

ELECTROCHEMICAL BEHAVIOUR OF SODIUM TUNGSTEN BRONZES IN SOLUTIONS OF SODIUM HYDROXIDE

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In solutions of sodium hydroxide, tungsten bronze is anodically oxidized at potentials higher than 0.2–0.3 V (RHE) under the formation of sodium ions and tungsten oxide which is then further dissolved. The amount of oxidic layer of WO_3 on the surface of sodium tungsten bronzes is therefore far less than in acid medium, and consequently also the inhibition effect of this layer on the course of both anodic and cathodic processes in their respective potential regions is much lower.

Sodium tungsten bronzes are non-stoichiometric compounds of the composition Na_xWO_3 in which the stoichiometric coefficient x can range between 0 and 1. They exhibit good conductivity and are relatively stable in acid solutions and therefore their electrochemical behaviour had been studied mostly in acid solutions. Contrary to this, little attention has up to now been paid to their electrochemical behaviour in alkaline medium, since they are easily dissolved under these conditions.

Dissolution of sodium tungsten bronzes in alkaline solutions of oxidizing agents forms the basis of analytical methods for the determination of alkali metals in bronzes in the wet way^{1,2}. Sienko³, too, found that tungsten bronzes undergo corrosion in alkaline medium which was also confirmed by Fukuda and coworkers⁴. Anodic corrosion of sodium tungsten bronzes was studied in more detail by Šepa and coworkers⁵. According to them the rate of anodic corrosion obeys in the range of potentials from 0.3 to 0.6 V the Tafel equation with the slope $b \approx 120$ mV and does not depend on the concentration of WO_4^{2-} ions in the solution, whereas the current density varies between 10^{-2} – 1 A/m².

The subject of the present communication is a more detailed investigation of the behaviour of sodium tungsten bronzes in sodium hydroxide solutions and comparison with their behaviour in acid medium.

EXPERIMENTAL

Materials and Working Procedures

Preparation and handling of electrodes made of sodium tungsten bronzes were described earlier^{6–9}. Crystals of sodium tungsten bronzes of various compositions were used for experiments, the remaining chemicals were of the reagent grade purity throughout. Solution of sodium hydroxide, used for measuring the electrochemical properties, was once more purified by preelectrolysis.

All electrochemical measurements were carried out with a potentiostat of our own construction, equipped with a voltage and current follower and a circuit for automatic *IR* compensation with phase error not exceeding 1° at 1 kHz. An analogue computer MEDA 40 A (Aritma, Prague) served as current integrator. Its function was improved by replacing the operating amplifiers Aritma TZP-4 by the newer type TZP-7. Impedance of electrodes was measured so that the electrode was charged by d.c. potential to which an a.c. component was superimposed from a generator Orion EMG 1117/4. This supplied two sinusoid signals whose amplitude and relative phase angle could be varied independently. The amplitude of the a.c. component on the output of the voltage and current followers were measured with a Tesla BM 450 oscilloscope or with a low-frequency millivoltmeter Tesla BM 494 and its phase angle was measured on the same oscilloscope by comparison with the reference output signal of the generator. The same generator and oscilloscope or an *x-y* recorder ENDIM 2200 (VEB Messtechnik, GDR) served for measuring the voltammetric curves.

Photoelectric properties of electrodes were measured using an electronic flash device, including a xenon discharge lamp IFK-120 (USSR), a parabolic mirror and a condensing lens of 120 mm diameter. The flash was equipped with a release device, allowing either a continuous sequence of 2–5 flash exposures per second of small intensity, suitable for focussing, or a single shot exposure of the intensity of 50–100 J, released by the time base of the oscilloscope and serving for the proper measurement.

Small amounts of tungsten compounds were determined spectrophotometrically using thiocyanate method¹¹. All electrochemical measurements were carried out at $20 \pm 1^\circ\text{C}$ and the potentials were related to standard hydrogen electrode (RHE) in the same solution. If not otherwise stated, 2M sodium hydroxide was used as electrolyte.

