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The Surface of Sodium Tungsten Bronze Electrodes in Acid Solutions*

M. V. Vojnović, D. B. Šepa, and D. S. Ovcin

Institute for Chemistry, Technology and Metallurgy, 11000 Beograd, Serbia, Yugoslavia

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At electrodes of sodium tungsten bronzes of cubic symmetry ($0.25 < x < 1$) in contact with acid electrolytes a hydrated layer of non-stoichiometric oxide is formed. On the base of comparative considerations of results of electrochemical and some other measurements the structure of the surface layer is proposed and the thickness of the surface layer estimated. Possible explanations of the nature of the rest potential and V — log i relationship are pointed out. On the base of study of kinetics and mechanism of some simple electron exchange reactions it is concluded that electrical properties of the surface layer are close to metallic.

INTRODUCTION

Crystal structure of sodium tungsten bronzes**, Na_xWO_3, where $0.25 < x < 1$, can be regarded as a close-packed cubic array of oxygen anions with a majority of oxygens, which are missing at their crystallographic sites, partly replaced by sodium ions. Remaining oxygens are linked to octahedra, which by the sharing of corners build the framework of the structure. Tungsten ions in this structure occupy octahedrally coordinated interstices. A valency of tungsten varies between 5 and 6, simultaneously with increasing amount of randomly distributed sodium in the lattice[1].

Due to the existence of highly symmetric tungsten sublattice, where tungsten ions are surrounded by octahedral field of oxygen anions, a conduction band of bronzes is formed by overlapping of the tungsten $5d\,(t_{2g})$ orbitals and oxygen p_π orbitals[2]. Therefore, cubic bronzes possess a behavior typical for metals such as metallic luster[1], single-crystal conductivity[3,4], magnetic susceptibility[5], Hall voltage[4,6] and Seebeck effect[7,8].

With lowering the content of sodium down to 0.25 the lattice parameter and electrical properties of the bronzes simultaneously are changed[3-6]. With further lowering of x value below 0.25 the highly symmetric structure, being responsible for overlapping of tungsten and oxygen orbitals, is replaced by a variety of complicated structures of lower symmetries[9]. The result is the qualitative change of electrical properties. Hence, the bronzes with x values below 0.25 are *n*-type semiconductors with energy gaps of about 0.5 eV[10].

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**Instead of »sodium tungsten bronze« the term »bronze« will be used for brevity.

Tungsten trioxide of distorted perovskite structure and monoclinic symmetry is obtained when sodium is absent from the lattice[11]. Tungsten trioxide is the *n*-type semiconductor with wide energy gap of about 2.5 eV[12].

So, if only electrical properties of crystals of the cubic symmetry with values of x higher than 0.25 are considered, it should be expected that the bronze electrodes would behave as metallic electrodes.

When left in contact with electrolyte, however, there is a possibility that the surface of the bronze will change chemically, structurally and physically. The evidence concerning these changes will be systematically presented in the following text.

The aim of this paper is to make a contribution to better understanding of the surface of the bronzes when used as electrodes in acid solutions.

EXPERIMENTAL

(i) The appearance of the crystals — It is known that freshly prepared crystals of the bronzes have beautiful, shiny surfaces of characteristic metallic luster. After some time, especially at sodium rich bronzes, the surface looses its shiny appearance being covered with a layer of bronze decomposition products[13,14]. If bronzes are treated in acid solutions at potentials more anodic to 1.0 V* the change of the appearance of the surface is more rapid[15,16].

(ii) The hydration of the surface. — Spitsyn and Kaschtanoff[17] found a certain amount of water strongly bonded to the surface of the bronze. The bronze releases this water at about 300^0 C. They found that this amount of water was not dependent on the composition of the bronze. Roughly calculated** the amount of this strongly bonded water is about 16 μ mole m^{-2}.

(iii) Transfer of sodium to solution. — Transfer of sodium to solution has been proved in the following experiment[16]: the bronze electrode, containing a thin layer of labeled sodium has been left in 1 *M* H_2SO_4, saturated with oxygen and potentiostated at 1.2 V. An increase of radioactivity of the solution was measured in time and the result, obtained after seven days of experiment is presented in Fig. 1.

