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TECHNICAL REPORT: MATERIALS AND CHEMISTRY

THE ELECTROLYTIC POLARIZATION OF BERYLLIUM

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TECHNICAL REPORT: MATERIALS AND CHEMISTRY

THE ELECTROLYTIC POLARIZATION OF BERYLLIUM

by D. J. LEVY

WORK CARRIED OUT AS PART OF THE LOCKHEED INDEPENDENT RESEARCH PROGRAM

Lockheed

MISSILES and SPACE DIVISION

LOCKHEED AIRCRAFT CORPORATION • SUNNYVALE, CALIF.

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FOREWORD

Beryllium is being used as a structural and heat-sink material at an increasing rate in the missile and spacecraft industry because of its desirable properties of high strength-weight ratio, high melting point, good thermal conductivity and outstanding stiffness. Naturally, technological problems arise concerning the surface properties of the metal in such areas as corrosion and corrosion control; pickling and cleaning treatments; electrolytic cleaning, polishing, and metal removal; conversion films, electrolytic coatings, and electrodeposition processes. The fundamental electrochemical phenomenon related to all of these processes is electrolytic polarization.

ABSTRACT

The anodic and cathodic polarization behavior of beryllium was determined in a number of unstirred aqueous electrolytes at 22°C with current densities in the range of 10^{-7} to 10^{-2} amps/cm². $\text{CrO}_4^{=}$ and $\text{PO}_4^{=}$ induced considerable anodic polarization. There was some evidence that the anodic potential was increased due to BeO film formation in the presence of $\text{CrO}_4^{=}$, NO_3^- , and AlO_2^- . A Flade Potential was not observed. Beryllium was activated and attacked anodically in the presence of Cl^- , ClO_3^- , F^- and $\text{SO}_4^{=}$. Other ions investigated were $\text{B}_4\text{O}_7^{=}$, $\text{C}_2\text{H}_3\text{O}_2^-$, $\text{CO}_3^{=}$, MnO_4^- , OH^- , and $\text{SiO}_3^{=}$. Na_2CrO_4 was an effective cathodic polarizer over a broad range of current densities. Most of the electrolytes exhibited a common Tafel region for hydrogen evolution. Some corrosion aspects of the solutions are also discussed.

CONTENTS

Section		Page
	Foreword	ii
	Abstract	iii
1	Introduction	1-1
2	Experimental	2-1
3	Results and Discussion	3-1
4	Summary	4-1
5	References	5-1

Section 1

INTRODUCTION

Thermodynamic data on beryllium, its oxides, hydroxides, and aqueous ions will be found in Latimer's book (Ref. 1). The equilibrium potential-pH diagram for the system Be-H₂O, and the influence of pH on the solubility of BeO and its hydrates have been calculated from these data by Pourbaix et al. (Ref. 2). Other studies of the electrochemical behavior of Be in aqueous media have centered on the formation and properties of anodic oxide films.

Electron diffraction studies by Kerr and Wilman (Ref. 3) revealed that the initial BeO films formed from a HNO₃-CrO₃ bath were amorphous up to thicknesses of 100 to 150 Å. Subsequent layers were randomly disposed BeO crystals 60 Å or more in diameter. Levin (Ref. 4) was not able to reproduce these amorphous films on vacuum-cast French flake beryllium from the bath used by Kerr and Wilman. Instead, he found the initial surface layers to be crystalline with a weak preferred orientation. Films were evident above 100 $\mu\text{a}/\text{cm}^2$ although current densities of 20,000 to 150,000 $\mu\text{a}/\text{cm}^2$ were more commonly used. Film adhesion was better with 10 percent than with 1 percent HNO₃. Crystal size was constant at 60 Å diameter and 20 Å thickness irrespective of current density or film thickness, although preferred orientation ceased as the thickness increased. The films were porous due to the solubilizing action of the electrolyte, as opposed to nonporous protective films which are thermally formed below 300°C.

It is reported that black films are formed by anodizing in 1 percent CrO₃, 70 percent HNO₃, 1 percent H₂SO₄, acidified Na₂CrO₄, or 5 to 10 percent NaOH (Ref. 5), but no details are given concerning the merits of such processes or the properties of the films formed. Whitby, et al. (Ref. 6) recently studied the parameters for chromic acid anodizing and measured some of the film properties. The bulk density of the

coating was the same as that of BeO, but ionic permeability was high and the process exhibited a very low electrical efficiency for film formation. X-ray and spark emission spectroscopy indicated that the black film was mainly BeO with a small amount of Cr.

