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## AN ELECTROCHEMICAL STUDY OF A LIQUID CRYSTAL USED IN INFORMATION DISPLAYS

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16. Abstract

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One parameter of liquid crystal displays which needs improvement is their operational lifetime. Electrochemical reaction at the electrodes of the display can cause failure after 2,000 to 3,000 hours of operation.

Cyclic voltametery is used to study the electrochemical reactions which occur in N-(p-methoxybenzilidene)-p-butylaniline, (MBBA), which is a nematic liquid crystal widely used for displays. Results of these studies indicate the presence of a reversible reduction of MBBA at the cathode and that the reduction product undergoes a further reaction leading to products which are not reversibly oxidized.

These results suggest that the degradation of the liquid crystal in displays can be reduced but not eliminated by addressing the cell with a suitable frequency of alternating voltage.

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## SUMMARY

Certain organic liquids, called liquid crystals, have optical properties akin to those of crystalline solids. Electrooptic effects in these materials allow them to be used in displays. Liquid crystal displays offer great advantages in size, power requirements, and cost over cathode ray tubes and electro-mechanical displays.

One parameter of certain liquid crystal displays which needs improvement is their operational lifetime. Electrochemical reaction at the electrodes of the display can cause failure after 2,000 to 3,000 hours of operation.

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## INTRODUCTION

Liquid crystals are one of the new materials being used as a display medium in the ever-expanding field of digital instruments. Liquid crystal displays went with amazing speed from their inception by Heilmeir (ref. 1) in 1968, to the market place. They are now found in clock radios, desk calculators, digital panel meters, and wrist watches.

NASA is interested in liquid crystal displays as replacements for the bulky and power consuming cathode ray tubes and for the many instrument readouts in aircraft cockpits.

The properties of liquid crystal displays which make them advantageous are:

1. Low power - 1 $cm^2$ of active display area requires as little as 1 microwatt of power for operation

2. Flat package - a complete liquid crystal display can be less than 2.5 mm thick. This is of great importance in today's heavily instrumented aircraft where space is at a premium and cathode ray tubes require so much space.

3. Multiple modes of operation - liquid crystal displays can be addressed with dc or ac signals, they can show black on white or white on black, they can be transmissive or reflective, and the decay time of the information can be adjusted from milliseconds to weeks.

4. No washout - when liquid crystal displays are operated in the reflective mode, the contrast ratio is independent of the ambient light and is not washed out, even by direct sunlight.

5. Low cost - a liquid crystal display can be made with two conductive glass plates and a 12 $\mu$m thick layer of liquid crystal. The primary cost is in the addressing circuitry.

Liquid crystal displays are, of course, not without their problems. The significant problems are:

1. Temperature range - the liquid crystal material exhibits its liquid crystal properties only in a particular temperature range. In the early materials, these ranges were narrow and above room temperature, e.g., 50° C to 70° C. Materials research has recently produced liquid crystals whose mesophase exists from 0° to 78° C (ref. 2).

2. Decay time - liquid crystals are relatively viscous liquids, and a certain amount of time is required for the liquid in a display to return from the cloudy "on" state to the clear "off" state after the voltage is removed. Some recently developed liquid crystals have room temperature decay times as short as 0.03-second and some as long as several weeks. The decay times of all liquid crystals are dependent on temperature and increase as the temperature decreases.

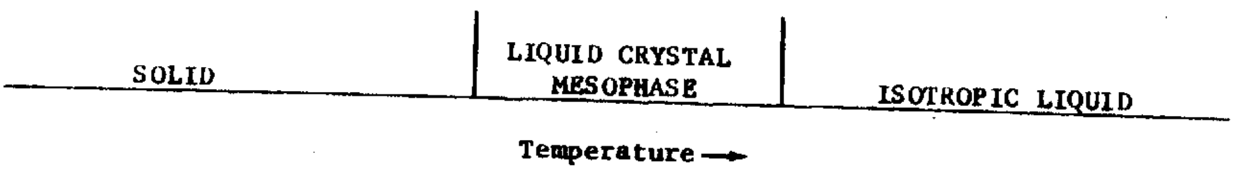
3. Opterating lifetime - the operating lifetime of a dynamic scattering display operated with a dc drive voltage is, at best, 3,000 hours. This can be extended to 20,000 hours by using an ac drive voltage. For some applications, however, the simplicity of dc operation is desired as well as a longer lifetime. It is also known that impurities in the material can markedly reduce the lifetime of the cell.

The goal of the experimental work reported in this paper was to determine possible failure mechanisms in liquid crystal displays through an investigation of the electrochemical processes which occur at the electrodes.

## LIQUID CRYSTALS

### Materials

A liquid crystal is a material which has the mechanical properties of a liquid and the optical properties of a crystalline solid. Certain chemical compounds possess a phase, called the liquid crystal mesophase, which exists in a temperature range between its solid phase and its isotropic liquid phase.




These compounds are long organic molecules which possess an electric dipole moment (figure 1). This dipole may or may not be parallel to the long axis of the molecule. The dipole-dipole interaction is strong enough to cause parallel alinement of the molecules within domains in the liquid, creating what amounts to a "polycrystalline liquid" (figure 2).

The property which makes liquid crystals useful is their behavior in an electric field. When a liquid crystal is placed in an electric field, all of the domains aline with the field because of their dipole moments, and we have what amounts to a "single-crystal liquid" (figure 3).

### Dynamic Scattering

Alinement of the domains in an electric field does not cause any visible change in the liquid crystal and, therefore, is not in itself sufficient for display applications.

For display applications, associated phenomena which occur when the domains aline with the field are used. One of the associated phenomena which occurs in nematic liquid crystals is called "dynamic scattering."

Dynamic scattering depends upon current flow by the movement of molecular ions through the liquid. In zero field, the domains are randomly oriented and the liquid is clear. When a voltage is applied to the cell, the domains aline with the field. The alined liquid is still clear, but ions immediately begin to move through the liquid. The moving ions disrupt the molecular order and cause microturbidity. These disrupted regions are the right size to scatter light in the forward direction, and the liquid becomes opalescent or white.

## Displays

An optical cell (figure 4) is made from the liquid crystal by placing a thin layer of the liquid between two glass plates which have transparent conductive coating on their inner surface. The plates are spaced 6 $\mu$m to 12 $\mu$m apart. A battery and switch are wired to the electrodes and the cell is complete. When the switch is closed a field appears across the liquid, and the cell changes from clear to opalescent.

