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## Abstract

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### PHYSICAL CHEMISTRY

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# PASSIVATION AND DEPASSIVATION OF A LEAD ANODE IN CONCENTRATED FLUOSILICIC, PERCHLORIC, AND FLUOBORIC ACIDS

*(Presented by Academician A. N. Frumkin, March 28, 1957)*

Recently the literature has described studies of the electrochemical system $PbO_2$/acid/Pb with an electrolyte of sufficiently concentrated perchloric, fluosilicic, or fluoboric acids ($^1$). Such cells operate at low temperatures and high discharge currents. However, the behavior of the lead anode and the conditions leading to its passivation in the indicated acids have not been studied in detail.

To investigate the process of passivation of lead (C–O), redistilled perchloric acid was used, as well as fluosilicic acid containing (in %): $H_2SiF_6$ 47, $SiO_2$ 0.14, $SO_4$ 0.01, and traces of As. Fluoboric acid was prepared from chemically pure $H_3BO_3$ and HF and had the following composition (in %): $HBF_4$ 49.5; $H_3BO_3$ 3.04; Pb 0.1. The experiments were carried out in polystyrene cells in special cryostats (temperature fluctuation not more than $±0.5°). The anode potential was measured by the compensation method or by means of a cathode voltmeter with resp
electrode in the same acid solution.*

In acid of a given concentration at constant temperature, the lead anode remains active and is only slightly polarized if the anodic current density ($i_a$) does not exceed a certain critical value ($i_{\mathrm{cr}}$), which depends on a number of factors. Experiments showed that the time after which the anode becomes passivated ($t_p$) depends on the chosen passivating current density and, over the interval of $t_p$ from several seconds to 1½ hours, is determined with good approximation by the known equation: $\lg t_p = A - B \lg i_a$, where $A$ and $B$ are constants.

Lowering the temperature in all cases greatly decreases the value of $i_a$ at which the anode becomes passivated in the same time. With a large decrease in acid concentration, this current density increases noticeably. Lead is most readily passivated in $H_2SiF_6$. In $HClO_4$ and $HBF_4$ at $t > -20°$ and $i_a < 100$ mA/cm$^2$, lead is not passivated.

Figure 1

Figure 1: Figure 1

The initial stage of passivation is undoubtedly a diffusion process. This follows from the fact that, other conditions being equal, stirring (rotation of the disk electrode) increases the passivation time. For example, in 7.9 N $H_2SiF_6$ at $i_a = 40$ mA/cm$^2$ and $t = -20°$:

| Number of revolutions | Without stirring | 300 | 450 | 520 | 650 | 800 |
|---|---|---|---|---|---|---|
| $t_p$, min | 0.86 | 3.26 | 7.25 | 13.3 | 34 | 60 |

At $i_a > i_{cr}$, the rate of ionization of lead is greater than the rate of electrochemical transfer of $Pb^{2+}$ ions and the rate of their diffusion into the solution under the influence of the concentration gradient that appears. As a result, the concentration of $Pb^{2+}$ increases and a porous phase layer is formed of a poorly conducting divalent lead salt of the given acid. The current density and the potential in the pores increase sharply, and in these regions a passivating layer of $PbO_2$ is formed.

Figure 1 shows a typical curve for the change of potential with time during passivation of a Pb anode in 7.9 N $H_2SiF_6$ at $i_a = 40$ mA/cm$^2$ and $t = -10°$ without stirring. In the initial stage of passivation, because of the resistance of the salt layer, the potential rises sharply, while the current falls from 40 to 5 mA/cm$^2$. Then, as a result of the formation in the pores of $PbO_2$, which has good electronic conductivity ($^2$), passage of current with evolution of oxygen becomes possible. Therefore the potential decreases and the current increases to its initial value. The passivating layer of $PbO_2$ soon spreads over the entire surface of the electrode, while the lead-salt layer, receiving no replenishment, rapidly dissolves in the acid, and a potential is established corresponding to the oxygen overvoltage on $PbO_2$ at the given $i_a > i_{cr}$.

**Fig. 1.** Change of potential with time during passivation of a lead anode in 7.9 N $H_2SiF_6$ at $t = -10°$

Figure 2 shows depassivation curves after switching off the passivating current of a lead anode passivated in 7.9 N $H_2SiF_6$ at $i_a = 40$ mA/cm$^2$ and $t = -10°$,

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* The measured potential of the $PbO_2$ electrode in 7.9 N $H_2SiF_6$ at 25° is 1.774 V, according to the hydrogen scale.

Fig. 2

Figure 2: Fig. 2

and held after passivation at the same value of $i_a$ for 1, 2, 4, 6, and 8 min. It is evident from this figure that, after the passivating current is switched off, the potential rapidly falls to $\varphi = 0.70 \div 0.66$ V on the normal hydrogen scale. This value, which characterizes the potential of passive lead, is maintained for a longer time the longer the current was passed through the passivated anode.

Rotation of the electrode accelerates depassivation; for example, at 700 rpm it is shortened by approximately a factor of 2.

If, after passivation, a current of low density ($i_a < i_{\text{cr}}$) is passed through the lead anode, the potential is maintained for some time at the same value ($\varphi = 0.70$—$0.66$ V on the normal hydrogen scale); for example, after holding at $i_a = 40$ mA/cm$^2$ for 4 min, the passive state was maintained at the indicated potential for 15 min at

$i_a = 1$ mA/cm$^2$, 27 min at $i_a = 4$ mA/cm$^2$, and 40 min at $i_a = 5$ mA/cm$^2$. At $i_a > 6$ mA/cm$^2$ the potential increases to a value corresponding to oxygen evolution ($\sim 2.2$ V)$^*$.