This paper presents the results of a study of the anodic and cathodic polarization behavior of beryllium in aqueous solutions of some common inorganic compounds. The chemicals are composed of acids, bases, and salts, and include halides, oxidizers, and ions capable of forming insoluble beryllium compounds.

Section 2 EXPERIMENTAL

The tests were made in 200 ml of electrolyte contained in a petri dish. A 5-in. rod of beryllium 1/2 in. in diameter, and a platinum inlay electrode, were partially immersed and electrically connected so that a voltage could be applied between them. The amount of voltage impressed by a group of dry cells was manually regulated by a potentiometer while the current was recorded on a strip chart recorder. The potential of the beryllium electrode was measured against a saturated calomel fiber-type reference electrode, using an electrometer of 10^{14} -ohm input resistance. A salt bridge, filled with the test electrolyte, was fabricated with an asbestos fiber sealed in the probe tip.

The surface of the beryllium test electrode was prepared by polishing the tip with 000 aluminum oxide paper prior to use in each electrolyte. The immersed cylindrical portion was masked with an air-curing silicone resin. Although a high quality QMV-grade hot-pressed powder metal was used, technology limits the purity of beryllium obtainable at this time. Table 1 lists the chemical composition of the beryllium electrode. It is essentially composed of 98.6 percent Be, 0.95 percent BeO, and lesser amounts of other metallic and non-metallic impurities.

All electrolytes were prepared from reagent grade chemicals and considering the purity level of the Be electrode, no effort was made to electrodeposit impurities from them before use. An attempt was made to compare the polarizing character of the various compounds in chemically equivalent concentrations. Normality is based on the simple hydrogen equivalent of each substance.

Measurements were made in unstirred solutions in air by the direct method at room temperature of $22 \pm 1^\circ\text{C}$. The tip of the Luggin probe was positioned at a distance of 4 times the external radius of the capillary from the beryllium test electrode to minimize the IR potential drop in the electrolyte and avoid shielding the electrode (Ref. 7). The high conductivity of the electrolytes produced low IR drops so the test measurements

Table 1

CHEMICAL ANALYSIS OF BERYLLIUM ELECTRODE**A. Metals by Spectrographic Analysis Percent**

Fe	0.2
Al	0.08
Mg	0.05
Ni	0.02
Cr	0.015
Si	0.01
Cu	0.007
Mn	0.002
Ca	0.001

B. Nonmetals by Vacuum Fusion

O	0.606
N	0.0093
H	0.0027

were not corrected for this effect. Correction for liquid junction potentials was also omitted.

Some polarization measurements were taken with a more sophisticated potentiostat (Ref. 8) substituted for the simple circuit described above, and the end results were unaffected.

The polarization data were obtained so as to encompass current densities of 0.1 to 10,000 $\mu\text{a}/\text{cm}^2$. A starting potential of about -2 v was used and the voltage was manually increased in the noble direction in steps of 0.1 to 0.5 v up to about +4 v and then returned to the origin of the anodic curve, about zero volt. It was found as other investigators (Refs. 9 and 10) have noted, that applying initially a strong cathodic potential to the test electrode serves to activate the electrode surface and ordinarily does not affect subsequent anodic polarization measurements. The current-recorder was a most invaluable tool since it indicated visually the approach of steady state conditions, a process normally requiring 10 to 30 minutes or more. It appeared that anodic polarization reached equilibrium more rapidly with decreasing current than with increasing current. A very small amount of hysteresis was observed between ascending and descending measurements, probably due to the time dependence of measurements.*

*Makrides (Ref. 10) found that hysteresis and time dependence are due to local action currents resulting from chemical impurities which adsorb on the electrode surface, and are completely absent when rigorous precautions are taken in the preparation of electrode and electrolyte.

Section 3

RESULTS AND DISCUSSION

The typical polarization response of beryllium induced by various electrolytes is illustrated in Fig. 1. Many substances caused a considerable anodic polarization similar to that caused by chromic acid (upper curve). Activators, such as the illustrated sodium chloride, produced no anodic polarization. A marked cathodic polarization, illustrated by the sodium chloride lower curve, was evident in a number of instances. Table 2 summarizes the experimental data, giving the polarizing current density at various potentials. The potential range is also listed within which the anodic and cathodic current density was less than $0.1 \mu\text{a}/\text{cm}^2$.

