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ULTRASONICS APPLIED TO ELECTRODE REACTIONS

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OBJECT OF THE STUDY

The problem is the use of ultrasonics produced by magnetostriction as a means of studying phenomena at the interface between electrode and electrolyte.

RESEARCH DURING THE PERIOD

Toward the close of the period covered by the last report, the photographs obtained through the use of the d-c amplifier and oscilloscope confirmed the effects previously noted with the potentiometer. However, the much greater detail obtained with the equipment showed hitherto unsuspected variations both with and without ultrasonic vibrations. Naturally, with this equipment substituted for the potentiometer, attention had to be given to the elimination of pick-up. This appeared to be accomplished most successfully by grounding the cathode.

Since even with the amplifier the possibility remained that the measuring equipment might itself alter the potential changes which it was desired to observe, an attempt was made to minimize such effects by introduction of a thermionic amplifier between the electrolytic cell and the measuring circuit. This device was a Leeds and Northrup instrument of very high impedance, specially designed to eliminate polarization effects in the measurement of hydrogen-ion concentrations. Use of this instrument, with which a grounding connection is recommended, required a restudy of the proper method of grounding the assembly in order to eliminate pick-up. The best location for the connection was found to be the input terminal of the d-c amplifier which was connected to the cathode. Even with this instrument the same unexplained variation in potential persisted.

Since the magnetostriction method involves the use of a coil surrounding the cathode subject to a plate potential of 700 volts d-c as well as a separate 45-volt d-c polarizing coil, it was considered possible that there was leakage of d-c potentials between these elements and the electrolytic cell. A very extensive study was therefore made of the resistances and potentials between all conceivable points involved in the measuring and electrolytic circuits, but no explanation of the anomalous potential variations observed was obtained.

It appeared possible that these variations were real effects on electrochemical potentials resulting from the application of ultrasonics. To study this possibility further, a standard Weston cell, with relatively unpolarizable electrodes, was introduced in place of the electrolytic cell, and in a further extended series of experiments the cell was replaced by as complete an electrical analog as possible involving potential dividers and primary batteries. With both these systems, in order to determine whether or not any extraneous potential is developed in the measuring circuits independent of the electrochemical potentials, a lead from the magnetostriction tube (the cathode in the original electrolytic cell system) was connected successively to various points corresponding to electrodes in the substitute cell system. With the simulated cathode grounded, in all cases oscillograms taken of the potential differences between various points of the substitute cell showed no variation when magnetostriction was applied.

From these results it was believed safe to assume that any changes observed on the application of magnetostriction to the cathode in the regular electrolytic cell represent changes in potential of an electrochemical nature.

It should be emphasized, however, that in order to obtain these results it was necessary to ground the cathode of the simulated cathode, since otherwise the potentials showed instability and drift and were influenced by the power input to the oscillator.

On the basis of this work it appeared that the preliminary results obtained with the electrolytic cell were not due to extraneous effects but rather represented a true effect of magnetostriction on electrode potentials. However, in this earlier work much difficulty had been experienced with the d-c amplifier, which showed persistent nonlinearity. Considerable time was therefore spent in attempts to detect and rectify the difficulty. However, at the high gain required for these measurements, it was not possible to secure linearity and reproducibility of calibration. An order was therefore placed for a high-precision d-c amplifier. In the meantime, in order to work with the amplifier at hand, it was necessary to run a complete calibration curve with each photograph. Naturally some time had to be spent in perfecting the photographic technique.

With this equipment and method, a large number of oscillograms was taken. Obviously in a complete investigation of this effect, many factors should be studied in relation to one another, such as

(1) variation of power input to oscillator,

(2) duration of magnetostriction,

(3) time interval between applications of magnetostriction,

(4) magnitude of electrolyzing current,

(5) duration of electrolysis prior to application of magnetostriction,

(6) duration of recovery period prior to re-application of vibrations,

(7) influence of the nature of the atmosphere above the solution, and

(8) material of the electrode.

Since the contract originally was scheduled to terminate on October 2, 1952, and the operator had an accumulated vacation period of one month, only one month remained for experimental work at this point. In view of this situation and the anticipation of a continuation of the project, it was decided to concentrate on preliminary exploratory investigations of the effects of several of these factors. Illustrative of the results obtained with a silver cathode in 2N H_2SO_4 are the oscillograms of Figs. 1, 2, and 3.

Figure 1 shows some of the best oscillograms obtained throughout the study. These particular photographs were taken at the same current of 25 microamperes, the solution being saturated with hydrogen. The upper traces of each pair (A, C, and E) show the potential differences between cathode and cathode reference during a sweep of two minutes taken from right to left. The spot was then readjusted, the direction of sweep reversed and the lower traces (B, D, and F) taken. Between points 1 and 2 magnetostriction was on for periods respectively of 7-1/2, 5 and 4 seconds. The respective potential changes were 21, 24, and 24 millivolts. The remainder of the traces shows the recovery following magnetostriction. The calibration dots at the right, differing (except for the top pair in each case) by 2,5,mv, show the distinct departure from linearity of the d-c amplifier, as discussed above. Traces A and B were taken after the electrolyzing current had been allowed to flow until the potential was reasonably steady; C and D were taken 45 minutes later, and E and F were taken after a further interval of 1 hour and 45 minutes.