A front lighted display such as numeric indicator (figure 5) would be made as follows: The electrode on the back plate covers the entire surface. The electrode on the front plate is segmented and each segment is addressed separately. The cell is placed over a black background. With no voltage applied to the electrodes the liquid is clear and the entire cell appears black. When a voltage is applied to a segment, the liquid beneath that segment scatters the ambient light, and the segment appears white. Thus, a white on black number can be displayed by addressing the correct segments.

The liquid crystal devices based on dynamic scattering make use of the nematic materials. Two of the most widely used nematic materials are N-(p-methoxybenzilidene)-p-butylaniline (MBBA) and N-(p-ethoxybenzilidene)-p-butylaniline (EBBA). The structure of these two molecules is represented in figure 6.

## EXPERIMENTAL PROCEDURE

### Basis of Experiment

A liquid crystal device based on dynamic scattering has two electrodes. Since a small current flows in these devices, some electrolysis of the liquid crystal material must occur, reduction of the liquid crystal at one electrode and oxidation of it at the other. If an ac voltage is applied, the respective electrochemical processes at the two electrodes alternate. Thus, it is necessary to examine the electrochemical reduction and oxidation processes along with any associated chemical reactions for the liquid crystal.

Since a current must flow in a dynamic scattering liquid crystal device and the liquid crystal is the only electrolyzable substance in the device, it is electrolyzed to new materials at each electrode. With the application of a dc voltage, this process leads to the formation of new materials at both electrodes with no reversal of the individual electrode processes. With the application of an ac voltage, at least some reversal of the electrode processes must occur since the lifetime of the device is considerably longer than with a dc applied voltage. This can be represented by the following reaction scheme:

$$\text{REDUCTION PROCESS: Liquid crystal} + e^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} \text{Product(s)} \quad (1)$$

$$\text{OXIDATION PROCESS: Liquid crystal} - e^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} \text{Product(s)} \quad (2)$$

The constants $k_f$ and $k_b$ are rate constants which are a measure of the rate at which the particular electron transfer process may occur. There is a limit to the speed at which an electron may go from an electrode to a molecule or ion, or from a molecule or ion to an electrode. Ideally the above process would occur with 100 percent efficiency, and no net change in the liquid crystal would occur. Unfortunately this is not true. Frequently, the initial product of an electrolysis is not stable. It may undergo some kind of internal rearrangement or decomposition, or it may react with something else. This possibility is represented schematically by the following:

$$\text{Liquid Crystal} \pm e^- \underset{k_b}{\overset{k_f}{\rightleftarrows}} \text{Product(s) A} \overset{k_c}{\rightarrow} \text{Products B} \quad (3)$$

The constant $k_c$ is a rate constant which is a measure of the rate of the associated chemical process. If some of the initial product of electrolysis, product A, undergoes the chemical change to products B before it is converted back to the liquid crystal by means of polarity reversal, then there will be a net destruction of the liquid crystal and the consequent generation of impurities. Elucidation of the processes is essential to understanding how and why dynamic scattering liquid crystal devices fail.

Both MBBA and EBBA belong to a class of compounds known as Schiff bases, characterized by the $-\overset{H}{\overset{|}{C}}{=}N-$ linkage in the molecule. Some early studies on the electrochemistry of this class of compounds have been done (refs. 3, 4, 5, 6). Although these workers were not concerned with these materials as liquid crystals, some of the basic aspects of the electrochemistry are given. Several recent publications on the electrochemistry of MBBA have considered directly the possible implications of its electrochemical properties to liquid crystal devices (refs. 7, 8). A brief review of the important aspects of some of these papers is useful.

Kononenko et. al. (ref. 3) have suggested that MBBA-like compounds undergo a two-electron reduction which occurs in two one-electron reduction steps. The first one-electron reduction step leads to a radical anion of MBBA. This is illustrated by equation (4).

$$CH_3OC_6H_4CH{=}N{-}C_6H_4{-}C_4H_9 + 1e^- \rightarrow \left[CH_3OC_6H_4CH{=}NC_6H_4{-}C_4H_9\right]^- \quad (4)$$

Kononenko et. al. propose that this radical anion may undergo further reduction or it may dimerize in accordance with the reaction shown by equation (5).

$$2\left[CH_3OC_6H_4CH{=}NC_6H_4{-}C_4H_9\right]^- + 2H^+ \rightarrow \begin{array}{l} CH_3OC_6H_4CH{-}\underset{|}{N}{-}C_6H_4{-}C_4H_9 \\ \quad\quad\quad\quad\; | \quad H \\ \quad\quad\quad\quad\; | \quad H \\ CH_3OC_6H_4CH{-}\overset{|}{N}{-}C_6H_4{-}C_4H_9 \end{array} \quad (5)$$

Two-electron reduction of the MBBA would lead to the reduction of the double bond between the carbon and nitrogen according to equation (6).

$$CH_3OC_6H_4CH{=}NC_6H_4{-}C_4H_9 + 2e^- + 2H^+ \rightarrow CH_3OC_6H_4{-}CH_2{-}NH{-}C_6H_4{-}C_4H_9 \quad (6)$$

This reaction may occur in steps involving the radical anion first and then the one-electron reduction of it to the N-(p-methoxytoluene)-p-n-butylaniline. The detection of this free radical anion was attempted by Scott and Jura (ref. 6). Lomax, et al (ref. 7) claim to have detected it by electron spin resonance, but their results were inconclusive.

There have been some recent studies on the electrochemical oxidation of Schiff bases both from a general point of view (ref. 4) and as liquid crystal materials (ref. 8).

The main effort of the studies reported in this paper was aimed at identifying the electrochemical processes occuring at the electrodes and the reduction products of MBBA, using cyclic voltametry.

## Cyclic Voltametry

In cyclic voltametry, a triangular voltage is applied to a stationary electrode called the working electrode. Usually this is accomplished with a third inert electrode so that the current flows between the electrode of interest (the working electrode) and the third electrode. This avoids passing current through the reference electrode. The instrumental set up used to accomplish it is shown in figure 7. In cyclic voltametry, the current flowing at the working electrode is measured as a function of the applied voltage that varies over the desired ranges. Typical cyclic voltamograms are shown in figures 8 and 9. As the potential is increased, the necessary potential for reduction (or oxidation) is reached, and a peak current occurs (figure 8 point A). The current begins to decrease due to depletion of the electroactive species at the electrode. The voltage scan is then reversed (figure 8, point B), and if the reaction is reversible, the new material formed at the electrode is reoxidized (or reduced) (figure 8, point C). However, if the reaction is not reversible, the peak corresponding to the oxidation will not occur or will be reduced in size (figure 9, point C). A diminished peak at "C" may also occur if the material formed at "A" undergoes a chemical reaction to form a new substance which cannot be oxidized at "C". A third possibility may appear in multiple sweep voltammograms. If the reduction process produces a product which undergoes a reaction to form another material which can itself be oxidized and 100 percent reduced, more than one peak will appear in the oxidation sweep (figure 10, point B), a new peak will show up in the reduction sweep of the second cycle (figure 10, point D), and the first reduction peak (figure 10, point A) will be reduced in size (figure 10, point E). These examples simply serve to give an idea of the usefulness of cyclic voltametry in characterizing electrode processes.

