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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Mercury Passivation Solutions of Potassium Chloride and Sodium Hydroxide and Hypochlorite

I. P. Sizeneva, Yu. A. Shchurov, and V. A. Val'tsifer

Perm State University, Perm, Russia
Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences, Perm, Russia

Abstract—Formation of anodic films on the surface of mercury in solutions of potassium chloride and sodium hydroxide and hypochlorite and the effect of these films on mercury passivation were studied by the potentiostatic method.

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At present, oxidation of mercury with strong oxidizing agents, to which belongs sodium hypochlorite (SHC), is a widely employed demercurization method. Demercurization is mostly performed with neutral and weakly acidic solutions, in which SHC shows a high oxidizing power, but decomposes exceedingly rapidly. Alkaline solutions of SHC are stable and belong to reagents that react with mercury to give its insoluble and low-volatile compounds. Such a treatment is necessary for eliminating fine mercury drops, which may remain unnoticed in crevices and irregularities after mechanical collection, and mercury adsorbed by various porous surfaces. However, formation of difficultly soluble compounds on the surface leads to passivation of mercury, which adversely affects the kinetics and completeness of demercurization.

It is known that there is no fundamental difference between the anodic passivation of a metal and its chemical passivation in solutions of oxidizing agents. The dissolution rate of the metal and, consequently, the degree of passivation of its surface are determined solely by the electrode potential. In this case, it is unimportant whether a given potential is maintained by polarization of the metal by an external current or by introduction of an oxidizing agent into a solution [1].

In this study, an electrochemical technique was used to examine in the potentiostatic mode the capacity of mercury for passivation in NaOCl, KCl, and NaOH solutions. The last two solutions were chosen for comparison, because formation of mercury oxide and calomel on the mercury surface is the most probable in alkaline solutions of SHC.

EXPERIMENTAL

The measurements were made on a stationary mercury electrode. Preliminarily degreased mercury for electrodes was subjected to additional purification by multiple passing of a dispersed metal through a 5% solution of $Hg_2(NO_3)_2$ in 5% HNO3 and bidistillate.

A NaOCl solution was prepared by passing chlorine at temperatures of –5 to 0°C through a sodium hydroxide solution containing no carbonates. Chlorine was obtained by reacting chemically pure hydrochloric acid with potassium permanganate [2]. The hypochlorite concentration was determined iodometrically for the active chlorine.

Polarization curves were recorded with a Pi-50 potentiostat. A V7-34A digital voltmeter served for additionally monitoring the potentials of the working electrode. In the electrochemical cell *1* (Fig. 1), the cathode and anode spaces are separated by a porous glass partition *2*. A saturated silver chloride reference electrode *3* was placed in the second lateral run-out whose nose is situated near the working electrode. The potential of the reference electrode was found experimentally to be 0.203 V (s.h.e.) at 20°C. A tube 4 mm in diameter was sealed in the cell bottom. Mercury was poured into the tube and acted as the working mercury electrode *4* with a surface area of 0.126 cm^2. An auxiliary platinum electrode 5 was introduced into the cathode space separated by the diaphragm. After the measurements, the solution under study and mercury were removed from the cell via a discharge tube equipped with a cock 6.

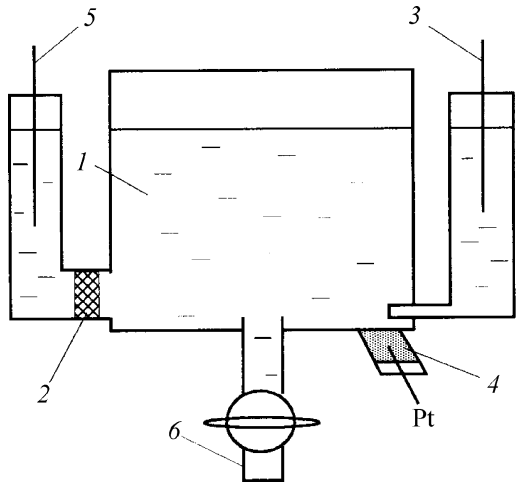

Fig. 1. Electrochemical cell.

