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ELECTROCATAYSIS BY THE BRONZES OF THE ELECTRODIC REDUCTION OF OXYGEN TO WATER

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Abstract

The increasing importance of the oxygen reduction reaction both to the fuel cell and to the storage battery makes the development of an economically feasible oxygen electrode an urgent problem. One approach is to find chemically stable substitutes for the noble metals now used as catalysts, and the so called "bronzes" have been investigated here for this purpose. These materials are nonstoichiometric mixed oxides with the general formula M_xTO_3 (where M is an alkali or alkaline earth metal, x lies between 0 and 1, and T is one of the transition metals Ti, V, Nb, Mo, Ta, W), and have electronic conductivities approaching those of metals. Particular emphasis was placed upon the tungsten bronzes. In acids, the bronzes exhibited eleoctrocatalytic activity comparable with that of platinum, *e.g.*, the exchange current density i_0 on Na_xWO_3 in solution of $pH=0.3$ under 1 atm. pressure of O_2 ranged from 0.5×10^{-9} to 5×10^{-9} A cm^{-2}. In this case, i_0 varied systematically with x, passing through two maxima at $x=0.4$ and 0.6 respectively. The two maxima are discussed in the light of related observations by other workers. In alkaline solution, electrodes of the tungsten bronzes were subject to chemical attack when used for oxygen reduction, while bronzes of niobium and tantalum proved stable, and exhibited i_0 values superior to those on platinum.

Introduction

The catalysis of oxygen dissolution to form water

The four electron reduction of oxygen to water is technically the most important reaction in electrochemistry today, not only because it finds such

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wide application in electrochemical energy converters, but also because of a growing emphasis upon the development of electrochemical energy storers in which one of the electrode reactions involves dissolution of oxygen on discharge, and evolution during charge.

The accelerative effect of the interfacial electric field at electrocatalysts has one disadvantage when one compares chemical and electrochemical interfacial reactions: the field tends to make atoms in the substrate take part in a charge transfer reaction and contribute to the net current flow, thus destroying the catalyst. The probability that the catalyst substrate itself will be used up increases with the increasing positive character of the (thermodynamically calculable) range of potentials in which the reaction to be catalyzed occurs.

Herein lies the difficulty of finding suitable catalysts for the oxygen dissolution reaction. The standard reversible potential for the reaction in acid solutions is +1.23 volts. Even when the electrocatalyst is giving electrons to oxygen, the potential still remains in the region +0.8 to +1.1 volts. In this range, most metals dissolve. Hitherto, it has been only the noble metals which have been known to retain sufficient stability under these conditions *i.e.*, to be effective catalysts for oxygen dissolution. The consequence that they alone have had to be used as electrocatalysts for the dissolution of oxygen in acid solutions (and sometimes also in alkaline solutions) has the obvious economic disadvantage.[*]

In addition, it has led to the misconception that "platinum is the only good catalyst for the electro-dissolution of oxygen". In fact, the exchange current density for the electro-dissolution of oxygen on Pt into acid solutions at 25°C is in the region of 10^{-10} A cm^{-2} (*i.e.*, about 3.10^{-16} moles cm^{-2} sec^{-1}).[2] By comparison, the exchange current density for the electro-dissolution of hydrogen on Pt is in the region of 10^{-3} A cm^{-2} (5.10^{-9} moles cm^{-2} sec^{-1}),[3] and, the *slowest* exchange current density for hydrogen evolution is in the region of 10^{-12} A cm^{-2}.[4] Thus, although noble metals are better than any previously known catalysts, they still catalyse the electro-dissolution of oxygen to form water very poorly. Their exclusive use hitherto as catalysts for the dissolution of oxygen in acid solution derives from their stability under the highly positive potentials at which cathodic oxygen dissolution characteristically

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[*] But *cf.* the recent work of BOCKRIS and CAHAN,[1] who used interferometric methods to measure the thickness of the meniscus in certain porous electrode analogues, and then set up electrode kinetic equations to find how the current varied with distance in pores. The essential result was that nearly all the current is obtained from a tiny area of the pore. A large fraction of the catalyst in present electrodes is wasted. Were it possible to make an electrode in which the noble metal catalyst is at the point of maximum activity only, about 1% of present catalyst loadings would be required.

occurs.

These observations lead to the following possibilities for improvement in the situation for oxygen reduction catalysis.

(1) By seeking conductive materials stable at potentials c. 1.0 volts anodic to the reversible hydrogen potential in the same solution.

(2) By synthesizing (or providing) redox systems (probably oxygenic) which will accept and reject electrons rapidly at conducting surfaces and then undergo fast homogeneous redox equilibrium with dissolved oxygen.

