A NEW APPROACH TO EXPLAIN THE ANODIC PASSIVATION AND PERIODIC PHENOMENA: THE PN JUNCTION AND SR MECHANISMS*

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IT is known[1] that when nickel is subjected to anodic polarisation under galvanostatic conditions the electrode displays oscillations in potential, under controlled conditions. These oscillations are very regular and persist for a considerable time. The occurrence of similar oscillations has been reported[2-9] in a number of passivating systems. There has been difficulty in giving a plausible mechanism for this phenomenon. One of the explanations given[2] is based on the idea that there is a periodic change in the thickness of the film by alternate dissolution and deposition. Another approach has been to interpret in terms of oxygen evolution which disturbs the stationary film adjacent to the electrode on the solution side and thereby enhances dissolution.[3] Another factor[4] which has been invoked to explain the periodicity is the rise of the pH which causes the increase in thickness of the film, leading to oxygen evolution which restores the original pH by agitation and facilitates solution of the film.

In all these explanations there has been no mechanism given as to why there are such sudden changes in the rate of formation or dissolution of the film. Furthermore[5] it is known that the amount of electricity to be passed between two oscillations often hardly corresponds to the building of a few unit cells of the film. It is difficult to understand how such a small amount of product formed can bring about such large differences in convection.

The present authors have repeated the experiments of Osterwald and Feller[1] on the anodic polarisation of nickel (A.R. quality) in half-molar sulphuric acid. Figure 1 shows the typical oscillogram of such oscillations. It appears to us that these phenomena are best understood in terms of solid state effects in the film formed. The importance of solid state effects has been directly or indirectly invoked by a number of earlier workers to explain anodic phenomena.[10]
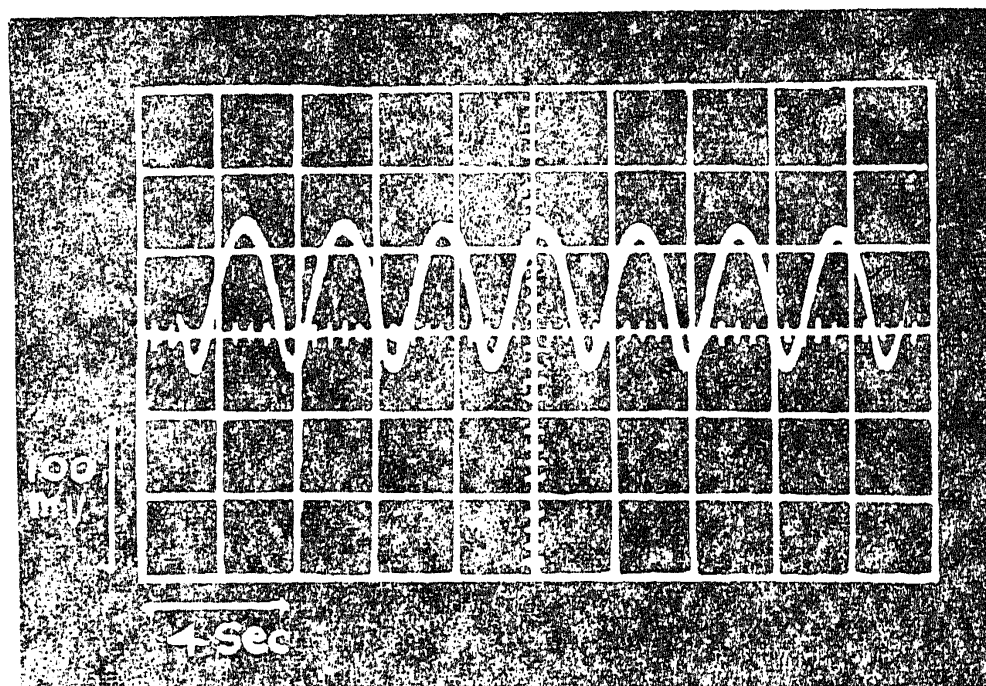

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FIG. 1. Anodic polarisation of nickel in 0·5 M sulphuric acid under galvanostatic conditions. Current density—7 mA/cm.²; Typical oscillations (anode potential 1·35–1·45 V. vs. N.H.E. at the end of 10 minutes polarisation. Voltage sensitivity—50 mV/cm. Time scale—2 sec./cm.

We shall first outline the general mechanism :—The basic mechanism is the formation of a high field domain consisting of either a stoicheometric region (SR) or a PN junction. The following detailed steps are postulated based on a logical application of the known solid state phenomena as well as about structure of nickel oxide (although they may require some revision on the basis of some specific information that may become available later):

(a) Cations move from the metal into the film thereby forming a cation excess layer at the metal/film interface.