All the potentials of the working electrodes were measured and are presented here relative to a saturated silver chloride reference electrode (s.s.c.e.). The solution temperature was maintained with a UTU-2 ultrathermostat. Anodic polarization curves were recorded with a step of 2 to 25 mV, depending on the nature of the curves. The electrode polarization started from the cathodic region from a potential $E = E_{cr} - 100$ mV to onset potentials of gas evolution. The curves obtained are shown in Figs. 2–5.

The anodic polarization curve of the mercury electrode in 1 M NaOH, measured at a temperature of 24°C (Fig. 2, curve *1*), shows a rise in the polarizing current density in the initial portion. According to [3], this active portion is due to partial dissolution of the forming oxide HgO upon a shift of the potential toward positive values. In addition, it was shown that the solubility of HgO in the alkaline solution is 10^{-5} M in the form of the $HHgO^{-2}$ anion, and 10^{-4} M as $Hg(OH)_2$. As a consequence, HgO is anodically formed at the mercury electrode and chemically dissolves in the alkali. After the critical passivation current density $i_{cr} = 5.06$ mA cm^{-2} is reached, a solid oxide film starts to be formed. Upon further shift of the potential in the positive direction, the current falls to the minimum value of the complete passivation current $i_{c.p} = 0.31$ mA cm^{-2}. The oxygen evolution onsets at a potential $E = 1.03$ V (s.s.c.e.), which is accounted for by the high overvoltage of oxygen evolution on mercury oxide. The oxygen evolution at the mercury electrode in 1 M KOH onsets at a potential close to 1.2 V (s.h.e.) [3, 4].

As temperature is raised to 50°C, the critical passivation current density increases to $i_{cr} = 13.7$ mA cm^{-2}, and the complete passivation current $i_{c.p}$ is 0.79 mA cm^{-2}. The oxygen evolution onsets at a potential $E = 0.920$ V.

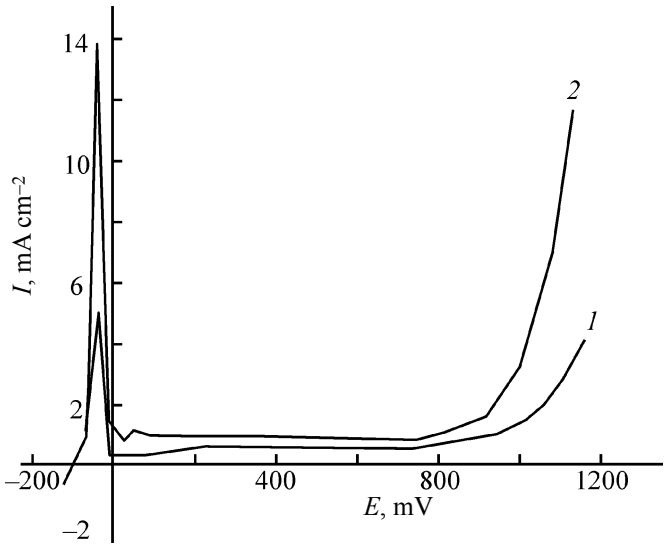

Fig. 2. Anodic polarization curves of a mercury electrode in 1 M NaOH. (*I*) Current density and (*E*) potential; the same for Figs. 3–5. Temperature (°C): (*1*) 24 and (*2*) 50.