(3) By the use of accelerative radiations (*cf.* radioactive emissions,-SCHWABE ;5) or photoacceleration-VESELOVSKII.6))

(4) By the use of very small quantities (*e.g.*, 1 gram per killowatt) of noble metal catalysts (BOCKRIS and CAHAN).1)

In respect to the search for new catalysts, the basic difficulty is that relatively little investigation of the rate-determining step of the oxygen dissolution reaction has hitherto been done. Even what *has* been done usually suffers from a fundamental limitation which makes much of the information obtained of little application to research on the electrodic dissolution of oxygen on platinum in a practical potential range. This situation does not arise in a simple way. The very low exchange current density of oxygen dissolution on noble metals means that, within, say, 0.2–0.3 volts of the reversible potential, the current density at an oxygen cathode is less than 1 μA cm^{-2}. Systems which have not been rigorously purified from electroactive constituents other than oxygen (the impurities are usually organic and are often present in the oxygen), contain adventitious substances at a sufficient concentration that *they deliver* electrons to the electrode surface at a rate comparable with that at which oxygen removes them. Hence, the currentless potential of the oxygen electrode differs from that which would be set up if the reactions across the interface were exclusively those of oxygen reduction and water oxidation at equal and opposite rates.

There is thus a region between about 1.23 and 1.0 volts, in which, except in superpurified situations the impurities contribute to the current and effectively decrease the rate of oxygen reduction (WROBLOWA, DAMJANOVIC, RAO and BOCKRIS7)).

The removal of the effective reaction zone to potential regions negative to +1.0 volt, has then the consequence that the oxygen *dissolution* reaction takes place on a surface which is free from oxide. (DAMJANOVIC, GENSHAW and BOCKRIS8)). However most of the mechanistic data on the reaction

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O$$

has been obtained with the reaction functioning *anodically*,—oxidizing water,— and thus on an oxidized surface (positive to 1.2 volt). Often, one *can* obtain information on the mechanism of a cathodic reaction from data concerning its anodic functioning and vice versa. However, it has been shown that the change of surface from metal to oxide changes both mechanism and rate (DAMJANOVIC and BOCKRIS⁹⁾). Only one study exists in which the mechanism of oxygen reduction was examined at surfaces prepared so that they were free from oxide, and hence that is relevant to the reduction of oxygen in acid solution (DAMJANOVIC, BRUSIC and BOCKRIS;¹⁰⁾ DAMJANOVIC and BRUSIC²⁾). The rate-determining step there suggested for the planar surface of Pt substrate was the first electron transfer. This background gives little information on which to orient oneself in the search for electrocatalysts more suitable than platinum. One must seek:

(a) Sufficient electronic conductivity so that currents may be passed up to 1 A cm^{-2}. If the thickness of the electrode material is as low as 10^{-4} cms (a feasible thickness for layers on more economical conducting substrates), then for an ohmic polarization of 0.01 volts, the specific resistivity can be as high as 10^2 ohms cm, and even organic semiconductors could be considered. However, a limitation for organic semiconductors is the minimum current associated with the flow of charge carriers to the interface.

(b) The velocity of dissolution of the substrate must be negligible (μA cm^{-2}) in potential regions as anodic as 1 volt (N acid solution). This implies maximizing the heat of sublimation and minimizing the solvation energy of the final state of the rate-determining step in the dissolution reaction.¹¹⁾

(c) The bond strength of the substrate and oxygen must be optimized. It is probable (*cf.*, *e.g.*, KUHN, WROBLOWA and BOCKRIS¹²⁾) that the plot of the rate of dissolution of oxygen at constant Galvani potential difference against heat of sublimation would pass through a maximum. This criterion of optimization may clash with the demand of (b) for maximum lattice energy, because the MO bond strength will tend to increase with increasing sublimation energy of the metal (PAULING¹³⁾) so that a sufficiently stable substrate may not be reached until the MO strength is passed that for maxium oxygen dissolution rate.

It follows from the above orienting material that a catalyst for the electrodissolution of oxygen with velocity greater than that on platinum should not be sought among the metals. Its likely origin could be among semiconductors (*cf.* MEHL and HALE¹⁴⁾); passive oxides, the electronic conductance of which has been raised by suitable additions; or inorganic compounds, which have a suitably large electronic conductivity. Here, an investigation is described which was focused upon the last aspect. A number of compounds were examined on the basis of high electronic conductivity and sublimation energy alone. Of these, $Na_{0.6}WO_3$ showed the greatest activity and led to the investigation of bronze-like compounds.15) Briefly the bronzes are non-stoichiometric compounds with the general formula M_xTO_3, where M is an alkali or alkaline earth metal, x lies between 0 and 1, and T is one of the transition metals Ti, V, Nb, Mo, Ta, W. A good survey of the bronzes is given by WADSLEY.16) At the basis of this investigation were three alternative working hypotheses.