Since pure MBBA or MBBA in a non-ionic solvent will not conduct, it is necessary to add an electrochemically inert, ionic material to the sample being studied. This is called the supporting electrolyte. In dynamic scattering-liquid crystal devices such a material is added to the pure liquid crystals material in order to make it conductive. Tetrabutylammonium perchlorate (TBAP) was used for the studies in this paper. Also, it is necessary to dilute the MBBA with a solvent in order to obtain meaningful current voltage relationships. The solvent chosen for these studies was dimethylformamide (DMF), $CH_3CON(CH_3)_2$. The studies were carried out using solutions which were 0.005 $\frac{\text{moles}}{\text{liters}}$ MBBA and 0.5 $\frac{\text{mole}}{\text{liter}}$ TBAP in DMF. The solvent was commercial spectrograde used without further purification. All experiments were conducted in a glove box with a dry nitrogen atmosphere. Operational amplifiers were used with standard circuits for cyclic voltametry.

## RESULTS AND DISCUSSIONS

Typical cyclic voltamograms of MBBA are shown in figures 11 and 12, each at different voltage scan rates. Current peak #1 corresponds to the reduction of MBBA. Reversal of the voltage scan leads to several oxidation current peaks. Peak #2 is the first oxidation current peak. Peak #2 is present at high scan rates but is absent or very small at low scan rates, indicating that the reversible reduction product of MBBA is unstable and undergoes some time-dependent chemical process. Peaks #3 and #4 appear at all scan rates. Peaks #3 and #4 do not appear unless MBBA is reduced and are therefore associated with the reduction products of MBBA. Peak #5 represents the oxidation of the solvent.

It is particularly significant that the ratio of oxidation current for peak #2 to the MBBA reduction current ($I_{p_a}/I_{p_c}$) increases with increasing scan rate, as shown in figure 13. This indicates that the unstable reduction product of MBBA undergoes a chemical reaction leading to products which are not reversibly oxidized or that the reduction product undergoes a chemical change with further reduction occurring at the same potential as that for reduction of MBBA. As a consequence, the faster scan rate allows less time for the unstable reduction products to undergo an irreversible change, and less impurities are produced. Applied to a liquid crystal display, this means that the lifetime of the display can be increased by addressing with an alternating voltage of the highest practical frequency. In the case of dynamic scattering displays, the frequency is limited by the rise time of the dynamic scattering to a few hundred hertz.

Kononenko et al (ref. 3) and Lomax, et al (ref. 7) propose that this unstable reduction product is a radical anion as shown in equation (4). This radical anion may undergo a chemical reaction such as the dimerization proposed by Kononenko and shown in equation (5). Although we have not yet identified the product of this chemical process, infrared absorption spectroscopy indicates that it is not the dimer. The radical anion may also undergo a further one-electron reduction to the product shown in equation (6). This stepwise process would probably involve protonation of the radical anion before the second reduction step.

Peaks 3 and 4 represent the oxidation of the products formed from the reaction of the intermediate and the two-electron reduction.

A sample of MBBA in 0.1M TBAP in dimethylformamide was reduced in an isolated chamber at a platinum electrode having a controlled potential corresponding to the potential of peak #1 of figures 11 and 12. The resulting mixture was separated by thin layer chromatography and by high pressure liquid chromatograph and found to contain three compounds; MBBA plus two products of the electrolysis process. This substantiates the cyclic voltrometric evidence that there are two routes of electrochemical decomposition for MBBA. One route is the electrochemical-chemical process resulting from a one electron reduction to form a product which undergoes a chemical reaction in solution. The other route is the product of the two-electron reduction of MBBA.

The products thus separated were examined by infrared absorption spectroscopy. There were not sufficient amounts of the products for positive identification, but the spectral data do show that neither product is the dimer predicted by Kononenko and indicate that one product is that given by the two electron process of equation (6).

## CONCLUSIONS

Based on the cyclic voltametric studies of this report, there are two processes leading to the decomposition of MBBA occurring as a result of electrochemical reduction. These processes are:

$$\text{MBBA} + 1e^- \rightarrow \left[\text{MBBA}^{\dot{-}}\right] \longrightarrow \text{Product \#1}$$

$$\text{and MBBA} + 2e^- + 2H^+ \longrightarrow \text{Product \#2}$$

These products have been separated, but not in quantities sufficient for positive identification. It is concluded from IR absorption spectra that Product #1 is not the dimer predicted by Kononenko (3). Absorption spectra of Product #2 indicates that it is

$CH_3OC_6H_4 - CH_2 - NH - C_6H_9 - C_4H_9$ as given by equation (6).

From the standpoint of the liquid crystal display devices, these results indicate that there is a net loss of MBBA at the electrodes due to the decomposition of the unstable reduction product and a corresponding production of impurities in the system. Since the decomposition of the unstable reduction product is time dependent, rapid reversal of the electrode polarity decreases the net decomposition of MBBA. Thus, the use of an alternating voltage prolongs the life of the dynamic-scattering liquid-crystal devices. The frequency of this alternating voltage is limited to a few hundred hertz because of the rise time of the dynamic scattering effect.

A study of the processes associated with the oxidation of MBBA is the next logical step in this investigation.

