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AN ELECTROCHEMICAL AND OPTICAL STUDY OF THE RUPTURE AND RESTORATION OF THE PASSIVATING HgO MULTILAYER ON A DROPPING MERCURY ELECTRODE IN AQUEOUS 1 *M* NaOH SOLUTION AT ANODIC POTENTIALS

M.M.J. PIETERSE, M. SLUYTERS-REHBACH and J.H. SLUYTERS

Van 't Hoff Laboratory of Physical and Colloid Chemistry, State University, Utrecht (The Netherlands)

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ABSTRACT

It is shown that the passivating layer on the surface of a dropping mercury electrode in 1 *M* NaOH at anodic potentials due to drop growth continuously is being mechanically ruptured and electrochemically repaired. This phenomenon is studied by means of microscopy, reflectometry and polarography. The latter technique allows current spikes to be measured. The relation between faradaic current during such a spike and time is discussed.

INTRODUCTION

The growth of the oxide layer on mercury during anodic polarisation in alkaline solution has usually been investigated at stationary electrodes, viz. the hanging mercury drop electrode or a mercury pool [1—5]. The shape of the current vs. time transient during the monolayer and multilayer HgO coverage following a potential step has been interpreted with Avrami's nucleation-growth model [1]. Barradas et al. [2,3] used also the linear potential scan and compared their experimental data with the result of a computer simulation of the growth of the layer.

The anodic dc polarogram of the dropping mercury electrode in 1 *M* NaOH shows a step that has been identified as the monolayer formation and a much larger step at more positive potentials due to formation of a HgO multilayer [4].

As we briefly reported in an earlier paper [6] reflectometry at a dropping mercury electrode in 1 *M* NaOH in the potential region where mercury becomes passivated led to an instable intensity of the reflected light. Cracking of the passive layer is a most probable explanation. It is the aim of this paper to report the results of some further experiments that show the validity of this hypothesis.

EXPERIMENTAL

1 *M* NaOH solution was prepared from twice-distilled water using NaOH pellets. Both the DME and the HMDE were made from fine-tipped capillaries. A

mercury pool served as the counter electrode and a saturated calomel electrode as the reference electrode. The latter was connected to the cell via a salt bridge filled with 1 *M* NaOH. The cell was connected to a PAR polarograph model 174 that was used in the dc mode, undamped. The current transients were recorded photographically from a Hewlett-Packard type 140A oscilloscope connected to the current output of the polarograph.

The details of the measurement of the reflectivity are given elsewhere [6].

Pictures of the HgO multilayer were taken through a microscope. The events on the surface of the mercury drop also were monitored on a video recorder with a TV camera situated immediately behind the microscope.

RESULTS AND DISCUSSION

The intensity of the light reflected from a dropping mercury electrode recorded as a function of time is reproduced in Fig. 1 for six successive drops. During the first two drops the metal surface was bare, the electrode potential being kept at −250 mV vs. SCE. The intensity of the reflected light increases according to $t^{2/3}$ as demanded by theory [6]. After the second drop fell off the electrode potential was increased to −50 mV vs. SCE which is within the passive region of mercury [3,6]. Evidently at these potentials the light intensity increases most irregularly because the part of the electrode surface that contributes to the reflected light at times is covered with an oxide layer, again being bare. The fifth and the sixth drop were allowed to grow regularly again at −250 mV.

Direct evidence for the occurrence of cracks in the oxide layer is given in Fig. 2. In this picture taken at 7 seconds after drop birth the cracks can be seen clearly. Observation of the drop during its growth shows heavy shocks to take place when a big crack springs up. This phenomenon explains the occurrence of

