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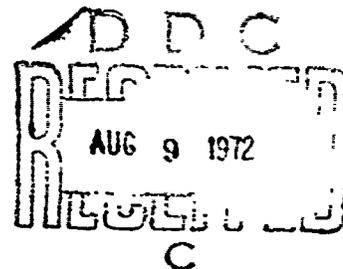
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ELECTROLYTIC PREPARATION AND EVALUATION
OF TUNGSTEN BRONZES

John A. Christopulos

June 1972



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13. ABSTRACT Mixed sodium-iron tungsten bronzes were electrolytically prepared from melts of tungstic oxide, sodium tungstate, and ferrous tungstate. Corrosion experiments indicated that these bronzes corrode at less than 10^{-6} g hr ⁻¹ cm ⁻² in 1F HClO ₄ and 1.25×10^{-3} g hr ⁻¹ cm ⁻² in 1F KOH under an oxygen pressure of 1 atm. The corrosion rate in 1F KOH appeared to be directly proportional to the oxygen partial pressure. Results of galvanostatic steady-state experiments for oxygen electroreduction in acid solutions are in agreement with existing knowledge that the rate determining step (r.d.s.) is a charge transfer step. In KOH, r.d.s. is not a simple charge transfer but some other process.			

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ELECTROLYTIC PREPARATION AND EVALUATION OF TUNGSTEN BRONZES

INTRODUCTION

Metal-air batteries and fuel cells have potential applications as power sources for Army communication and surveillance equipment. The need of a low-cost air-cathode for these systems is important since the present air-cathodes use expensive platinum or platinum alloys which increase unit cost. The difficulty of finding suitable catalysts for air-cathodes lies in the fact that most electronically conductive materials corrode at potentials at which oxygen is reduced (1.23 V vs SHE in an acid solution). The question of chemical and electrochemical stability, therefore, appears to be of primary importance in selecting suitable substitutes for presently used precious-metal catalysts. The tungsten bronzes offer promise of satisfying some of the requirements for an oxygen electrode¹ with properties such as good electronic conductivity and fair chemical stability over at least a limited pH range. The tungsten bronzes^{2,3,4} are nonstoichiometric compounds with the empirical formula, M_xWO_3 , in which M is an alkali metal (Na) and x has a value of between 0 and 1. The tungsten bronze, Na_xWO_3 , is known to have perovskite structure (Fig. 1). The cell is a body-centered cube with tungsten at the center and orthogonally surrounded by six oxygen atoms at the face centers. The corners of the cube are the eight interstitial sites available for, but not completely occupied by, sodium atoms.

The tungsten bronzes have shown to be good catalysts for oxygen electroreduction in acid electrolytes.^{1,5} Their performance can be improved by doping with trace amounts of tantalum and zirconium oxides.⁶

This report describes a study of the electrolytic preparation of mixed sodium-iron-tungsten bronzes and their chemical and electrochemical properties during oxygen reduction in both acid and alkaline solutions. The technique for the electrolytic preparation of these bronzes is similar to that employed by others⁶ except that "dopant" additives were introduced into the melt as tungstates instead of oxides.

EXPERIMENTAL PROCEDURE

Preparation of Bronzes

The assembled cell is shown in Fig. 2. The cell consisted of 57 mm outer-diameter quartz tubing (A), 16" long, rounded at the bottom, and a ground-glass flange at the top. Attached is a side arm tube with a ball joint for outlet gas, located near the flange. High purity alumina crucible (B) (McDanel ACN100) was used for the melt and was placed at the bottom. The top (C) of the cell was made of pyrex and contained four standard tapered ($\frac{3}{8}$ 19/38) joints equipped with gas-tight Teflon swagelok fittings. This top contained a ground glass flange joint which was sealed with Apiezon wax to the lower quartz flange assembly. A small blower fan was projected toward the wax seal to prevent its melting during the heating