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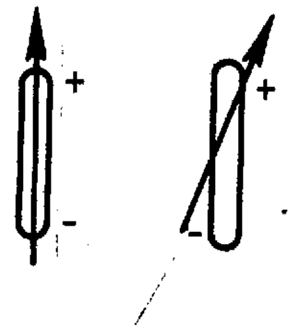



FIGURE 1. ELECTRIC DIPOLES ON LIQUID CRYSTAL MOLECULES

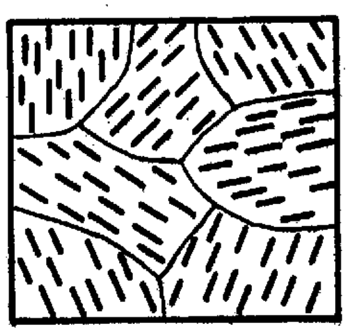


FIGURE 2. LIQUID CRYSTAL MOLECULES ALINED IN DOMAINS

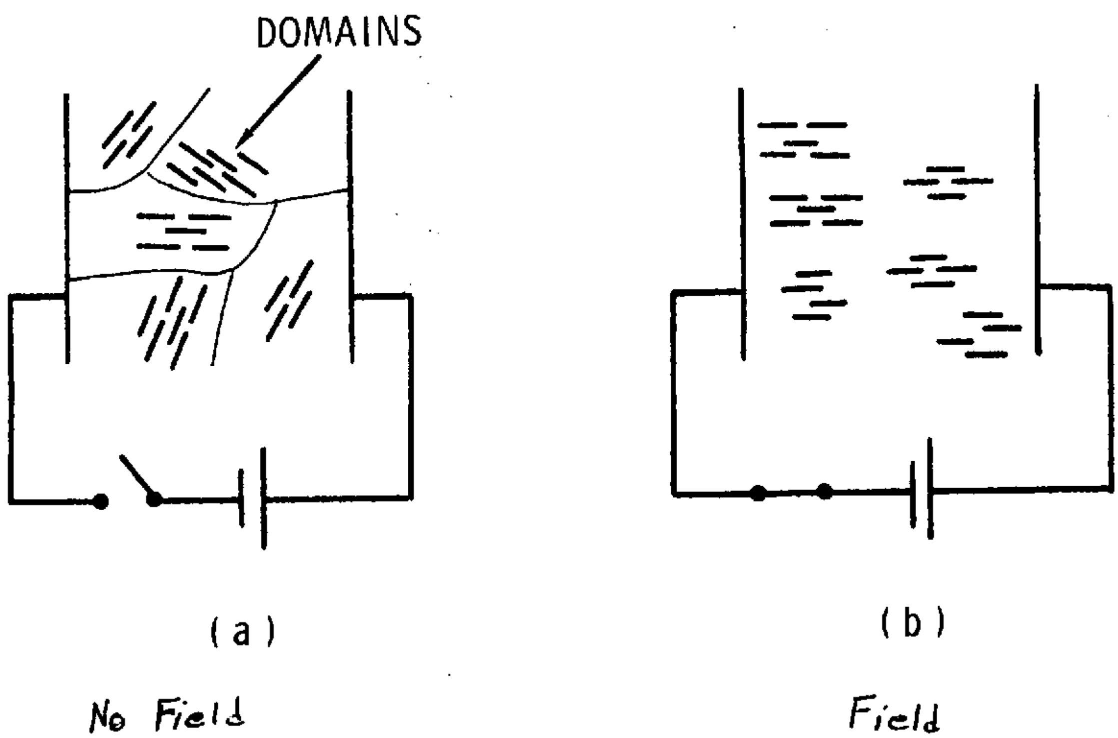



FIG. 3. BEHAVIOR OF LIQUID CRYSTAL DOMAINS IN AN ELECTRIC FIELD

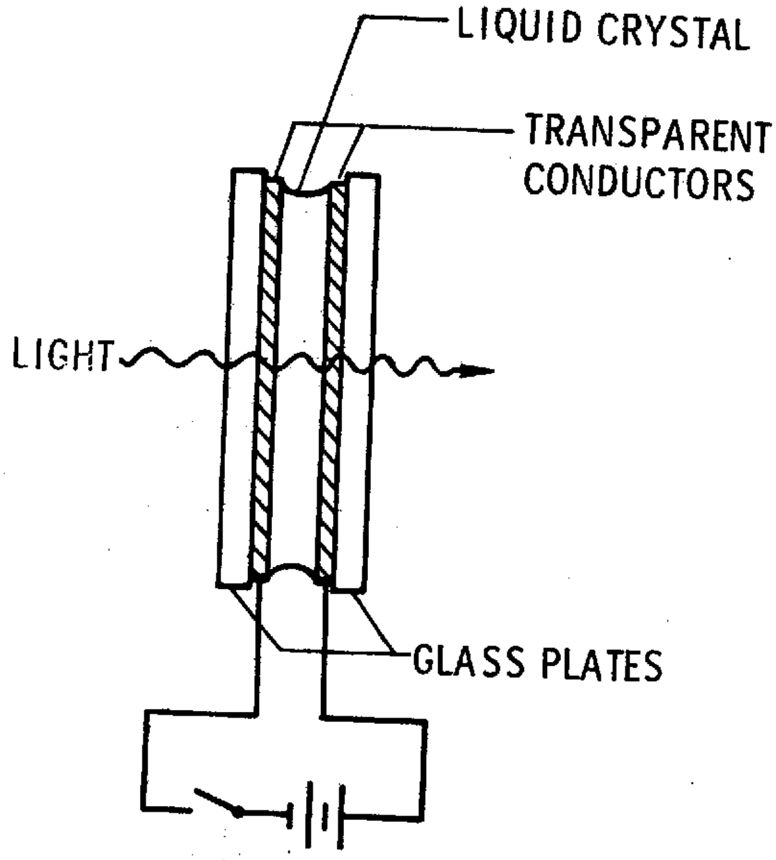



FIG. 4. LIQUID CRYSTAL OPTICAL CELL

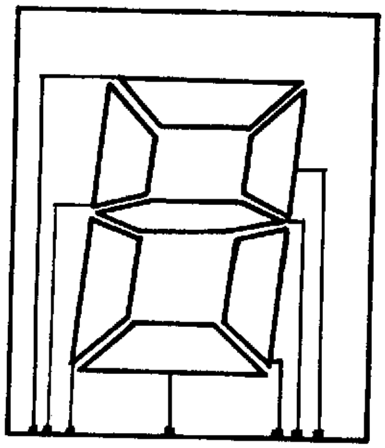
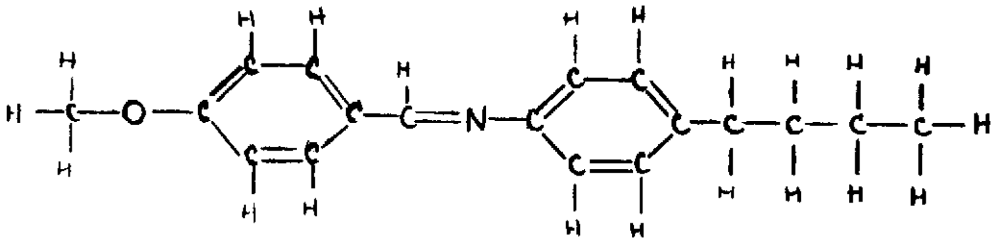
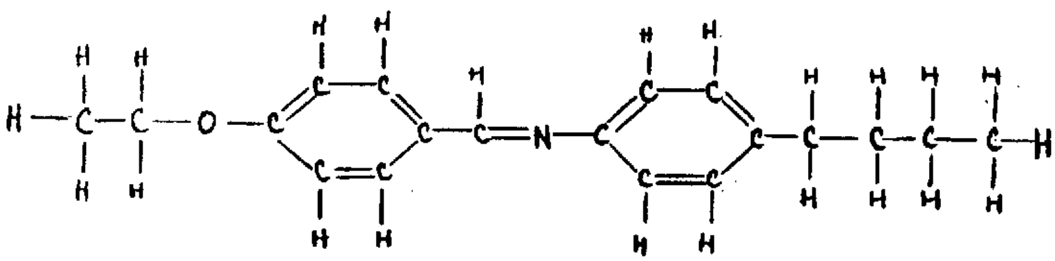