RESULTS

Open Circuit Potentials

Sodium tungstate is the product of anodic oxidation of sodium tungsten bronze in a solution of sodium hydroxide. Therefore, our first task was to find whether the open circuit potential of bronze electrode in a solution of sodium hydroxide containing sodium tungstate has the characteristics of an equilibrium potential. The open circuit potential was found to be poorly reproducible, its value had a scatter of ± 50 to ± 100 mV and was independent of the tungstate concentration over the whole studied range of concentrations, *i.e.* between 0.05M–0.5M. Contrary to this, its value was strongly influenced by the presence of gases in the solution. In solutions freed from oxygen by a stream of nitrogen or argon the potential is about +50 to +150 mV, without any apparent dependence on the composition of either bronze or solution. In solutions saturated with hydrogen its value is by several tens of mV more negative. The open circuit potential in solutions saturated with oxygen is more positive and depends also on the composition of the bronze electrode, decreasing from *c.* +0.6 V found with bronze of the composition $\text{Na}_{0.46}\text{WO}_3$ to +0.24 V measured with an electrode of the composition $\text{Na}_{0.81}\text{WO}_3$. The establishing of stationary potential in oxygen was accompanied by a clearly visible corrosion of the electrode surface.

Voltammetric Curves

Voltammetric curves were measured on electrodes whose surface was polished with fine emery paper No 6/0 prior to each measurement. The starting potential was approximately -0.5 V and first the anodic and then the following cathodic branch of the curve were recorded.

Fig. 1 shows an example of anodic and cathodic curves measured with bronze $\text{Na}_{0.72}\text{WO}_3$ at the rate 0.2 V/s in a solution of the composition $2\text{N-H}_2\text{SO}_4$, 1M-KHCO_3 , $1\text{M-Na}_2\text{CO}_3$ and 2M-NaOH . Two well distinguished anodic waves can be seen on all four curves. Maximum of the first wave lies on the anodic curve approximately at -0.15 V, maximum of the second wave lies on anodic curves between $+0.2$ and $+0.3$ V. The second wave is rather elongated. In solution of sulphuric acid the current decreases with increasing potential, after passing a maximum, almost to zero value (see Fig. 1, curve 1, see also ref.⁶⁻⁹) whereas in all alkaline solutions a further increase of anodic current is observed after the end of the second wave (Fig. 1, curves 2-4). This current increases roughly exponentially with potential and also increases with increasing pH of the solution. This increase, independent of the mixing of solution at the electrode, is evidently due to anodic dissolution of sodium tungsten bronze in alkaline solution.

Fig. 2 shows the effect of the scanning rate of voltammetric pulse v (V/s) on the shape of voltammetric curves in 2M-NaOH . In measurements performed with the lowest scanning rate nearly no hysteresis was observed between the branches of the curve in ascending and descending potential, whereas at higher scanning rates the difference between the two branches of the voltammetric curve is the greater, the

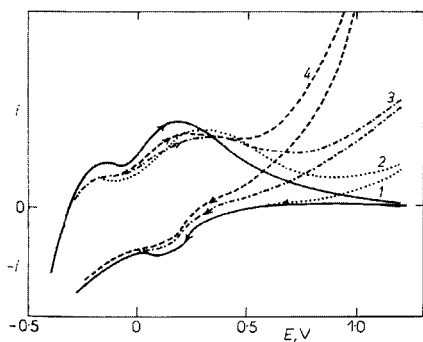


FIG. 1
Voltammetric Curves of $\text{Na}_{0.72}\text{WO}_3$ Electrode in Various Electrolytes

1 $1\text{M-H}_2\text{SO}_4$, 2 1M-KHCO_3 , 3 $1\text{M-Na}_2\text{CO}_3$,
4 2M-NaOH . Current i in arbitrary units.

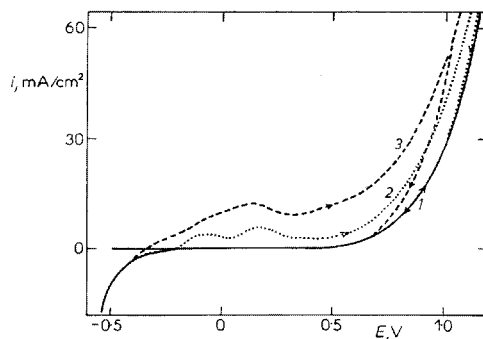


FIG. 2
Effect of Scanning Rate of the Potential Pulse v (V/s) on the Shape of the Voltammetric Curve of $\text{Na}_{0.72}\text{WO}_3$ Electrode in 2M-NaOH
1 0.004 V/s, 2 0.04 V/s, 3 0.4 V/s.

higher is the steepness. Besides, a higher anodic current passes through the electrode than when the curve is measured at the slowest rate. The current increases especially in its ascending branch, whereas the descending cathodic branch more or less approximates the voltammetric curve found with the slowest pulse. Current i , found in the region of anodic corrosion, can thus be considered to be a sum of a stationary component i_s and a nonstationary component Δi . The stationary component can be measured on voltammetric curves with the scanning rate $v \leq 0.004$ V/s; the dependence of the stationary corrosion current density on potential obeys in the potential range 0.5–+1.2 V the semilogarithmic relation $E = -0.4 + 0.4 \log i_s$ (V, A/m²). Contrary to this, the nonstationary component of the corrosion current i has a complicated course, its ascending branch being approximately proportional to \sqrt{v} . This is demonstrated in Fig. 3 where the quantity $\Delta i \cdot v^{-1/2}$ vs. potential is plotted for the values of scanning rate v . Both curves are practically identical.