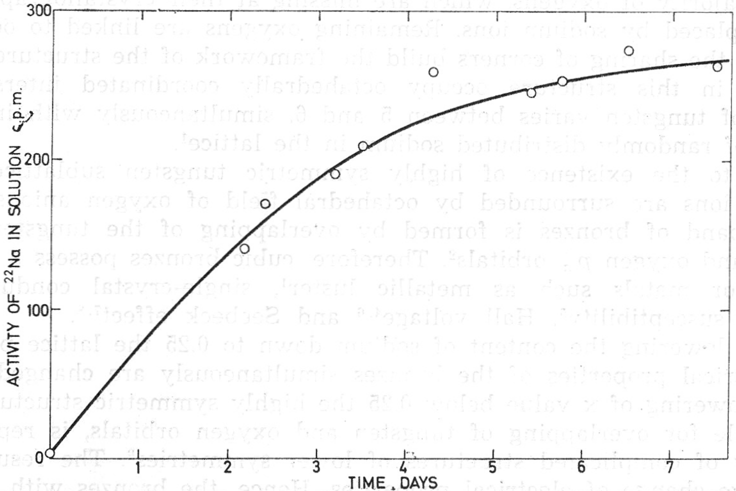

Fig. 1. Increase of the radioactivity of solution due to dissolution of ^{22}Na from labeled $Na_{0.63}WO_3$ electrode[16].

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* Potentials are referred to the standard hydrogen electrode scale unless otherwise stated.

** In these calculations values of 0.15% of strongly bonded water and 5 $m^2 g^{-1}$ for specific area[18] have been taken.

(iv) Transfer of tungsten to solution. — One of the features of the bronzes, frequently stressed in the literature, is their chemical resistance to attack by non-oxidizing acids[1,19]. It is proved quantitatively, however, that the bronzes slowly dissolve in acid solutions[16,20]. Fig. 2 shows an amount of tungsten accumulated for eight days in air-saturated 1 N H_2SO_4[20].

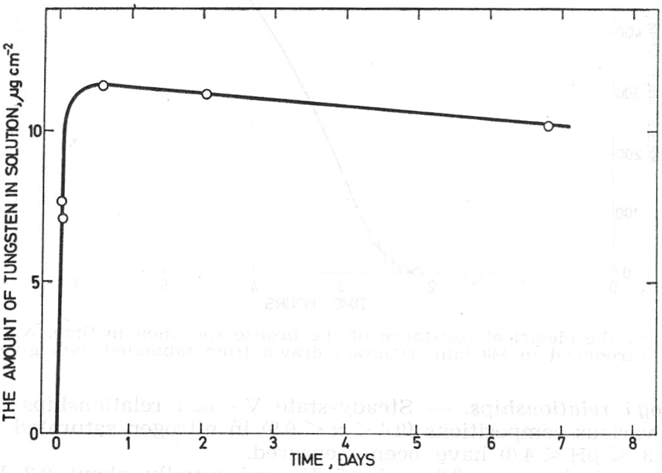

Fig. 2. Increase of the amount of tungsten in solution due to dissolution of the $Na_{0.52}WO_3$. Area of the electrode 3 cm². Volume of the solution 10 cm³. (Ref. 20).

(v) Electrical resistance of the bronze powders. — It is known in the literature that the electrical conductivity of polycrystalline powders is strongly dependent on the state of contacts among grains[21,22].

Specific resistivities of the bronze powders, measured in vacuum, are higher for about two orders of magnitude when compared to monocrystals of the same composition, indicating that the surface of grains is different from the bulk (*cf.* Table I). Qualitatively the same picture is obtained when bronzes of lithium[23] or potassium[24] are considered. It should be noted that metallic type of electrical conductivity for the bronze powders has been reported[14,25].

TABLE I

Values of Specific Resistivities of Sodium Tungsten Bronze Powders and Monocrystals at Room Temperature

Sample	Specific resistivity ohm cm		Reference
	$Na_{0.8}WO_3$	$Na_{0.9}WO_3$	
Powder	2.5×10^{-3}	2.7×10^{-3}	14
Monocrystal	2.0×10^{-5}	1.6×10^{-5}	4

The formation of the surface layer at powder grains of the bronze has been demonstrated by Straumanis and Dravnieks[14]. They left the bronze specimen in contact with moist air and measured its resistance in time. A considerable change of the resistance of the specimen, as presented at Fig. 3, they explained by an oxidation of the bronze and formation of tungstates at the surface of powder grains. If powders, prior to measurements, are treated with alkalies, acids and water, considerably higher specific resistivities (for instance[26] 0.123 ohm cm for $Na_{0.78}WO_3$), as well as behavior typical for n-type semiconductors, are reported[26,27].

