transferred to the dissolution medium after being washed quickly and gently with distilled water, where the measurements were carried out immediately.

The electrode capacitance, C_m, was measured by means of a high precision standardized bridge of the Wien type. The bridge and electrolytic cell were essentially the same as those described elsewhere [11]. The input a.c. voltage to the bridge was 1000 Hz. The potential of the tungsten electrode was measured by means of a valve voltmeter. Measurements were made in a double wall air thermostat at $30 \pm 0.5°\,C$ unless otherwise stated.

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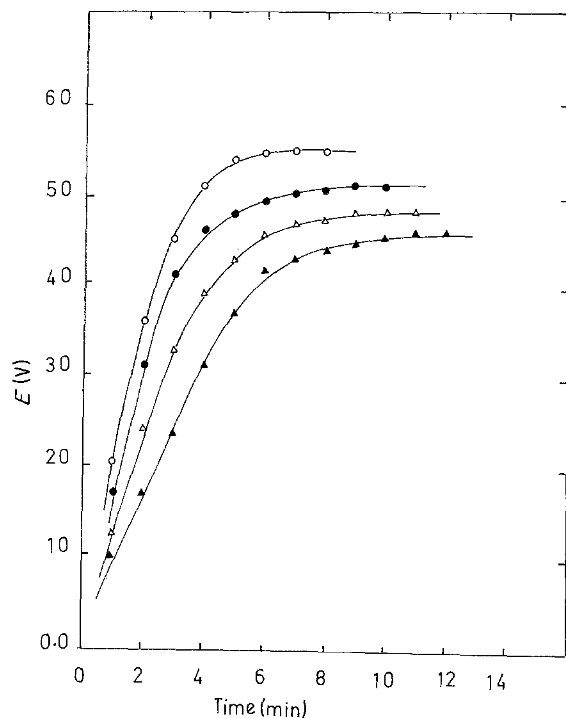


Fig. 1. Anodic charging curves for tungsten in 0.1 M HCOOH at different current densities: (▲) 8.0×10^{-4}, (△) 1.0×10^{-3} A cm^{-2}, (●) 1.2×10^{-3}, (○) 1.4×10^{-3} A cm^{-2}.

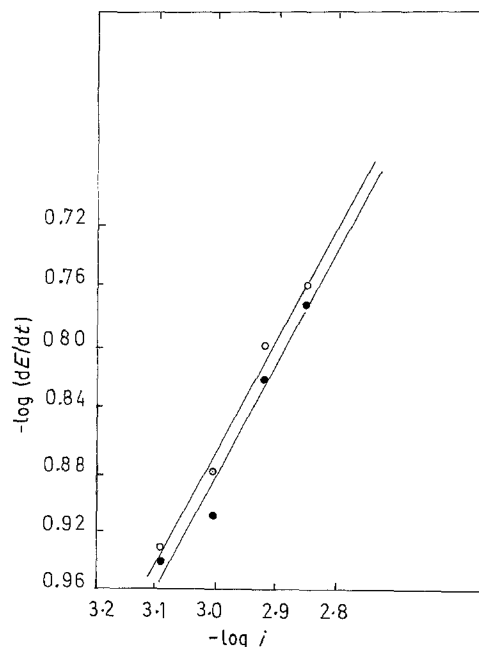


Fig. 3. Relation between log oxide formation rate and log current density at 30° C: (○) HCOOH, (●) CH_3COOH.

