

Thickness of Inhibiting Films on Glass Electrode Surfaces

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The thickness of voltage-inhibiting films produced on glass surfaces by heat treatment after leaching has been studied by means of the glass electrode and the interferometer procedure previously used for determining the chemical durability of glasses. The glass electrode gave conspicuous voltage departures (errors) and alterations (swelling) of the surface that were just detectable by the interferometer. This corresponds to approximately 0.01 fringe, or four times the unit cell dimension for cristobalite. The inhibiting effect of films of electric conductors, such as metallic silver, has been qualitatively compared with the inhibiting effect of films prepared from electric nonconductors, such as petrolatum and silicone stopcock grease.

I. Introduction

Considerable interest in the general subject of glass surfaces has been aroused by many industrial and scientific problems involving glass solution interfaces. Examples of these problems include the commercial practice of improving the chemical durability of inferior glasses by various surface treatments, the application of nonreflecting films to the surfaces of optical elements, and the effect of nonhygroscopic films on the hydrogen-electrode function of the glass electrode.

From earlier work it is obvious that the glass electrode is an extremely sensitive indicator capable of detecting the presence of inhibiting films thinner than 6×10^{-8} cm, and the interferometer can readily detect alterations of an optically flat surface of less than one-tenth this value. The voltages of glass electrodes [1, 2, 3]¹ prepared from Corning 015 [4] or other glasses of adequate hygroscopicity [5, 6, 7] and satisfactory chemical durability [7, 8] follow approximately the straight-line relation of the Nernst equation [9] over an extended range of hydrogen-ion activities [10]. Normally, the glass electrode exhibits voltage departures from the theoretical in the extreme acid [11, 12] and alkaline ranges [3, 13]. However, under special conditions of annealing or other controlled heat treatments after aging (leaching in acid solutions) the electrodes develop very large voltage departures (errors) over the entire pH range [14, 15, 16].

In extreme cases the hydrogen-electrode function (pH response) of the glass disappears almost completely, and the electrodes behave similarly to electrodes prepared from glasses of low hygroscopicity [6, 17]. This loss of pH response is brought about by the formation over the entire surface of the electrode bulb of a thin, nonhygroscopic, silica-rich layer [16]. With the interferometer method previously used for the determination of the chemical durability of glasses [7, 18, 19, 20], the maximum thickness of these inhibiting layers was estimated to be approximately 6×10^{-6} cm [16].

The present investigation was undertaken to determine what further information concerning the thickness of these films might be obtained from the combined use of the glass electrode and the interferometer.

II. Experimental Procedure

A series of mercury-filled glass electrodes [6, 21, 22] prepared from Corning 015 glass was leached in Britton-Robinson universal buffer [23] at pH 4.6 for various periods of time at 80° C. With the mercury removed, these leached electrodes were heated to 550° C, held 10 minutes and cooled slowly to 400° C, then cooled more rapidly to room temperature [16]. This series was prepared in order to ascertain the time of leaching necessary to develop an inhibiting film sufficiently thick to

¹ Figures in brackets indicate the literature references at the end of this paper.

bring about detectable voltage departures. Other glass electrodes, without previous leaching or annealing, were coated with inhibiting films of non-hygroscopic materials, such as silicone stopcock grease, petrolatum, and metallic silver.

The hydrogen-electrode function of all experimental electrodes was determined with a Beckman pH meter model *G*, using a well-conditioned glass electrode as the reference electrode. The voltage-departure measurements [16] were confined to a pH range over which the glass electrode is known to give reliable readings.

In order to determine the alterations of the electrode surface during the period of leaching, pitch-polished, optically flat specimens (approximately 2.5 by 1.5 cm) of Corning 015 glass were partially immersed in the same buffer as the electrodes and given identical treatment. The surface of the buffer was covered with a thin layer of liquid petrolatum to prevent evaporation of the solution during the period of exposure. The magnitude of the swelling of the glass surface was determined by observing the displacement of the interference fringes when the specimens were placed under an optical flat of fused silica [7, 20]. This displacement was converted to centimeters by the formula

$$\text{Swelling in centimeters} = \frac{N}{2} \times 5,876 \times 10^{-8},$$

where N is the number of orders (fringes), and 5,876 angstroms is the wavelength of the principal helium line.