Other points to be noted in connection with these oscillograms are (1) the relatively rapid fall in potential when magnetostriction is applied, (2) the indication that the effect might be still greater if the period of application were increased, and (3) the unexpected variations in the type and extent of recovery under substantially identical conditions.

The oscillograms of Fig. 2 show especially the effects of re-application of magnetostriction after a short recovery period under a considerably larger current - 90 microamperes. In all cases the solution was saturated with hydrogen. Traces C and D were taken 45 minutes after A and B, while traces E and F were taken 15 minutes later. Again A, C, and E, taken with the sweep from right to left, are traces of the potential differences between cathode and cathode reference without the application of magnetostriction and show clearly the marked stability of the cathode potential at this higher current density. After a brief interval during which the spot was relocated, the traces (B, D, and F) were taken in the reverse direction. At the points marked 1, magnetostriction was applied for a period of 2 seconds, during which the potentials dropped by about 6-8 mv to the points marked 2, at which time the magnetostriction was removed. After a recovery period of about 1-1/4 minutes, during which the potential returned nearly to its original value, magnetostriction was again applied at the points indicated "3". For traces B and D the vibrations were maintained for 15 seconds, whereas for trace F the duration was 30 seconds, after which the recovery, starting from points "4" was again practically complete within the remaining sweep period.

Additional observations with respect to this figure are as follows: (1) The effect of magnetrostriction increases with time of application, reaching a maximum of about 12 millivolts at this current density between 15 and 30 seconds. (2) At this higher current density the recovery is complete and regular, in distinct contrast to that at lower current densities. (3) At the higher current density the potential decrease due to magnetostriction is distinctly smaller than that at the lower current density.

Figure 3 shows some results at a very low current (8.9 microamperes), indicating again the effects of variation in duration of magnetostriction and also the influence of a hydrogen atmosphere. A and C without, and, B and D with, magnetostriction (sweep direction opposite to those in other figures) were taken with no hydrogen bubbling through the solution; C and D were taken 45 minutes after A and B. The potential decreases of 10 and 14 mv, respectively for a 30-second application of vibration show the lack of reproducibility in the absence of a hydrogen atmosphere. The other two traces show the magnetostriction effect observed subsequently after hydrogen saturation, trace E for a 30-second vibration period and trace F taken 45 minutes later for a 15-second; the potential decreases were respectively 24 and 10 mv. At this lower current density both the magnetostriction effect and the recovery are much smaller than at higher current densities.

These selected photographs confirm qualitatively the earlier potentiometric observation that magnetostrictive vibrations definitely produce a depolarizing effect at the cathode. This effect has been shown to depend on the current density, the duration of the vibration, and the presence or absence of a hydrogen atmosphere. It must be pointed out, however, that during the period many other observations, both photographic and visual, showed distinctly ambiguous, erratic, and unexplained results as well as a lack of reproducibility under supposedly identical conditions.

Such observations mean that there must be present several disturbing factors of a totally unknown nature which at times exert a pronounced influence on the results. Before this method can be relied upon to furnish results justifying definite conclusions, the causes of these spurious effects must be located and eliminated.

In this connection the present complex assembly involving many separate components has evolved gradually as the need for a greater variety of measurements and control of conditions has become evident. Each separate unit of this assembly should be restudied, redesigned, and relocated if necessary to improve its functioning both alone and in conjunction with other components. There are already strong indications of a disturbing interaction between some of the elements of the system and of unsatisfactory operation of individual units; among the latter reference has already been made to the d-c amplifier, for which a replacement is on order. In connection with new equipment necessary for quantitative measurements which would add materially to the value of the results, it may be mentioned that a so-called "Dynagage" is also on order; this instrument, as shown by tests with a similar unit borrowed from the General Motors Research Laboratory, should be satisfactory for the determination of the amplitude of vibration of the magnetostriction tube.

Once the above has been done, not only could the work under the present proposal be completed, but also the very broad field of polarization phenomena, both theoretical and practical, could be brought under study from this point of view.

It is therefore recommended that the project be continued for another year.