FIG. 5. SEGMENTED FRONT ELECTRODE FOR NUMERIC DISPLAY



MBBA



EBBA

FIG. 6. STRUCTURE OF MBBA AND EBBA MOLECULES

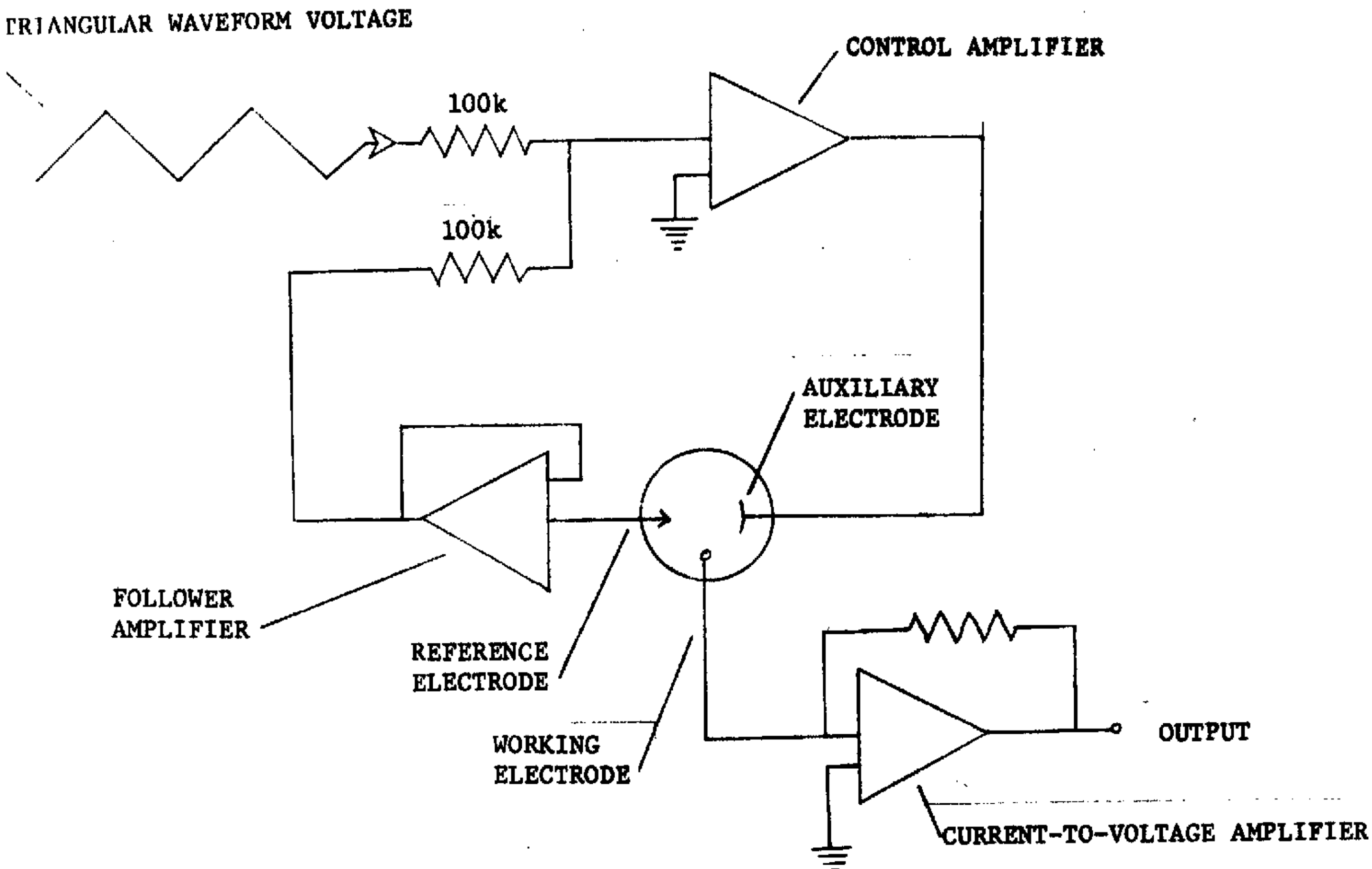



FIG. 7. DIAGRAM OF CYCLIC VOLTAMETRY CIRCUIT