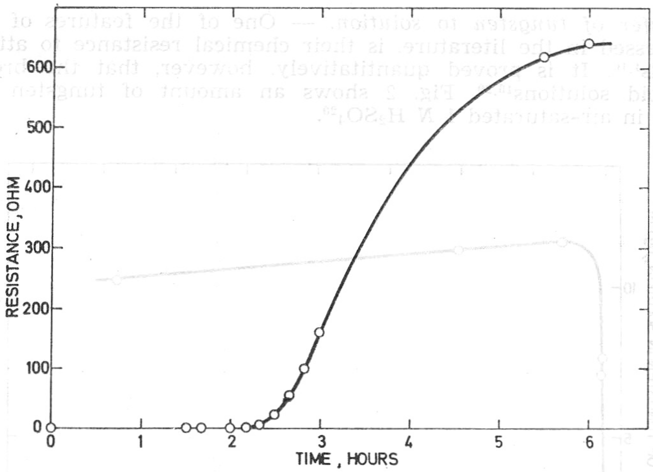

Fig. 3. Increase of the electrical resistance of the bronze specimen in time. Air saturated with water vapor introduced in 140 min. Diagram drawn from tabulated data given in Ref. 14.

(vi) V - log i relationships. — Steady-state V - log i relationships at the bronze electrodes of various compositions ($0.4 < x < 0.9$) in nitrogen saturated acid solutions (H_2SO_4, $-0.3 < p\mathrm{H} < 4.0$) have been measured.

Rest potentials between 0.2 and 0.5 V, and usually about 0.3 V, have been established at the bronze electrodes. Any definite relationship between the rest potential and the composition of the bronze, or *p*H of solution could not be visualized. Reproducibility of measurements has been low, and a prior history of the electrode influenced the final result.

Steady-state V - log i relationships, however, have a characteristic form. Typical V - log i relationship is presented at Fig. 4. The line below approximately — 0.1 V corresponds to the hydrogen evolution reaction[28], while the line above approximately 2.0 V represents the oxygen evolution reaction[16]. The complex V - log i line in the potential region between these limits is the result of electrochemical

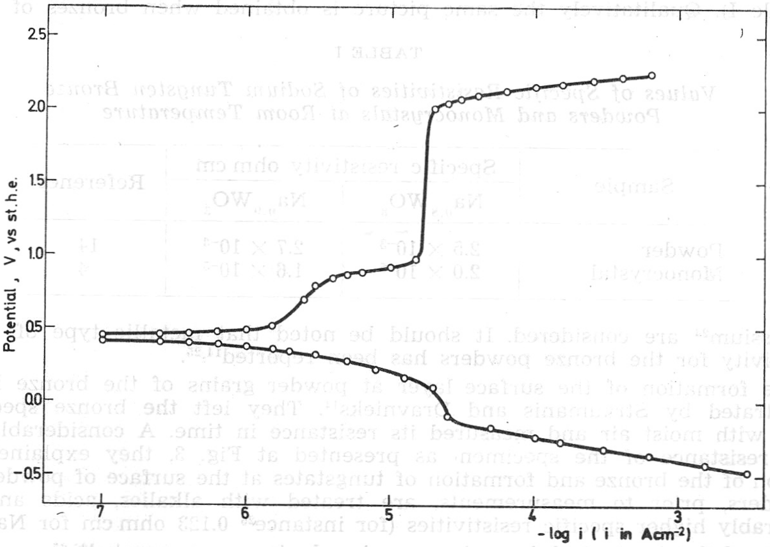

Fig. 4. Typical V-log i relationship at $Na_{0.83}WO_3$ in nitrogen saturated 1N H_2SO_4.

processes which are following changes of the bronze. Rather simple cathodic line is obtained between the rest potential and approximately —0.1 V. Anodic line, of stepwise form, is obtained between the rest potential and approximately 2.0 V. Two limiting currents of the anodic line appeared to be dependent only on the composition of the bronze. It is not possible, however, to visualize these relationships quantitatively, because of low reproducibility of measurements. The results have been influenced by a prehistory and possible pretreatments of the electrode. Usually electrodes previously held at potentials more positive than 1.0 V exhibited lower limiting currents and more positive rest potentials.