(i) There is no special electrocatalytic activity of the bronzes and the main point about them is the resistance to anodic dissolution. Thus tungsten bronzes, for example would be no worse than platinum. (In watts per unit of initial investment in an electrochemical generator, they would be greatly advantageous). This hypothesis can be tested by examining variables which alter the heat of sublimation of the substrate (*e.g.*, change of W to Ta, *etc.*). One would expect little change of rate with MO bond strength.

(ii) The rate-determining step for this O_2 dissolution is

$$T-O_2+e \longrightarrow O_2^-$$

(*cf.* DAMJANOVIC and BRUSIC2)). It will pass through a maximum at relatively small $T-O_2$ bond strengths. There will be a strong dependence on T, where T is the transition element, *e.g.*, W, Ta, *etc.*

(iii) The rate depends largely upon the Fermi level of the substrate, which will be affected by the content and nature of the alkali metal. This does not seem a likely hypothesis in view of the primary independence of electrodic reaction rates (measured by the exchange current densities) upon work function.*) The view can be tested by obtaining rate as a function of alkali metal content with constant transition metal.

Experimental

1. Preparation of Samples

The alkali metal tungsten bronzes for this investigation were prepared in two ways: by electrolytic reduction,17,18) and by thermal reduction.19,20) Bronzes of niobium and tantalum were synthesized by the U. S. Bureau of Mines, Pittsburgh Coal Research Center, using the thermal method.21,22)

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*) It is the heat of activation for the reaction which remains independent of work function (BOCKRIS, DAMJANOVIC and MANNAN3)). There may be a secondary dependence on work function, even in weakly-bonding situations, because of the relation of Φ to the potential of zero charge and hence a connection of Φ to the potential of the layer of reactant charges at the electrode.

Bronzes of molybdenum and vanadium were prepared using the electrolytic reduction method[23,24] in the Institute for Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia.

i. Preparation of tungsten bronzes by electrolytic reduction

Sodium tungsten bronzes, Na_xWO_3 of compositions $0.37<x<0.89$, were prepared by electrolytic reduction of a fused mixture of reagent grade sodium tungstate and purified tungsten trioxide (Fisher Sci. Co.). Electrolysis was performed in a platinum crucible, because porcelain and quartz crucibles were attacked by the melt. Wires of tungsten, platinum or gold were used as cathodes in different experiments. The anode was a cylindrically shaped sheet of platinum or gold.

Depending on melt composition, electrolysis was carried out at temperatures between 700–750°C. The temperature was monitored with a Pt-PtRh (13%) thermocouple.

The crystals were grown on the cathode at current densities of about 10 mA cm^{-2}, applied potential being altered appropriately during growth. The product of electrolysis was firmly attached to the cathode. The size of individual crystals varied with the composition of the melt and increased with the proportion of sodium. The crystals in sodium rich samples were cubes, the largest being about 10 mm along an edge, while the crystals in samples with lower contents of sodium were rhombohedra, the largest being 2–3 mm along an edge. The change in morphology of sodium tungsten bronze crystals from cubes to rhombohedra was observed between $0.63>x>0.60$.

Samples removed from the fused mixture of sodium tungstate and tungsten trioxide were covered with a thick layer of solidified melt. The cleaning procedure consisted of alternate washings in hot concentrated solutions of sodium hydroxide and sulfuric acid, followed finally by thorough rinsing with distilled water. The sodium content in tungsten bronzes was determined by X-ray measurements of the lattice parameters using the relation,[25~28]

$$a_0 = 0.082x + 3.7845 \ (\text{Å}).$$

Some attempts were made to synthesize lithium, potassium and cesium tungsten bronzes by the same procedure. The resulting samples dispersed into small grains upon washing.

ii. Preparation of tungsten bronzes by thermal reduction

The electrolytic reduction method could not be satisfactorily used for the preparation of samples of sodium tungsten bronzes with compositions $x<0.37$, or for tungsten bronzes with alkali metals other than sodium. These bronzes were prepared by a thermal reduction method. A mixture of fine powders (particle size less than 40 microns) of tungsten, tungsten trioxide and alkali metal tungstate (K & K, Rare and Fine Chemicals) in the stoichiometric ratio for the wanted composition, was heated in an alumina boat in a Burrell furnace, model H–1–9. Reaction occurred in an atmosphere of prepurified argon at 1000°C. The substances were kept in contact for about 6 hours. Thereafter, reaction products were cooled in a stream of argon. The products were fine crystalline powders, a substantial fraction being less than 50 microns. Washing procedure consisted of alternate boiling in 1 M NaOH to which H_2O_2 had been added, and in 1 M HCl, to remove all unreacted materials. Finally, the powder was washed with repeated decantations of distilled water.