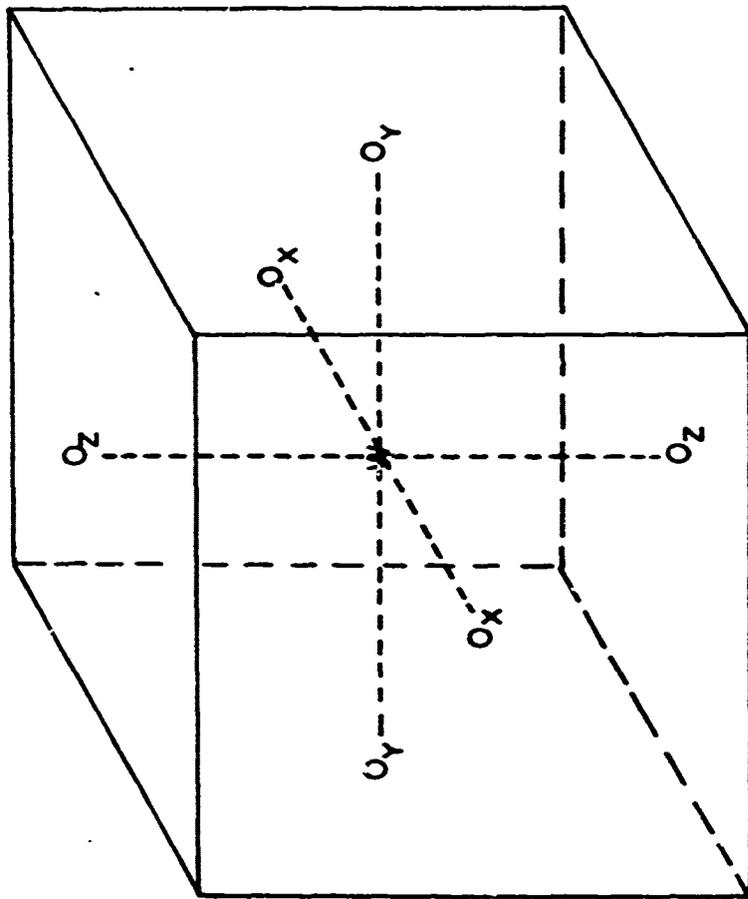


FIG. 1. STRUCTURE TUNGSTEN BRONZE M_xWO_3 $x=0$

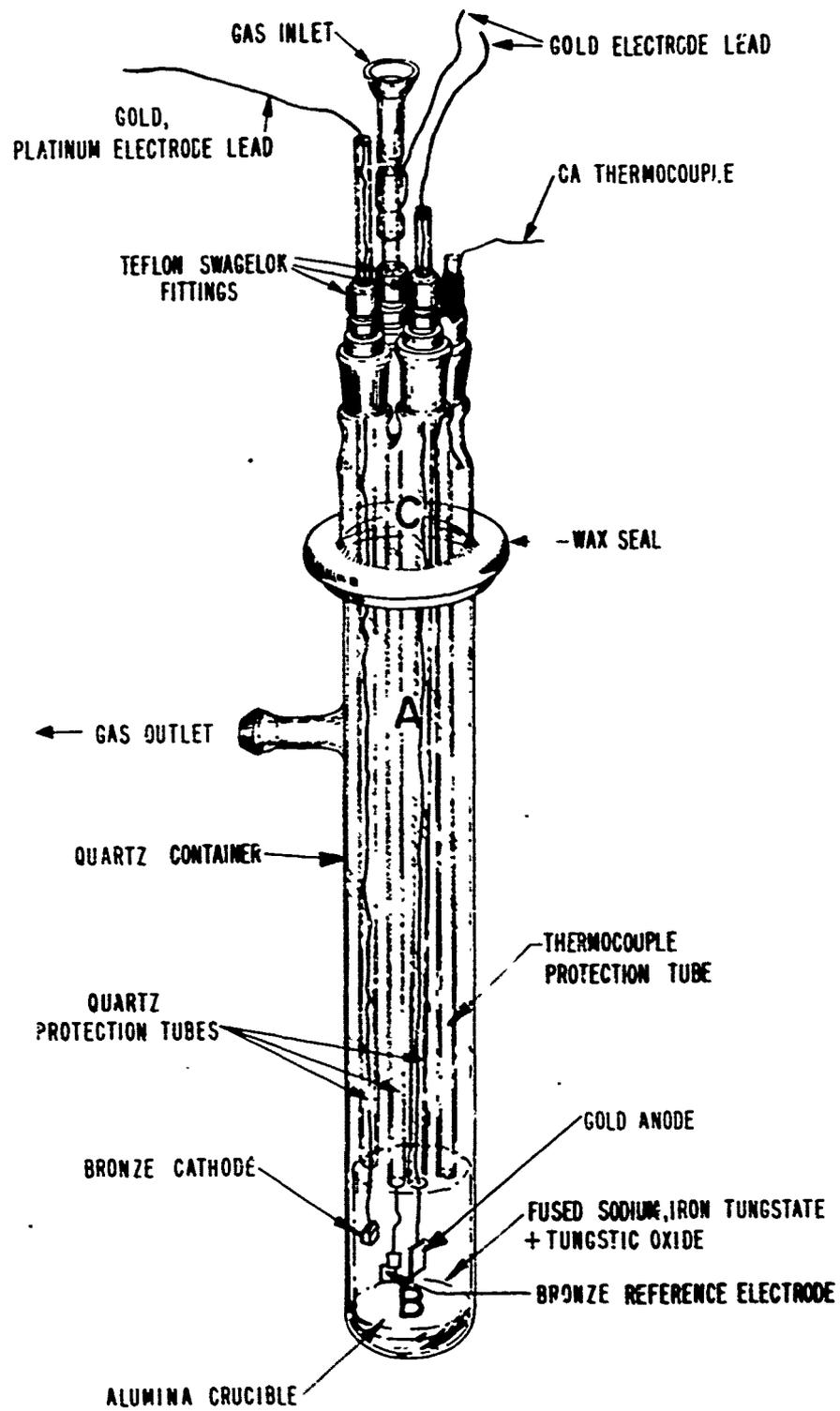


FIG. 2. CRYSTAL PREPARATION CELL

process in the furnace. All electrodes, one thermocouple, and the gas inlet were inserted into the cell through the Teflon swagelok fittings. The cell was heated in a vertical furnace and the temperature controlled to $\pm 3^\circ\text{C}$ by a West control unit (Model J.P.). A chromel-alumel thermocouple sheathed in alumina was used for temperature measurements of the melt. Reagents consisted of sodium tungstate (99.9%), tungstic oxide (99.9%) (both obtained from Fisher Scientific Company), and ferrous tungstate (99.9%) obtained from Alfa Inorganics, Inc. These reagents were dried at 110°C for 24 hours prior to use. Prepurified argon was obtained from Air Products.