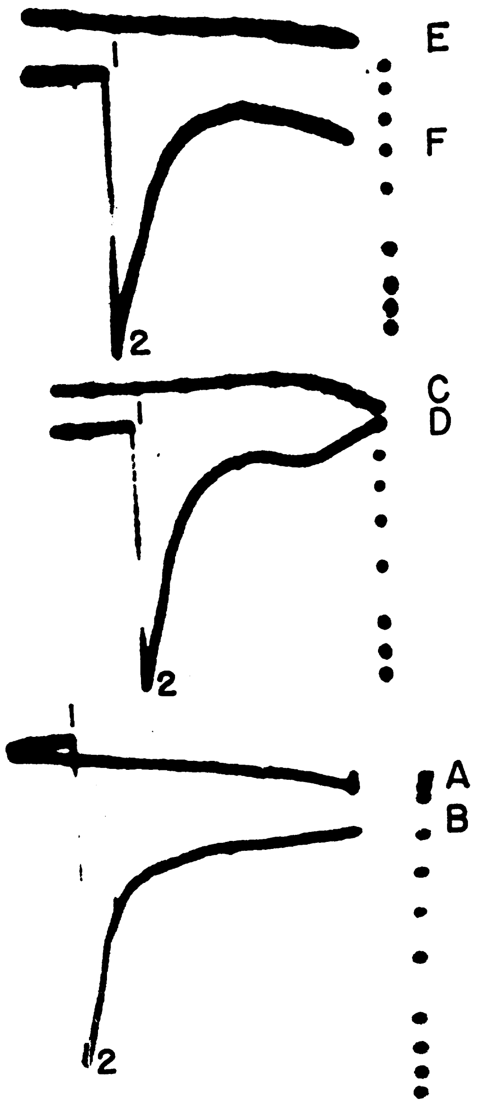

FIG. 1

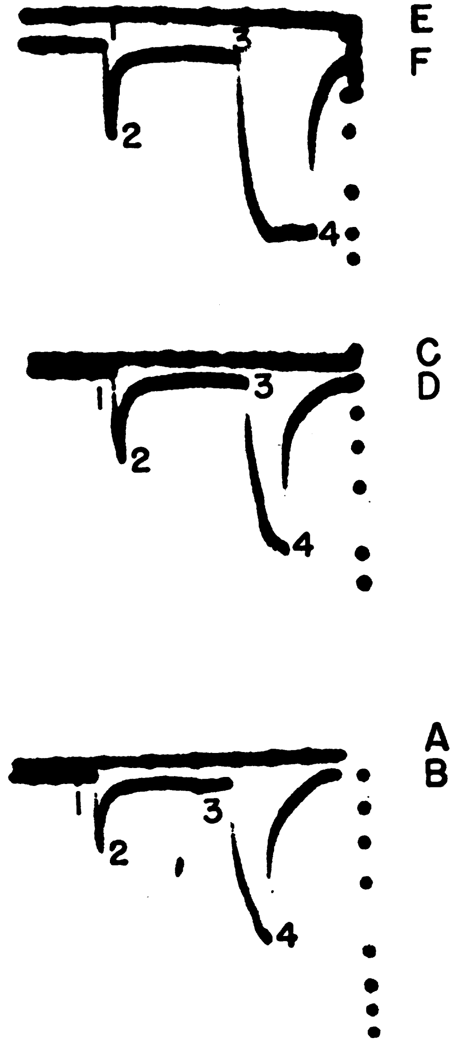

FIG. 2

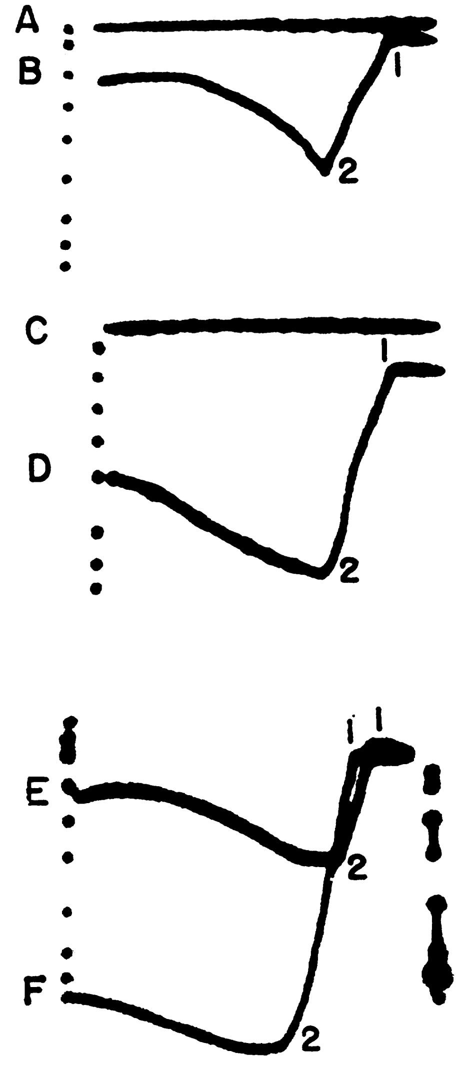

FIG. 3