ELECTROLYTIC REDUCTION OF OXYGEN ON ELECTRODES CONTAINING TUNGSTEN BRONZES

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The electric and electrochemical properties of hydrophobic porous electrodes prepared from sodium or lead tungsten bronzes mixed with ground graphite were studied from the point of view of cathodic reduction of oxygen in sulphuric acid. Both the electric and electrochemical properties of such electrodes are determined in the first place by the properties of graphite and only to a small extent by the properties of the bronzes. The ability of the bronzes to catalyze the cathodic reduction of oxygen is below that of their mixtures with graphite. The catalytic activity of neither material is therefore high enough to be used in fuel cells operating with an acid electrolyte.

The reduction of oxygen on electrodes prepared from tungsten bronzes was first studied by Bockris, Šepa, and Damjanovič[1⁻3], and it was their very promising results that initiated further investigations by many other workers in the field. The possibility of employing some of these bronzes as catalysts for the above reaction was confirmed by the semiquantitative experiments made by Broyde[4]. Fukuda and coworkers further suggested that tungsten bronzes be used in catalytic electrodes operating on gaseous fuels[5,6]. Niedrach and Zelinger[7], Fishman, Henry, and Tessore[8], and recently also Heffler and Böhm[9] studied electrodes which contained small quantities of platinum besides tungsten bronzes; the platinum was added in the form of platinum black, or, it was introduced by impregnating the electrodes with a solution of chloroplatinic acid. The results obtained were, however, not too favourable. Similar results were then reported by Armstrong and coworkers[10], Randin[11,12], Voïnov and Tannenberger[13], and Vondrák and Balej[14,15], all working with single crystals of various bronzes. Their results have shown that the reduction of oxygen in an acid medium proceeds only at potentials below $+0.5$ V.

The present paper is devoted to studying the behaviour of sodium and lead tungsten bronzes, and of tungsten di- and trioxide, in porous hydrophobic electrodes for the reduction of oxygen in 2N sulphuric acid. As was shown by preliminary measurements, the electric conductivity of powdered tungsten bronzes bonded with plastic agents is low. For this reason, it was necessary to study the influence of graphite on the conductivity and the electrochemical properties of tungsten bronze porous hydrophobic electrodes. Since carbon is known to have a catalytic activity for the reduction of oxygen and would consequently contribute to the overall activity of the mixture, two series of electrodes were prepared: one from mixtures of tungsten compounds with graphite, the other from mixtures containing equivalent quantities

of graphite but with chemically inert and electrically nonconductive $BaSO_4$ in the place of the tungsten compounds (the density of the two species being next to equal).

EXPERIMENTAL

Preparation of the electrocatalytic substances. The sodium tungsten bronze was prepared by electrolyzing a molten mixture of sodium tungstate and tungsten trioxide[16]. The bronze was obtained in the form of crystals which were then pulverized in a vibrating agate grinder. The lead tungsten bronze was prepared by the modified Bernoff and Conroy[17] method: a mixture of PbO, WO_3, and WO_2 was heated under argon to 800°C for 40 h. Tungsten trioxide was prepared by heating tungstic acid (Fluka) to 500°C. Tunsten dioxide was obtained by reducing WO_3 under the conditions given by the $W-WO_x-H_2O$ phase diagram[18,19] (690°C, hydrogen saturated with water vapour at 85°C). $BaSO_4$ was precipitated from a solution of barium chloride with sulphuric acid. All chemicals used were of reagent grade purity. The compounds, in a selected ratio, were mixed and ground in a vibrating agate grinder. The powder was then made into a thick suspension (to be spread with a brush) in a solution prepared from 20 ml of a storage solution thinned with 60 ml 1 : 1 benzene–xylene mixture to which 0·2 g of paraffine was added. The storage solution contained 10 g of white rubber sheet RSS-2 in 200 ml benzene and 200 ml xylene.