Sodium iron-tungsten bronze was prepared by weighing 88.25 g Na_2WO_4 (58.8 mole %), 46.5 g WO_3 (39.24 mole %), and 3.03 g FeWO_4 (1.96 mole %) into an alumina crucible³ (B). The alumina crucible was placed into the quartz tube (A) and the tube sealed. The assembly was then placed into the vertical furnace and heated slowly, approximately 3 hours, to $735\text{--}750^\circ\text{C}$ at least 15°C higher than the fusion point of melt. When the reagents fused, the cell was flushed continuously with argon at a rate of $10\text{--}15\text{ cm}^3$ per minute. The thermocouple, sheathed completely in alumina, was well immersed into the reagents in the crucible from the beginning since these reagents contract upon melting. Two gold wires (.020" outside diameter (O.D.)), protected with quartz tubing, were then immersed into the melt and a constant current of 6 mA was passed through this melt for 28 hours. A bronze of multiple crystals was formed at the cathode (Fig. 3). A few small crystals of 1.5 mm cube were cut from the cathode using a diamond wafering machine. These cut crystals were used as seeds for potentiostatic growth of larger crystals. The original cathode bronze was then reimmersed and subsequently used as a reference electrode. A bronze seed was attached to a flattened platinum wire (.010" O.D.) by winding the wire around the seed. Larger crystals of 5 mm cube were first drilled using a S.S. White "airbrasive" unit producing a hole of .02" diam and then attached to a gold wire (.02" O.D.) by stringing and beading (melting) the end of the wire. If the seed were not a perfect cube, the potential was again cathodically adjusted to give a current of 2 mA until all the imperfections were filled in with bronze. Otherwise, the seeded cathode was lowered into the melt (contact was checked by using a conductivity bridge in conjunction with the immersed anode) and the bronze grown by maintaining the cathode potential at -78 mV with respect to the reference electrode using a Tacussel Potentiostat PRT 10-0.5. The anode again was gold foil (2 cm^2 area) attached to a gold lead. A Tacussel Generator GSTP 2 was used to offset the potential in conjunction with the potentiostat. Two Keithley 602 Electrometers were used to measure the potential and the current. Cathode versus anode measured -1.153V and the anode versus reference measured $+1.075\text{ V}$. After 24 hours, a perfect bronze cube had grown (Fig. 4). This crystal was reddish-brown in color and measured 5 mm on the side. The melt was washed from the crystal by boiling in distilled water. The platinum or gold lead was then sheathed with heat-shrinkable Teflon tubing to the point of contact with the bronze. Bronzes prepared in this fashion were used for both oxygen electroreduction and corrosion studies.



FIG. 3. GALVANOSTATICALLY GROWN BRONZE (MULTIPLE-CRYSTAL)

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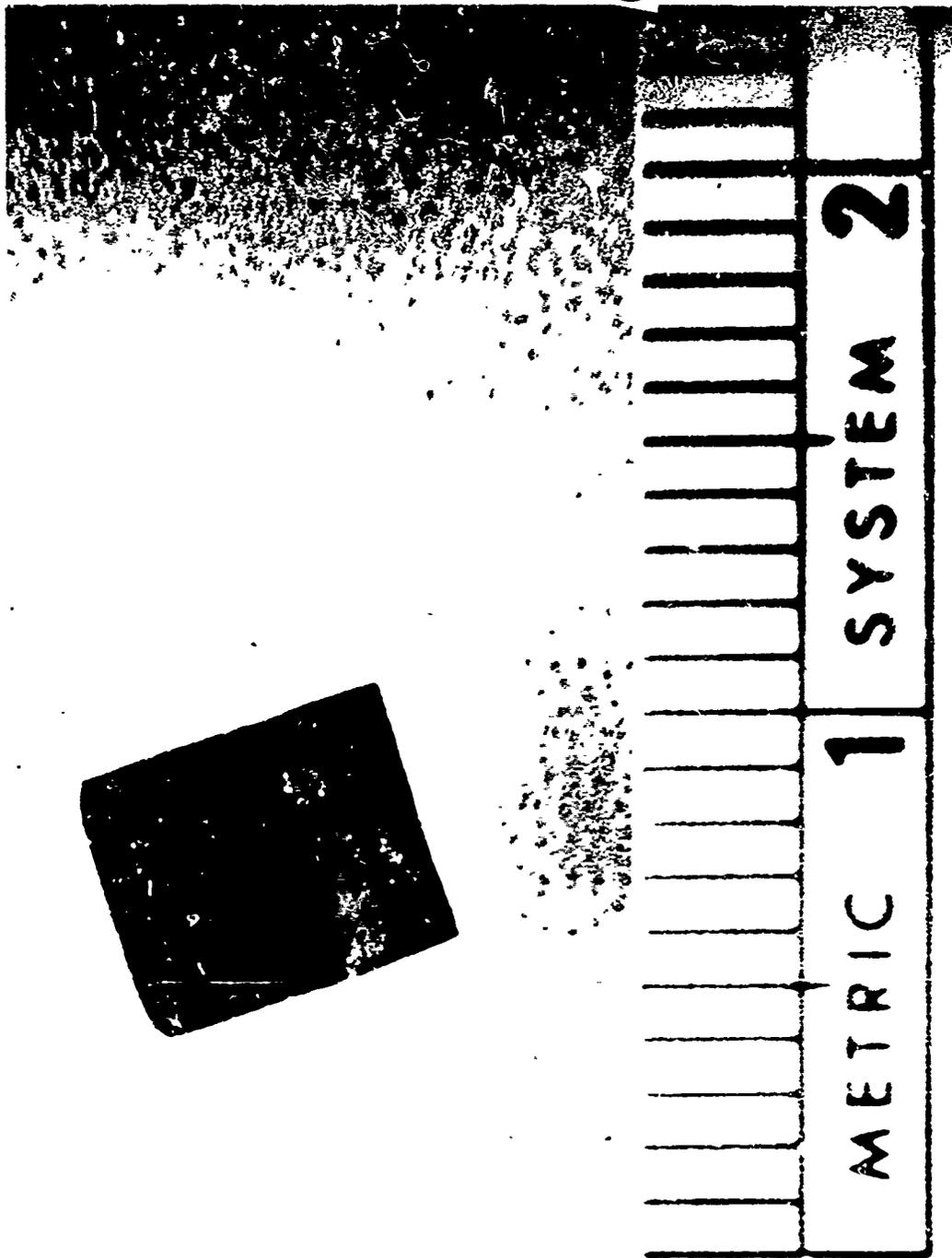


FIG. 4. POTENTIOSTATICALLY GROWN BRONZE (SINGLE-CRYSTAL)