(b) Schottky interaction would take place at the film/solution interface leading to the formation of surface cations and cation deficiency layer in the film near the film/solution interface.

(c) Surface cations enter the solution by interacting with an acceptor in the solution (The acceptor may be entities such as solvent cage, anions, complexing ions, etc.).

(d) Transport of cation vacancies and excess cations occurs in opposite directions aided by the field.

(e) Somewhere in the middle, the excess cations and the cation vacancies, combine to form a thin stoichiometric or nearly stoichiometric layer.

(*f*) Across the stoichiometric layer, there is a field created by the positive charge of the cation excess region and the negative charge due to cation vacancy region.

(*g*) Tunnelling of electrons in the film takes place from the vacancy side of the stoichiometric layer to the cation excess side of the layer. This gives rise to holes on the cation vacancy side and the electrons on the cation excess side. This partially or fully neutralises the space charges on the two sides of the boundary.

(*h*) The stoichiometric layer grows into a large stoichiometric region (SR).

(*i*) The SR offers a high resistance for ion transport and causes a high IR drop and the potential rises.

(*j*) The enhanced thickness of SR being high, the tunnelling of electrons referred to in (*g*) will stop and builds up an electrostatic field.

(*k*) The high field causes an internal field emission from the valency band in the film from the cation vacancy side to the cation excess layer and causes a sudden breakdown of the stoichiometric region leading to creation of large number of defects such as cation vacancy and cation excess regions thereby causing good ionic conduction across the region. The potential, therefore, falls.

(*l*) The building up of the SR starts again by transport of vacancies and excess cations.

In the above mechanism, it has been assumed that the electrons or holes generated by tunnelling or by internal field emission are mostly in traps and are not taking part in conduction. The conduction is, therefore, entirely or mostly ionic. Alternatively, the development of appreciable concentration of cation excess or deficit and the corresponding high concentration of elections and holes may lead to electronic conductivity of p and n type in the two regions separated by a p–n junction in the stoichiometric region. In such a case, the field due to applied potentials would be mostly at the p–n junction. The cation transport, therefore, would be by a diffusion process in the cation excess and cation deficiency regions and would be field-controlled in the p–n junction. If the latter is fast enough due to the high field present, the overall transport may be mostly solid state-diffusion controlled in the two regions and would be *independent of potential*. This may correspond to the passivation current plateau[11] in the i–e curve of nickel in sulphuric acid obtained under potentiostatic conditions.

If a thick p–n junction builds up, it may lead ultimately to a breakdown and cause oscillations.

In the above discussion, we have considered that the transport becomes slow in the stoichiometric region as compared to that in non-stoichiometric region. This is largely true except under very exceptional circumstances involving small changes in stoichiometry.

In the present note, we confine ourselves to a new line of experimental evidence in support of the breakdown which is the basis of the general mechanism given in this paper.

A nickel electrode (1 sq. cm.) (A.R. quality E merck) was subjected to anodic polarisation by the galvanostatic technique in 1 N sulphuric acid (A.R.). We were able to reproduce oscillations observed earlier by Osterwald and Feller. A typical oscillogram obtained at a c.d. of 7 mA./cm.[2] in 1 N H_2SO_4, is given in Fig. 1. In these oscillations, the peaks are due to the build-up of stoichiometric or p–n junction region as per the above mechanism. The existence of such a barrier can be proved if the barrier can be more effectively destroyed by an additional current pulse by discharging through a condenser. This experiment was done by using a circuit given in Fig. 2.
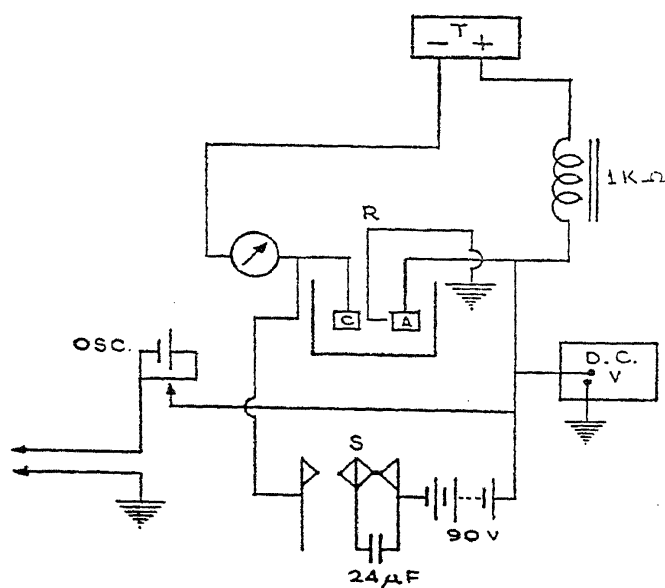

FIG. 2. Experimental set-up and circuit used for studying the periodic oscillations: T—Transistor base constant current regulator; A—Nickel anode 1 sq. cm.; C—Platinum cathode; R, Reference electrode Hg/Hg_2SO_4 1 N H_2SO_4; V—D.C. V.T.V.M.; S—Mercury wetted relay switch; Osc.—Type 531 A tektronix oscilloscope.

