LOWERING OF HYDROGEN OVERVOLTAGE ON GRAPHITE BY TUNGSTEN COMPOUNDS

J. VONDRÁK and J. BALEJ

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

Received May 29th, 1974

Cathodic polarization of graphite electrodes in potassium or sodium metatungstate solutions leads to the formation of a layer on the electrode surface which accelerates the evolution of hydrogen by 2—3 orders of magnitude. The electrocatalytically active component of this layer is probably a hydrogen tungsten bronze, H_xWO_3.

The presence of tungsten compounds in the electrolyte can accelerate the evolution of hydrogen on electrodes on which this reaction is normally slow. This effect is observed, *e.g.*, in polarographic studies of tungstates[1] and it is the cause of the rising content of hydrogen in chlorine during amalgam cell electrolysis of alkali metal chlorides[2]. In this case it is assumed that traces of tungstates are reduced to give a suspension of insoluble lower-valency tungsten compounds or even metallic tungsten, and on their particles the evolution of hydrogen proceeds more easily than on the amalgam. W(VI) oxide is reduced to hydrogen tungsten bronze[3-8], H_xWO_3, which is considered as the active substance of hydrogen electrodes containing platinum and this oxide[9-11]. Hydrogen is relatively easily evolved also on lower oxides of tungsten[12-14], on metallic tungsten[12,14-16] and on sodium tungsten bronzes[17,18], which can also be used as catalytic electrode for the anodic oxidation of hydrogen[19].

According to Thiesz[20] a layer of tungsten bronze can be deposited electrolytically on solid electrodes from extremely concentrated solutions of metatungstates at elevated temperatures, *e.g.*, 80 wt.% barium metatungstate at 70°C. The aim of the present work was to check this method of tungsten bronze preparation and to determine whether the obtained layer has a lower overvoltage for the evolution of hydrogen than the supporting material.

EXPERIMENTAL

Preparation and Identification of Metatungstates

Sodium and potassium metatungstates were prepared by boiling a suspension of tungstic acid in sodium or potassium hydroxide solution under stirring. The obtained solution was filtered and evaporated to a viscous liquid. The potassium salt of the composition $K_2W_4O_{13}.5\,H_2O$ was isolated by precipitating with ethanol with a yield of about 85%, whereas the sodium salt was isolated by crystallization in an exsiccator filled with sulphuric acid. Barium metatungstate

was prepared by conversion of a potassium metatungstate solution with barium perchlorate and crystallization in an exsiccator above sulphuric acid. The metatungstates were analyzed polarographically; the shape of the polarograms was in accord with published data[1]. The high solubility of the barium salt is also an evidence of the presence of metatungstate since other isopolytungstates of barium are insoluble in water.

Preparation of Electrodes

The supporting materials were platinum, copper and graphite, the latter in the form of electrodes for spectral analysis. Active layers of tungsten bronzes were deposited by cathodic reduction of 70—80% solutions of metatungstates in a vessel of 10 ml holding capacity at 80°C. The electrochemical properties of the electrodes thus prepared were measured in 1M-H_2SO_4 at (20 ± 1)°C.

RESULTS

Appearance and Composition of Deposited Layers

Cathodic polarization of metal electrodes in solutions of alkali metal tungstates leads to the formation of a dark blue, in the dry state rather well adhering layer, which can be easily removed by means of water. A blue layer formed on graphite under the same conditions is not entirely removable with water. Further electrochemical measurements were therefore made only on graphite electrodes covered with the blue active layer, while a layer deposited on a smooth platinum electrode from a potassium metatungstate solution was chemically analysed by two methods. The gravimetric analysis yielded the composition of the product 8·26% K and 63·45% W. The content of reductants was in the product of electrolysis determined by the van Duyn method[21] proposed for the analysis of sodium tungsten bronzes and based on dissolution of the sample in an alkaline solution of potassium hexacyanoferrate(III) of a known concentration:

$$M_xWO_3 + x\,Fe(CN)_6^{3-} + 2\,OH^- =$$
$$= WO_4^{2-} + x\,Fe(CN)_6^{4-} + 4\,H_2O + x\,M^+ .$$

The amount of unreacted hexacyanoferrate(III) was determined after acidifying and adding zinc sulphate and potassium iodide by titration with a thiosulphate solution. This way, it was found that the reduction product contained $2{\cdot}52 \,.\, 10^{-3}$ equivalent of reductants in 1 g.