Corrosion Stability of Bronzes

The rate of corrosion of the tungsten bronzes was determined gravimetrically in an oxygen or air saturated solution of either acid or alkali. The corrosion tests were performed in the same test cell (Fig. 5) as the oxygen electroreduction studies. The cell consisted of a single cylindrical Teflon compartment (250 ml capacity) with provisions for passing gas through or over the electrolyte. The cylindrical Teflon top is secured to the compartment with a Teflon gasket and six (6) stainless steel screws to insure gas-tight seals. The bronzes to be tested were all cubes of approximately 1 cm^2 (geometric area), immersed in the solution, and suspended from the top by a Teflon sheathed platinum or gold wire. This test cell was operated with a constant gas rate through the solution of $1 \text{ cm}^3 \text{ sec}^{-1}$ at $20 \pm 1^\circ\text{C}$. The acid or alkaline solution was always saturated with either oxygen or air. The length of time of any one experiment in alkali was between 22-48 hours. All experiments in acid solution required at least 100 hours duration to obtain measurable results. Before and after each experiment, the bronze electrode was first washed three times with distilled water and then oven dried at 110°C until a constant weight is observed ($\pm 0.05 \text{ mg}$). The tungsten bronzes were not found to be hygroscopic but were thermally stable within the temperature range ($20-110^\circ\text{C}$) utilized; therefore, minimum protection from the atmosphere was required during drying or gravimetric measurements. The rate of corrosion was defined as the loss in weight (grams) of the bronze on immersing in acid or alkaline solution divided by both the time (hours) of the experiment and the geometric surface area (cm^2) of the bronze.

Oxygen Electroreduction on Bronzes

The experimental cell for oxygen electroreduction studies is illustrated in Fig. 5. The Teflon cell (250 ml capacity) consisted of a central bronze working electrode (1 cm^2), an adjacent Luggin capillary with closed stopcock connecting either a saturated calomel or hydrogen reference electrode for potential monitoring, and an enclosing cylindrical gold foil counter electrode ($1\text{-}1/2$ " high x 2" diameter). The temperature, measured by a mercury thermometer, was maintained at $20 \pm 1^\circ\text{C}$.

The acids employed in these studies were 0.1F HClO_4 and 1F HClO_4 . All solutions were made with triply distilled water. Extensive purification was employed using constant potential preelectrolysis at large surface platinum electrodes (1.65 V between electrodes) for at least 16 hours at 20°C prior to the experiment. The purified electrolyte was transferred to the test cell in situ to avoid contact with the atmosphere. The alkali used was reagent grade 1F KOH without further purification. The gases used were purified oxygen and air from Air Products. In addition, all gases were bubbled through a solution identical to that in the cell prior to passage, thus maintaining a constant electrolyte composition. Both the temperature of the cell and the prebubbler were at 20°C .

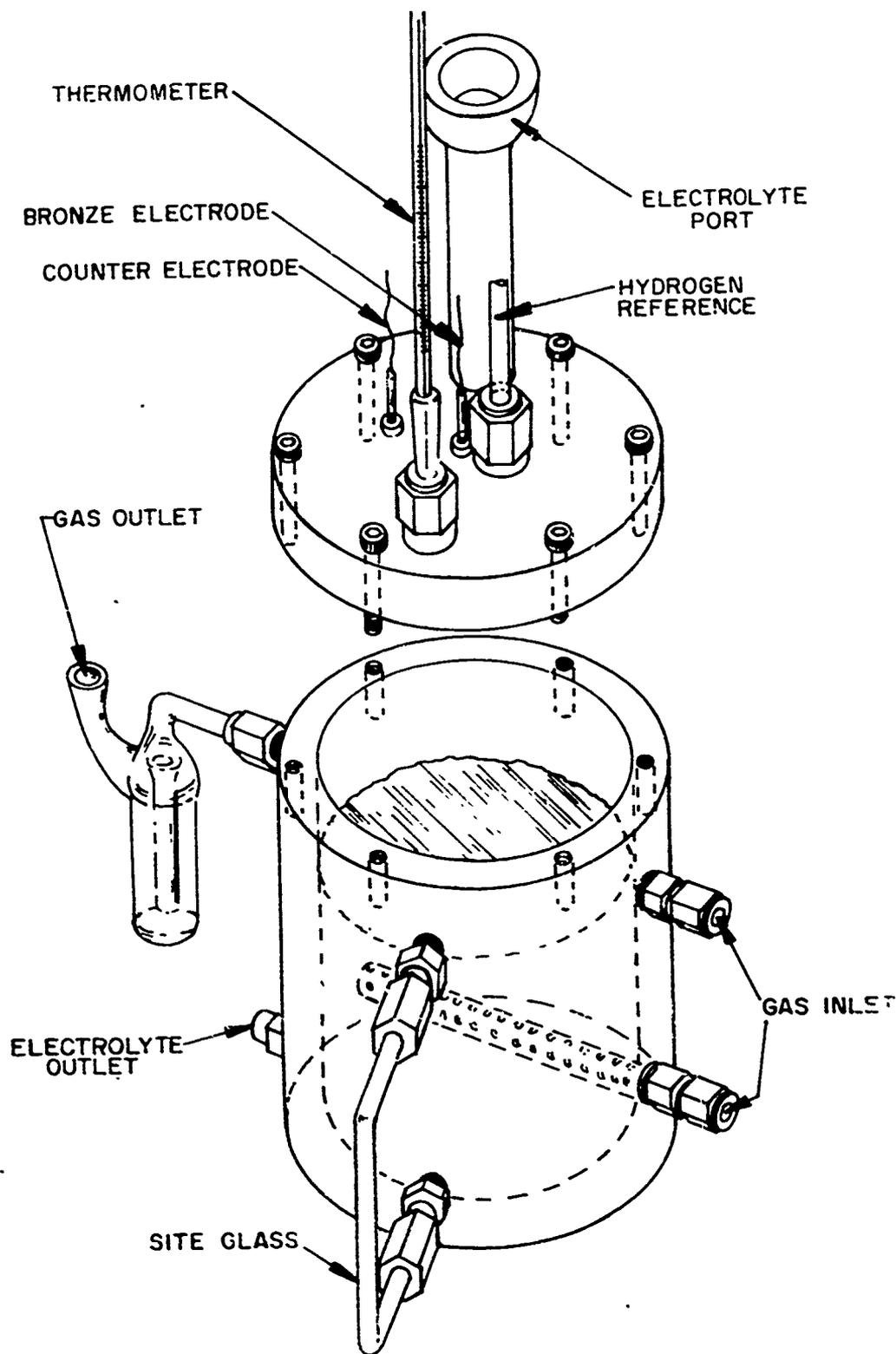
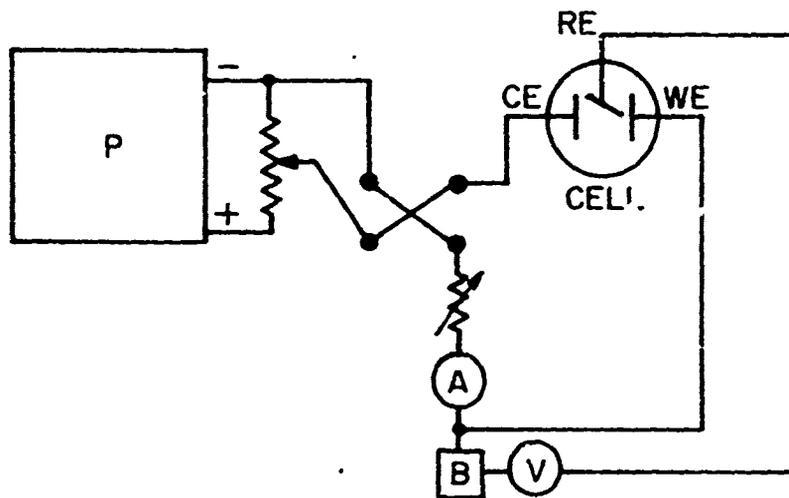