(vii) Potentiokinetic measurements. — Potentiokinetic measurements have been performed at the bronzes of various compositions ($0.6 < x < 0.9$) in nitrogen saturated acid solutions, using potential sweeps between 0.3 and 3.0 V s^{-1}. From a current-potential trace, obtained during potential sweep measurements at the bronze electrodes a difference in an amount of the charge for anodic and cathodic sweeps is observed[29,30]. An amount of the charge for the anodic sweep usually exceedes corresponding amount for cathodic process.

The amount of the charge is dependent on a prior treatment of the electrode, the range of potentials where sweeps are applied, and the sweep rate. The results, in the function of these variables vary between limiting values of 200 and 2000 µC cm^{-2}. On the base of our results and comparing the results of other authors[30], for the potential range —0.1 to 2.0 V and lower sweep rates (0.3 V s^{-1}) the amount of electricity of approximately 500 µ C cm^{-2} can be taken as the representative value for charging the bronze electrode.

(viii) Kinetics and mechanism of electron exchange reactions. — Kinetics and mechanism of electron exchange reactions Fe^{3+}/Fe^{2+} . $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and $W(CN)_8^{3-}/W(CN)_8^{4-}$ have been studied by measuring V - i and V - log i relationships by pulse and steady-state galvanostatic methods[31,32]. The bronze electrodes of various compositions ($0.5 < x < 0.9$) and nitrogen saturated acid solutions of relatively high concentration of supporting electrolyte (1 *N* H_2SO_4) have been used. Electrodes of gold and some platinum metals have been used parallelly. Solutions of various ratios of oxidized and reduced forms of ions have been selected, together with electron exchange reactions, to cover the region of potential between approximately 0.3 and 1.0 V.

Reversible potentials for these electron exchange reactions have been established quickly at the bronze electrodes in all solutions examined, as presented at Fig. 5. This has been observed by other authors also[31,33,34].

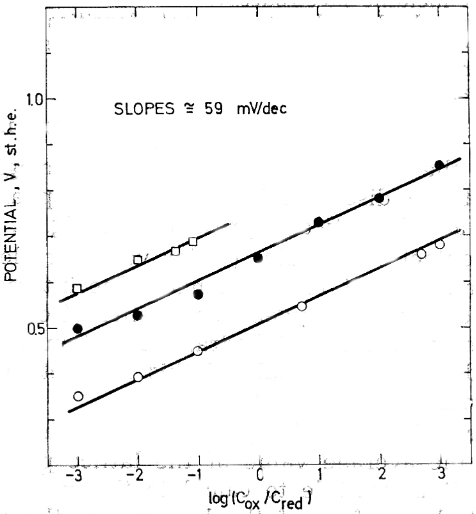

Fig. 5. Reversible potentials of some electron exchange reactions at sodium tungsten bronze electrodes. (□) Fe^{3+}/Fe^{2+}; (●) $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, and (○) $W(CN)_8^{3-}/W(CN)_8^{4-}$. All points are mean values for three bronzes with x values 0.5, 0.7 and 0.9.

No qualitative difference in V - i and V - log i relationships at the bronze electrodes and metallic electrodes (Au, Pt, Rh) have been observed. Divergences indicating the behavior typical for semiconductors, as reported by Vondrak[29], have not been observed at the bronze electrodes.

From exchange current densities, obtained from V - i and V - log i relationships in the usual manner, and from various ratios of concentrations of oxidized and reduced forms of ions, functions log i_0/C_{ox} and log (C_{red}/C_{ox}) were calculated and graphically correlated as shown at Fig. 6. The slope of the straight line obtained in this way defines the transfer coefficient[35]. The value of transfer coefficient is equal to 0.5, being in accordance with theoretical predictions for one-electron exchange reactions at metallic electrodes[36].