Measurements of the electric properties of the active substances. The suspension of the electrode material was evaporated to dryness and then pressed into a tablet of 6 mm diameter and 4—5 mm thickness; the tablet was then placed between two flat copper elements one of which was cooled with water and the other heated with a resistance heater immersed in ethylene glycole. The temperature of the two elements was measured with mercury thermometers; the thermoelectric tension was measured with a voltmeter-pikoamperemeter Tesla BM 483. The electric conductivity exhibited a marked dependence on the pressure under which the sample was held during the measurement. For this reason, the measuring device was supplemented with a micrometric screw enabling one to measure the electric resistance at the given relative compression of the sample.

Preparation of the electrodes and measurement of their electrochemical properties. A previously compressed grid of an alloy 90% Pt and 10% Rh (10 holes/mm^2) was spread with 2—3 layers of the suspension of the electrode material. The quantities of the dry electrode material per 1 cm^2 of the geometrical area of the electrode are given in Table II. A fully dried electrode was then fastened into an acrylic glass holder thus forming one wall of a gas chamber where an overpressure $\leqq 0·3$ atm was maintained with the aid of a manostat. The current was collected with a platinum wire connected to the electrode in such a way as to be out of contact with electolyte. The holder was then placed into one arm of a H-shaped vessel; the other arm separated with a fritted glass contained an auxiliary electrode made of bright platinum. The electrode potential was measured against a Hg/Hg_2SO_4 reference electrode, whose Luggin capillary was fastened to the holder of the electrode to be measured. All potential values presented are, however, referred to the reversible potential of a hydrogen electrode operating in $2N-H_2SO_4$ which was used as electrolyte.

The electrode which was fed with pure nitrogen or with oxygen was polarized with a potentiostat to various potential values until steady state currents were attained; this lasted from 30 min to 10 h, depending on the material of the electrode measured and on the potential used. The rate of the reduction of oxygen was calculated from the difference between the values of the current obtained from the electrode operating on oxygen and nitrogen.

RESULTS

Electric Properties of the Mixtures for Preparing the Electrodes

The electric properties of some of the electrode mixtures used are compiled in Table I. None of these measurements were made on mixtures of $C + WO_3$ and WO_2. The Seebeck coefficient of the thermoelectric tension α is an excellent measure of the type of conductivity. This is seen for instance in the case of the mixtures of $BaSO_4 + C$ whose conductivity, after adding non-conductive $BaSO_4$, strongly decreases whereas their Seebeck coefficient remains constant and approaches the value of the coefficient of pure graphite. Similarly, the mixtures of bronzes and graphite have an equal thermoelectric coefficient as that of pure graphite, although their conductivity

TABLE I
Electric Properties of Mixtures of Graphite with Tungsten Compounds (or $BaSO_4$)

C, %	Tungsten compound, %	α, $\mu V/°C$	R_1, Ω cm^a	R_5, Ω cm^a
		Pure C		
100	0	$-18\cdot5$	$6\cdot0$	$3\cdot5$
		$C + Na_{0\cdot6}WO_3$		
0	100	$8\cdot5$	$1\cdot6$	$0\cdot5$
50	50	$-20\cdot2$	$2\cdot5$	$0\cdot48$
70	30	$-18\cdot1$	$7\cdot0$	$0\cdot92$
80	20	$-19\cdot1$	32	
		$C + Pb_{0\cdot25}WO_3$		
0	100	$+12\cdot3$	700	—
20	80	$-18\cdot5$	$3\cdot3$	$0\cdot9$
50	50	$-18\cdot0$	—	—
70	30	$-19\cdot5$	$9\cdot5$	$1\cdot1$
80	20	$-20\cdot1$	17	$0\cdot7$
		$C + BaSO_4$		
15	85	$-20\cdot7$	17 000	3 500
20	80	$-22\cdot3$	290	b
30	70	$-23\cdot9$	60	$9\cdot5$
50	50	$-23\cdot2$	$6\cdot3$	b

^{a} R_1 specific resistance at a relative compression of 1%; R_5 — 5%. ^{b} The tablet crashed before the relative compression of 5% was reached.