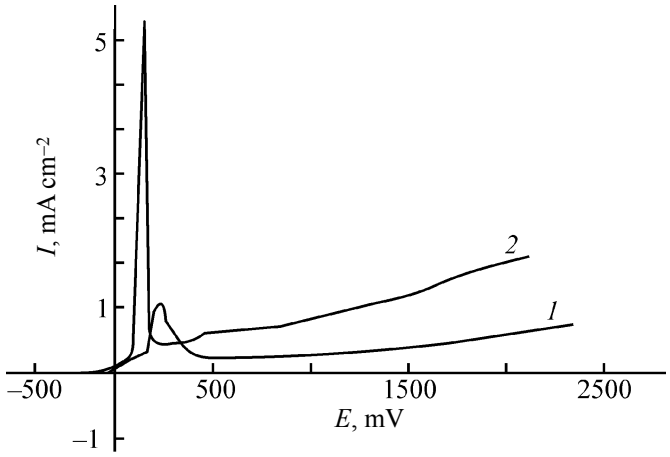

Fig. 3. Anodic polarization curves of a mercury electrode in 1 M KCl. Temperature (°C): (*1*) 25 and (*2*) 50.

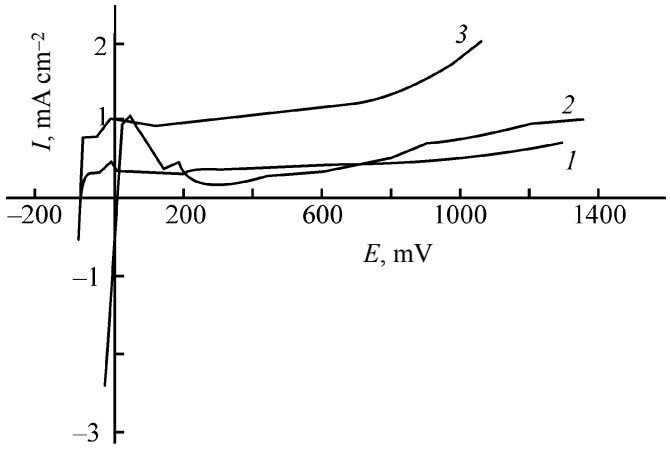

Fig. 4. Anodic polarization curves of a mercury electrode in 1 M NaOCl. pH: (*1, 2*) 13 and (*3*) 10 (HCl). Temperature (°C): (*1, 3*) 25 and (*2*) 50.

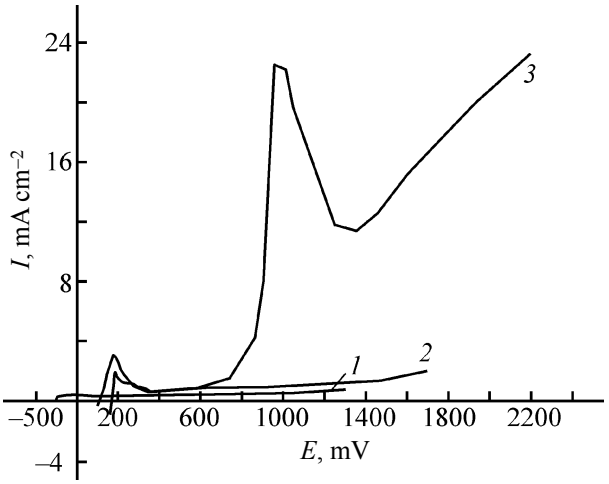

Fig. 5. Anodic polarization curves of a mercury electrode in 1 M NaOCl at 24°C. (*1*) Without orthophosphoric acid (pH 12.5); with orthophosphoric acid, pH: (*2*) 11 and (*3*) 9.5.

The anodic polarization curve of the mercury electrode in 1 M KCl also has the form characteristic of the anodic passivation of metals (Fig. 3). At a temperature of 25°C, the passivation onsets at a potential $E_{p.o}$ = 0.230 V, the critical passivation current density i_{cr} = 1.03 mA cm^{-2}, and the complete passivation current ic.p = 0.20 mA cm^{-2}. At 50°C, the critical current density and complete passivation current are higher: i_{cr} = 5.31 mA cm^{-2} and $i_{c.p}$ = 0.43 mA cm^{-2}. In anodic polarization of mercury in a neutral solution containing chloride ions, calomel is formed on its surface. In the complete-passivation region, the mercury surface is fully blocked by a calomel film. It is visually observed that a light gray film appears on the mercury surface and becomes darker as the potential shifts into the anodic region. A shift of the electrode potential as far as 3 V, does not lead to a steep rise in current, i.e., no oxygen evolution is observed in the potential range studied.