3. Results and discussion

3.1. *Polarization measurements*

Figures 1 and 2 show the charging curves of tungsten in HCOOH and CH_3COOH, respectively. They consist of a linear portion and a plateau zone. The slope of the linear portion represents the rate of growth of the oxide [12]. This increases with current density as shown in Fig. 3. The same figure also indicates that, during the initial stage of polarization (until a thickness corresponding to 25 V), the oxide is more readily formed in the formic acid solution than in the acetic acid solution since dE/dt for a given current density, i is higher in HCOOH than in CH_3COOH (Fig. 3). E is the electrode potential at time t during current flow. Thus the amount of oxide formed per unit of charge is higher in formic acid than in acetic acid. This can be attributed to the difference in reducing properties, acidity and adsorbability of these solutions. Since the steady-state voltage, Fig. 4, is higher in CH_3COOH than in HCOOH, one may conclude that the steady-state thickness of the film in CH_3COOH is higher than that in HCOOH. Over the region of the steady voltage,

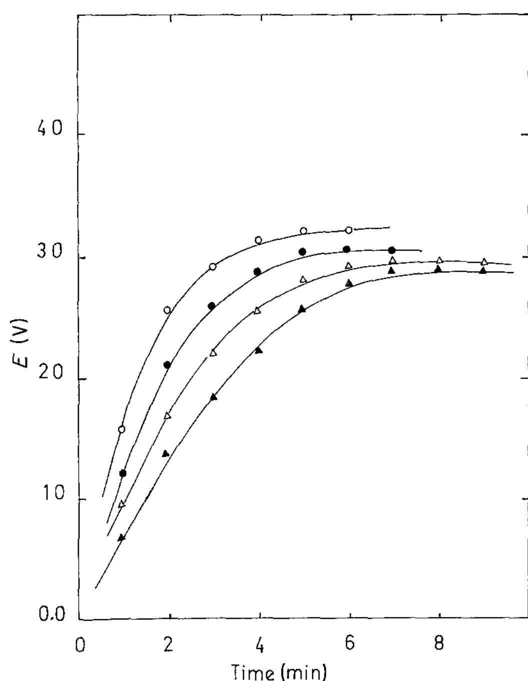


Fig. 2. Anodic charging curves for tungsten in 0.1 M CH_3COOH at different current densities: (▲) 8.0×10^{-4}, (△) 1.0×10^{-3} A cm^{-2}, (●) 1.2×10^{-3}, (○) 1.4×10^{-3} A cm^{-2}.

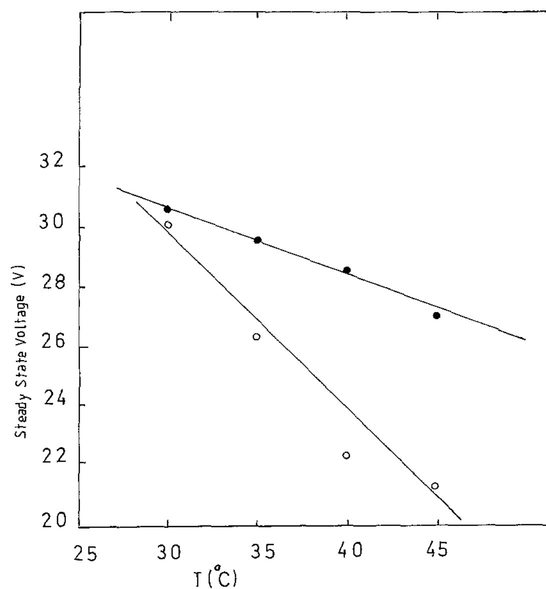
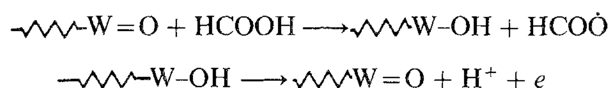


Fig. 4. Effect of temperature on the steady-state voltage: (○) HCOOH, (●) CH_3COOH.

the reactions occurring are oxide dissolution and electrolyte oxidation. The effect of temperature is more pronounced in HCOOH (Fig. 4). This indicates a difference in the current efficiencies of the processes occurring in the region of the steady-state voltage. Thus, in HCOOH, the probability of electrolyte oxidation increases with temperature together with the oxide dissolution. Hence an appreciable drop of the steady voltage occurs.

Since at lower formation voltages tungsten oxide is more readily formed in HCOOH than in CH_3COOH (Fig. 3) whereas the steady-state voltage is low (Fig. 4), it is likely that other reactions occur on the thick tungsten oxide film. It has been reported previously that as the film thickness increases it becomes more defective [13] hence more ready for participation in chemical reactions such as dissolution or catalysis of the oxidation of HCOOH.