The thickness of the silver layers deposited on the electrodes was determined by the interferometer on optical flats of Corning 015 glass coated simultaneously along with the glass electrodes. A small area of silver was stripped from these silver-coated flats by the use of chromic acid, and the displacement of interference fringes was observed. No satisfactory method was developed for determining the thickness of the petrolatum and silicone layers.

III. Results and Discussion

1. Films Formed by Leaching and Annealing

The data listed in table 1 and plotted in figure 1 show the voltage departures brought about by heat treating at 550° C a series of Corning 015 glass electrodes previously leached at pH 4.6 for

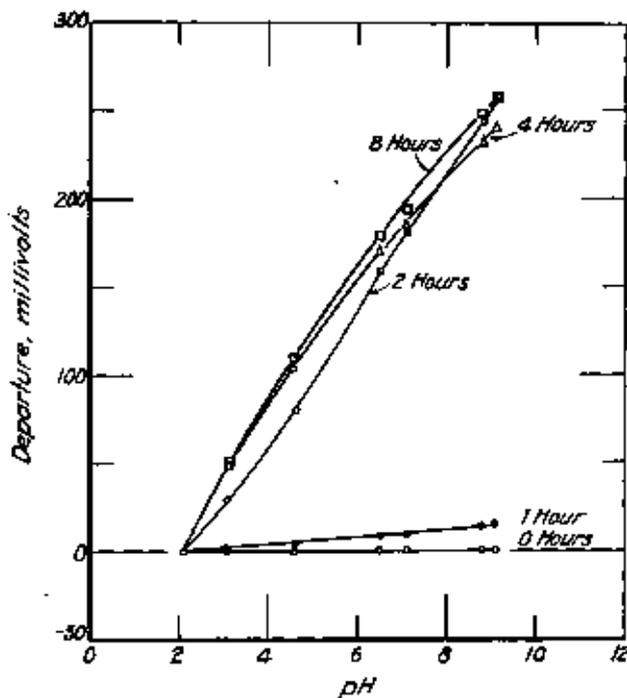


FIGURE 1. Voltage departures of glass electrodes, leached for various periods of time in Britton-Robinson universal buffer (pH 4.6 at 80° C) and then heated for 10 minutes at 550° C.

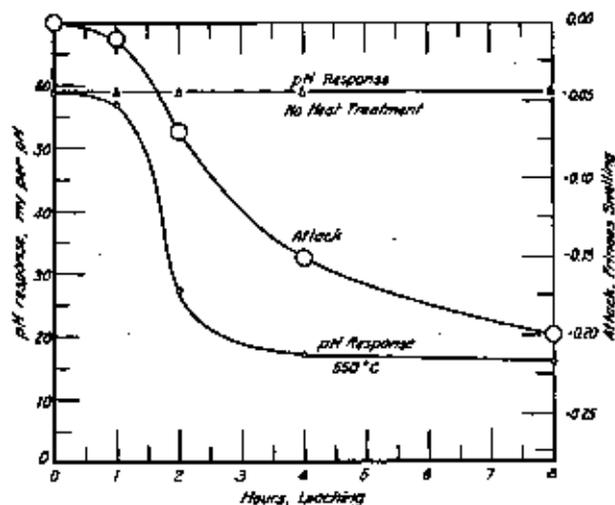


FIGURE 2. Effect of leaching (pH 4.6 at 80° C) and subsequent heat treatment at 550° C on the pH response of glass electrodes, compared with the attack (swelling) accompanying the leaching.

0, 1, 2, 4, and 8 hours at 80° C. The most conspicuous feature of this series is the marked increase in the voltage departures that appears between the electrodes given 1- and 2-hour leach-

ing periods. Although there is some overlapping of the voltage-departure curves for the electrodes given 2-, 4-, and 8-hour leaching, it is obvious that most of the effective inhibiting layer is formed within 2 hours. Converting the voltage departures between pH 2.1 and pH 4.6 to pH response (millivolts per pH) gives the value for the depar-

ture curve plotted for 550° C in figure 2. From this curve the loss in hydrogen-electrode function with increasing duration of leaching treatment can be compared directly with the amount of swelling of the glass (listed in table 1 and plotted as negative values in figure 2) brought about by the same period of leaching.