The anodic polarization curves of a mercury electrode in an SHC solution at two temperatures and different pH values are shown in Figs. 4, 5. The critical current density in the anodic region at 25°C for 1 M NaOCl (Fig. 4, curve *1*) is i_{cr} = 0.48 mA cm^{-2}, and the complete passivation current $i_{c.p}$ = 0.40 mA cm^{-2}. At the higher temperature (50°C), as also in sodium hydroxide and chloride solutions, these currents are higher: i_{cr} = 1.04 mA cm^{-2}, $i_{c.p}$ = 0.79 mA cm^{-2}. The run of the polarization curve (presence of two peaks) before the onset of complete passivation indicates that a mixed film composed of calomel and mercury oxide can be formed on the electrode surface.

At low overvoltages, the forming deposit has a light yellow color corresponding to that of mercury oxide, and at E > 0.7 V, the surface of the mercury electrode becomes darker. It is known that addition of an alkali to a solution of a mercury(I) salt results in that a black deposit, a mixture of highly dispersed metallic mercury and mercury(II)oxide, is formed by the reaction

$$Hg_2 + 2OH^- = Hg + HgO + H_2O.$$

Probably, the same process occurs at the surface of an anodically polarized mercury electrode. In the course of further anodic polarization, the thickness of the dark surface layer increases.

The stability of the depolarizer-ion ClO^- and of the forming oxide film, and, consequently, the passivation of mercury and the corrosion rate are affected by the pH of the medium. To study this effect, the starting 1.3 M NaOCl solution was neutralized with solutions of hydrochloric or orthophosphoric acid (acid dilution 1 : 1), with the pH value controlled potentiometrically. With the known volume of the acid added, the starting solution was diluted with a calculated amount of water to obtain 1 M NaOCl.

In the case of neutralization of the starting solution with hydrochloric acid, the concentration of Cl^- ions increases upon correction of the pH value and no other anions that could affect the structure of the double layer and the qualitative composition of the passivating film appear in solution. The anodic polarization curve for an SCH solution neutralized with hydrochloric acid to pH 10 is shown in Fig. 4 (curve *3*). It can be seen that, compared with the starting SCH solution, the stationary potential and the passivation onset potential are shifted in the positive direction. The first peak in the polarization curve corresponds to coverage of the electrode surface by an oxide film and is observed at $E_{1p.o}$ = 0.040 V and current density i_{1cr} = 1.07 mA cm^{-2}, which twice exceeds the critical current for the starting SCH solution. As the potential shits in the positive direction further, two dips and one peak appear in the polarization curve. The second peak ($E_{2p.o}$ = 0.18 V, i_{2cr} = 0.47 mA cm^{-2}) is associated with the formation of a calomel film. The first dip in the current, $i_{1c.p}$ = 0.39 mA cm^{-2} at a potential $E_{1c.p}$ 0.140 V corresponds to preferential coverage of the mercury surface by an oxide film, the second dip $i_{2c.p}$ = 0.17 mA cm^{-2} at $E_{2c.p}$ = 0.30 V is associated with the most complete blocking of the surface by calomel. The last example most clearly points to the complex composition and structure of the passivating film and its transformation in the course of anodic polarization of mercury in the SCH solution.