The composition of each sample was deduced from the lattice parameter (obtained from an X-ray powder photograph) using information in the literature.24)

2. Stability determinations

Chemical stability of some sodium tungsten bronzes was determined as a weight loss of crushed crystals (about 1 mm in diameter) upon prolonged extraction with hot azeotropic HCl in a soxhlet apparatus, through which oxygen was bubbled.

The electrochemical stability was also investigated, using a radiotracer technique. Crystals of $x=0.57$, containing Na^{22}, were submitted to 1.9 V anodic potential in perchloric acid solutions of $pH=0.1$ and 1.8. Readings of counting rates were taken daily for 15 to 20 days. Qualitative evidence about the stability of other bronzes was also acquired by observing their resistance to dissolution in 1 M H_2SO_4.

3. Electrochemical Investigations

i. Electrodes

Two types of electrode were used.*) All sodium tungsten bronzes in the composition range $0.37<x<0.89$ were used as electrodes in the form in which they were prepared. The wire on which the crystal grew was isolated from solution by teflon or polyethylene, as is shown in Fig. 1. The area of these electrodes was determined by measuring the surface area of each crystal plane, and adding the areas together. All of this geometric area was assumed to be available to the current.

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*) It is important, if the primary objective be the investigation of the electrocatalysis of the situation, that investigations are made on clearly defined surfaces and not *e.g.*, on any of the several types of porous electrode structures because of the lack of definition of what is the active zone in such arrangements.30)

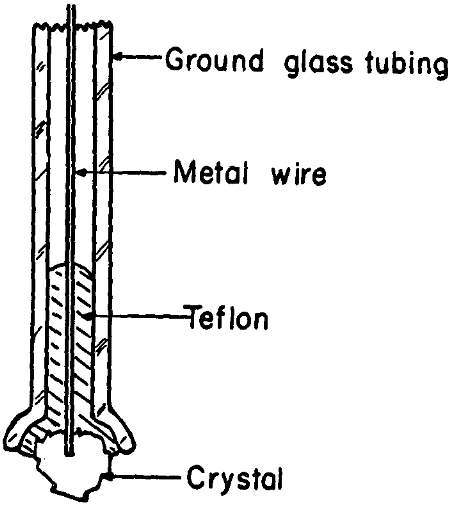

Fig. 1. Sodium tungsten bronze crystal electrode

The materials outside the above composition range were investigated with a second type of electrode in which bronze particles were embedded in a matrix of gold. The gold did not appreciably affect the results obtained because it is a very poor electrocatalyst for oxygen dissolution: The equilibrium oxygen dissolution rate on gold is only about 10^{-12} A cm^{-2} in acid solution.[29,30] Bronze powders were sieved. The size of particles used in these specimens was between 53 and 149 microns, with the exception of sodium, potassium and rubidium tungsten bronzes, when particle size was less then 37 microns. A mixture of gold (Fisher Sci. Co.) and bronze powders was homogenized and then pressed into a solid cylinder. Samples were pressed with approximately 12 ton/cm^2 at room temperature, and at a 2:1 volume ratio of gold to bronze.

The porosity of a pressed sample of pure gold was evaluated in the following way. The density of the pressed gold specimen was 7% less than that of solid gold. The volume of water that could be taken up by the gold specimen was 8% of its total pore volume. The influence of such pores on the total working area of the electrodes was considered to be insignificant, because of the severe limiatation upon diffusion of the reaction species.[31]

After pressing, the samples were treated with a high anodic current in concentrated HCl solution, to remove all loose particles on the surface and to dissolve some layers of gold in order to open more sites for the catalyst.

Thereafter, samples were boiled in approximately 1 N HCl solution to dissolve gold oxide. Finally, after rinsing with distilled water, the samples

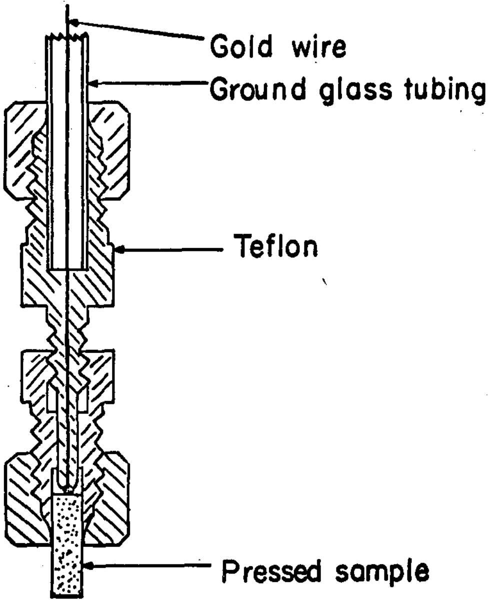

Fig. 2. Pressed powder electrode

were mounted in a teflon holder (Fig. 2). The area of the catalyst on the surface was estimated from a low power photo micrograph of a representative part of the surface.

ii. Cell, gases, solutions

Experiments were carried out in an all-glass, three compartment cell, essentially the same as described previously.[32,33)]

Oxygen, and all mixtures of oxygen and nitrogen, were purified by passage through a heated platinum asbestos column, and dry ice cold-traps with molecular sieves (Linde, types 4A and 13X).