The catalysis of the oxidation of HCOOH by the anodic oxide film on tungsten is interesting on account of its occurrence without significant oxygen evolution. The oxygen evolution reaction is of minor importance at the anodically formed oxide film on tungsten [14]. Thus the oxidation of HCOOH may occur by a mechanism similar to that suggested by Meyer [15]. So in the chemical oxidation the following steps may occur:



$$\sim\!\sim\text{W=O} + \text{HCOOH} \longrightarrow \sim\!\sim\text{W–OH} + \text{HCO}\dot{\text{O}}$$

$$\sim\!\sim\text{W–OH} \longrightarrow \sim\!\sim\text{W=O} + \text{H}^+ + e$$

since the intermediate ∼∼W–OH is probable on account of the fact that tungsten oxide forms a hydrated oxide film [16]. Apart from the chemical oxidation of HCOOH there is a possibility for the electrochemical oxidation in which tungsten oxide only plays the role of a semiconducting electrode [17]. The formation of ∼∼W–OH may account for the high solubility of tungsten oxide in HCOOH after interruption of the anodizing current, since the hydrated oxides are more soluble than the less hydrated ones [16].

3.2. *Capacitance measurements*

An oxide film was formed in 0.1 N H_2SO_4 up to 30 V and at a current density of $8 \times 10^{-4}\,\text{A cm}^{-2}$ on the tungsten electrode. The electrode was then withdrawn from the polarization cell, washed with distilled water and immediately immersed in the dissolution medium. This consisted of formic acid or acetic acid solutions of different concentrations covering the range from 0.1 to 10 M. The open circuit (currentless) dissolution of the oxide was followed by measuring the electrode capacitance, C_m, as a function of immersion time, t. The relation between log $1/C_m$ and t forms two intersecting straight lines, Fig. 5. The break is due to the fact that the oxide film on tungsten consists of two layers [18, 19]. Therefore, an average rate for the dissolution of the whole oxide $\bar{k}$ has been introduced [20]

$$\bar{k} = (l_1 k_1 + l_2 k_2)/(l_1 + l_2)$$

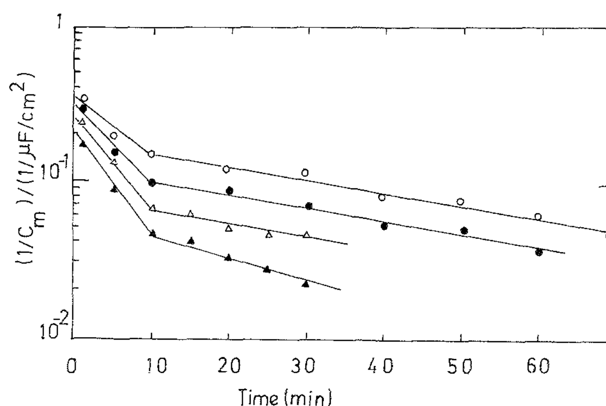
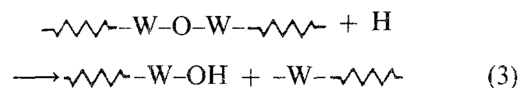


Fig. 5. Variation of log $1/C_m$ with time t during dissolution of the oxide film formed in 0.1 N H_2SO_4 in different HCOOH concentrations: (○) 0.1, (●) 1, (△) 5, (▲) 10 M HCOOH.

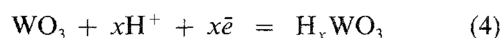
where k_1 and l_1 are the slope of the first linear segment and its length, respectively; k_1 and l_1 characterize the outer layer of the film and k_2 and l_2 similarly characterize the inner layer. The linear relationship between log $(1/C_m)$ and t indicates that the rate of dissolution is a first order process with respect to the thickness of the remaining film [3].