The anodic polarization curves of a mercury electrode for solutions with pH 11 and 9.5, produced by neutralization of the starting SCH solution with orthophosphoric acid, are shown in Fig. 5. A decrease in the pH value and increase the concentration of phosphate ions result in that the stationary potential and the passivation onset potential are shifted in the positive direction and the current density of a completely passivated electrode, ic.p, increases. The current of mercury passivation onset in a solution with pH 11 has the maximum value (i_{cr} = 3.9 mA cm^{-2}), which exceeds that in the starting SCH solution. Lowering the pH value to 9.5 leads to a decrease in the critical current to 1.95 mA cm^{-2}, with the passivation onset potential (0.190 V) changing only slightly. These facts indicate that the forming passivating film contains, in addition to the oxide and calomel, also mercury phosphate. This leads to additional "loosening" of the film and to an increase in the current ic.p.

At pH 9.5 and potential of 0.80 V (Fig. 5, curve *3*), a steep rise in the anode current is observed, which probably corresponds to oxidation of the hypochlorite ion to the chlorite ion:

$$ClO + 2OH^- - 2e \rightarrow ClO_2^- + H_2O.$$

The maximum current density of 22.7 mA cm^{-2} corresponds to the electrode potential of about 1.0 V. Further shift of the potential in the positive direction leads to a decrease in the current. It can be assumed that this "secondary passivation" is associated with the formation of mercury peroxide HgO_2.

The values found for the stationary potential E_{st}, passivation onset potential $E_{p.o}$, critical passivation current icr, and complete passivation current of mercury are listed in the table for all of the solutions studied.

It follows from these results that the stationary potentials of the mercury electrode in SCH solutions are a compromise between the potentials of a calomel and metal oxide electrodes, calculated for the corresponding solution compositions. The current for the fully passive state of mercury in the SCH solutions is 1.3 and 2 times those for sodium hydroxide and potassium chloride, respectively. This indicates that, as a result of anodic polarization in an SCH solution, a mixed calomel–oxide film is formed on the mercury surface and this film has a "looser" structure than a purely oxide or calomel film. At potentials close to the stationary value, oxidation (corrosion) of mercury brought in contact with an SCH solution should occur at boundaries between oxide and calomel parts of the film, and, apparently, should do so at a higher rate than that in sodium hydroxide or potassium chloride solutions.

Main characteristics of the passivation process of a mercury electrode at 25°C

1 M solution	pH	E_{st}	$E_{p.o}$	i_{cr}	$i_{c.p}$
		V (s.s.c.e.)		mA cm^{-2}	
NaOH	~13	–0.164	–0.010	5.06	0.31
NaCl	6.3	–0.030	0.230	1.03	0.20
NaOCl	~13	–0.077	0.090	0.48	0.40
NaOCl+ + HC1	10	0.001	0.040 0.183	1.07 0.47	0.39 0.17
NaOCl+ + H_3PO_4	11	0.110	0.170	3.09	0.60
NaOCl+ + H_3PO_4	9.5	0.162	0.192	1.95	0.71

Introduction of phosphate ions into the SCH solution and lowering the pH value shift E_{st} and $E_{p.o}$ in the positive direction and hinder passivation of mercury, because the bulky and multi-charged phosphate ions not only affect the structure of the double layer, but also are incorporated into the passivating film and thereby loosen it. It should be kept in mind here that the solubility of mercury phosphate markedly exceeds that of calomel and mercury oxide. All these factors lead to a pronounced increase in the current in the passive state of mercury.

CONCLUSIONS

(1) It was found that the current of the completely passive state of mercury in a sodium hypochlorite solution is 1.3 and 2 times that in a sodium hydroxide or potassium chloride solution, respectively. The mixed passivating film composed of mercury oxide and calomel, formed on the surface of mercury brought in contact with a sodium hypochlorite solution, has a looser structure than films of pure mercury oxide or calomel.

(2) It was shown that the mixed oxide–calomel film has poorer protective properties, compared with films composed of pure mercury oxide and calomel, which makes it possible to recommend an alkaline solution of

sodium hypochlorite for demercurization by conversion of mercury into low-volatile compounds.

(3) Introduction of phosphate ions and lowering of the pH of the sodium hypochlorite solution shift the stationary potential and the passivation onset potential in the positive direction and hinder the passivation of mercury.

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