TABLE 1. Voltage departure and pH response of electrodes in solutions of various pH values after leaching in a solution at pH 4.6 for various times at 80° C and heat treating at 550° C

[The attack (swelling) exhibited by the glass under these conditions of leaching is given]

Leaching time	Voltage departure at pH—							pH response ¹		Attack (swelling)		
	2.1	3.1	4.6	5.6	7.1	8.6	9.1	No heat treatment	Heated to 550° C	Observed	Used in calculation	Plotted in figure 2
hr	mV	mV	mV	mV	mV	mV	mV	mV/pH	mV/pH	Fringes	Fringes	cm
0.....	0	0	0	0	0	0	0	59	59	0	0	0
1.....	0	2	5	8	9	14	16	59	57	Detectable	0.01	6.3×10 ⁻³
2.....	0	29	79	159	161	243	257	59	27.4	<0.1	.07	2.1
4.....	0	49	105	171	185	232	239	59	17	>.1	.15	4.4
8.....	0	51	108	179	195	243	257	59	15.8	<1/4	.2	5.9

¹ pH response calculated from voltage departures at pH 2.1 and 4.6.

Figure 3, which was also plotted from the data in table 1, gives an over-all picture of the effect of thickness of the inhibiting film on the pH response of these glass electrodes. From this curve, it is obvious that the major portion of the inhibiting effect takes place for film thicknesses between 0.29×10^{-6} and 2.05×10^{-6} cm.

If the edge of the unit cell of cristobalite (7.0×10^{-8} cm. [24]) is used as a reference scale, the thickness of the inhibiting layer after 1 hour of leaching is $29.0 \times 10^{-8} / 7.0 \times 10^{-8} = 4.1$ unit cells. That some of this swollen layer does not contribute to the effective voltage-inhibiting layer was shown in the earlier work [16] by the hygroscopicity of the annealed leached film. In that investigation the outer layer was found to be strongly water absorbent, showing that the nonhygroscopic, voltage-inhibiting film was confined to a layer formed by reaction between the base glass and the lower level of the silica-rich layer. Just what portion of this swollen surface contributes to the inhibiting layer is merely conjecture, but the evidence indicates that a layer thinner than four unit cells of cristobalite was readily detected by the glass electrode in the present investigation.

These inhibiting films were removed by im-

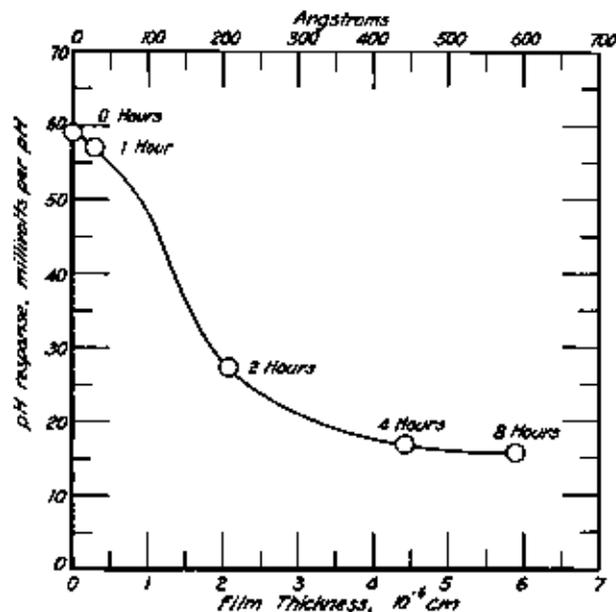


FIGURE 3. pH response of annealed, leached glass electrodes and the accompanying limiting thickness of the inhibiting layer on the surface of the glass brought about by leaching at 80° C.

mersing the electrodes for a few seconds in 1:1 hydrofluoric acid, thereby restoring the electrodes to their correct pH response [16].

2. Films of Petrolatum and Silicone

Other examples of nonhygroscopic films [25] that inhibit the pH response of the glass electrode are given in table 2 and figure 4. Curve A gives the voltage performance of the electrodes before the films of the electric nonconductors, silicone (stopcock grease), and petrolatum, were applied and also after these films were removed. The extent of the departures is not an indicator of the relative inhibiting capacity of the materials, as no method of film-thickness control was available. The petrolatum coatings often rendered the electrode so insensitive that no readings could be obtained with the electrometer.

