FORMATION OF PEROXY COMPOUNDS ON ANODICALLY POLARIZED SODIUM TUNGSTEN BRONZE ELECTRODES

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On anodically polarized electrodes of sodium tungsten bronzes in solutions of sulphuric acid a small amount of peroxydisulphate ions is formed in addition to gaseous oxygen and to the products of electrode corrosion. The electrode is covered by a passive semiconducting layer, so that its potential approaches the value of 40 V at the current density 1 A/cm². Capacity of the electrode complies with the Mott-Schottky relation up to 20 V. Peroxydisulphate is probably formed by electron mechanism, whereas both the corrosion of the electrode and the evolution of oxygen proceed on the surface of the passive layer via the hole mechanism.

Sodium tungsten bronze is covered in solutions of sulphuric acid at potentials more positive than c. $+0.4$ V (RHE) by a passive layer[1,2]. This layer, having the characteristics of a semiconducting barrier layer, entirely blocks cathodic processes and significantly slows down anodic processes. McHardy and Bockris[3,4] found that this process is accompanied by a decrease in the concentration of sodium in the bronze as well as by its transition into the electrolyte. According to Randin[5] the potential of electrodes made of sodium tungsten bronzes attains at a current density c. 0.1 A/cm² the value up to several tens of volts and in this respect the behaviour of tungsten bronzes resembles that of valve-effect metals, e.g. titanium and tantalum.

At such high anodic potentials the possibility arises of the formation of peroxy compounds via anodic oxidation of the electrolyte, of the electrode or of its corrosion products. The object of the present communication is the study of the formation of peroxy compounds on sodium tungsten bronzes, in solution of various inorganic oxyacids and their salts.

EXPERIMENTAL

The experiments were carried out using either electrodes of monocrystalline sodium tungsten bronzes of the composition $Na_{0.60}WO_3$, or electrodes, prepared by sintering the tablets of powder sodium tungsten bronzes at about 900°C in pure argon. The preparation of powder and mono-crystalline bronzes as well as the analytical methods for the determination of electrode composition were described earlier[6]. The measurements were carried out in a cooled electrolytic vessel which allowed to measure the volume of oxygen evolved electrochemically on the bronze electrode. The vessel was supplied from an d.c. current source with an attached transistor interrupter,

permitting to evaluate, by using the interruption technique, both the actual potential of the current loaded electrode and its differential capacity.

Analysis of the solution for peroxy compounds was performed according to Le Blanc and Eckardt[7]: after the experiment had been finished, all the electrolyte or its aliquot part was transferred into a reaction vessel, treated with 0·1N solution of ferrous sulphate, heated to c. 40°C and the remaining non-oxidized bivalent iron was titrated with 0·1N solution of potassium permanganate. The content of peroxymonosulphuric acid (Caro acid) was determined using the Palme's method[8] based on the difference betwen the rate of oxidation of potassium iodide with Caro acid and with peroxydisulphuric acid. The sample of electrolyte was added to c. 500 ml of water, containing 1 g potassium iodide and about 1 ml of starch gel. Time was measured from the moment when the components had been mixed and the amounts of iodine were titrated in one-minute intervals with 0·05M solution of sodium thiosulphate. The content of Caro acid was then evaluated by extrapolation of the dependence of the total amount of liberated iodine for zero time.

The experiments were carried out in sulphuric, perchloric and phosphoric acids of various concentration and in an electrolyte containing 20% $(NH_4)_2SO_4$ and 23·5% H_2SO_4. This electrolyte is similar to those recommended for industrial production of ammonium peroxydisulphate as intermediate in the electrochemical preparation of hydrogen peroxide[9].

RESULTS AND DISCUSSION

The highest yields of peroxy compounds on a monocrystalline electrode were obtained in sulphate electrolyte of the above-mentioned composition. They were lower in sulphuric acid, lowest in phosphoric acid and no peroxy compounds were formed in perchloric acid. Besides, preliminary experiments showed that sintered electrodes behave essentially like the smooth monocrystallinic electrodes. All further experiments were therefore carried out in sulphate electrolyte and with a monocrystallinic electrode of the composition $Na_{0.60}WO_3$. As can be seen in Fig. 1, partial current density i_1, corresponding to the rate of formation of peroxy compounds, increases both with increasing total current density i and with increasing temperature. Measurement of the volume of anodically evolved oxygen revealed, however, that the total current is always by 5—20% higher than the partial current densities of the formation of peroxy compounds and of oxygen. The remaining current is probably consumed by oxidation of the electrode surface.