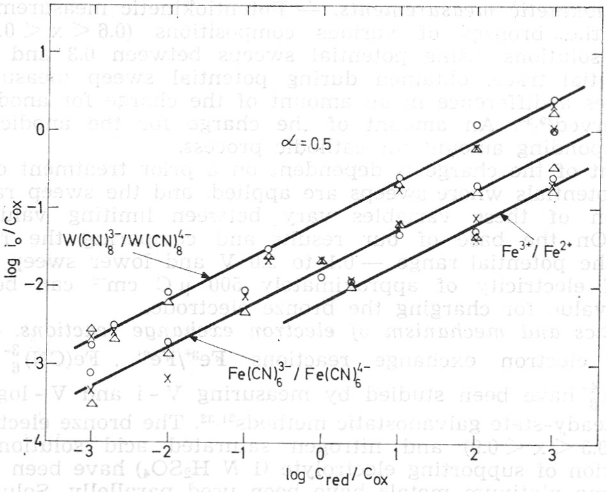

Fig. 6. Transfer coefficient for the electron exchange reactions $W(CN)_8^{3-}/W(CN)_8^{4-}$, $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ and Fe^{3+}/Fe^{2+} at sodium tungsten bronze electrodes: (○) $Na_{0.9}WO_3$, (×) $Na_{0.7}WO_3$ and (△) $Na_{0.5}WO_3$.

The values of standard exchange current densities calculated from experimental data indicate the differences among materials studied. So, the standard exchange current densities at the bronzes and gold are systematically lower than at platinum metals, as illustrated in Table II.

A MODEL OF THE SURFACE OF THE BRONZE ELECTRODES IN ACID SOLUTIONS

The surface of the cubic bronze can be easily imagined if the idealized (1/2, 0, 0) plane at the discontinuity of the bulk phase of the perovskite structure is taken, as schematically presented at Fig. 7.

When left in contact with water (water vapor or electrolyte) the surface of the bronze as presented at Fig. 7 changes. The interaction will occur preferentially at sites of missing oxygens, or at sites of coordination-unsaturated oxygens (outer corners of WO_6 octahedra). Formation of hydroxyl groups, as at some other oxides[40], is the result of this interaction. Changed, hydrated surface of the bronze is shown at Fig. 8.

If the structure of the surface, as presented at Fig. 8, is taken into account and using the average value of the lattice parameter of the bronze (3.8 Å, *cf.* Ref. 1), it is possible to calculate the maximum concentration of hydroxyl groups at the surface of the bronze. So, the surface concentration of 24 μ mole m^{-2} of hydroxyl groups is obtained. This is equivalent to 12

TABLE II

Values for Standard Exchange Current Densities for some Electron Exchange Reactions at Different Electrode Materials

Electron exchange reaction	Electrode material					
	Sodium tungsten bronzes			Gold	Rhodium	Platinum
	x = 0.5	x = 0.7	x = 0.9			
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	1.5×10^{1}[a]	2.3×10^{1}[a]	2.9×10^{1}[a]	—	—	$(0.4—1.5) \times 10^{4}$[b]
$W(CN)_8^{3-}/W(CN)_8^{4-}$	6.5×10^{1}	5.7×10^{1}	7.8×10^{1}	1.8×10^{2}	1.5×10^{3}	—
Fe^{3+}/Fe^{2+}	6.3×10^{0}[c]	1.2×10^{1}[c]	1.0×10^{1}[c]	2.5×10^{1}[c]	2.2×10^{2}[c]	$(2.5—5.2) \times 10^{2}$[d]

[a] see Ref. 32; [b] see Ref. 37 and 38; [c] see Ref. 31; [d] see Ref. 31, 37, and 39.