Stoichiometry of Anodic Corrosion

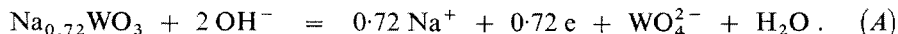
The nature of anodic corrosion reaction was studied by determining the amount of tungsten compounds transferred from electrode into solution after a known amount of electricity of the value 0.5–1 C had passed at different electrode potentials. The results are presented in Table I, in terms of the values of electrode potential, passed electric charge, the amount of tungsten transferred into solution and the calculated amount of tungsten, transferred into solution by a charge equal to 1 C. The found amount of tungsten agrees well with the theoretical value 2.650 mg/C for

TABLE I

Stoichiometry of Anodic Corrosion of Na_{0.72}WO₃ Electrode in 2M-NaOH
Electrode surface area approximately 50 mm².

Potential V	Charge C	mg W in solution	W per 1 C, mg
0.4	0.421	1.297	2.945
0.5	0.463	1.310	2.754
0.6	0.907	2.475	2.690
0.7	0.942	2.640	2.765
0.8	0.877	2.300	2.583
0.9	0.895	2.104	2.312
1.0	0.943	2.432	2.542
1.1	0.872	2.048	2.308
<i>Mean</i>			2.619
<i>Theory</i>			2.650

the given composition of the sodium tungsten bronze used, as it is given by the stoichiometry of dissolution according to equation



At low potentials the amount of tungsten transferred into solution is about by 10% greater, whereas at higher potentials it is by about 10–15% lower than the theoretical value. Times, necessary for passing the quantities of electricity according to Table I, ranged between tens of min (at 0.4 V) to 3 s (at 1.1 V).

Impedance of the Electrode

Impedance of sodium tungsten bronze of the composition $\text{Na}_{0.72}\text{WO}_3$ was measured in the potential range 0 to 1 V, when the rate of corrosion is still not great enough to change the condition of the electrode surface during measurement. Impedances were measured in the interval 0.1 to 1100 Hz. The series resistance of the electrolyte was determined by extrapolation to infinite frequency.

Fig. 4 shows the course of electrode impedance at different potentials. Up to 0.4 V the impedance is prevailing of capacitance character; at higher potentials the faradaic component becomes more pronounced, due to anodic dissolution. The interpretation of curves in Fig. 4 was successfully performed using an equivalent

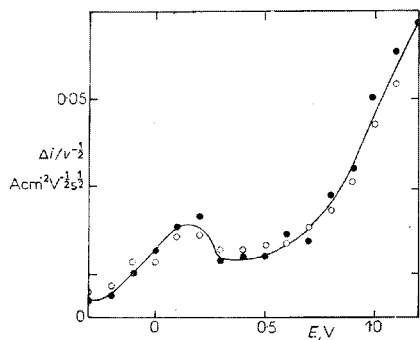


FIG. 3

Dependence of the Expression $\Delta i.v^{-1/2}$ on the Potential of $\text{Na}_{0.72}\text{WO}_3$ Electrode at Scanning Rate $v = 0.04$ V/s (○) and 0.4 V/s (●)

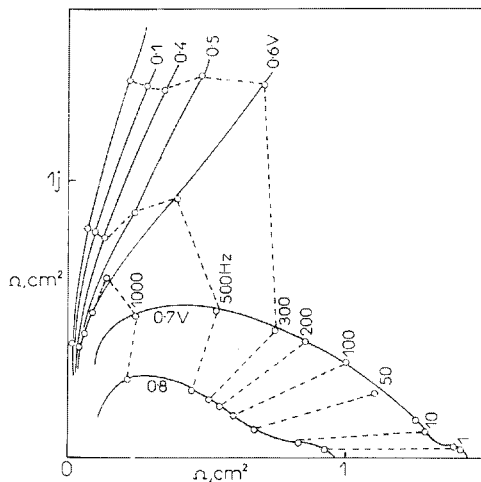


FIG. 4

Impedance of $\text{Na}_{0.72}\text{WO}_3$ Electrode at Different Potentials in 2M-NaOH