The measurements at various partial pressures of oxygen were achieved by using appropriate mixtures of gases, made up by Baker Chemical Co.

Acid solutions were prepared with analytical grade sulfuric acid or perchloric acid, and conductivity water. Sulfuric acid was treated with H_2O_2 as recommended by VISSCHER and DEVANATHAN,[34)] but no differences in the behavior of the system were observed. Anodic pre-electolysis was carried out in some experiments but no appreciable influence on the rate of the electrodic reactions was noticed.

iii. Measurements

Galvanostatic measurements of cathodic and anodic Tafel lines were carried out. Potentials were measured with Keithley 600 or 610 electrometers, and recorded on a Hewlett Packard 7000A X–Y recorder. Potentials were measured against a hydrogen electrode in the same solution or, in some experiments, against a saturated calomel electrode. Steady state potential readings were taken, which were achieved after 1/2 to 5 minutes, depending on current density. Currents were measured with a Keithley 414 microammeter.

In the case of electrodes sintered with gold, only cathodic Tafel lines for the dissolution of oxygen were measured because gold dissolves at potentials where the anodic Tafel line would lie. Measurements were also made on pure gold electrodes, prepared under the same conditions, to confirm that reaction on the electrode in the presence of the catalyst was as least 10 times faster than on pure gold.

Results

Chemical stability of bronzes

The stability of the bronzes to chemical dissolution is summarized qualitatively in Table I. Quantitative results obtained on a series of Na–W bronzes appear in Fig. 3. The stability depends primarily on crystal structure and on the stability of the corresponding transition metal oxide. Bronzes of Nb, Ta and W which had the Perovskite structure exhibited good stability in acids even at the high positive potentials of oxygen evolution. An effect of sodium content on the stability of the Na–W bronzes was observed (Fig. 3). Samples dissolved at an average rate of only 0.5 gms cm^{-2} $year^{-1}$ (0.05 cms per year). The dissolution rate at +1.9V in perchloric acid solution as measured by the radio tracer technique was of the order of 0.2 g cm^{-2} yr^{-1} at pH=0.1 and 0.001 gm cm^{-2} yr^{-1} at pH=1.8. Bronzes of V and Mo, which had distorted Perovskite structures, dissolved readily in concentrated acids and alkalies, a fact that eliminated them from further consideration.

TABLE I Chemical stability of bronzes under various conditious

	M_xVO_3	M_xNbO_3	M_xTaO_3	M_xMoO_3	M_xWO_3
Acid	Poor	Good	Good	Poor	Good
Acid, oxygen, anodic potential	—	Good	Good	—	Good
Alkali	Poor	Good	Good	Poor	Good
Akali, oxygen	—	Good	Good	—	Fair
Alkali, oxygen, anodic potential	—	Good	Good	—	Poor