FIG. 5. GALVANOSTATIC TEST CELL

The galvanostatic test circuit employed is illustrated in the block diagram shown in Fig. 6.



- A, V - Keithley 602 Electrometers
- B - Battery plus Resistors, Voltage Offset
- P - D.C. Power - Northhills Electronics Model CS-11
- RE - Hydrogen Reference Electrode
- CE - Cylindrical Gold Foil Counter Electrode
- WE - Bronze Working Electrode

FIG. 6. GALVANOSTATIC TEST CIRCUIT

The geometric area of all bronzes was used without any corrections for surface roughness. Before each experimental run, the bronze working electrodes were rinsed in triply distilled water. The quasi-steady state measurements were performed as follows: current was gradually increased cathodically from 10^{-7} A at 2 minute intervals to 10^{-3} A, then retrogressed to 10^{-7} A. Next, the current was increased in the same way anodically from 10^{-7} A to 10^{-3} A then retrogressed to 10^{-7} A. Plots of voltage vs log i were prepared to obtain the necessary kinetic parameters for oxygen electroreduction.

DISCUSSION AND RESULTS

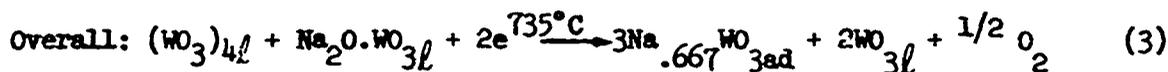
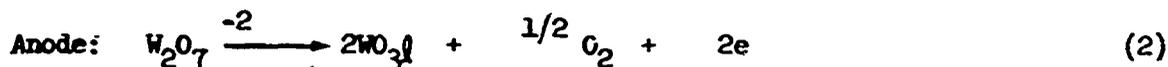
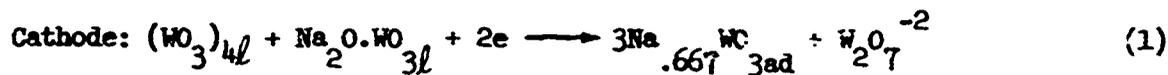
Preparation of Bronzes

Table I lists the compositions of prepared bronzes with their corresponding melt compositions.

Table I. Composition of Bronzes: $\text{Na}_x, \text{Fe}_y, \text{Ni}_z, \text{WO}_3$

Crystal No.	Temp. °C	Melt WO_3 Mole %	Composition FeWO_4 Mole %	Bronze Composition			Lattice Constant Å
				x	y	z	
0	735	40	0	.689	--	--	3.841
1	735	39.24	1.96	.690	.002	.04	3.842
2	750	39.24	2.20	.690	.003	--	3.842
3	745	39.24	1.96	.689	.002	--	3.841
4	740	39.24	2.20	.690	.004	--	3.842

The compositions of the crystals and melts were obtained from emission spectroscopy. The crystal structure was elucidated by X-ray diffraction studies. The formation of the $\text{Na}_{.667}\text{WO}_3$ bronze is apparently favored during reduction and adsorption at the cathode. Two factors which may influence this bronze formation are its greater electroconductivity and symmetry when compared to bronzes with less sodium content.³ The formation of this bronze may be explained by the following electrode reactions:

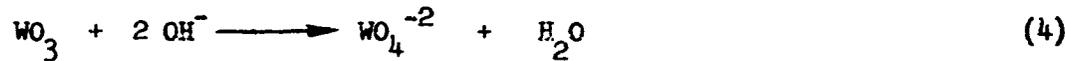


The sodium content determined by X-ray diffraction⁵ is close to the sodium content of 0.667 according to the above mechanism. Several mechanisms for tungsten bronze preparation were proposed by E. Banks, et al.⁷ Crystal No. 1 is a mixed bronze ($\text{Na}_{.69}\text{Fe}_{.002}\text{Ni}_{.04}\text{WO}_3$) which was prepared from a melt containing only the dopant iron (FeWO_4); the nickel was added from a

gold-plated nickel foil anode. Attempts to add nickel or iron through an unprotected nickel or iron wire anode were unsuccessful. Only two different melt compositions with FeWO_4 additive were used to prepare crystals numbers 1-4. Attempts to increase the FeWO_4 composition above 2.2 mole % were unsuccessful. In the process of depositing a crystal at the cathode, it was necessary to maintain the temperature at least 15°C higher than the fusion temperature. The reason being that solid reagent sometimes occluded in the bronze thereby spoiling the crystal. All crystals prepared had resistivities in the range $5.6 - 6.0 \times 10^{-3} \Omega \text{cm}$ at 25°C , and a density of $6.62 - 6.67 \text{ g cm}^{-3}$ at 20°C .