The dependence of current yields on the composition of electrolyte shows that the anions of the electrolyte participate in the formation of peroxy compounds on electrodes made of tungsten bronzes. Hence, what can be expected is either the formation of peroxydisulphuric acid or the formation of some peroxy compounds containing in addition to sulphuric acid also tungstic acid, *i.e.* heteropolyperoxytungstenosulphuric acids of some kind. Their formation is theoretically possible, since tungstic acid dissolves slowly in mixtures of hydrogen peroxide and diluted sulphuric or phosphoric acid. The resulting solution decomposes under heating and in the presence of platinum black, yielding a nonsoluble hydrated tungstic acid. In the absence

of hydrogen peroxide or in the mixture of hydrogen peroxide with perchloric acid, tungstic acid does not dissolve.

To elucidate the nature of the formed peroxy compound in more detail we carried out the following decisive experiments: *1*) Anolyte prepared by electrolysis of a sulphate electrolyte was precipitated by excess solution of barium nitrate, so that all remaining sulphate and sulphuric acid were removed as barium sulphate. The filtrate was diluted by 20% (vol.) and boiled in the presence of platinum black. A new portion of white, crystalline precipitate was formed, resembling barium sulphate. In another experiment a sample of the anolyte after electrolysis was boiled with platinum black, however, without addition of barium nitrate. No precipitate of hydrated tungstic acid was formed, which is an evidence that the anolyte did not contain any peroxy compounds of tungsten.

2) 5 ml of anolyte prepared by electrolysis were diluted to 100 ml with $2N\text{-}H_2SO_4$ and after removing the formed oxygen the solution was analyzed polarographically on a mercury dropping electrode. The polarogram shows a limiting current over the whole potential range from zero up to the potential of hydrogen evolution the height of which corresponds to the limiting current in a solution containing peroxydisulphate of the same total concentration of active oxygen, both fresh and hydrolyzed to Caro acid to c. 50%. Evidently, polarographic behaviour of the peroxy compounds formed on anodes made of tungsten bronzes is similar to that of peroxydisulphate ions in concentrated initial electrolytes according to Krjukova[10]. On the other hand, no waves were observed of isopolytungstic acids, as were described by Launay, Souchay and Boyer[11].

3) Provided that peroxydisulphate ions are formed on anodically polarized electrodes of sodium tungsten bronzes in hydrogen sulphate electrolytes its hydrolysis o Caro acid must be considered according to equation

$$S_2O_8^{2-} + H_2O = HSO_5^- + SO_4^{2-} + H^+ . \qquad (A)$$
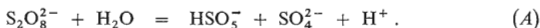
If we denote k the rate constant of the above reaction and x and y the instantaneous concentrations of the peroxydisulphuric and Caro acid, respectively, then the rate of hydrolysis is described by equation $dy/dt = kx$. The total amount of peroxy compounds at time t can, in the first approximation, be taken as $x + y = k't$, where k' is the rate of anodic formation of peroxydisulphate which we assume to be constant and independent of the amount of the product formed. By joining these equations we obtain a differential equation whose solution for the initial condition $x = = y = 0$ gives for the ratio of the undecomposed peroxydisulphate to the total amount of peroxy compound the expression

$$x/(x + y) = (1/kt)\left[1 - \exp\left(-kt\right)\right] . \qquad (1)$$

In this equation k is the rate constant of hydrolysis of peroxydisulphate. Its value in the used sulphate electrolyte was found to be $k = 1\cdot01 \cdot 10^{-5}\ \text{s}^{-1}$. The anolyte prepared by electrolysis for 20 and 24 hours at $20 \pm 1\cdot5°C$ contained, of the total amount of peroxy compounds, 22 and 37% of substances, giving the same reactions as Caro acid. Under the mentioned conditions, 29·5 and 33% of Caro acid should theoretically be formed. Although the theoretical degree of hydrolysis of peroxydisulphate to Caro acid does not exactly agree with the experimentally found one, the qualitative accordance is fairly good, so that even this experiment may be considered a further proof of the formation of peroxydisulphate on a bronze electrode. One of the causes of the discrepancies between the measured and the calculated values is obviously the inconstancy of temperature during electrolysis. Owing to the high overvoltage an energy of about $20-40\ \text{W/cm}^2$ is generated at the anode in the form of heat, which makes the regulation of temperature of the electrolyte difficult. This can affect both the current yields and the rate of reaction (A). Another cause may be the considerable corrosion of the electrode which changes its properties and hence also the current yields.