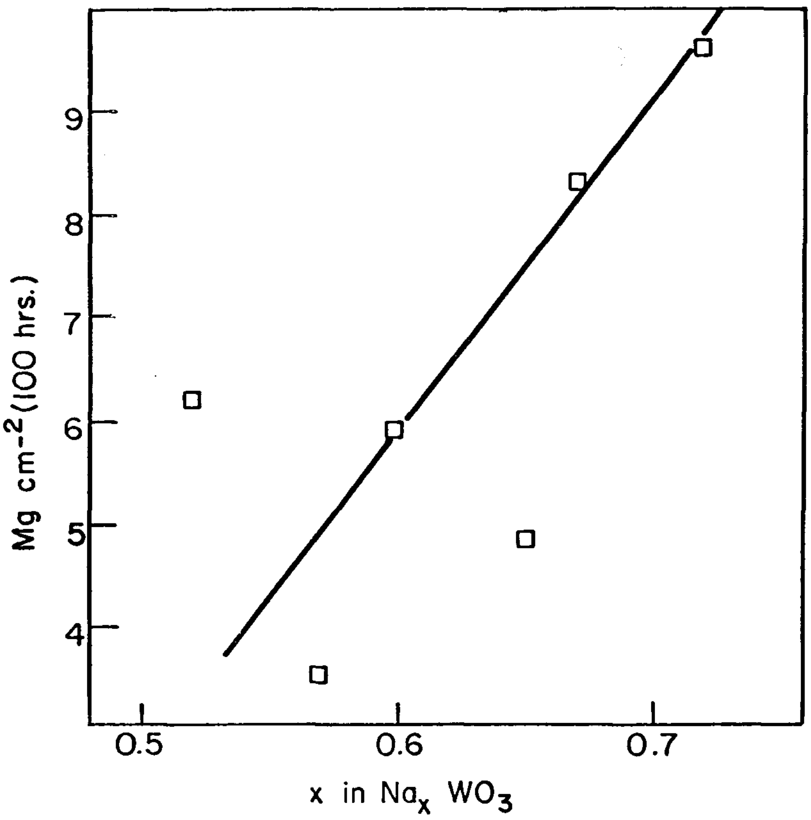

Fig. 3. Loss of weight of sodium tungsten bronzes in oxygen saturated hot azeotropic HCl.

The niobium, tantalum and tungsten bronzes all resisted dissolution in alkaline solution when oxygen was excluded, but the tungsten bronzes were visibly attacked in oxygen saturated solution, and dissolved readily at the high positive potentials of oxygen evolution. The niobium and tantalum bronzes showed no signs of attack under any conditions.

Reaction order with respect to O_2

A current-potential plot typical of all those obtained is shown in Fig. 4. Tafel lines were apparent on both anodic and cathodic branches. The position of the cathodic Tafel line could be shifted by changing the partial pressure of oxygen, and the cathodic current density at any given potential changed in direct proportion to the change in oxygen pressure. It follows that the reaction was of first order with respect to oxygen, and this fact eliminates the possibility that oxidation or reduction of the electrode material was re-

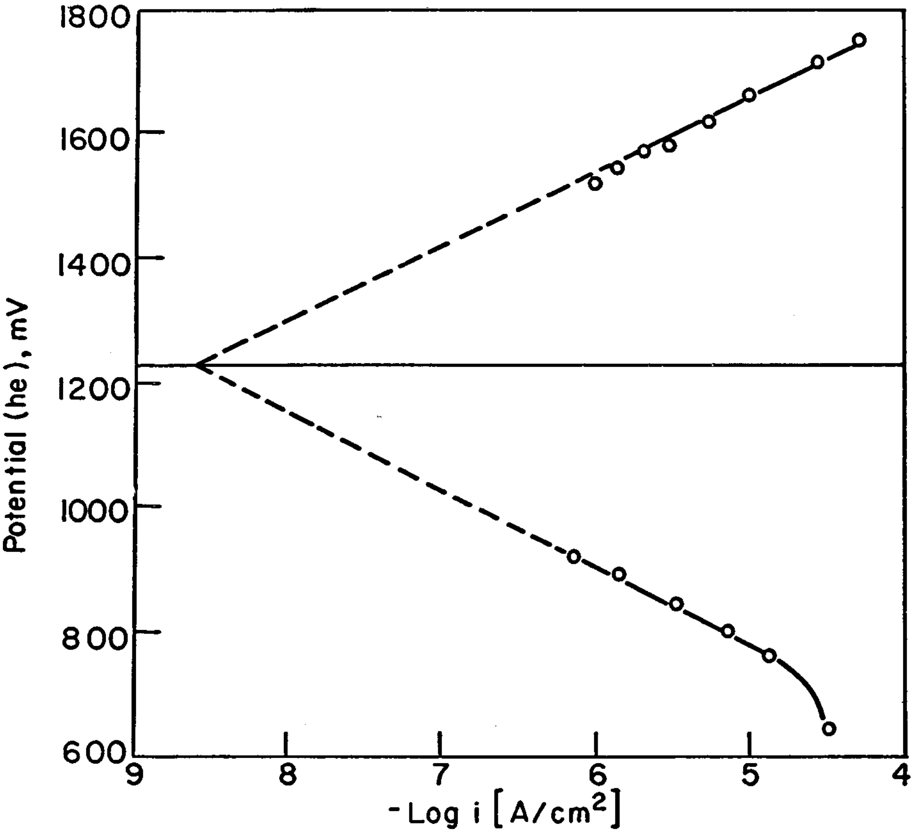

Fig. 4. Typical Tafal plot for oxygen reaction on tungsten bronzes

sponsible for the currents observed.

Reaction order with respect to H^+

Three types of pH effect were observed, depending on the composition of the bronze. The effects are summarized in Table II in terms of the rate of change of cathodic and anodic partial currents respectively with pH at constant potential. This comparison is more meaningful than a simple comparison of i_0 values at different pH's because the reversible potential itself is a function of pH.

The results in Table II were deduced from the observed influence of pH upon i_0 and the values of anodic and cathodic Tafel slopes $(dV/d\log i)$ which were equal to $2RT/F$ in all cases examined. Bronzes of type III, being powders, were all made into electrodes with gold. Consequently anodic Tafel lines were not obtained for them and $(\partial \log i_a/\partial\, \mathrm{pH})_V$ could not be calculated.