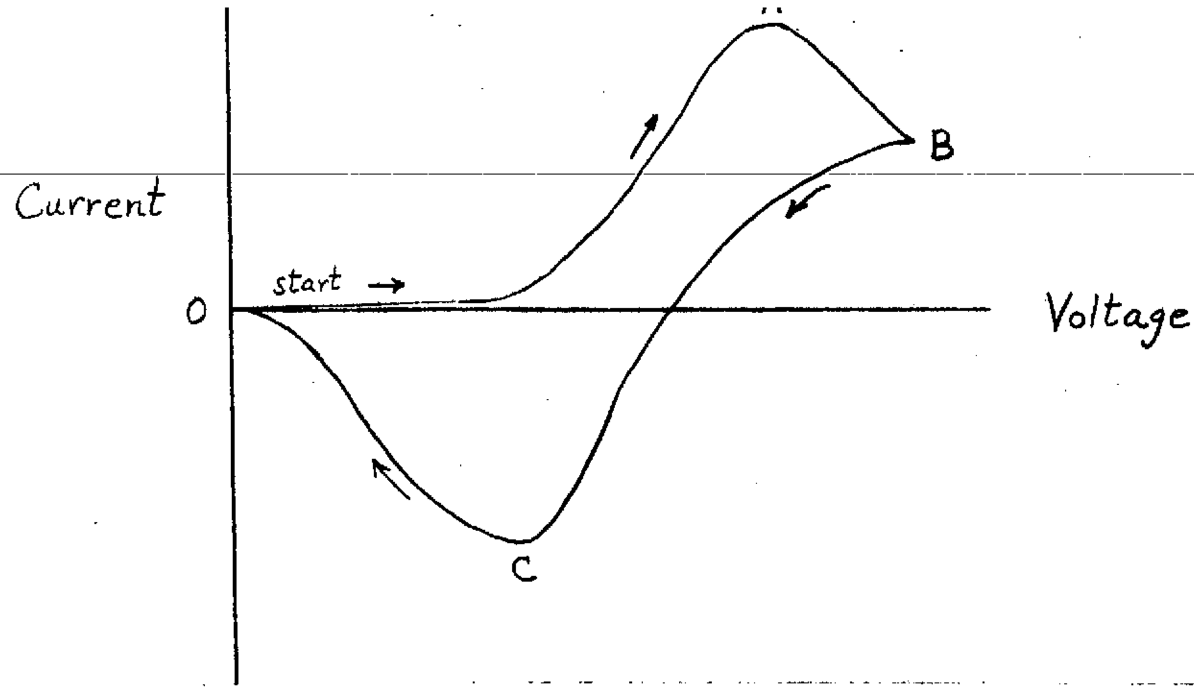



FIG. 8. CYCLIC VOLTAMOGRAM OF REVERSIBLE REACTION

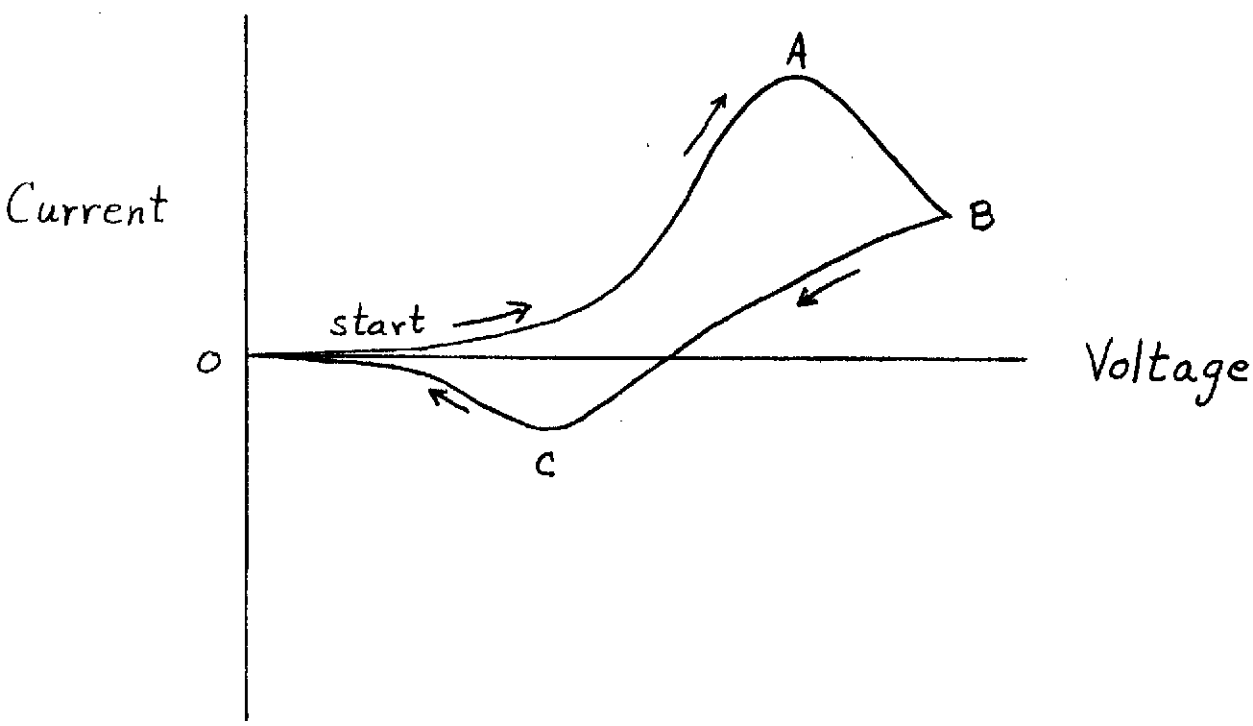



FIG. 9. CYCLIC VOLTAMOGRAM OF IRREVERSIBLE REACTION