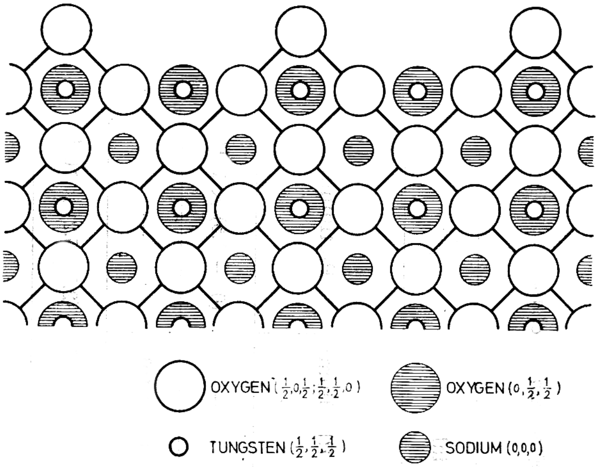

Fig. 7. Idealized (1/2, 0, 0) plane of $Na_{1.0}WO_3$

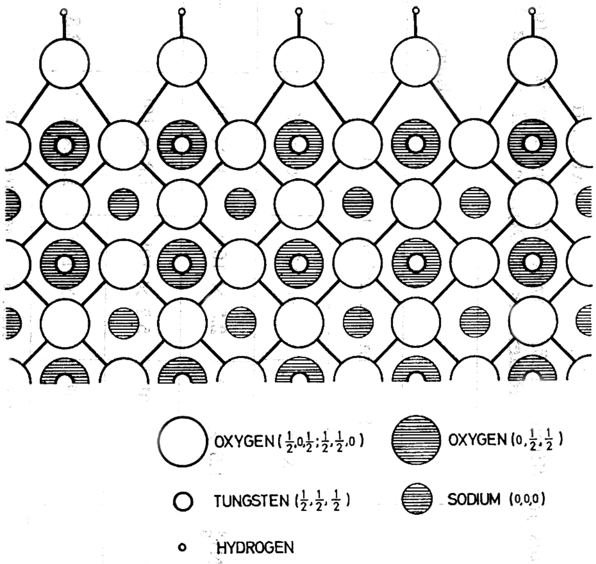

Fig. 8. Hydrated idealized (1/2, 0, 0) plane of $Na_{1.0}WO_3$.

μ mole m^{-2} of structurally bonded water, the value being comparable with already mentioned 1·6 μ mole m^{-2} (*cf. ii*). The agreement between these values is considered to be satisfactory to support the model of the hydrated surface of the bronzes as presented at Fig. 8.

The strongly bonded water, being in the form of hydroxyl groups at the surface of the bronze, influences changes of bond lengths within the first layer of WO_6 octahedra, as already emphasized at Fig. 8. This perturbation within the first layer obviously changes the energy of sodium ions in the adjacent layer and favours the migration of sodium ions out of the lattice[16].

Hence, the result of changes at the surface of the bronze in contact with acid solution would be the formation of a layer of deformed WO_6 octahedra, deficient in sodium ions. Deficiency of positive charge in the surface, caused by the exit of sodium ions is balanced in the most simple way — by the replacement with hydrogen ions from the solution[16,28]. So, the surface layer will have the composition resembling a hydrated non-stoichiometric tungsten oxide species with mean valency of tungsten between 5 and 6. Therefore, initial, highly symmetric structure of the bronze can not exist any more within the surface layer, as already proved in crystallographic studies of bronzes with lower sodium contents[9]. Transformation which have to occur in the surface layer should be the formation of domains of WO_6 octahedra sharing edges, to resemble structurally the non-stoichiometric higher tungsten oxide. It is shown[41] that such structural transformation, known in the literature as crystallographic shear[42] really occurs at tungsten oxides in the way schematically presented at Fig. 9 (ReO_3, the structural type-oxide is used as a model).

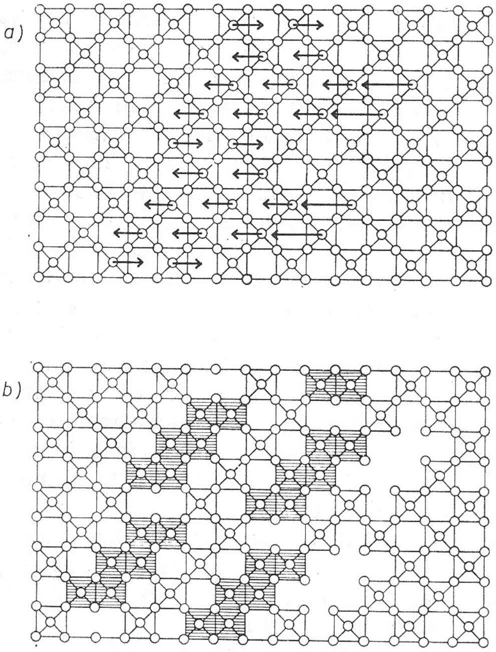

Fig. 9. Crystallographic shear at ReO_3 structure.

If the surface layer of the bronze is rearranged by crystallographic shear in the way presented at Fig. 9, characteristic groups of six WO_6 octahedra, sharing edges among themselves, are formed. As the consequence the surface layer contracts. Simultaneously, in the first surface layer appear holes — areas where the same sequence of changes can occur at the next layer of the bronze. Hence, the thickening of the surface layer can continue.