The observed polarization may be due to the formation of an insoluble beryllium oxide or salt film, adsorbed films of hydrogen or oxygen gas, slow chemical reactions, or other factors which can interfere with charge transport phenomena. Detailed studies of the polarization mechanism in each case were not conducted and are beyond the scope of this investigation.

Table 2 shows considerable anodic polarization of beryllium by currents of less than $1 \mu\text{a}/\text{cm}^2$ in the presence of chromates. Some of the effect may be due to the known ability (Refs. 4 and 5) of this medium to produce anodic BeO films, and indeed the characteristic black film was visually apparent with Na_2CrO_4 after the test. H_2CrO_4 produces somewhat less anodic polarization than Na_2CrO_4 and fails to exhibit any visual evidence of anodic film. This is possibly due to the solubilizing action of the more acid solution. Other electrolytes which produced a dark anodic film indicative of BeO were NaNO_3 and NaAlO_2 .

The anodic curve of chromic acid, illustrated in Fig. 1, indicates a Tafel region at potentials more noble than +2.5 v (S.C.E.). This portion of the curve represents oxygen evolution as the dominant reaction.

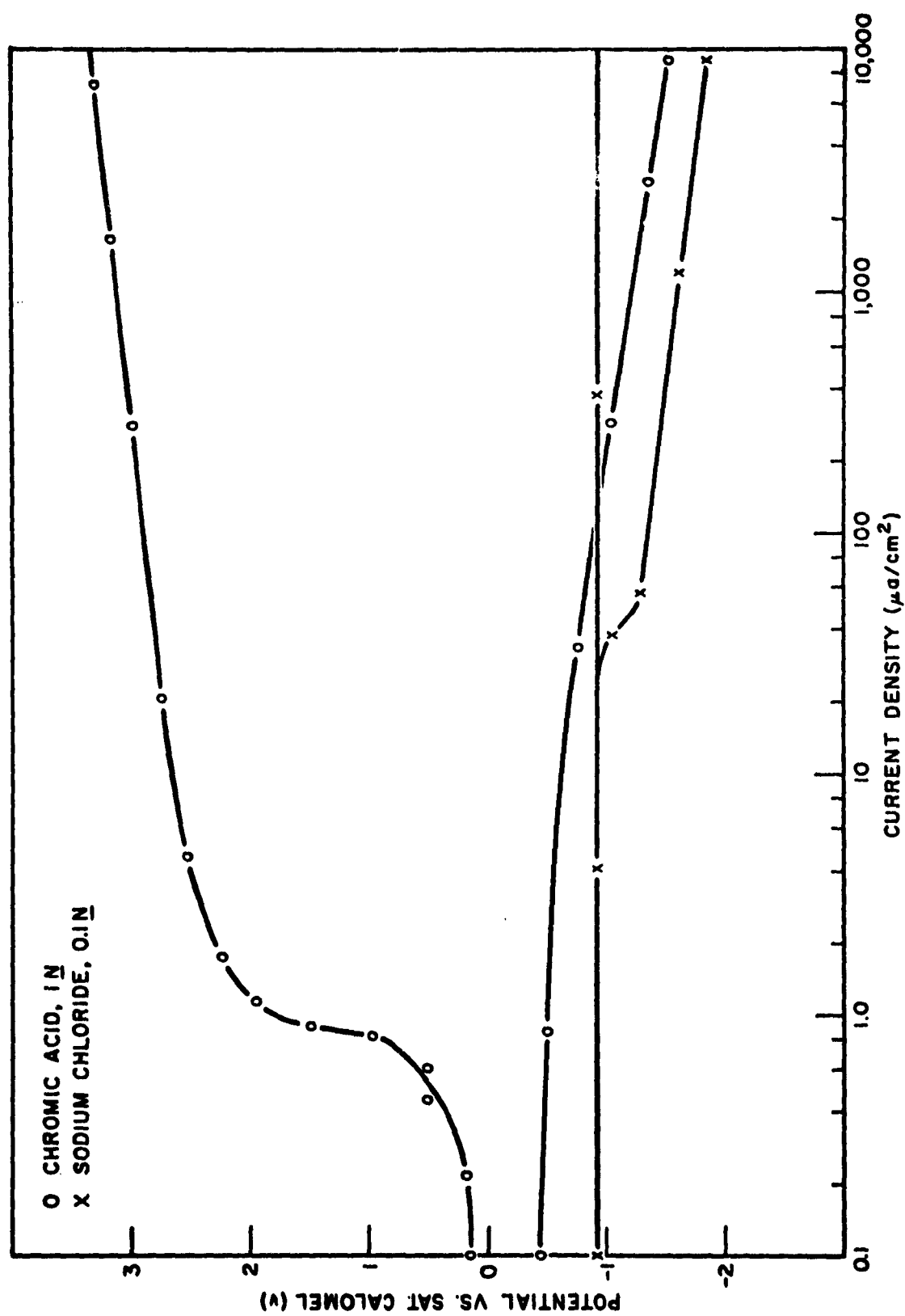


Fig. 1 Typical Polarization Curves

Table 2
POLARIZATION DATA

POTENTIAL (S.C.E.) (Volts)	ELAS N/I	P ₂ CrO ₄ N/I	P ₂ PO ₄ N/I	NaAc N/I	Na ₂ CrO ₄ N/I	Na ₃ PO ₄ N/I	NaAlO ₂ N/I	Na ₂ CO ₃ N/I	NaNO ₂ N/I	NaOH N/I	Na ₂ SiO ₃ N/I	NaNO ₃ N/I	NaOH N/I	EDSO ₄ N/I	KCl N/I	NaF N/I	NaSO ₄ N/I
	Polarizing Current Density, [†] ma/cm ²																
4.0	3200	•	•	200	•	100	•	250	•	•	660	•	•	•	•	•	•
3.5	1500	•	•	110	•	80	7600	200	•	•	310	•	•	•	•	•	•
3.0	700	270	•	33	160	24	4000	130	1900	9100	340	900	130	130	•	•	•
2.5	300	4.5	275	30	5	3	320	70	16	1100	140	300	40	90	•	•	•
2.0	120	1.1	170	15	1.2	2.4	61	25	2.5	35	45	230	11	15	•	•	•
1.5	50	0.9	150	6	0.4	0.7	45	5	0.7	4.9	15	110	4	4	•	•	•
1.0	20	0.5	140	4	0.2	0.2	30	3	0.4	3.5	5	0.7	1.2	1.1	•	•	•