Figure 3 gives a typical oscillogram obtained in such an experiment. The current pulse is given at the 7th crest of the oscillations in Fig. 3. The first

effect of the injection of charges by the pulse is to increase the potential of the electrode by 50 mV, which mostly goes to increase the field in the barrier region; this leads to a severe breakdown of the SR. As a result of this, it is seen that the minimum of potential dips down by about 100 mV.

The effect of current pulse in the trough position is also indicated in Fig. 3. The current pulse is given at the 4th trough in the figure. The first effect of the pulse is again to raise the potential by about 50 mV momentarily. But, since the destruction of barrier region is more or less complete at the normal minimum of the oscillation, the anodic pulse at the normal minimum point would not have much of influence on the oscillation. Thus the trough position following the pulse is only slightly affected as can be seen in Fig. 3.
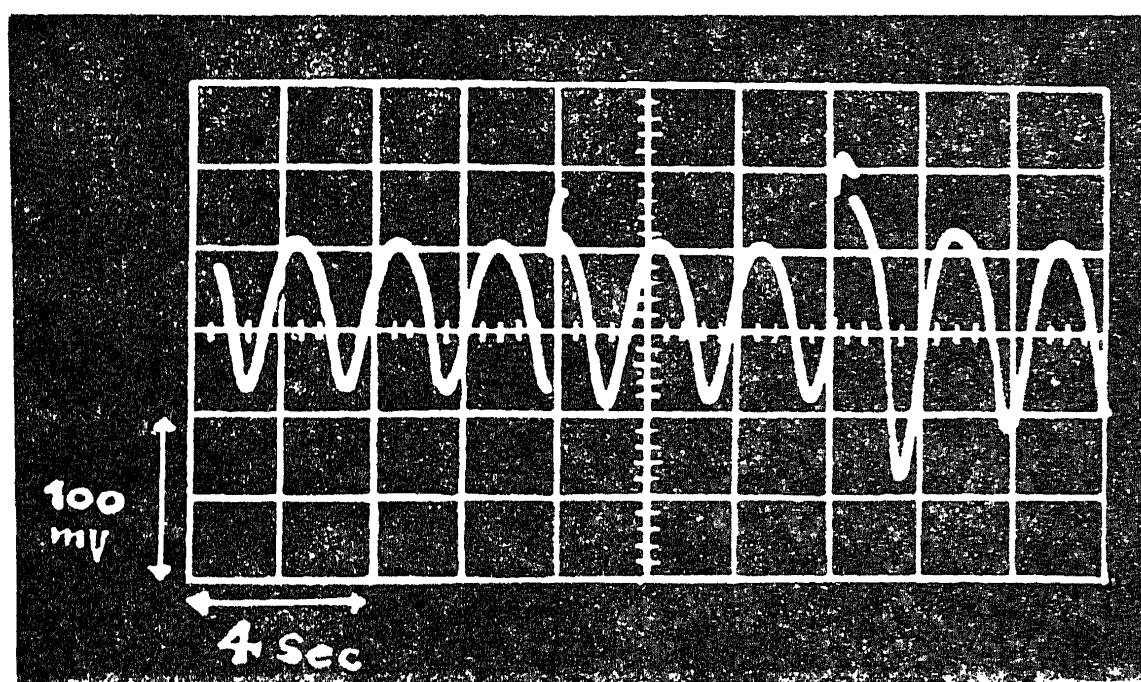

Fig. 3. The effect of an anode pulse (24 × 90μc.) at the crest and trough of the oscillation. (*a*) Voltage sensitivity—50 mV/cm.; Time scale—2 sec./cm.; Current pulse given at (1) 4th trough; (2) 7th crest.