Corrosion Stability of Bronzes

Factors which required close control during corrosion experiments were the rate of aeration and convection, temperature, and electrolyte composition. Even with close control of all of these factors, an additional factor, time of immersion, had to be resolved before sample bronzes in duplicate would show a percent difference in weight loss less than $\pm 5\%$. This minimum immersion time was experimentally determined to be about 12 hours in alkali. Acid solutions required at least 100 hours of immersion before gravimetric measurements could be taken. The reason for erratic corrosion results with short immersion time ($\ll 12$ hours) in alkali may be related to nonhomogeneity of bronze surfaces. If interstitial sodium or iron at the surface is less than that in the bulk crystal, there appears to be an initial increased attack on the WO_3 matrix:



This proposed corrosion reaction would soon stabilize itself with either uniform dissolution of sodium or some other diffusion process in control:

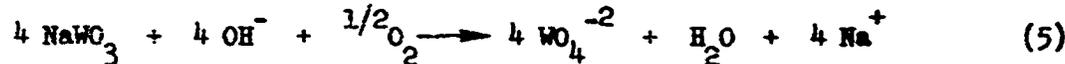


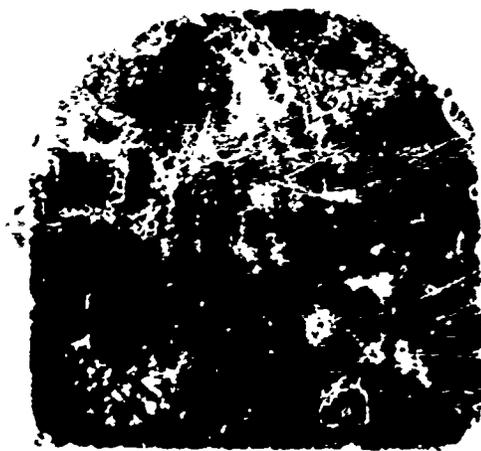
Table II lists the chemical corrosion rates of prepared bronzes in 1F HClO_4 and 1F KOH. Each value reported is an average of two runs. The length of time of an experiment in 1F HClO_4 was between 117-144 hours and in 1F KOH was between 22-48 hours. The results, in general, show that the rate of corrosion in acid is less than $10^{-6} \text{ g cm}^{-2}\text{hr}^{-1}$. Some positive influence of oxygen pressure on the rate of corrosion is also shown. A close inspection of the crystals after exposure (144 hours) to acid revealed a white surface film, probably tungstic acid; this film could possibly explain the reduced corrosion rate. The results in alkaline solution indicate that the corrosion of tungsten bronzes is almost directly proportional to the oxygen pressure. The bronzes corroded at approximately $2.5 \times 10^{-4} \text{ g cm}^{-2}\text{hr}^{-1}$ under 0.2 atm pressure of oxygen, and $1.2 \times 10^{-3} \text{ g cm}^{-2}\text{hr}^{-1}$ under 1 atm pressure of oxygen.

Table II. Chemical Corrosion Rates of Bronzes

CRYSTAL NO.	Corrosion Rate, * g hr ⁻¹ cm ⁻² at 20°C			
	1F HClO ₄		1F KOH	
	$\frac{O_2}{P = 2 \text{ atm}}$	$\frac{O_2}{P = 1.0 \text{ atm}}$	$\frac{O_2}{P = 2 \text{ atm}}$	$\frac{O_2}{P = 1.0 \text{ atm}}$
0	5.7×10^{-7}	1.8×10^{-6}	2.56×10^{-4}	1.28×10^{-3}
1	NON UNIFORM DECOMPOSITION			
2	4×10^{-7}	8.7×10^{-7}	2.42×10^{-3}	1.13×10^{-3}
3	5×10^{-7}	1.1×10^{-5}	2.4×10^{-4}	1.03×10^{-3}
4	5×10^{-7}	8.7×10^{-7}	2.54×10^{-4}	1.21×10^{-3}

*Aeration 1 cm³ sec⁻¹

Figures 7a and 7b show a bronze crystal before immersed in 1F KOH and after 25 hours, respectively. The central portion of the crystal in Figure 7b was protected with Teflon during the experiment. Attempts to measure the corrosion effect of electrical currents on the bronzes in acid were unsuccessful inasmuch as they showed little or no difference from that of chemical corrosion. In alkali, however, the results indicated that, upon applying a constant cathodic current of -1×10^{-4} A cm⁻² (.45 V vs HE) under oxygen pressure of 1 atm, the rate of corrosion for No. 3 bronze was 3×10^{-3} g hr⁻¹ cm⁻². At double this current density, -2×10^{-4} A cm⁻² (.34 V vs HE), the rate of corrosion for No. 3 bronze was halved to 1.48×10^{-3} g hr⁻¹ cm⁻². Anodic currents of $+1 \times 10^{-4}$ A cm⁻² (.68 V vs HE) produced a corrosion rate 2.2×10^{-3} g hr⁻¹ cm⁻². Upon doubling this current to $+2 \times 10^{-4}$ A cm⁻² (1.59 V vs HE), the corrosion rate was again reduced to approximately 1×10^{-3} g hr⁻¹ cm⁻².



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FIG. 7a. BRONZE BEFORE IMMERSION IN 1F KOH



FIG. 7b. BRONZE AFTER 25 HOURS IN 1F KOH

Oxygen Electroreduction on Bronzes

Bronzes Numbers 0, 2, 3, and 4 all behaved similarly in acid solution during oxygen electroreduction and evolution. Figure 8 shows a typical steady state Tafel curve where cathodic current density i_c was much less than i_L the limiting current density ($5 \times 10^{-4} \text{ A cm}^{-2}$). The points plotted at $i_c < 5 \times 10^{-6} \text{ A cm}^{-2}$ were not included in the curve since trace impurities (ppm) in the electrolyte can influence these current densities.