circuit according to Fig. 5, consisting of a parallel combination of a capacity of a double layer, C , faradadic conductance G , Warburg admittance W and a series term R_A and C_A which could be observed only at potentials $+0.7$ V and higher. Dependence of the values of the equivalent circuit according to Fig. 5 on potential is presented in Table II; the capacity components C and C_A and active components G_0 and R_A are summarized together with the values of real or imaginary component of Warburg admittance W_1 at unit frequency 1 Hz, in $S\ m^2\ Hz^{-1/2}$; thus, the following relation holds between W_1 and the Warburg admittance in complex representation \vec{W}

$$\vec{W} = (1 + j) \cdot \omega^{1/2} \cdot W_1.$$

According to this Table the electrode capacity exhibits a rather small maximum between 0.1 and 0.2 V, decreasing towards both sides. Contrary to this, the faradadic conductance increases monotonously with increasing potential which is accompanied by an approximately parallel increase of Warburg admittance W_1 . The values of the series combination $R_A + C_A$ do not depend considerably on potential in the range of potentials where these elements of the equivalent circuit are measurable.

Redox Reactions

The course of redox reactions in alkaline medium yields further information on the behaviour of the electrode surface. Fig. 6 shows voltammetric curves measured on a stationary electrode made of $Na_{0.72}WO_3$ bronze both in a medium of bi- and

TABLE II
Components of the Impedance of $Na_{0.72}WO_3$ Electrode

Potential V	Double-layer capacity F/m^2	Diffusion impedance W_1 $S\ m^{-2}\ Hz^{-1/2}$	Con- ductance S/m^2	R_A $10^{-4}\ m^2$	C_A F/m^2
0	2.39	1.8	210	—	—
0.1	2.82	0	190	—	—
0.2	2.82	0	290	—	—
0.3	2.61	9.0	400	—	—
0.4	1.97	13.0	630	—	—
0.5	1.70	17.0	860	—	—
0.6	1.04	17.0	1 460	—	—
0.7	0.516	47.0	5 750	13.8	7.75
0.8	0.550	83.0	8 800	13.8	9.70
0.9	0.222	71.0	9 000	11.9	9.00
1.0	0.118	59.0	9 700	15.7	6.70

trivalent iron in triethanolamine and in chromate solutions, as measured by voltammetric pulse of the scanning rate $v = 0.04$ V/s. Similarly as in acid medium⁶⁻⁹, also in alkaline solutions reduction of hexavalent chromium is inhibited at potential more positive than $+0.4$ V, *i.e.* at a potential, shifted by about 0.3 V in cathodic direction from the equilibrium value. The behaviour of the system $\text{Fe}^{2+}/\text{Fe}^{3+}$ is quite different. Whereas in acids its reduction is inhibited by the presence of corrosion products on the electrode surface, at potentials higher than $+0.4$ V, in alkaline medium a well developed voltammetric curve is obtained. Oxidation of bivalent iron in sulphuric acid proceeds at a very low current density, whereas in sodium hydroxide a well developed wave can be seen, prolonged up to $+1.2$ V, whose quantitative evaluation is very difficult, since the dependence of the position of maximum as well as of the other parameters on the steepness of the voltammetric pulse do not obey the relations according to Honz and Mareček¹⁰.

Photoelectric Effect

No photoelectric effect was found with electrodes of sodium tungsten bronzes in alkaline solutions, whereas in acid solutions this effect can easily be observed at potentials higher than $+0.5$ V (see^{6,12}).

Hydrogen Evolution

Investigation of cathodic evolution of hydrogen on tungsten bronze electrodes encounters great difficulties. In the region of overvoltage up to -0.4 V a satisfactorily steady

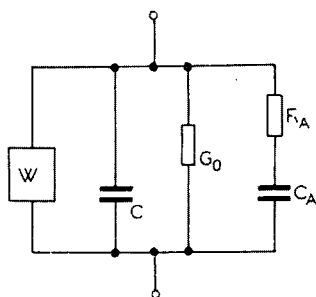


FIG. 5
Equivalent Circuit for Electrodes of Sodium Tungsten Bronzes

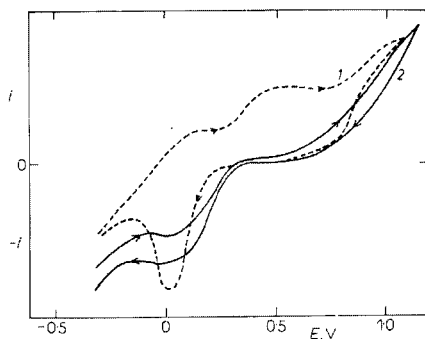
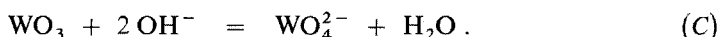
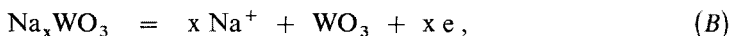