Another interesting feature of the phenomenon is that the time for repair or build-up of the layer is nearly independent of the amount of electricity (coulombs) injected as can be seen from Fig. 4. At the second crest, two successive current pulses were given. At the seventh crest, a single pulse was given. On application of two quick successive pulses, the dip is higher as compared with that of a single pulse; but the time for restoration of normal oscillation is not altered appreciably. These interesting features are difficult to be interpreted in terms of the classical theories. In order to explain on the basis of older mechanisms of the larger dip with a

larger injection of charge, it would be necessary to assume an enhanced thinning of the film. The time required for building up of the film should also increase with the extent of damage. This is contrary to what is observed experimentally. Furthermore, whereas the present mechanisms give a clear picture of the cause of the oscillations, the older mechanisms do not give any reason for the overshoot of the formation and dissolution of the film postulated in the mechanisms.
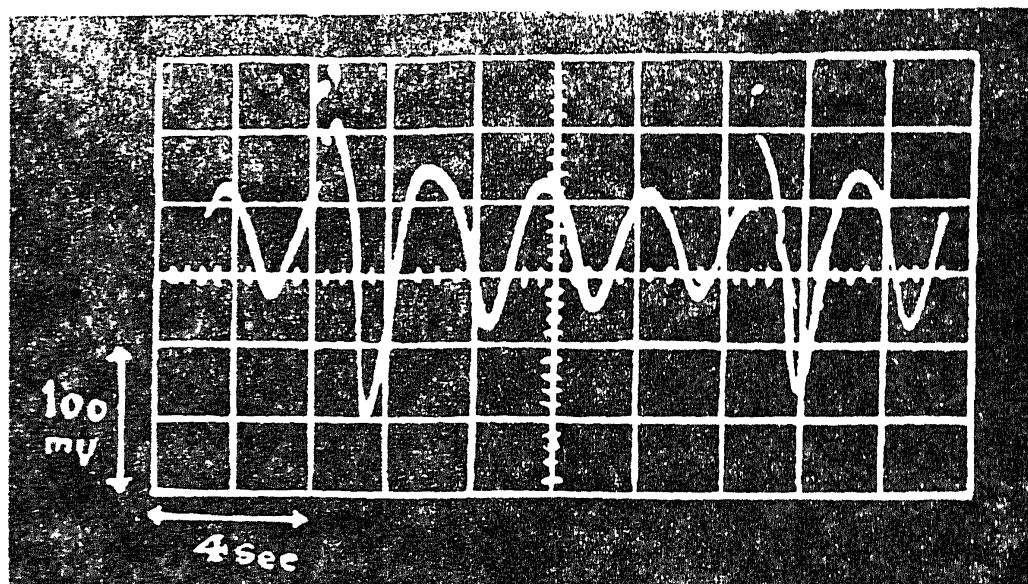

FIG. 4. The effect of number of anodic pulses $(24 \times 90 \mu c.)$ on the oscillations: 2 pulses at the 2nd crest; 1 pulse at the 6th crest; Voltage sensitivity—50 mV/cm.; Time scale—2 sec./cm.

It is interesting to point out that in the anodic polarisation of silver in hydrochloric acid, two types of breakdown occur.[9] At medium current densities $(2-10 \text{ mA/cm.}^2)$ the breakdown is mainly of the first type involving the stoichiometric region. At higher current densities $(> 10 \text{ mA/cm.}^2)$ the breakdown is of the PN junction. Further work would be needed to definitely establish whether it is internal field emission or avalanche break-down.

That the stoichiometric region should have minimum diffusion rate has been based on the assumption that such a region has mainly the Frenkel defects. Schottky type of defects would require a different treatment particularly at small departures from stoichiometric.[12] Similarly the mobilities of anions are considered negligible in the cases under discussion.

It appears to us, the PN junction and SR mechanisms developed by us may have a much wider application. If the PN junction or SR happens to be very close to the film/solution interface, it may lead to large changes in

the rate of dissolution of the film during oscillations, leading to visually observable changes in the appearance of the surface during oscillations. If under these conditions, the potential is near the gas evolution region and the vacancy and cation excess regions are electronically conducting, it may lead to sudden bursting of gas evolution corresponding to the peaks of the potential oscillations. As a third possibility, if an effective PN junction gets formed very near the film/solution interface, the breakdown of the PN junction may cause a dielectric breakdown in the solution causing the anode effects (anodoluminiscence).[13]

The interesting abnormal transfer coefficients observed by Macrides[14] is to be connected with the changes in the structure of SR or PN junction in the film brought about by even small deviations of potential from the equilibrium values. In cases where the relaxation time for such structural changes are long enough, it may be possible to get the correct transfer co-efficients by transient techniques.

Similarly, it is possible to picture the conditions favouring (*a*) anodic dissolution and polishing, (*b*) formation of anodic films of different types, (*c*) oxygen evolution and (*d*) changes in the ratio of ionic to electronic conductivity of the film.

Future work would have to concentrate on the different aspects of the film such as, nature and concentration of carriers, their mobilities, their distribution, the position and thickness of the SR and/or PN junction and the relaxation times, in relation to the different types of films met with; experimental determination of current efficiencies for film formation, dissolution and other reactions, if any, would be useful from this point of view. It would then be possible to work out the detailed mechanism for each individual system showing its own specific behaviour, on the basis of the above general mechanism.

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