The results of steady state experiments on prepared bronzes in acid solutions are summarized. The open circuit voltages of these bronzes ranged from 0.4 - 0.52 V versus hydrogen reference in the same solution. The nature of this open circuit voltage appears to be a mixed potential composed of some oxygen reduction process coupled with an anodic process. The anodic process has been attributed to sodium dissolution,⁸ however, it could be an anodic reaction encompassing the complex (WO_3) bronze matrix. The Tafel slopes $(\partial V / \partial \log i_c)_{T,P,pH}$ for oxygen electroreduction at constant temperature, oxygen pressure, and pH were approximately -120 mV for all bronzes except bronze number 1, which decomposed rapidly in acid solution. The electrochemical reaction orders $(\partial \log i_c / \partial \log P(\text{O}_2))_{T,V,pH}$ were collectively close to 1; actual values were between 1.1 - 1.3. Previously mentioned data plus the relationship of $(\partial \log i_c / \partial \text{pH})_{V,P,T} = -1/2$ appear to verify the results found by Bockris et al.⁶ concerning most tungsten bronzes.

These specific kinetic parameters indicate that the rate determining step in oxygen electroreduction on tungsten bronzes in acid is a charge transfer step which can be expressed by the rate equation:

$$i = ZFV = ZFkP(\text{O}_2)(C_{\text{H}^+})^{1/2} e^{-2 VF/RT} \quad (6)$$

where $i = \text{A cm}^{-2}$

$ZF = \text{sec mole}^{-1}$ of products

$V = \text{rate of product moles cm}^{-2} \text{ sec}^{-1}$

$k = \text{rate constant atm}^{-1} \text{ sec}^{-1} \text{ moles}^{1/2} \text{ cm}^{-1/2}$

$P(\text{O}_2) = \text{pressure of oxygen, atm}$

$(C_{\text{H}^+}) = \text{concentration of hydrogen ion mole cm}^{-3}$

$-2VF/RT = \text{cathode Tafel slope, } \partial V / \partial \log i_c$

A typical steady state Tafel curve of prepared bronzes during oxygen electroreduction in alkali is shown in Figure 9. The open circuit was low and varied between .39 - .52 V versus a hydrogen electrode in the same solution. The cathode Tafel slopes $(\partial V / \partial \log i_c)_{T,P,pH}$ at constant oxygen pressure of 1 atm and constant pH were -8 mV. This value is interpreted to mean that some process other than simple charge transfer