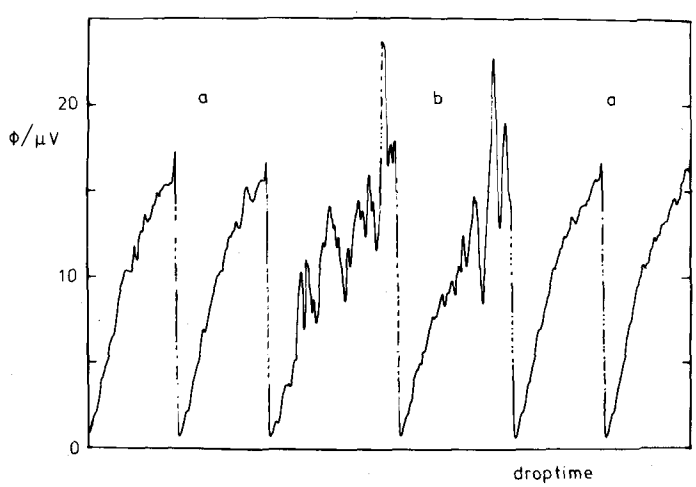

Fig. 1. The light intensity reflected from a DME in 1 *M* NaOH at (a) −250 mV vs. SCE (film-free state), and (b) at −50 mV (HgO multilayer coverage) (6 successive drops).

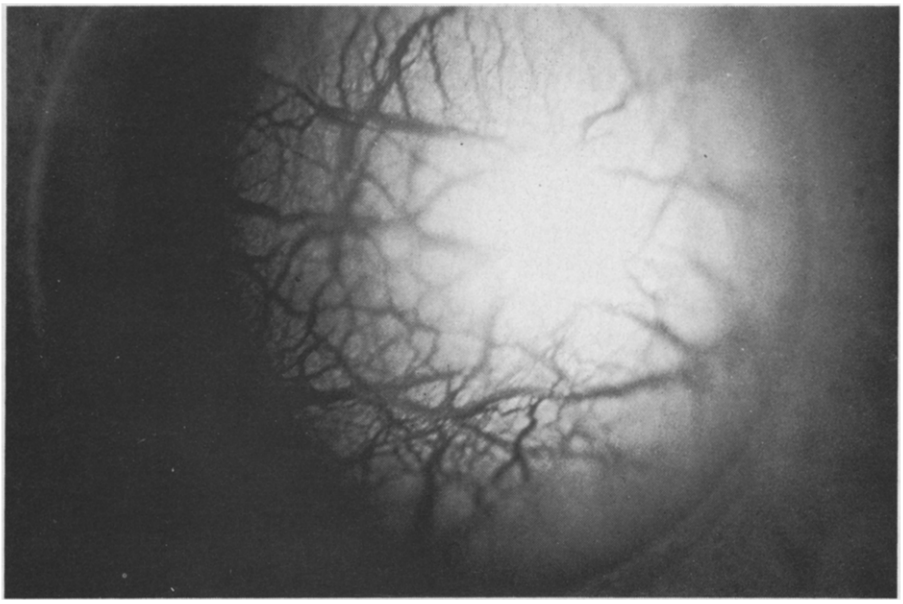

Fig. 2. Cracks in the HgO multilayer covered DME in 1 *M* NaOH at −50 mV vs. SCE. Magnification: 50×.

light intensities in Fig. 1 at −50 mV exceeding those observed at −250 mV.

For comparison in Fig. 3 a hanging mercury drop is shown at −50 mV, evidently without cracks.