0.5	6	0.3	135	0.9	0.1	•	0.6	1	0.2	0.9	1.5	0.1	0.2	0.3	•	•	•
0.0	1.3	-0.8	120	•	•	•	•	0.5	0.1	0.2	0.6	•	•	•	•	•	•
-0.5	-40	-200	95	-25	•	-0.1	•	-6	-0.6	•	0.2	-12	-0.1	-0.2	•	•	•
-1.0	-400	-8000	-2100	-31	-0.6	-30	-5	-17	-100	-20	-25	-61	-36	-500	-35	-30	-40
-1.5	-1500	•	•	-400	-130	-200	-200	-600	•	-200	-500	-1600	-100	-1300	-400	-170	-250
-2.0	-3000	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•

Current	POTENTIAL (S.C.E.) (Volts)																
<0.1 ma/cm ²	-0.3	-0.45 to +0.15	-0.5	-0.05 to +0.3	-0.5 to +0.3	-0.5 to +0.6	-0.3 to +0.2	-0.45 to -0.05	-0.3 to -0.1	-0.75 to -0.2	-0.65	-0.1 to +0.5	-0.5 to +0.2	-0.5 to +0.4	-0.95	-0.35	-0.4

Symbol: • > 10,000
• < 10,000

[†] Positive Polarizing Current is Anodic, Negative is Cathodic.

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Some media are known to cause the formation of insoluble beryllium compounds and one might expect these surface films to influence polarization behavior. The presence of carbonates causes the formation of insoluble basic salts of the type $\text{BeCO}_3 \cdot x\text{Be(OH)}_2$ wherein the exact composition depends upon the alkali used, temperature, and concentrations. Acetates form an insoluble basic salt with the definite composition $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$. Table 2 shows that both carbonates and acetates produced some anodic polarization. However, both acetic acid and sodium acetate created an unusual condition; the beryllium was polarized to an unstable and fluctuating anodic and cathodic potential. Acetic acid also caused the formation of a dark surface film.

Beryllium, in the presence of sulfates, normally forms water insoluble BeSO_4 . However, if the metal presents an anodic potential, the sulfate ion causes strong activation of the metal surface. This situation emphasizes that solubility of metal salts is not a basis for predicting polarization behavior. Other electrolytes which caused anodic activation were N/10 concentration of NaF, NaCl, and the oxidizer NaClO_4 .