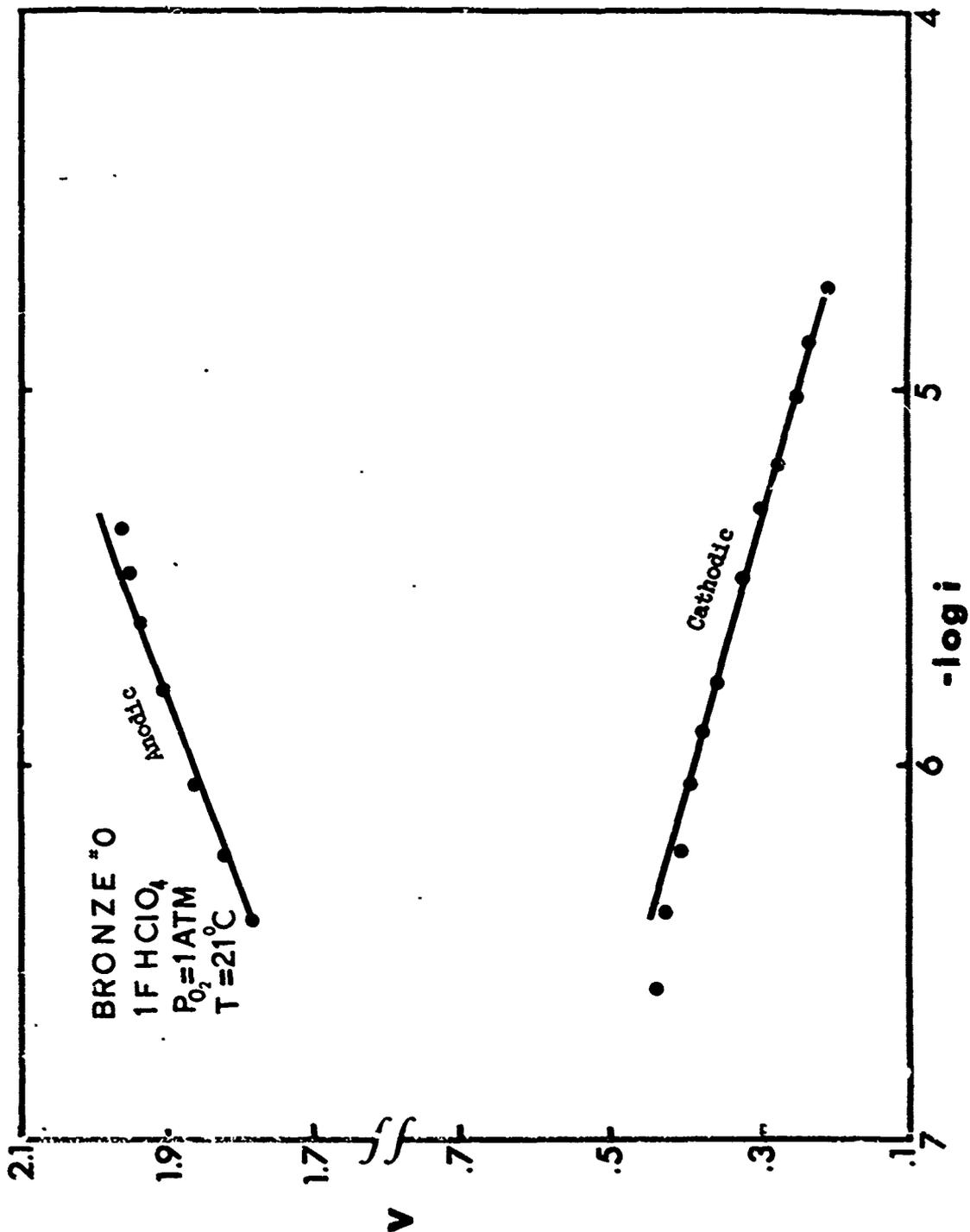


FIG. 8. VOLTAGE vs LOG I IN 1F HClO₄

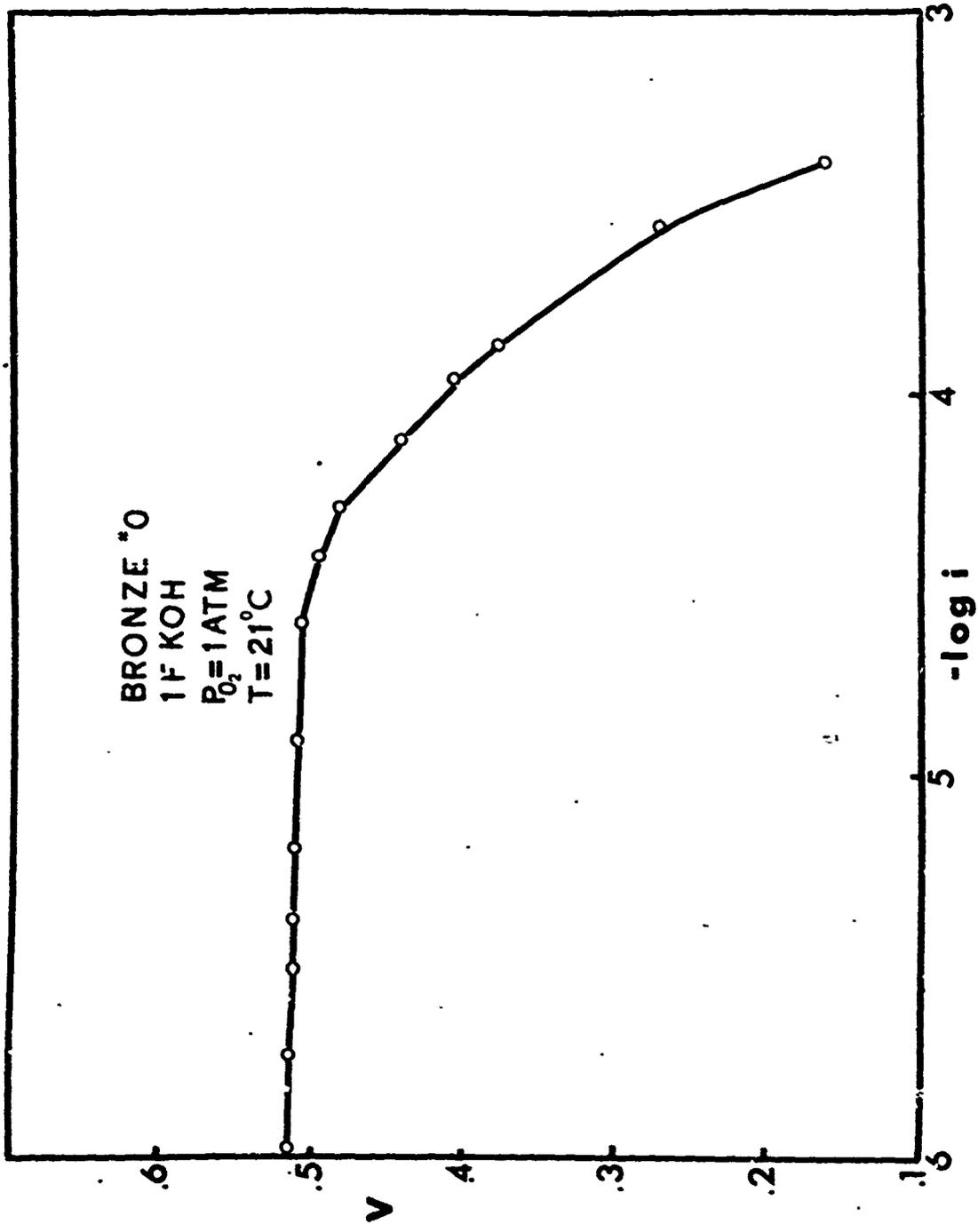


FIG. 9. VOLTAGE vs LOG I IN 1F KOH

is occurring. Since the rate of corrosion in alkali was so great, $1.25 \times 10^{-3} \text{ g hr}^{-1} \text{ cm}^{-2}$, no further kinetic parameters were determined.

SUMMARY AND CONCLUSIONS

The electrolytic preparation of mixed sodium-iron bronze was accomplished using a melt composition of approximately 39.24 mole % WO_3 , 58.8 mole % Na_2WO_4 , and 1.96 mole % FeWO_4 at $735\text{--}750^\circ\text{C}$ under an argon atmosphere. These bronzes were fairly stable in perchloric acid showing a corrosion rate $< 10^{-6} \text{ g hr}^{-1} \text{ cm}^{-2}$ under an oxygen pressure of 1 atm. The corrosion rate in potassium hydroxide was high, $1.25 \times 10^{-3} \text{ g hr}^{-1} \text{ cm}^{-2}$, and appears to be directly proportional to oxygen pressure. The results of galvanostatic steady state experiments performed in acid are in agreement with other workers in that the rate determining step for oxygen electroreduction is a charge transfer step.

The steady state results for oxygen electroreduction in potassium hydroxide were masked by the excessively high corrosion rate of the tungsten bronzes and, thus, could not be interpreted as simple charge transfer.

It is concluded that these tungsten bronzes are not stable enough to be used as cathodes for oxygen electroreduction in alkaline solutions. However, other bronzes (Ba_5NbO_3), which are stable in alkaline solutions, should be examined as support of substrate for the optimization of precious metal (catalyst) loading.

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