These groups of six WO_6 octahedra are bonded to the surface by sharing some oxygens at outer corners of WO_6 octahedra. If the number and type of these bonds are considered a definite stoichiometry can be ascribed to these groups. It is well known[43] that groups of definite number of WO_6 octahedra, sharing edges, with hydroxyl groups instead of coordination unsaturated oxygens, exist in acid solutions as polytungstates. Hence, the groups of six WO_6 octahedra at the surface of the bronze can be considered as surface analog of polytungstates. In the following text the term »surface hexatungstate« will be introduced arbitrarily for the groups of six WO_6 octahedra sharing edges among themselves.

In the development of the model of the surface of the bronze in acid solutions it is assumed that the valency of tungsten in the surface layer is the same as in the bulk phase of the bronze (*i. e.* between 5 and 6). An interesting feature of polytungstates, however, is that the mean valency of their tungsten can be changed stepwise, being compensated by transforming the corresponding number of oxygen anions to hydroxyl groups, while the structure of the species is remaining principally the same [43]. Therefore, polytungstates posses a large redox capacity. The surface hexatungstates, on the other side, should behave analogously. If the mean valency of tungsten in the surface hexatungstate is considered a number of species of different composition can be imagined. In the Table III possible formulas of idealized surface hexatungstates (*cf.* Fig. 9) are listed, as well as corresponding electrochemical reactions for possible changes from one hexatungstate to another. All surface hexatungstates from Table III are existing at the surface — independently on the composition of the bronze. This is consequence of the initial statistical distribution of sodium in the bronze[1]. Concentrations of possible surface hexatungstates, however, obey the statistical distribution curve for sodium in the bronze, *i. e.* the species with the mean valency of tungsten the closest to the bronze composition prevail at the surface.

Chemical and/or electrochemical processes occuring at the interface bronze/electrolyte may influence the original distribution of the surface hexatungstate concentrations. Interaction with water, as main chemical process, giving rise to dissolution of the surface layer (*cf. iv*) influences the original distribution of the surface hexatungstate concentrations. It can be supposed that water interacts preferentially with the surface hexatungstates of lower mean valency of tungsten, which can be hydrated to higher degree.

The existence of possible electrochemical reactions of the surface hexatungstates (*cf.* Table III) indicates that original distribution of their concentrations will be potential dependent. For instance, at more positive potentials, referring the rest potential, the surface hexatungstates of higher mean valency of tungsten will accumulate at the surface.

It is following from the foregoing text that the bronze electrode in acid solutions will behave similarly to metallic electrodes covered with a layer of non-stoichiometric oxide[44].

Rest potentials established at the bronzes in acid solutions can be determined by any one of possible reactions among the surface hexatungstates given in the Table III, or by the corresponding overall process:

$$W_6O_{11}(OH)_8 = W_6O_{17}(OH)_2 + 6\,H^+ + 6\,e \qquad (1)$$

No matter which one of these reactions is considered there is an analogy with typical oxide potential[44].

According to this model V-log i relationship (*cf.* Fig. 4) within the range of potentials between — 0.1 and 2.0 V represents complex kinetics of overall reaction (1), which can proceed through successive one-electron steps listed in the Table III. It is possible to propose reaction paths which would qualitatively explain the form of V-log i relationship. Quantitative analysis of kinetics and mechanism, however, does not improve available information due to experimental limitations *(cf. vi).*

TABLE III

Possible Stoichiometry and Electrochemical Reactions of Surface Hexatungstates

No	Mean valency of tungsten in the surface hexatungstates	Formula of the surface hexatungstate	Electrochemical reactions of surface hexatugstates
1	5.000	$W_6O_{11}(OH)_8$	$W_6O_{11}(OH)_8 = W_6O_{12}(OH)_7 + H^+ + e$
2	5.167	$W_6O_{12}(OH)_7$	$W_6O_{12}(OH)_7 = W_6O_{13}(OH)_6 + H^+ + e$
3	5.333	$W_6O_{13}(OH)_6$	$W_6O_{13}(OH)_6 = W_6O_{14}(OH)_5 + H^+ + e$
4	5.500	$W_6O_{14}(OH)_5$	$W_6O_{14}(OH)_5 = W_6O_{15}(OH)_4 + H^+ + e$
5	5.667	$W_6O_{15}(OH)_4$	$W_6O_{15}(OH)_4 = W_6O_{16}(OH)_3 + H^+ + e$
6	5.833	$W_6O_{16}(OH)_3$	$W_6O_{16}(OH)_3 = W_6O_{17}(OH)_2 + H^+ + e$
7	6.000	$W_6O_{17}(OH)_2$	