Beryllium orthophosphate is water soluble, although some references (Ref. 2, for example) suggest that a number of other beryllium phosphates are insoluble. In any case the greatest anodic polarization observed was produced by Na_3PO_4 .

NaOH and NaNO_3 were studied at two different concentration levels. Dilute NaOH produced significantly more anodic polarization than the more concentrated solution. The concentration effect of sodium nitrate was exactly opposite. Obviously, concentration per se is not the controlling factor. In the case of sodium hydroxide, one might reason that increased concentration causes increased solubility of surface films (forming beryllates), a factor opposing polarization. On the other hand, the sodium nitrate media at pH 5.1 and 5.5 (see Table 3) presented only a mild corrosive environment. Polarization in this instance probably varied directly with concentration because of the oxidizing character of the media. The black surface films, presumably BeO , produced by NaNO_3 were mentioned earlier.

Table 3
CORROSION DURING ELECTROLYTIC TEST

<u>pH</u>	<u>Electrolyte</u>	<u>Normality</u>	<u>Observed Corrosion</u>
0.4	H_2CrO_4	1	none
1.3	H_3PO_4	1	matte etched
2.4	$\text{HC}_2\text{H}_3\text{O}_2$	1	local pitting
5.1	NaNO_3	1	none
5.4	NaCl	0.1	yes
5.5	NaNO_3	0.1	none
5.6	Na_2SO_4	0.1	yes
8.1	KMnO_4	0.1	none
6.9	NaF	0.1	yes
8.2	$\text{NaC}_2\text{H}_3\text{O}_2$	1	---
8.9	Na_2CrO_4	1	none
11.8	Na_2CO_3	1	none
12.3	Na_3PO_4	1	none
12.6	NaOH	0.1	---
12.8	NaAlO_2	1	none
13.1	Na_2SiO_3	1	slight
13.5	NaOH	1	none

The cathodic curves with most electrolytes show a reproducible sharp increase in polarization at 15 to 40 $\mu\text{a}/\text{cm}^2$ indicative of a change in reaction type at this point. This pronounced effect is illustrated by NaCl in Fig. 2 (lower curve). The polarization increase was less sharply defined with HAc, H_2CrO_4 , and Na_2CrO_4 . It is proposed that this zone represents a transition from polarization caused by films of $\text{Be}(\text{OH})_2$ or adsorbed hydrogen gas and that caused primarily by hydrogen evolution. Cathodic polarization above the transition zone exhibits a Tafel region common to the electrolytes, regardless of type, with a slope of 0.18 v. Extrapolating this region to the reversible hydrogen potential of -0.241 v (S.C.E.) indicates a relatively low exchange current for hydrogen evolution of only $10^{-11} \text{ a}/\text{cm}^2$.

The equilibrium potential--pH diagram for the system $\text{Be}-\text{H}_2\text{O}$ (Ref. 2) is reproduced in Fig. 2. Pourbaix has used a concentration of 10^{-6} ionic species for the solubility limit which defines the regions of corrosion, passivation, and immunity. He proposes that the chemical resistance of beryllium to other electrolytes can be estimated provided complexing and insolubilizing ions are absent. Table 3 lists the observed corrosion of Be resulting from the various test solutions. It is apparent that chloride, fluoride, and sulfate ions interfere with the formation of the protective $\text{Be}(\text{OH})_2$ film normally found in the 4.0 to 10.7 pH range. Corrosion in the more alkaline media was generally absent (or very slow). This might be attributed to the complexing or insolubilizing character of carbonates, phosphates, and aluminates. In the case of NaOH at pH 13.5, it is more probable that the reaction is merely slow. The effectiveness of chromates in passivating beryllium in low pH solutions is also evident.

