814. *Anodic Processes. Part III.* The Passivation of Mercury in Hydrochloric Acid.*

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The continued polarisation of the mercury anode in 0·1N-hydrochloric acid leads to passivation. A quantitative relation has been established between the time required to effect passivation and the current density for an electrode in 0·1N-hydrochloric acid at 25°. The course of passivation has also been followed oscillographically and some comments are made upon the state of an electrode approaching passivation and in the passive state.

The anodic passivation of mercury in aqueous hydrochloric acid was observed by Paschen in 1890 (*Wied. Ann.*, 1890, **39**, 61), but, somewhat surprisingly, has been given no systematic study. Yet, in relation to passivation and indeed to other electrode phenomena, mercury may well be of more theoretical interest than any other metal, since it can be more readily brought to a standard state, has a homogeneous surface, and shows passivation as striking and sudden in onset as almost any other. This supposition is confirmed in a recent paper by Thirsk (*Proc. Phys. Soc.*, 1953, **66**, *B*, 129), who has shown that the passivating film of calomel consists of crystals with a unique orientation with respect to the metal surface. This orientation is such that the {110} planes alone lie parallel to the surface: these contain Cl·Hg·Hg·Cl entities (Cl–Hg, 2·52 Å; Hg–Hg, 2·53 Å; Cl–Cl, 3·33 Å), forming an approximately hexagonal array of " mercury and chlorine ion pairs."

The films examined by Thirsk were, on the assumption of 100% current efficiency in the anodic production of calomel, some 60—200 Å thick. It has been found in the present work that a quite invisible film only 22 Å thick will effect passivation, which occurs more readily the higher the purity and deoxygenation of the system.

Such perfectly orientated crystalline films must have grown in an orderly manner from more elementary structures, the formation of which was discussed in the previous paper. The present intention is to present such systematic results on passivation as have been obtained in this preliminary work, in order to complete the survey of the sequence of anodic phenomena: it would be altogether premature to attempt any extensive theoretical treatment.

The " passivation time " may be defined as the time between switching on of a constant current and the incidence of passivation. It has been found to be systematically related to current density in the manner shown in Fig. 1; the logarithmic plot is seen to be linear and has, under the experimental conditions (25°; 0·1N-HCl), a slope consistent with a law $it^{0·75} =$ a constant. All the results included in this plot, covering passivation times from 0·5 sec. to 40 min. and current densities from 2400 to 5 μA/cm.^{2}, were obtained from experiments conducted in hydrophobic vessels. Similar data, showing a wider scatter about the same straight line, were provided by experiments made in normal vessels (*i.e.*, not treated with Silicone; see previous paper) for passivation times up to 90 min. No definite lower limit has been determined for the current density that will effect passivation.

Two oscillographic records of passivations are shown in Fig. 2. The peak, discussed in the previous paper, is discernible at the beginning of a long trace of sensibly constant potential, which rises somewhat before the catastrophic increase which marks the onset of passivation. This sudden increase of potential is interrupted by a rapidly traversed arrest, indicated on the oscillogram by a " kink " at about 0·8 v. The potential at which this occurs, and the potential of the electrode in the passivated state, have not been systematically studied, and all that can be said about them at present is that they do not seem to be strongly dependent upon current density.

The long section of uniform potential already discussed requires some further comment from the aspect of this paper. There can be no doubt that calomel generation starts at

* Part II, preceding paper.

the beginning of this section and it clearly proceeds by a mechanism which has no effect on the current-carrying powers of the electrode for a comparatively long time. This precludes a layer-by-layer deposition of calomel over the whole electrode surface. The only alternative is the growth of calomel islands. It does not seem likely, however, that the calomel islands grow to a height exceeding 20 Å, approximately the thickness of the minimal passivating film. Lateral growth must therefore occur, and must progressively decrease the effective working area of the electrode. Since the current is maintained at a constant value, the current density at the surface not covered by the islands must increase, yet there is no increase in the working electrode potential until this process approaches its final stages. This is clearly related to the observations that the potential is almost independent of apparent current density over a very wide range and exceeds the reversible calomel potential by only a small margin which does not appear to correspond with any known kind of overpotential.

There can be no doubt that in this region of the polarisation curve the electrode reaction is still composite. The slow decay of overpotential and the secondary reaction occurring on resting suggest that mercuric entities are still being generated, and it is these which, from their potential-determining effect, are thought to be largely responsible for the " overpotential," at least in the earlier sections of the level region. It must be noted,

FIG. 1.