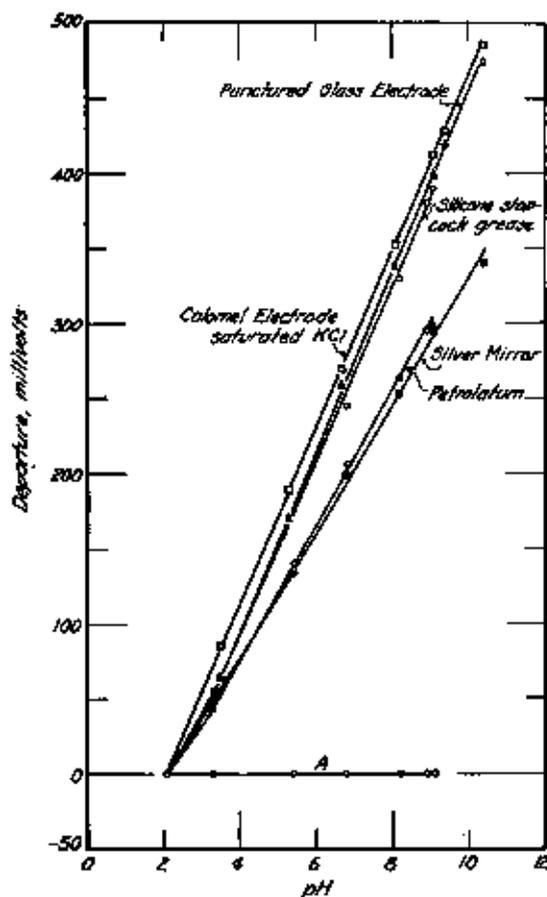


FIGURE 4. Voltage departures of the glass electrode brought about by films of silicone stopcock grease, petrolatum, and silver compared with the voltage response of electrodes having little or no hydrogen-electrode function.

The voltage departures brought about by a film of metallic silver are included in figure 4 to emphasize that films of electric conductors are

also effective in destroying the hydrogen-electrode function of glass electrodes.

TABLE 2. Voltage departures of glass electrodes brought about by thin films of nonhygroscopic materials, compared with the voltage performance of the saturated calomel half-cell and punctured, mercury-filled glass electrode.

pH	Voltage departure of glass electrodes coated with—			pH	Voltage performance of—	
	Silicone	Petrolatum	Silver		Calomel half-cell	Punctured glass electrode
2.1	mp	mp	mp	2.1	mp	mp
3.3	0	0	0	3.5	35	66
5.4	53	42	48	6.3	180	171
5.4	171	141	133	6.7	270	240
6.8	245	207	199	8.1	362	338
8.2	330	263	252	9.1	412	399
8.9	381	295	9.4	432	419
9.1	389	299	295	10.3	485	475
10.4	340			

It is interesting to observe that the voltage departures of these electrodes with inhibiting films approach the voltage departures observed for punctured glass electrodes (mercury filled) and the saturated calomel half-cell, figure 4. The limiting departure seems to be that dictated by an electrode having no response to hydrogen ion activity.

3. Films of Metallic Silver

The data plotted in figure 5 from table 3 show the voltage departures brought about by metallic silver films of different thicknesses. The voltage departures for these silver-coated electrodes, especially for the thinner silver coatings, demonstrated a tendency to drift toward zero departure prior to the recorded observations, particularly in the acid buffers. This feature was attributed to the presence of pinholes in the silver coatings. Hence the severe bow shown by two of the curves in figure 5 is believed to be spurious.

The inhibiting effect of silver films of different thicknesses on the pH response of glass electrodes is shown by the data given in table 3 and plotted in figure 6. The effect of the electrically conducting silver films applied to the outer surface of these electrodes is qualitatively similar to that for the silica-rich nonhygroscopic films obtained by leaching and annealing, and is also similar to the water-repellent coatings of petrolatum and silicone stopcock grease.