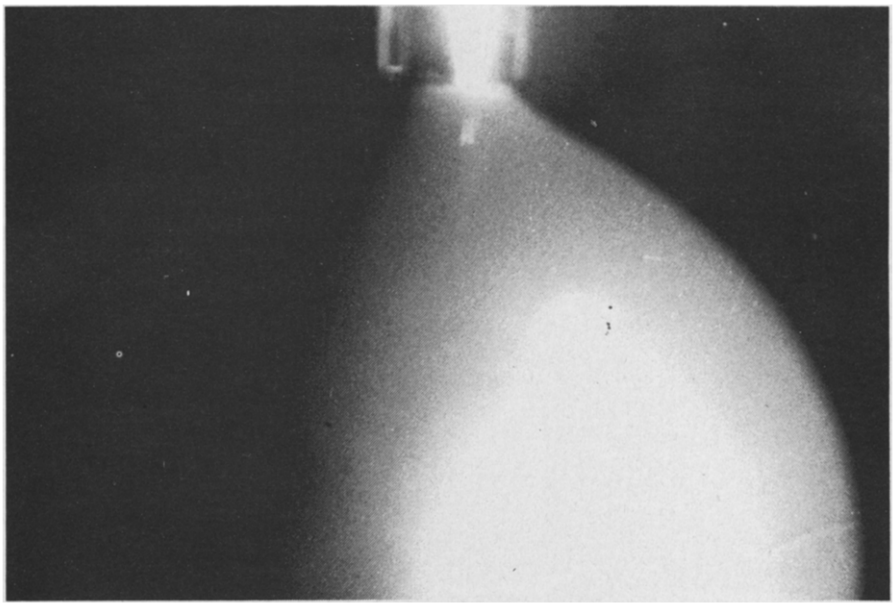

Fig. 3. Rigid HgO multilayer on the HMDE in 1 *M* NaOH at −50 mV vs. SCE. Magnification: 50×. The top of the drawn-out glass capillary is at the top of the picture.

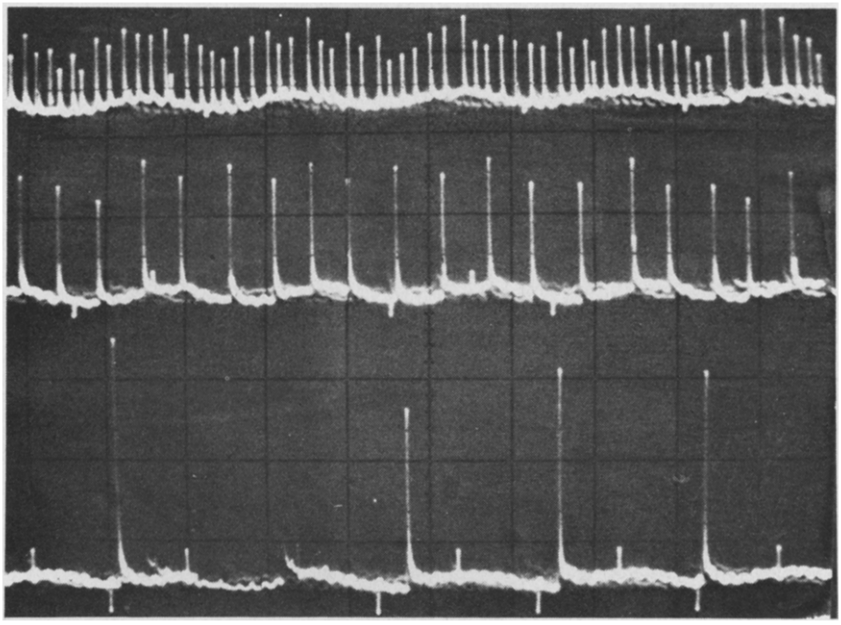

Fig. 4. Oscillographic picture during the anodisation of the DME in 1 *M* NaOH at −50 mV vs. SCE. Upper: current peaks (frequency ~600 Hz) about 0.2 s after formation of the drop; middle: after ~2 s (f ~ 190 Hz); lower: just before the drop fall, after ~10 s (f ~ 50 Hz). Horizontal axis: 10 ms/div.; vertical axis: 40 μA/div.

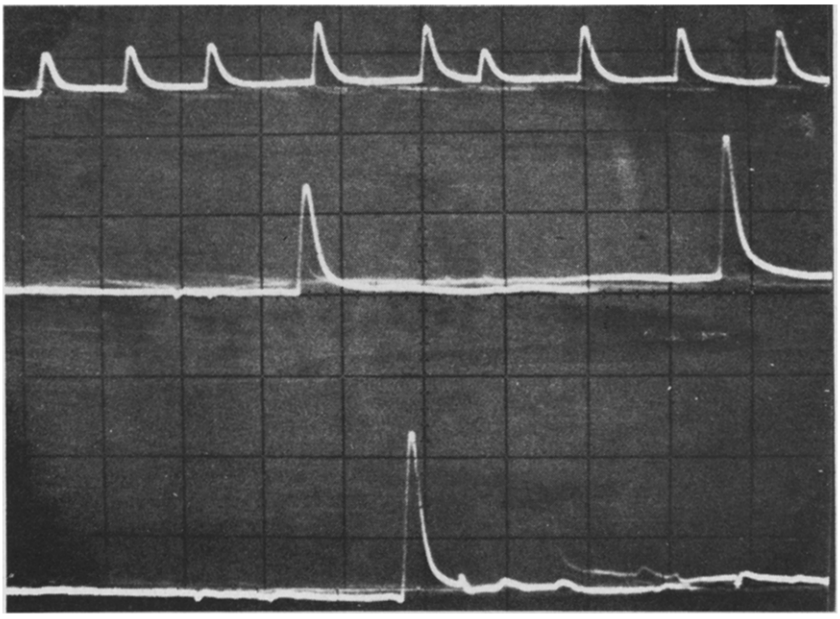

Fig. 5. See text Fig. 4. Horizontal axis: 1 ms/division.