FIG. 6
Voltammetric Curves of the Course of Redox Reactions on $\text{Na}_{0.72}\text{WO}_2$ Electrode
1 $0.005\text{M-Fe}^{2+} + 0.005\text{M-Fe}^{3+} + 1\text{M}$
triethanolamine; 2 0.1N-CrO_4^{2-} , 2M-NaOH ;
 $v = 0.04$ V/s, Current i in arbitrary units.

state is not attained even after three days; the current density decreases steadily to values of the order 10^{-5} A/m² at -0.3 V. On increasing the overvoltage over -0.4 V the cathodic current increases considerably and later on is governed by the Tafel equation, even after restitution to the region of lower overvoltages. During this process the electrode is covered by a clearly visible grey coating. Its formation is probably the cause of the change of the surface properties of the electrode. For this reason further studies of the tungsten bronze in the region of hydrogen evolution was abandoned.

DISCUSSION

In alkaline medium sodium tungsten bronze easily undergoes corrosion the products of which are sodium and tungstate ions. In a stationary state the rate of this reaction obeys the semilogarithmic relation. In the potential range 0.5 to 1.2 V its slope is $b = 0.4$ V, whereas in the interval 0.3 to 0.6 V a lower value (0.12 V) was found by Šepa and coworkers⁵. This difference can be caused *e.g.* by accumulation of corrosion intermediates on the electrode surface at higher current densities and by the following partial inhibition of anodic oxidation of the bronze. Study of the stoichiometry of anodic dissolution in stationary state showed that this process follows stoichiometric equation (A). In measuring the anodic voltammetric curves, recorded with steeper pulses ($v > 0.004$ V/s), always a higher than stationary current was found. At the same time in non-stationary measurements a somewhat less amount of tungstate ions is transferred into solution than would correspond to Eq. (A). The explanation could be that oxidation of sodium tungsten bronzes proceeds in two steps:



Thus, reaction (B) yields tungsten(VI) oxide which is transformed in reaction (C) into tungstate anion. As long as reaction (C) is slow, a certain excess of tungsten oxide is formed on the electrode at any potential. In nonstationary measurement a certain part of the current is consumed in the formation of this surface layer whereas in a stationary state the amount of tungsten oxide on the electrode is constant and the amount of tungstate in the solutions corresponds to the electric charge passed according to the over-all equation (A). The formation of tungsten oxide is probably governed only by diffusion within the electrode and therefore the nonstationary component of anodic current has some characteristics of a diffusion current, especially the proportionality to the square root of the steepness $v^{1/2}$ and, on the other side, it does not depend on mixing of the solution. The presence of WO_3 layer on the surface of tungsten bronze considerably inhibits the course of reactions on bronze electrodes.

In acid medium^{8,9,12} the corrosion layer is stable and resembles oxidic layers on valve-effect metals, so that at anodic current densities 10^{-5} to 10^{-4} A/m² oxygen overvoltage amounts to several tens of V and mineral acids are oxidized on the electrode surface, e.g. sulphuric acid to peroxydisulphuric acid¹³. This layer shows some characteristics of semiconductor electrodes; its capacity is governed by the Mott-Schottky relation and it exhibits a photoelectric effect^{8,10}. Contrary to this, in alkaline medium the primarily formed layer is continuously dissolved and regenerated in further anodic process and consequently the total amount of tungsten oxide present at the electrode surface is lower in alkaline than in acid medium. Thus, the inhibition of anodic reactions is less pronounced, the impedance of the electrode at potentials over +0.7 V is much lower and is almost of ohmic character, whereas in acids it increases and is almost totally capacitive⁸. Therefore the semiconductive character of this compound is not so much effective so that in alkaline solutions no photoelectric effect can be observed in anodic region. The low frequency component of impedance found at frequencies lower than 15 Hz is assumed to be due to the formation of this layer.

According to our results anodic dissolution of sodium tungsten bronzes can be applied to electrolytic polishing of these materials in solutions of 1–2M-KOH in glycerol, diluted with water in the ratio 2 : 1.

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