TABLE II

Type	Bronze compositions	$\left(\frac{\partial \log i_c}{\partial \mathrm{pH}}\right)_V$	$\left(\frac{\partial \log i_a}{\partial \mathrm{pH}}\right)_V$
I	Na_xWO_3 for $0.37 < x < 0.6$	0	1
II	Na_xWO_3 for $0.5 < x < 0.78$	$-1/2$	1/2
III	M_xWO_3 for M=Li, K, Rb, Cs; $Na_{0.3}WO_3$; $Ba_{0.5}TaO_3$; $Sr_{0.8}NbO_3$	$-1/4$	—

Dependence of i_0 upon the transition metal constituent of the bronze

Table III provides a comparison of the exchange current densities observed on bronzes with niobium, tantalum and tungsten respectively, in solution of $pH = 0.3$ and under 1 atm. pressure of oxygen. Any difference in the value of i_0 among bronzes of comparable interstitial metal contents is probably less than one order of magnitude.

Dependence of i_0 upon the interstitial metal content of the bronze

Exchange current densities on a number of tungsten bronzee appear in Table IV. The dependance of i_0 upon the sodium content of sodium-tungsten bronze is shown for solutions of two pH values in fig. 5. Tungsten bronzes containing sodium support exchange currents of one order of magnitude higher than those on tungsten bronzes with other alkali metals. Two maxima exist at about $x = 0.4$ and $x = 0.6$ respectively. The maxima reflect neither crystal

TABLE III Values of exchange current densities of oxygen reduction at bronzes of different transition metal ($pH = 0.3$; $p_{O_2} = 1\,\mathrm{atm}$)

Bronze	$i_0\,(\mathrm{A \cdot cm^{-2}})$
M_xWO_3*)	1 to 50×10^{-10}
$Sr_{0.8}NbO_3$	1.5×10^{-10}
$Ba_{0.5}TaO_3$	3×10^{-10}

*) Range of values for bronzes of different alkali metals and alkali metal contents ranging between 0.3 and 0.8.

TABLE IV Exchange current densities on tungsten bronzes in solution of pH = 0.3

Substance	A·cm^{-2}
$Li_{0.40}WO_3$	1.5×10^{-10}
$Li_{0.30}WO_3$	1×10^{-10}
$Na_{0.78}WO_3$	2×10^{-9}
$Na_{0.70}WO_3$	1×10^{-9}
$Na_{0.67}WO_3$	1×10^{-9}
$Na_{0.62}WO_3$	5×10^{-9}
Na_xWO_3	2×10^{-9}
$Na_{0.37}WO_3$	5×10^{-9}
$Na_{0.30}WO_3$	5×10^{-10}
$K_{0.50}WO_3$	1.5×10^{-10}
$K_{0.30}WO_3$	1×10^{-10}
$Rb_{0.30}WO_3$	2.5×10^{-11}
Cs_xWO_3	4×10^{-10}

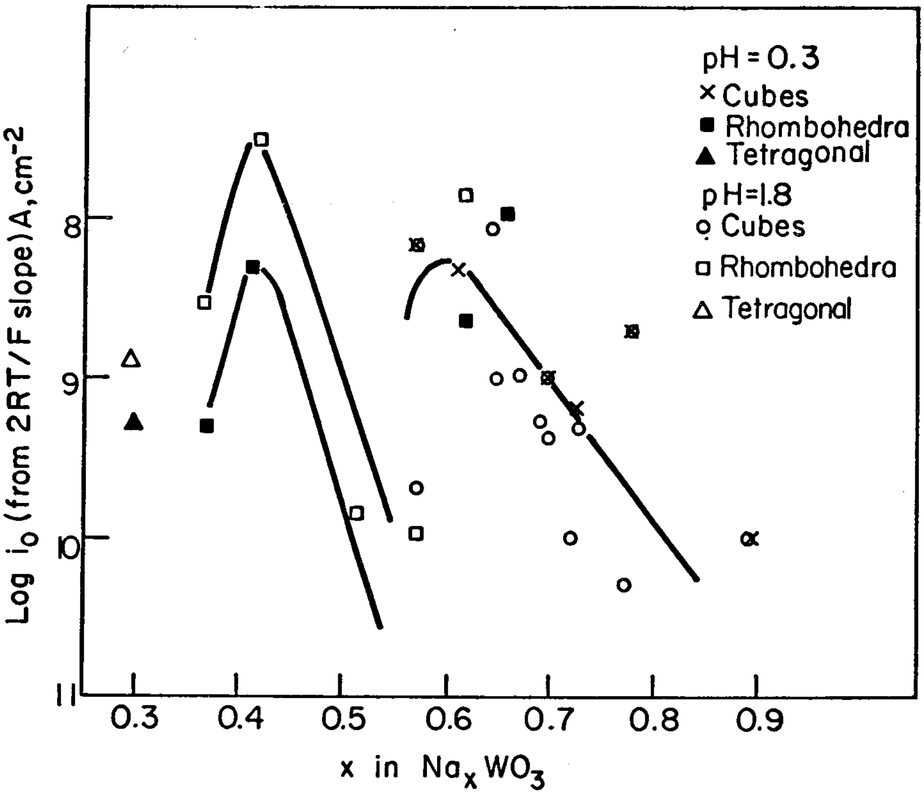

Fig. 5. Variation of i_0 values with composition.