By electrolysis of a barium metatungstate solution, a thin blue layer was deposited on the electrode which was covered by a thick white layer, the formation of which caused a considerable decrease of current and which had to be removed mechanically before measuring the electrochemical properties of the graphite electrode with the blue layer.

Evolution of Hydrogen

The rate of hydrogen evolution on pure graphite without and with the active layer prepared under various conditions is given in Table I. The exchange current density for this reaction on this material is of the order of 10^{-7} A/cm^2 and the overvoltage up to -500 mV is given by the Tafel equation with a slope $b = 100-115$ mV in close agreement with the data of Drossbach and Schulz[22]. The hydrogen evolution is accelerated by the cathodic deposition of the active layer, especially from the potassium metatungstate solution, and to the smallest extent from the barium metatungstate solution. However, the Tafel equation applies only for overvoltages up to -300 mV when the slope of the polarization characteristics increases to 200–300 mV.

Anodic Voltammetric Curves

Anodic voltammetric curves for pure graphite and graphite polarized for 1·5 h by a cathodic current density of 0·08 A/cm^2 in a potassium metatungstate solution are shown in Fig. 1. The voltammetric curve for pure graphite shows a single wave at about +0·2 V, whereas the graphite electrode coated with the active layer gives in addition to this wave also another one with a maximum between -250 and -280 mV. Its position and charge, equal to 270 μC/cm^2, do not depend on the sweep rate up to 100 V/s. In Table I are also given the electrode capacities at +0·5 V found from the voltammetric curves.

DISCUSSION

The kinetic parameters (Table I) indicate that the evolution of hydrogen is accelerated by the presence of the layer of tungsten compounds on graphite. No drop of the

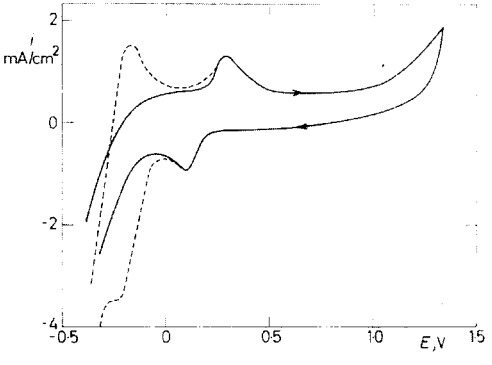

FIG. 1

Voltammetric Curves for Graphite Electrode without (dotted line) and with an Active Deposit (full line) from Potassium Metatungstate Solution

Electrolyte 1M-H_2SO_4, sweep rate 0·03 V/s.

TABLE I

Rate of Hydrogen Evolution and Capacity of Graphite Electrodes Activated by Cathodic Polarization in Metatungstate Solutions

Mode of activation			Evolution of H_2		C
Cation	A/cm^2	time h	i_0 A/cm^2	b mV	μF/cm^2
—	—	0	0·29	105	44
—	—	0	0·20	110	—
—	—	0	0·21	110	—
K	0·08	1·5	53	115	300
K	0·08	1·5[a]	186	115	—
K	0·08	2	25	115	—
K	0·10	2	21	110	—
Na	0·08	0·5	1·8	120	—
Na	0·12	2·5	22·5	113	—
Ba	0·005	1	1·6	120	—

[a] Electrode from the preceding experiment after measurement of anodic voltammetric curves.

electrode activity was observed after a 200 hour-test of the electrode. The voltammetric curves show a distinct wave of an adsorption character with a charge of 270 μC/cm^2 in the region of hydrogen evolution. Its maximum lies approximately in the potential region where the polarization curve bends and its slope increases. Therefore, the wave can be ascribed to adsorbed hydrogen and the growth of the slope of the polarization curve is explained in terms of blocking of most of the active surface area by atomic hydrogen.

The capacity of the electrode with and without the active layer at +0·5 V shows that the electrode surface is moderately rough. Its roughness factor can be estimated as $\sigma = 10-50$. Consequently, the charge of the wave of adsorbed hydrogen related to a unit of the true surface area is equal to 5·4–27 μC/cm^2, which is at least by one order of magnitude smaller than in the case of metals. The exchange current density for the hydrogen evolution related to 1 cm^2 of the true surface area of the active layer is accordingly in the range $(1-20) \cdot 10^{-6}$ A/cm^2, which is by nearly two orders of magnitude more than in the case of single crystals of sodium tungsten bronzes[17,18]. Also the shape of the polarization curve is different. Still more different are the anodic voltammetric curves of the active layer and of sodium tungsten bronzes[23,24]. The difference in the characteristics of these materials is so considerable that the products of the cathodic reduction of concentrated solutions of metatungstates cannot be regarded as alkali metal or barium tungsten bronzes. This con-

clusion is supported by the work of Souchay and coworkers[1,25] and Tourner[26] concerning polarography of metatungstates.