From the potentiokinetic measurements a rough estimate of the thickness of the surface layer is possible. From the idealized structure of the surface layer (*cf.* Fig. 9) the concentration of the surface hexatungstates within a monolayer can be calculated. The value of 2.4×10^{13} cm^{-2} is obtained. If it is supposed that during anodic sweep between —0.1 and 2.0 V six electrons are transferred per one surface hexatungstate (mean valency of tungsten changed from 5 to 6), it is easy to calculate that 24 μC cm^{-2} are needed to charge all surface hexatungstates in the monolayer. Taking into account the average value of charge of 500 μC cm^{-2} used in anodic sweep in the same range of potentials *(cf. vii),* 20 monolayers or 76 Å would be the corresponding thickness of the surface layer of the bronze.

When electrical properties of the surface layer of the bronzes are considered a parallellism with bronzes of low sodium content ($0 < x < 0.25$) and with tungsten trioxide, typical *n*-type semiconductors of energy gaps varying between 0.5 and 2.5 eV, respectively, usually is made. On the base of this analogy the surface layer of the bronzes should be semiconductor of *n*-type with relatively wide energy gap.

Results of studies of kinetics and mechanism of simple electron exchange reactions at the bronzes, however, indicate the behavior close to theoretically expected for metallic electrodes[2-6] (*cf. viii*). The difference in the values of standard exchange current densities, when compared with platinum metals, can be explained on the base of existing theory for metallic electrodes[32].

If the surface layer of the bronze would be an intrinsic semiconductor, from the theory of electron exchange reactions for electrodes metal/film of semiconductor/electrolyte[45] the next properties would follow: (*i*) V-log i relationship typical for the semiconductor; (*ii*) transfer coefficient, generally different from 0.5, dependent on the film thickness, and (*iii*) standard exchange current density dependent on values of work functions of metal and semiconductor and on the thickness of the film. No one of these points has been proved experimentally at the bronze electrodes.

The surface layer of bronzes, however, could be a semiconductor with behavior close to metallic electrode in the following two cases: (*i*) if it is semiconductor with »metallized surface«[46] (the Fermi level intersects either the valence or the conduction band) and, (*ii*) if it is intrinsic semiconductor with high concentration of the surface states[46,47]. In these cases the transfer coefficient is equal to 0.5. The standard exchange current density, however, is dependent on the work function and is lower from the corresponding value at metallic electrode (approximately for factor exp $(-\Delta/2\,kT)$, where Δ is the energy gap of the semiconductor[47]).

Hence, when experimental data are considered (cf. *v* and *viii*) it can be concluded that the surface layer of the bronzes in acid solutions is not intrinsic semiconductor, but has electrical properties close to metallic. From the experimental data available, however, it is not possible to distinguish between electrical properties either of metal, or of the semiconductor with »metallized surface«, or of the semiconductor with high concentration of the surface states.

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IZVOD

Površina natrijum volframovih bronzi kao elektroda u kiselim rastvorima

M. V. Vojnović, D. B. Šepa i D. S. Ovcin

Na elektrodama od natrijum volframovih bronzi kubne simetrije ($0{,}25 < x < 1$) u kontaktu sa kiselim rastvorima dolazi do formiranja hidratisanog oksidnog sloja nestehiometrijskog sastava. Na osnovu uporednog razmatranja rezultata elektrohemijskih i drugih merenja predložena je struktura površinskog sloja, ocenjena njegova debljina i ukazano je na mogućnosti objašnjenja prirode stacionarnog potencijala i oblika V-log i zavisnosti. Na osnovu ispitivanja kinetike i mehanizma nekih prostih reakcija izmene elektrona došlo se do zaključka da su elektronske osobine ovog površinskog sloja bliske osobinama metala.

INSTITUT ZA HEMIJU, TEHNOLOGIJU
I METALURGIJU
11000 BEOGRAD

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