The anodic current of a DME at −50 mV in 1 M NaOH was registrated on a storage oscilloscope (single-sweep and ac mode) at different times after drop fall. The current spikes observed and reproduced in Figs. 4 and 5 originate from the cracks being repaired by oxidation of the generated bare mercury surface.

During drop growth both the time interval between two spikes and the amplitude of the spikes can be seen to increase. So in the early stage of drop growth many small cracks are generated and later a fewer number of large cracks. A most clarifying demonstration can be made by a video recording with the camera behind the microscope and a simultaneous registration of the faradaic current spikes on the audio track.

The shape of a current spike as demonstrated in Fig. 5 closely resembles the current transient that occurs after a potential step from the film-free region up to the multilayer region. Armstrong et al. [1] derived an equation for the growth of a thick layer of HgO on Hg from Avrami's random distribution activation-nuclei growth model. The individual nuclei are approximated as right circular cones expanding on the electrode surface. The current response after the potential step perturbation was found to be

$$i = nFk_2[1 - \exp(-\beta t^3)] \exp(-\beta t^3)$$

where $\beta = \pi M^2 k_1^2 A/3\rho^2$, k_1 is the crystal growth rate constant parallel to the electrode, k_2 that orthogonal to the electrode, M = molecular weight of HgO, A is the nucleation rate constant and ρ is the density of HgO.

The current has a maximum equal to $i_m = nFk_2/4$ that occurs at $t_m = [\ln 2)/\beta]^{1/3}$ [1].

The normalized equation

$$i/i_m = 4[1 - \exp(-\alpha)] \exp(-\alpha)$$

where $\alpha = (t/t_m)^3 \ln 2$ has been plotted in Fig. 6, together with the experimental normalized curve of a spike.

In the case of a potential step Armstrong et al. [1] found good agreement

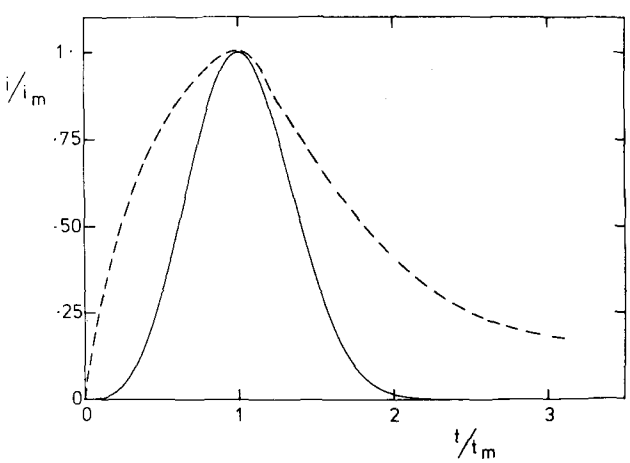

Fig. 6. Theoretical curve of the normalized equation (see text) and experimental normalized (dashed line) of a current spike.

between theory and experiment at $t < t_m$. At large values of t the experimental curve was found to descend more slowly than predicted by theory, which was ascribed to diffusional control. From Fig. 6 it can be seen that the latter behaviour also occurs in the case of the repair of a crack in the passivating layer. Here, however, also at $t < t_m$ the current is higher than the value predicted by theory. We think this to be due to crystal growth on the edges of the HgO crack and to the presence of nuclei on the mercury surface that were created during the vigorous act of the rupture.

Our main conclusion is that polarograms obtained in a passive potential region and with a damped instrument should be interpreted with great care. Preferably the measurements should be performed with zero time constant on an oscilloscope.

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