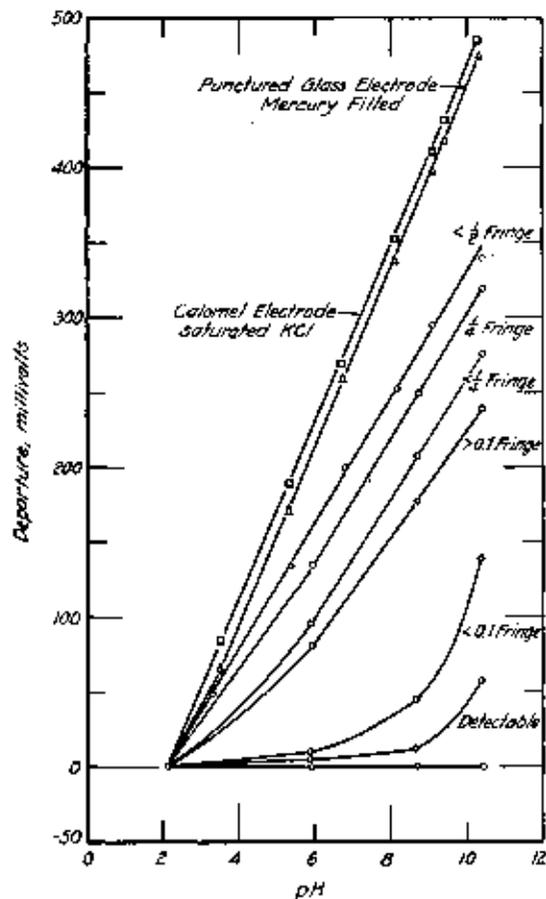


FIGURE 5. Voltage departures of glass electrodes brought about by thin films of metallic silver compared with the voltage departure of electrodes having little or no hydrogen-electrode function.

TABLE 3. Voltage departures and pH response of glass electrodes brought about by metallic-silver films of various thicknesses

Film thickness observed	Voltage departure at pH—				pH response ¹	Film thickness	
	9.1	5.9	9.1	10.4		Used in calculation	Plotted values
Fringes	me	mu	ms	me	ms/pH	Fringes	cm
0	0	0	0	0	59	0	0
(?)	0	6	12	57	62.1	0.01	0.3×10^{-4}
< 0.1	0	10	36	139	43.2	.07	2.1
< 1	0	81	177	239	30.2	.16	4.4
< 1/4	0	95	207	276	29.7	.2	5.9
1/4	0	134	242	319	26.6	.26	7.3
< 1/2	(?)	(?)	(?)	(?)	18	.46	13.2

¹ pH response calculated from voltage departures at pH 2.1 and 10.4.

² Detectable.

³ See table 2, column 4.

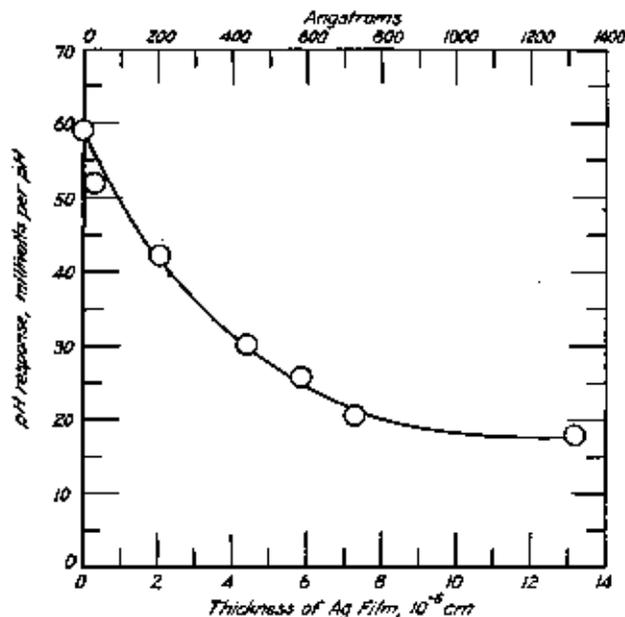


FIGURE 6. Inhibiting effect of silver films of different thicknesses on the pH function of glass electrodes.

4. Voltage Departure with Reference to Sodium-Ion Concentration

Voltage departures exhibited by glass electrodes have frequently been accredited to an equilibrative response to ions other than hydrogen [26] such as Na^+ . In the present investigation, there is no theoretical reason for attributing the voltage departures of the glass electrode brought about by the inhibiting films to a response of the electrodes to $[\text{Na}^+]$ of the buffers used. However, it is obvious that a thickness for any of the inhibiting films could be selected that would present a pseudo-correct response to the $[\text{Na}^+]$.

IV. Conclusions

The glass electrode readily detects the presence of certain voltage-inhibiting films as thin as 30 angstroms. This sensitivity approaches the practical limits of resolution of the electron microscope and the interferometer. Films of electrical conductors, such as silver, and electrical nonconductors, such as petrolatum, when applied to the outer surface, appear to be equally effective in inhibiting the pH function of the glass electrode. A study of the nature of these films may lead to a more satisfactory picture of the mechanism of the glass electrode.

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