Fig. 2. Curves of the change in potential with time during the depassivation of lead in 7.9 N $H_2SiF_6$ at $t = -10°$ after holding the passivated anode at $i_a = 40$ mA/cm$^2$: 1—1 min, 2—2 min, 3—4 min, 4—6 min, 5—8 min.

The indicated value of the potential of passive lead is close to the value 0.666 V reported by Lander (4) for the reaction

$$\mathrm{Pb} + 2\mathrm{H_2O} = \mathrm{PbO_2} + 4\mathrm{H^+} + 4e.$$

Taking this reaction for the passive state of lead, we must assume that a porous layer of $\mathrm{PbO_2}$ in contact with the clean lead surface is responsible for passivation. Hence depassivation is the discharge of a short-circuited galvanic cell $\mathrm{PbO_2}$/acid/Pb. In this case the following reactions take place: the anodic reaction

$$\mathrm{Pb} + \mathrm{SiF_6}^{2-} \rightarrow \mathrm{PbSiF_6} + 2e$$

and the cathodic reaction

$$\mathrm{PbO_2} + 2e + \mathrm{SiF_6}^{2-} + 4\mathrm{H^+} \rightarrow \mathrm{PbSiF_6} + 2\mathrm{H_2O}.$$

From the results of our experiments it may be concluded that, as the holding time of the passive anode at constant current density ($i_a > i_{\text{kp}}$) is increased, the $PbO_2$ layer thickens, the length of the pores increases and their diameter decreases, as a result of which diffusion of the reaction products in the pores becomes more difficult and the depassivation time increases (see Fig. 2).

When an anodic current of magnitude $i_a < i_{\text{kp}}$ is passed, depassivation is slowed, which is evidently associated with retardation of the cathodic process of $PbO_2$ reduction, as well as with an increase in the ohmic resistance of the operating galvanic cell owing to an increase in the concentration of lead ions in the pores of the passivating layer.

Potentiostatic measurements of the current at a constant potential value were also carried out. A passivated lead anode at $i_a = 40$ mA/cm$^2$ and $t = -10°$ in 7.9 N $H_2SiF_6$ was held at the same current density for various times (4, 8, and 12 min). Then, by decreasing the value of $i_a$, the potential was lowered to $\sim 0.75$ V and, beginning from this value, was gradually increased while simultaneously measuring the current under established stationary conditions. The results of these measurements are shown in Fig. 3. From the curves in this figure it is seen that, in order to maintain any stationary value of the potential in the range from 0.8 to 2.2 V, a preliminarily

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* At $i_a = 6$ mA/cm$^2$ under the stated experimental conditions, before the potential assumes the value corresponding to oxygen evolution ($\sim 2.1$ V), a delay appears on the $\varphi(\tau)$ curve at $\varphi = 1.15$ V. According to Lander (4), the system

$$\mathrm{PbO} + \mathrm{H_2O} = \mathrm{PbO_2} + 2\mathrm{H}^+ + 2e$$

has a potential of 1.100 V; it may therefore be supposed that, before transition to the potential of oxygen evolution at $i_a > i_{\text{kp}}$, metallic lead in the pores is covered by a layer of PbO or of divalent lead salts, which soon pass into $PbO_2$.

for a passivated anode, an anodic current of one and the same magnitude is required. At $\varphi < 0.8$ V the current tends to decrease as a result of depassivation; at $\varphi > 2.2$ V oxygen begins to be evolved and the current increases sharply with increasing potential. The stationary current in the potential interval from 0.8 to 2.2 V, since it prevents depassivation, may be identified with the corrosion current of the galvanic couple $PbO_2$—Pb. A decrease in the corrosion current

**Fig. 3.** Dependence of current density on the potential of passive lead in 7.9 N $H_2SiF_6$ at $t = -10°$, measured by the potentiostatic method after holding following passivation at
$i_a = 40$ mA/cm$^2$: **1** –4 min., **2** –8 min., **3** –12 min.

with increasing time of preliminary holding of the passive electrode at high current density ($i_a > i_{\text{kp}}$) is caused by an increase in the thickness of the passivating layer and in the ohmic resistance of the galvanic couple (see Fig. 3). The constancy of the corrosion current over a broad range of potentials is

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also apparently connected with the fact that an increase in the potential in the interval indicated above leads to a commensurate increase in the thickness of the passivating layer and in the length of the pore channels.

Passivation of lead in concentrated $H_2SiF_6$ has an external similarity to the passivation of iron in sulfuric or nitric acids described by Bonhoeffer and co-workers ([3],[5] ). However, as follows from the foregoing, the mechanism maintaining the passive state of the lead anode and the process of its depassivation are of a different nature. The difference consists, first of all, in the fact that in the case of iron the anodic stationary current required to preserve passivity is 3 orders of magnitude smaller than in the case of lead in $H_2SiF_6$, and it is expended on the formation of iron oxide, which dissolves at a constant rate, and not on suppressing the operation of the galvanic couple consisting of the porous layer of lead dioxide, acid, and metallic lead.

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*Note: Figure translations are in progress. See original paper for figures.*