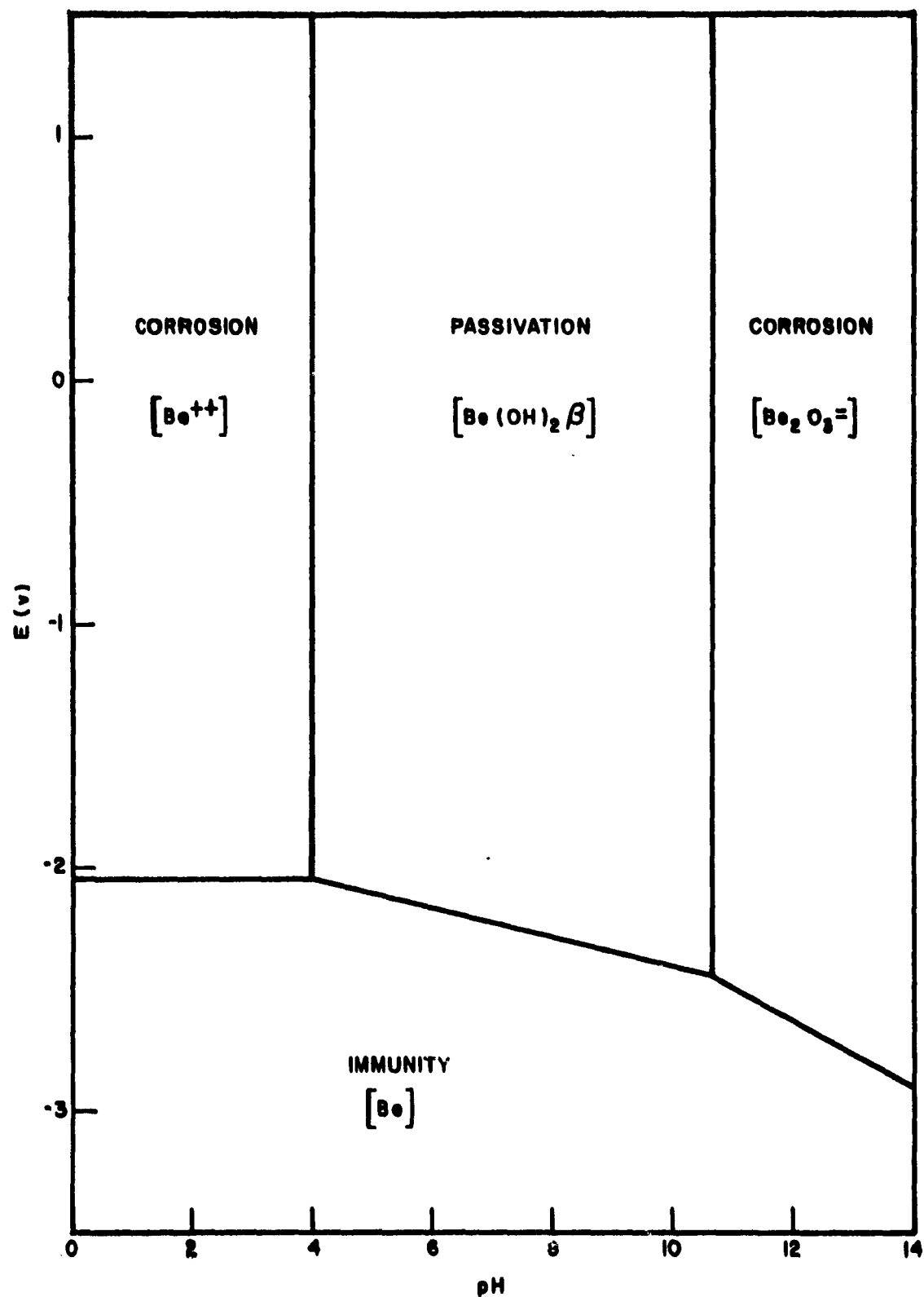


Fig. 2 Equilibrium Potential - pH for the System Beryllium - Water at 25°C
(Reproduced from Ref. 2)

Section 4 SUMMARY

The electrolytic polarization of beryllium in the presence of a number of common aqueous electrolytes has been determined. Chromates and phosphates, particularly in neutral pH solutions, induced considerable anodic polarization. It is believed that a beryllium oxide film contributes appreciably to the polarization observed with chromate, nitrate, aluminate and hydroxide solutions.

Cathodic polarization was less pronounced than anodic, and all electrolytes exhibited a similar Tafel region for hydrogen evolution.

None of the systems studied caused the beryllium to develop a Flade potential and the accompanying passive region.

Fluoride, chloride, chlorate, and sulfate all activate and attack beryllium anodically by some process which interferes with the normal formation of a protective $\text{Be}(\text{OH})_2^\beta$ film in neutral pH solutions. Also, there was no relation between insolubility of a beryllium salt and anodic polarization. Very little corrosion was observed in alkaline media.

Section 5
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