is higher than that of the mixture $BaSO_4$ + C. The Seebeck coefficient of pure pulverized tungsten bronzes is far away with respect to both the value and sign. The Seebeck coefficients obtained on pure pulverized sodium tungsten bronze tally with the values tabullated for monocrystalline sodium tungsten bronzes of a similar composition[20-22] and with the value $\alpha = 9{\cdot}075$ obtained by us for a single crystal of $Na_{0.6}WO_3$ which was later ground to be used for preparing the electrodes. The Seebeck coefficient for pure pulverized lead tungsten bronze is higher than that obtained for sodium tungsten bronzes (Table I); this value can be used for calculating (according to Shanks[22]) the concentration of conductivity electrons corresponding to the liberation of $1{\cdot}87$ conductivity electrons from each lead atom present in the lead tungsten bronze. The value suggests that the majority of lead atoms in lead tungsten bronzes is ionized to the second degree forming Pb^{2+} which is in conformity with the present views of the electronic character of tungsten bronzes[22].

Electrode Activity of the Mixtures of Tungsten Compounds with Graphite for the Reduction of Oxygen

The behaviour of porous hydrophobic electrodes containing tungsten bronzes may be described by several characteristic points. Firstly, even when feeding the electrode with nitrogen, a current of a considerable density is obtained. At potentials more positive than $200-300$ mV, the current is anodic, at more negative potentials it is cathodic. Secondly, this "basic" current is strongly dependent on previous polarization of the electrode and after a change in the potential it changes in a way reminiscent of the behaviour of single crystal sodium tungsten electrodes[21]. In the potential range from zero to $+500$ mV and on a freshly prepared electrode, one can observe a slight oxidation of hydrogen but its rate decays rapidly to a very low steady state value of 10^{-5} to 10^{-4} A/cm^2 at $0{\cdot}5$ V; since, moreover, the phenomenon exhibits a rather bad reproducibility it is not dealt with in the present paper.

The reduction of oxygen obeys the Tafel equation only at above $+0{\cdot}4$ V; at lower potential values the polarization curves (drawn in the usual semi-logarithmic coordinates) are curved. The rates of the reduction of oxygen at various potentials, and the slope of the linear portion of the Tafel curves b are listed in Table II. The results induce that the behaviour of pure graphite and that of the mixture graphite and sodium or lead tungsten bronzes, or of graphite and small quantities of tungsten trioxide are close to one another. The activity of the lead tungsten bronzes and partly also of the pure sodium tungsten bronze is visibly lower. Contrary to that, electrodes made of pure WO_3 are active at a potential $\leq 0{\cdot}5$ V; in the vicinity of the zero potential they undergo an easy electrolytic reduction and yield a deeply blue product. The activity of the electrodes containing $BaSO_4$ in the place of tungsten compounds was decreasing as the quantity of the sulphate increased. Electrodes made of pure WO_2 were — in the range up to $0{\cdot}4$ V — of an equal activity as were those of the mixtures

TABLE II
Kinetics of Reduction of Oxygen on Mixtures of Graphite with Tungsten Compounds

Composition of mixture		Active substance g/cm²	Tafel constants		$\log i_{O_2}$ (A/cm²) at potential, V					
C, %	Tungsten compound, %		a	b	0	+0.2	+0.3	+0.4	+0.5	+0.6
					Pure C					
100	—	0.0540	0.107	0.120	−2.00	−2.34	−2.616	−3.060	−3.530	−4.217
					$C + Na_{0.6}WO_3$					
0	100	0.1110	−0.028	−0.120	−2.522	−2.691	−3.284	−4.017	−4.699	−5.854
50	50	0.0412	−0.103	−0.120	−3.276	−3.546	−3.887	−4.127	−4.951	—
70	30	0.0440	0.047	−0.120	−2.677	−3.031	−3.357	−3.653	−4.036	−4.855
80	20	0.0488	0.000	−0.115	−2.275	−3.854	−3.252	−3.818	−4.552	−5.301
					$C + Pb_{0.25}WO_3$					
0	100	0.330	−0.236	−0.110	−2.222	−4.046	—	—	—	—
20	80	0.062	0.087	−0.120	−2.000	−2.684	−3.032	−3.537	−3.872	−4.398
50	50	0.044	0.112	−0.120	−2.198	−2.693	−3.000	−3.451	−4.123	−4.854
70	30	0.60	0.125	−0.115	−2.003	−2.292	−2.696	−3.234	—	—
80	20	0.060	0.057	−0.120	−2.102	−2.391	−2.719	−3.225	−3.822	−4.515