The electrolysis products of barium metatungstate can show the probable mechanism of formation of the layers and their composition. The layer formed in this solution consists of a blue deposit adhering to the electrode surface and a white precipitate insoluble in water. Barium tungstates are insoluble in water except for the metatungstate. Alkaline solutions of metatungstates decompose to isopolytungstate with a lower number of W atoms or to normal tungstates. During cathodic reduction of a metatungstate, always a parallel hydrogen evolution reaction proceeds. As a result, the solution at the electrode becomes alkaline, the barium metatungstate decomposes and the electrode surface becomes covered with a precipitate of insoluble barium tungstate. This is one of the electrolysis products, whereas the blue colour, electric conductivity and electrochemical activity are an evidence for the presence of a small amount of some reductive compound, most probably hydrogen tungsten bronze, H_xWO_3.

The formation of layers during electrolysis of other metatungstates proceeds probably analogously. Alkalization of the electrolyte near the cathode causes the formation of lower polytungstates, which are almost insoluble in the concentrated (70–80%) metatungstate solution and are deposited on the cathode surface together with the reduction product of the metatungstate. This explanation is supported also by the results of chemical analysis of the deposit obtained by electrolysis of potassium metatungstate. The content of potassium, tungsten and reductants can be interpreted by the following composition of the layer: 17% $H_{0.35}WO_3$, 79% $5\,K_2O.12\,WO_3.11\,H_2O$ (sparingly soluble potassium paratungstate) and 4% H_2O.

REFERENCES

1. Launay J. P., Souchay P., Boyer M.: This Journal *36*, 740 (1971).
2. Balej J., Paseka I., Koudelka V.: Chem. průmysl *13*, 466 (1963).
3. Glemser O., Sauer H.: Z. Anorg. Allgem. Chem. *252*, 144 (1943).
4. Glemser O., Naumann K.: Z. Anorg. Allgem. Chem. *265*, 288 (1951).
5. Glemser O., Lutz G.: Z. Anorg. Allgem. Chem. *264*, 17 (1951).
6. Benson J. E., Kohn H. W., Bondart M.: J. Catalysis *5*, 307 (1966).
7. Dickens P. G., Hurditch R. J.: Nature *215*, 1266 (1967).
8. Sienko M. J.: J. Am. Chem. Soc. *90*, 6568 (1968).
9. Hobbs B. S., Tseung A. C. C.: Nature *222*, 556 (1969).
10. Tseung A. C. C., Hobbs B. S.: Platinum Met. Rev. *13*, 146 (1969).
11. Hobbs B. S., Tseung A. C. C.: J. Electrochem. Soc. *119*, 580 (1972).
12. Heumann T. H., Stolica N.: Electrochim Acta *16*, 643 (1971)
13. Feuillade G., Bonet J., Chenaux B.: *Compt. Rend. 3èmes Journées Internat. d'Etude des Piles Combust.*, p. 300. Bruxelles 1969.
14. Niedrach L. W., Weinstock J. B.: Electrochem. Technol. *3*, 270 (1965).
15. Vondrák J., Balej J.: Electrochim. Acta *15*, 1653 (1970).

16. Trčunjan A. A.: Izv. Akad. Nauk Armen. SSR *7*, 71 (1954).
17. Vondrák J., Balej J.: Electrochim. Acta, in press.
18. Šepa D. B., Ovcin D. S., Vojnovič M. V.: J. Electrochem. Soc. *119*, 1285 (1972).
19. Broyde B.: J. Catalysis *10*, 13 (1968).
20. Thiesz E.: US-Pat. 1 896 022 (1933).
21. Van Duyn D.: Rec. Trav. Chim. *61*, 661 (1942).
22. Drossbach P., Schulz J.: Electrochim. Acta *9*, 1391 (1964).
23. Armstrong R. D., Douglas A. F., Williams A. E.: Energy Convers. *11*, 7 (1971).
24. Vondrák J., Balej J.: Electrochim. Acta *18*, 1017 (1973).
25. Teze A., Souchay P.: Rev. Chim. Miner. *7*, 539 (1970).
26. Tourne C.: Bull. Soc. Chim. France *9*, 3214 (1967).

Translated by K. Micka.