The results shown in Fig. 6 indicate an increase of the average dissolution rate of films formed in sulphuric acid with the concentration of HCOOH and a decrease with the concentration of CH_3COOH. The presence of the reducing agent may give rise to the creation of active sites in the film which increase its susceptibility to dissolution. These active sites are created by the breaking of a bridging tungsten–oxygen bond according to



$$\sim\!\sim\text{W–O–W}\sim\!\sim + \text{H} \longrightarrow \sim\!\sim\text{W–OH} + \text{–W}\sim\!\sim \quad (3)$$

or by the trapping of $H^+ + e$ according to [17]



$$\text{WO}_3 + x\text{H}^+ + x\bar{e} = \text{H}_x\text{WO}_3 \quad (4)$$

Thus according to Equation 3 a dispersed structure will result [8] which can account for: (i) the early high rate of growth of the oxide in HCOOH during anodic current flow; (ii) the increase of the rate of dissolution

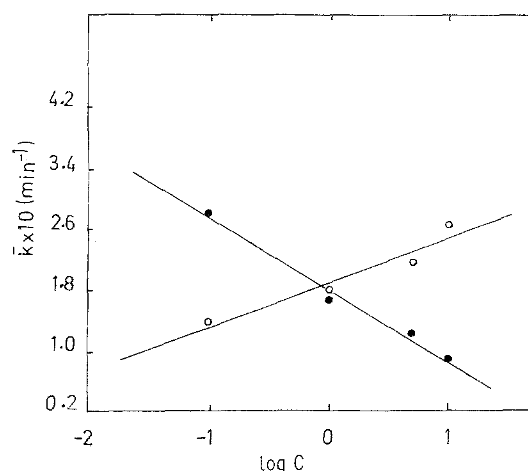


Fig. 6. Dependence of the average rate of dissolution, $\bar{k}$ on composition of the dissolution medium: (○) HCOOH, (●) CH_3COOH (the oxide was prepared in 0.1 N H_2SO_4).

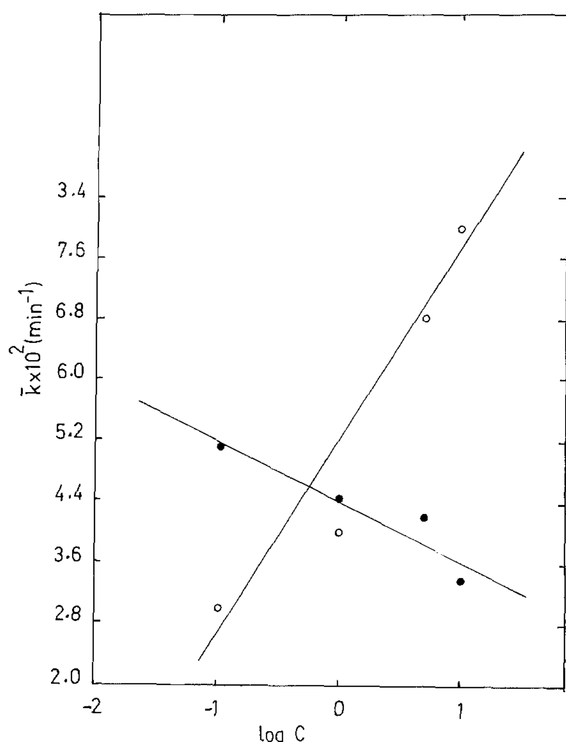


Fig. 7. Dependence of the average rate of dissolution, $\bar{k}$ on composition of the formation medium: (○) HCOOH, (●) CH_3COOH (the oxide was dissolved in 0.1 N H_2SO_4).

in sulphuric acid of oxides formed at different concentrations of HCOOH (Fig. 7).

Thus, anodization of tungsten in the reducing agent, formic acid, gives an oxide with some degree of dispersion inasmuch as repetitive potentiodynamic cycling produces hydrated oxide films whose features have been described previously [8, 21]. Hence the galvanostatic oxidation of a metal in a reducing medium can be considered as a novel technique for the preparation of this class of oxides.

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