					C + WO₃					
0	100	0·0346	—	—	—3·300	—3·522	—3·850	—	—	—
50	50	0·0560	—	—	—3·793	—3·193	—	—	—	—
70	30	0·0600	0·047	—0·120	—2·097	—2·546	—2·867	—3·346	—4·016	—4·168
80	20	0·0620	—0·080	—0·115	—2·075	—2·674	—3·222	—3·585	—4·620	—5·525
					C + BaSO₄					
0	100	0·1210	—	—	—4·086	—5·398	—5·921	—5·778	—	—
20	80	0·0691	—	—	—3·657	—4·550	—5·050	—5·650	—	—
30	70	0·0721	—	—	—3·319	—3·77	—4·162	—4·301	—5·797	—
50	50	0·0594	—	—	—2·477	—3·25	—3·600	—4·000	—4·300	—
					Pure WO₂					
0	100	0·328	—0·250	0·130	—2·699	—3·180	—3·642	—4·237	—	—

of graphite and tungsten bronzes, above 0·5 V their activity rapidly decreased similarly to the electrodes containing larger quantities of WO_3.

DISCUSSION

The conductivity of pure powdered tungsten bronzes is low for use in porous diffusion electrodes and has, therefore, to be raised by adding graphite. As is seen from the change of the Seebeck coefficient after adding graphite, the current in these electrodes is conducted mostly *via* graphite, the Seebeck coefficient of the graphite-bronze mixtures being close to that of pure graphite. The bronzes, however, do contribute to the conductivity as was proved by comparing electrodes of bronze–graphite mixtures with electrodes made of graphite and $BaSO_4$.

Between the electric properties and the electrode activity of tungsten compounds for the reduction of oxygen there exists an analogy. The electrochemical activity of mixtures containing $Na_{0.6}WO_3$, $Pb_{0.25}WO_3$, or small quantities of WO_3 is close to that of pure graphite electrodes whereas the activity of the mixtures of graphite and the inert $BaSO_4$ decreases with the quantity of the sulphate present. This shows that the electrochemical reduction proceeds mostly on graphite and only to a small extent on the compounds of tungsten. This holds mainly for mixtures containing the lead tungsten bronze whose activity is maintained up to the content of 80% $Pb_{0.25}WO_3$ on the same level as that of the pure graphite electrodes.

The behaviour of pure WO_3 shows that above $0.5-0.7$ V no oxygen is reduced; this is in agreement with measurements made with sodium tungsten bronze single crystal electrodes. The basic analogy between the behaviour of electrodes containing bronzes and WO_3 has recently been confirmed by Randin[12], and is probably due to the fact that above 0·3 V the surface of the bronzes is oxidized and the composition of its surface layer is close to WO_3. The surface of WO_2, too, seems to be oxidized at higher potentials and its electrochemical activity thus falls. Contrary to that, pure WO_3 is, at lower potentual values, reduced to form H_xWO_3 which is probably a conductor and seems to be responsible for the electrochemical activity of WO_3 found below 0·3 V.

It follows from the above results that sodium and lead tungsten bronzes both pure and mixed with graphite, if employed for preparing hydrophobic porous gas diffusion electrodes for the reduction of oxygen in an acid medium, exhibit equal properties as they do in the form of single crystals; this makes the previous promising results[1−3] rather dubious. The results presented in this paper further imply that an addition of electric conductors, for instance graphite, may greatly influence the electrochemical properties of the resulting mixtures. The contribution of the individual components of such mixtures on the electrode activity should, therefore, be considered with caution.

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