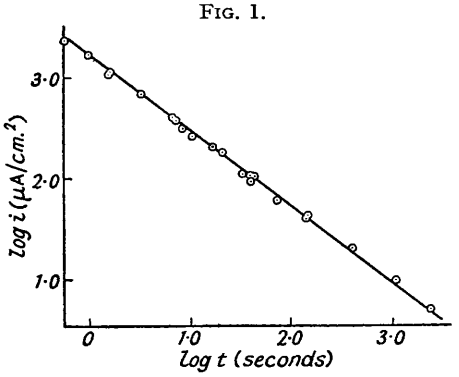
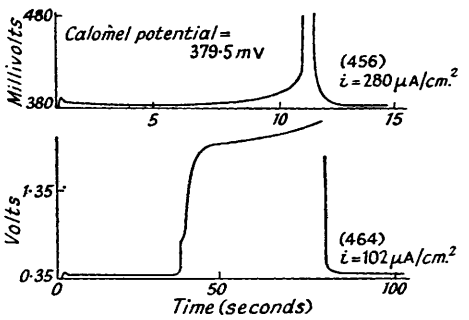


FIG. 2.



however, that the overpotential decay becomes faster as this section is traversed and it is probable that a continuous improvement in electrode reversibility and decrease of " chemical overpotential " is being masked by a rising concentration overpotential as the calomel islands close together and the effective current density increases. The signs of such an effect are always apparent before the occurrence of passivation and, indeed, some of the polarisation curves at low current densities show flat minima which could be well explained by the supervention of one kind of overpotential by another.

It is clear that the whole of this region of level polarisation potential requires to be investigated in detail, but, although this has not yet been done, it is felt that there is compelling reason for the postulation of a two-fold electrode process. Thus, if the whole of the current were devoted to the production of calomel, it might be understandable that a very low current could generate a passivating film without undue congestion of the electrode surface (" congestion " necessarily being reflected in electrode potential) in the earlier stages. But it is incredible that a current some powers of ten greater should cause very little more congestion : it is true that passivation occurs earlier (in terms of coulombs passed) with the heavier current, but, before the actual passivation, the potential is only a very little greater. This fact seems to require an electrode reaction scheme of a kind able to maintain a steady state at the electrode surface, corresponding with the steady potential. Such a scheme, involving the concurrent generation of mercuric chloride, may be tentatively suggested.

After traverse of the initial peak, the primary electrode reaction is thought to be the discharge of chloride ions (mechanism II; cf. preceding paper), giving first the disordered chloromercury film which " condenses " to form calomel. When established, however,

this film can initiate another anodic reaction; the charging of chloromercuric ions, $HgCl^+$, which, when disengaged, will instantly become mercuric chloride molecules (or their anionic derivatives) which will diffuse away and subsequently take part, as opportunity allows, in secondary, non-electrochemical, generation of calomel at the electrode surface. The joint operation of these two reactions, one tending to maintain and the other to deplete the population of the chloromercury film, might maintain a *status quo* at the mercury surface for each current density. Thus, since the rate of increase of population is proportional to the difference, whereas the current density is proportional to the sum, of the rates of these reactions, there could arise a steady state with a total population of chloromercury on the whole electrode surface directly proportional to the total current. This, at present, is felt to be over-simplified for any further theoretical development.

It will be noted that this argument proposes another mechanism (III) for the anodic formation of mercuric chloride, differing from mechanism I, previously invoked; it is suggested that it can occur only secondarily to chloride-ion discharge and may be easier because it involves only single-electron transfer steps.

Few observations have been made on the electrode in the passive state, but it is certain that an extremely small current continues to flow and is, indeed, required to maintain the passivity. There is no sign of any change in the anodic products in this state, for no solid substance other than calomel has been detected in the passivating films (Thirsk, personal communication). Switching off the polarising current causes an instant fall of potential, but not directly to the calomel potential, which is reached asymptotically after a short delay (Fig. 2). This may be due either to " chemical overpotential " arising from continued generation of mercuric chloride in the passive state, or to concentration polarisation of a special kind. Restoration of the current causes rapid, but not instantaneous, reinstatement of the high potential characteristic of passivity. At present the scanty evidence available suggests that this high potential is either an extreme concentration overpotential arising in minute pores and fissures in the film, or an ohmic potential difference due to the traverse of the film itself by ions. It is not known whether the structure of the film is sufficiently open to allow this to occur through the interionic interstices, or whether it might occur by a Grotthus mechanism.

A single experiment has been conducted which may be significant in relation to this problem. An electrode already passivated was subjected to closely controlled polarisation and it was found that there was a tendency for it to adopt alternative states with an unstable transition region in between. Thus, on reducing the polarising current just below the limit to maintain full passivity, it was found that 0·58 μA/cm.^{2} would maintain the potential at a steady value of 1·33 v. Further reduction of the current allowed depassivation to occur, with a fall of potential to about 0·40 v. Cautious increase of the current again to the same value as before, 0·58 μA/cm.^{2}, then maintained the electrode at a steady potential of 0·47 v. Two steady states involving the same current density but with a wide difference of potential in between were therefore realised, and were evidently characterised by different rate-limiting factors. This observation may not be unconnected with the " kink " previously noted in the steeply rising oscillographic record of passivation. Such singularities as a general rule mark a change of electrode process or state. It is tempting to think that this might be the change over from a " film fissure " to a " film permeation " mode of ion transfer between mercury and solution.

In conclusion, it is stressed, that many of the conjectures made in this preliminary survey may require subsequent revision, and are advanced for the main purpose of lending some coherence to the numerous new phenomena reported.

The experimental methods used in this work were identical with those described in the previous paper.

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