The anodic polarization curve was measured using the current interruption technique. Over the whole range of current densities $(0\cdot006-0\cdot7\ \text{A/cm}^2)$ the dependence of the anode potential on current density can formally be described by a semilogarithmic relation

$$E = 38\cdot5 + 17\cdot6 \log i \quad (\text{V, A cm}^{-2}). \tag{2}$$

The unusually high values of both constants indicate the existence of a barrier layer on the surface of a bronze electrode in which the main part of the potential drop between the electrode and the solution is concentrated. This part has no effect on the rate of electrochemical reactions and, moreover, it also brings about the evolution
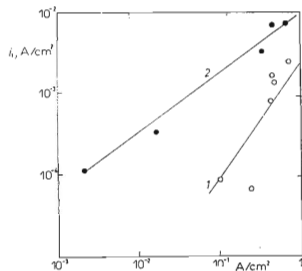

FIG. 1

Dependence of Partial Current Density i_1 on Total Current Density and on Temperature on the Sodium Tungsten Bronze Anode in Mixed Sulphate Solution

$1 - 2$ to $+2°C$, 2 30 to 40°C.

of a great amount of heat on the electrode surface. The dependence of the capacity of semiconductor electrode, C, related to surface unity, on potential E, is usually expressed by the Mott–Schottky equation[12,13]

$$1/C^2 = (2/\varepsilon\varepsilon_0 n)(E - E_{FB}),\qquad(3)$$

where ε is the relative dielectric constant of the medium, ε_0 is the permittivity of vacuum, n is the number of donors in a volume unit and E_{FB} is the flat band potential at which the space charge in the semiconductor just vanishes, so that the bands in the electron energy spectrum are no more curved at the surface. As can be seen in Fig. 2, the capacity of a bronze electrode complies with this equation up to potential c. 20 V and to current density c. 0·1 A/cm². At higher potentials its value increases again. The found value of the slope of the linear part equals 0·0037 F^{-2} cm⁴ . V^{-1}, which is about three times less than the value 0·012 F^{-2} cm⁴ V^{-1}, found by Randin[5] in the potential range to 2·5 V. The difference can be caused *e.g.* by an intense corrosion of the electrode surface at higher potentials which causes an increase of the roughness factor of the electrode surface. Linear dependence of $1/C^2$ on potential indicates, however, that up to $20-25$ V bronze electrodes behave like semiconductors with a relatively high donor concentration of the order of magnitude of $10^{20}-10^{21}$ cm^{-3}. An exact determination of the donor concentration is difficult owing to the fact that the precise value of the dielectric constant of the barrier layer, ε, is not known.

At higher potentials the capacity of the electrode increases again. As shown in Fig. 1, in the same potential range also the partial current density of the peroxydisulphate formation increases. Consequently, the formation of peroxydisulphate may be accompanied by injection of electrons into the conductive band of the semiconductive layer on the surface of the bronze electrode. These excess electrons diminish the effective thickness of the barrier layer, increasing in this way its capacity.
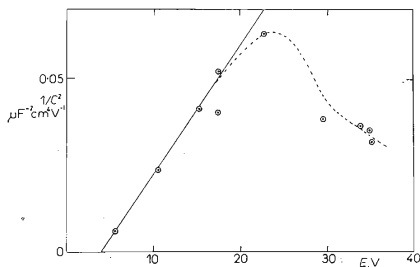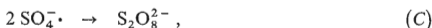

Fig. 2

Behaviour of Sodium Tungsten Bronze Electrode in the Parameters of the Mott–Schottky Relation

Thus, peroxydisulphate is probably formed *via* the following mechanism

$$SO_4^{2-} \rightarrow SO_4^-\cdot + e,\qquad (B)$$

$$2\,SO_4^-\cdot \rightarrow S_2O_8^{2-},\qquad (C)$$

similarly as on platinum electrodes. Contrary to this, neither the evolution of oxygen nor the oxidation of the surface of the tungsten bronze causes an injection of conductive electrons, as follows from the validity of the Mott–Schottky equation in the potential range where the rate of peroxydisulphate formation is small and where the prevailing reactions are the two above mentioned processes. Therefore, both these anodic reactions proceed probably under the participation of the holes in the valence band of the semiconductor, analogously as it is in the case of germanium electrodes[14].

On the basis of the experiments the conclusion can be drawn that the formation of peroxy compounds on anodes made of sodium-tungsten bronzes, polarized to high anodic potentials (over 20 V) can take place only in solutions containing substances, able to be oxidized to the respective peroxidic forms, *e.g.* sulphates. No peroxy compounds of tungsten are formed in these anodic reactions and the anodic oxidation of tungsten bronzes as electrode materials proceeds evidently only *via* oxidation of sodium in the surface layer under the formation of a barrier layer with the properties of a semiconductor of the N type.

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