structure nor crystal morphology: points corresponding to rhombohedra overlap considerably with those corresponding to cubes.

Comparison of electrocatalysis on bronze and platinum

Fig. 6 is a comparison of current-potential curves for oxygen dissolution on platinum and on a sodium-tungsten bronze in 0.05 molal H_2SO_4 solution.

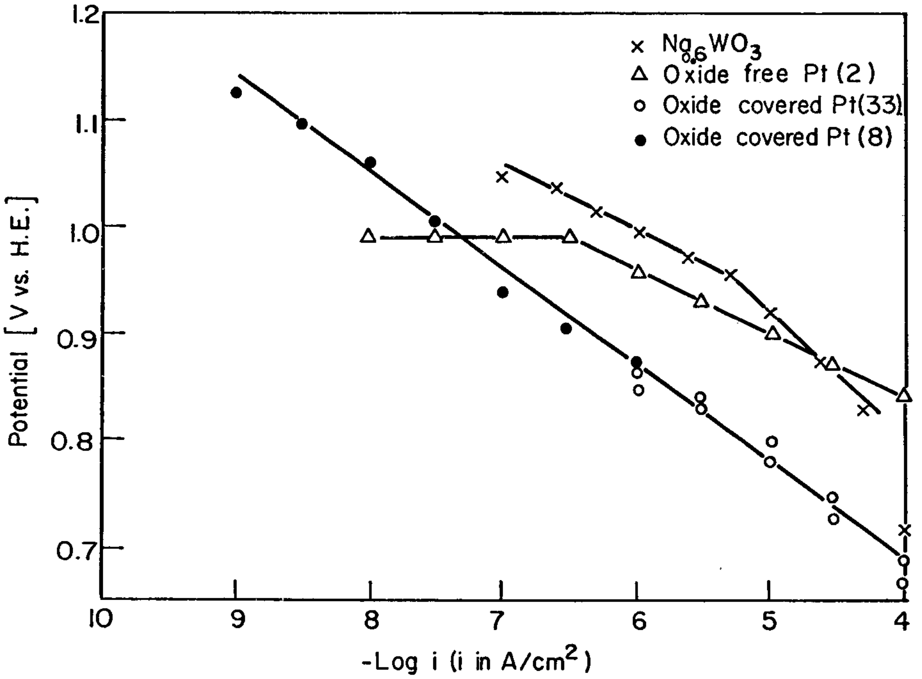

Fig. 6.

TABLE V Comparison of Pt with two bronzes as oxygen electrodes in solution of pH = 12.5

	i_0	Cathodic Tafel slope $\left(\frac{dV}{d \log i_c}\right)$
Pt[1]	2.5×10^{-12}	120 mV
Au	1.0×10^{-9}	120 mV
$Sr_{0.8}NbO_3$	3.0×10^{-7}	120 mV
$Ba_{0.5}TaO_3$	1.5×10^{-6}	120 mV

1) R. Parsons, *Handbook of Electrochemical Constants*, Butterworths, London, 1959.

Table V provides a comparison of electrochemical parameters for oxygen dissolution on platinum, strontium-niobium bronze and barium-tantalum bronze in alkaline solution. Using overvoltage at a given current density as the criterion, these comparisons show that in acid solution, electrocatalysis is quite similar on bronze and platinum. *In alkaline solution, however, electrocatalysis is considerably better on some bronzes than on platinum.*

Conclusions

1) Bronzes based on WO_3, Nb_2O_5, and Ta_2O_5 provide stable substrates for the oxygen electrode reaction in acid solutions and bronzes based on Nb_2O_5 and Ta_2O_5 provide stable substrates in alkaline solutions.

2) Electrocatalytic activity of the stable bronzes is similar to that of platinum in acid solutions, but is superior to that of platinum in alkaline solutions.

3) In acid solution, electrocatalytic activity of Na_xWO_3 varies somewhat with x, and two maxima in i_0 occur at $x=0.4$ and 0.6 respectively. The first maximum is apparently related to the bronze-oxygen bond strength, and the second may be related to the Fermi energy of the bronze.

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