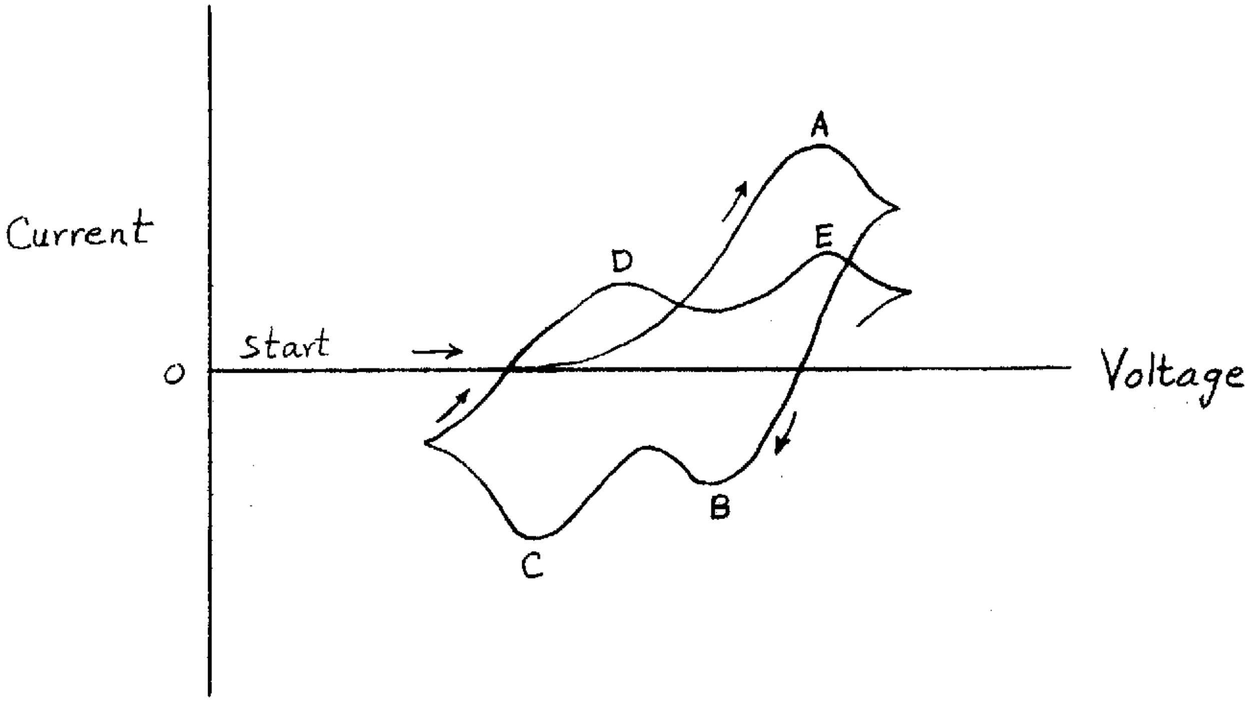



FIG. 10. MULTIPLE SWEEP VOLTAMOGRAM

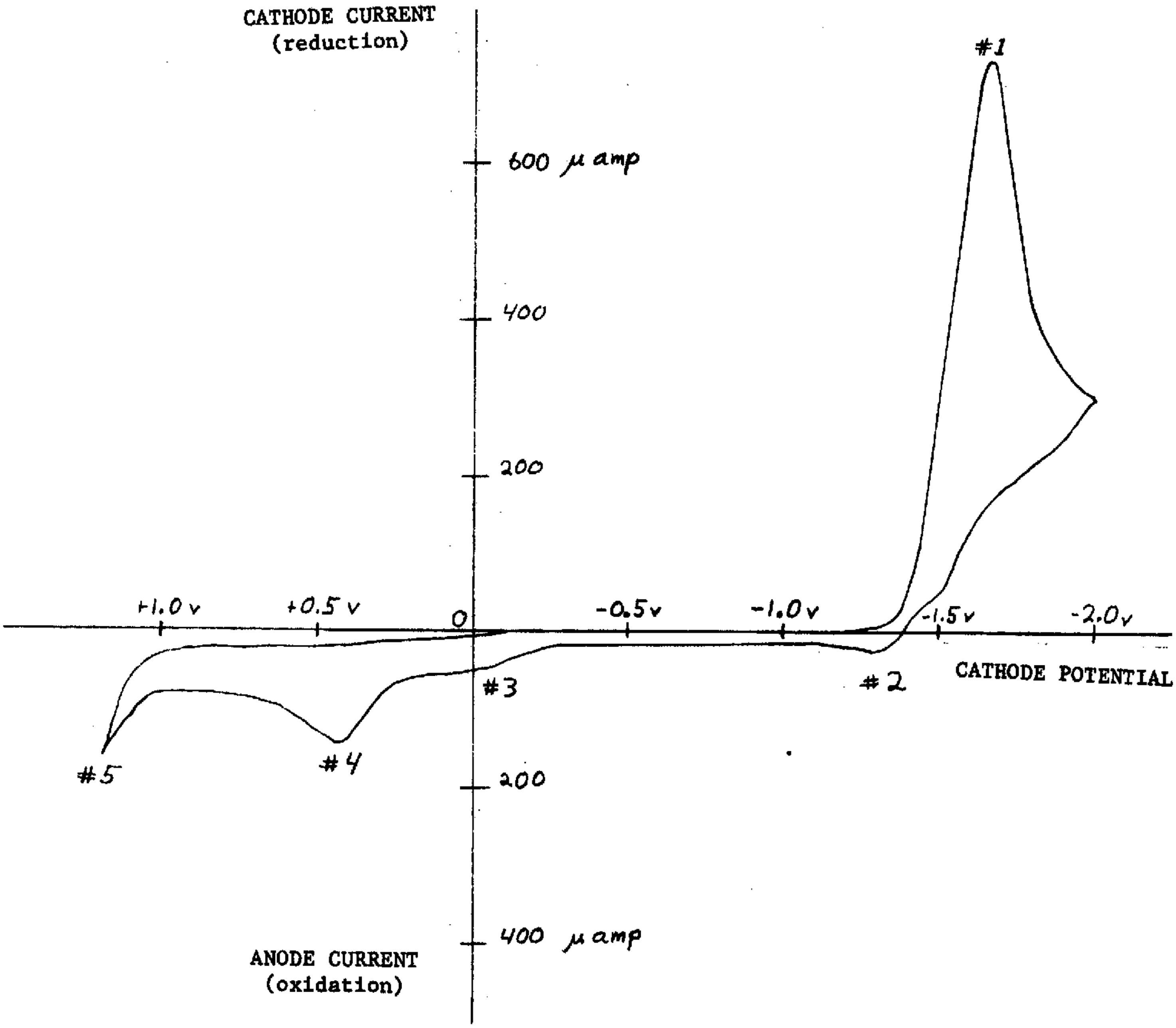



FIG. 11. CYCLIC VOLTAMOGRAM OF MBBA AT 0.1 VOLT/SEC SCAN RATE

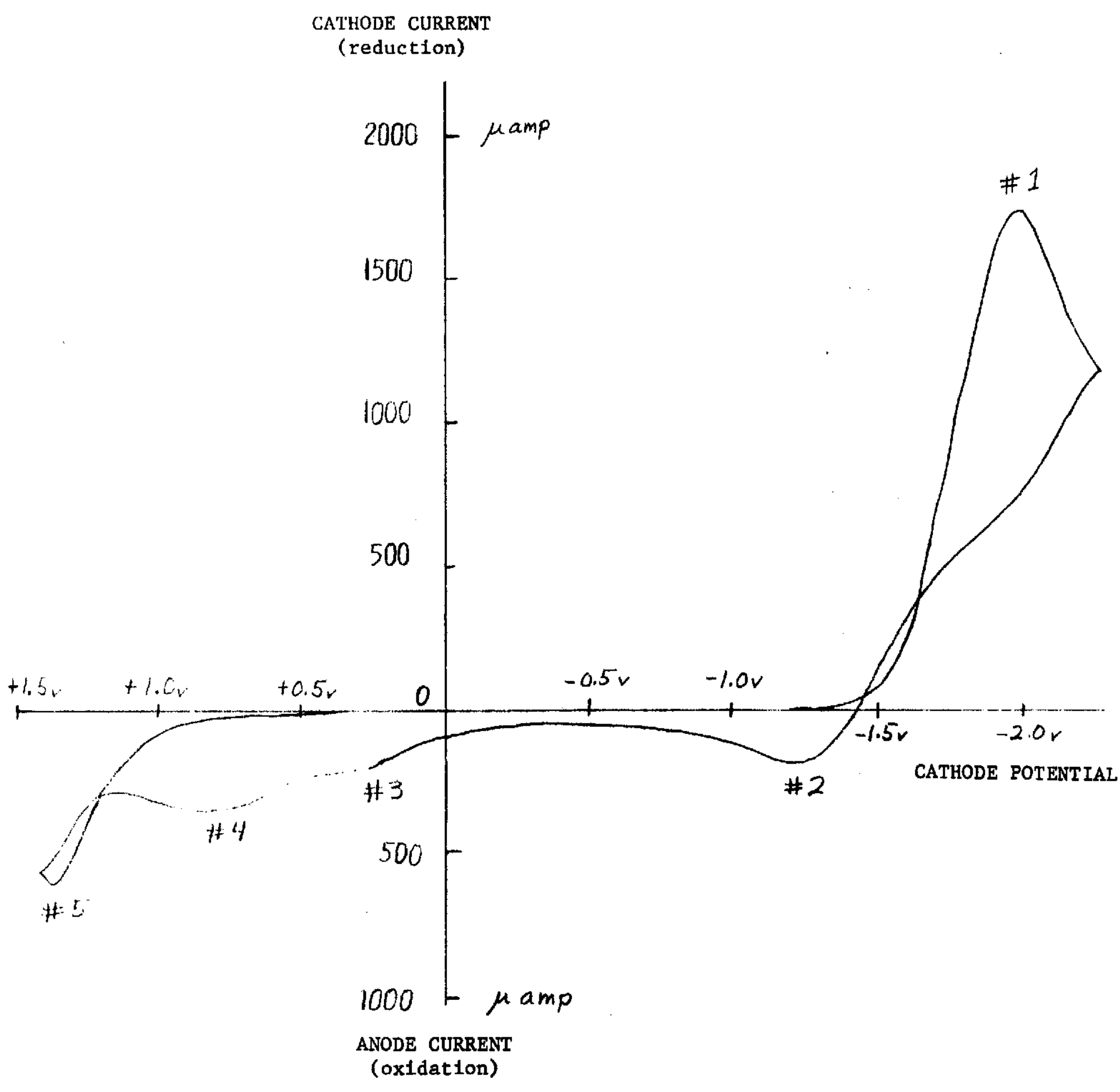



FIG. 12. CYCLIC VOLTAMOGRAM OF MBBA AT 1.0 VOLT/SEC SCAN RATE

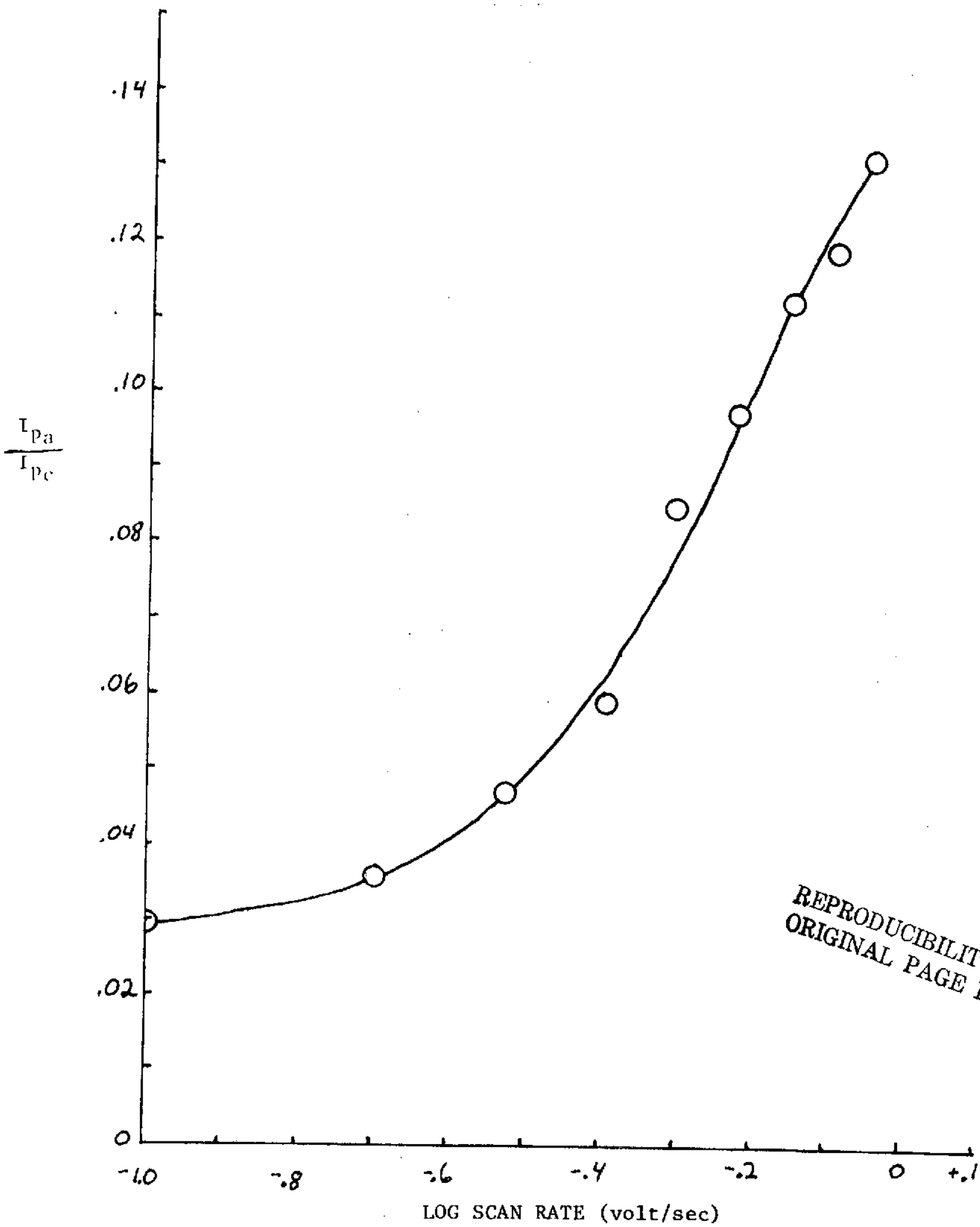



FIG. 13. OXIDATION-REDUCTION CURRENT RATIO VS SCAN RATE FOR PEAK #2 IN MBBA