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ELECTROCHROMIC DISPLAY DEVICE

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Semi-Annual Report for Period 1 March 1975 to 31 August 1975

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Electrochromic Display Device
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OBJECTIVES

The objective of the program is to develop and evaluate the performance characteristics of a solid state electrochromic device such that after the conclusion of this program a rational decision can be made on the scope and future uses of this new technology in military applications.

The work is divided into three separate phases:

(i) Physico-Chemical Investigation of Known Electrochromic Devices; (ii) Incorporation of Solid State Super-Ionic Conductors into Electrochromic Devices; (iii) Electrochromic Phenomena in Multilayer Transition Metal Oxide Structures.

In the first phase the objective is to optimize the fabrication process of known solid state electrochromic devices and to evaluate their performance characteristics. In phase (ii) the objective is to demonstrate the feasibility of incorporating a solid state super-ionic conductor into the electrochromic, to study their operational characteristics and to optimize the fabrication process. In phase (iii) the objective is to study a new concept, that of using a variable valence state transition metal oxide film in conjunction with a known electrochromic oxide such as WO_3 to form a novel electrochromic device.

SUMMARY

This semi-annual report covers the work performed under ARPA contract No. DAAB07-75-C-1310 during the period of March 1, 1975 to August 31, 1975. The work has been concentrated on the optimization of the fabrication process of known solid state electrochromic devices and on the evaluation of their performance characteristics. Significant progress has been made in the successful routine fabrication of an improved structure consisting of $\text{SnO}_2\text{-WO}_3\text{-MgF}_2\text{-Au-MgF}_2$. This structure appears to have superior electrochromic properties when compared to the corresponding devices such as $\text{SnO}_2\text{-WO}_3\text{-SiO-Au}$ which have been studied earlier. Although the lack of reproducibility of the electro-optical characteristics among samples prepared under apparently identical conditions still remains a major enigma, considerable insight has been obtained on various parameters which affect the performance of solid state electrochromics.

The solid state electrochromic devices that are being investigated consist of a multilayer thin film structure. Each of the constituent layers can critically affect the electro-optical characteristics and therefore the major part of the work had to be directed toward the optimization of each layer with respect to parameters such as: substrate preparation, Electrochromic material selection, methods of film preparation, control of deposition parameters such as rate of evaporation, substrate temperature, selection of suitable insulating material, development of a transparent counter electrode and the protection

of the device against mechanical damage and chemical contamination. A standard method of fabrication has been established and the functional parameters of assembled structures are routinely evaluated.

Thin films of superionic conductors such as RbAg_4I_5 have been prepared by different techniques - (i) direct evaporation of the compound and (ii) by coevaporation of RbI and AgI in the appropriate molar ratio and by synthesis of the compound in situ by solid state reaction. Electrochromic devices have been fabricated by incorporating this material into the standard solid state structure. The characteristics of such devices are being evaluated. Attempts are also being made to synthesize thin films of β -alumina for this purpose.

The literature survey on the preparation and properties of transition metal oxides to be used in conjunction with known electrochromic materials has been completed and efforts are beginning to fabricate an electrochromic structure based on this novel concept.

TECHNICAL DISCUSSION

1. Introduction

A great deal of interest has been generated in recent years in exploiting various technological developments for the purpose of information processing and display by using selected materials in devices that change their optical properties such as light emission, reflection or scattering and the state of polarization, when subjected to an external electric field. Some of the most widely studied systems for this purpose are the light emitting diodes, the plasma discharge in gases and the liquid crystals. Many of these systems suffer from major disadvantages such as lack of adequate storage, low contrast in high ambient lighting conditions, poor field of view, high voltage requirements, unacceptable power consumptions, poor resolution or lack of grey scale.

There is a need to develop new systems which do not have these disadvantages and at the same time will operate in the more stringent requirements of displays for military applications. A number of materials have been studied sporadically during the last few years which when excited by an electric field or current will change their light absorption properties in the visible range. Devices based on these materials, henceforth called electrochromics, promise to fulfill most of the requirements of an ideal display system ^(1,2).

The basic concept of the electrochromic display device is shown in Figure I. On a transparent substrate, such as glass, a transparent conductive electrode is deposited in a pattern required for a given application. The electrochromic material where the color change is induced, is then deposited on top of the conductive coating. A thin layer of a selected insulating material which is typically an ionic conductor with very little electronic conductivity, is then deposited over the electrochromic layer. The device is completed by depositing a second electrode layer on top of the insulating film. This layer not only serves as the electrode but depending upon its thickness the device can be made to operate either in a reflective mode or in a transmissive mode. An additional layer can be applied on the top electrode to make it abrasion resistant.

The purpose of this program is to carry out a research and development work leading to the generation of a solid state electrochromic technology which may be utilized in military display applications. The approach taken involves the optimization of the fabrication parameters and the characterization of the devices by measuring the relevant optical, electrical and other physical properties. The work is conveniently divided into three categories and these are: (i) Fabrication and characterization of the existing device, (ii) Incorporation of superionic conductors, and (iii) new approach based on variable valence state oxide multilayer structure.

The successful fabrication of a device of this kind depends on the optimization of each constituent layer with respect to film thickness, deposition parameters and mutual compatibility of the layers with respect to inter-diffusion, solid state chemical reaction, etc. This report covers the work performed under ARPA Contract No. DAAB07-75-C-1310 during the period March 1, 1975 to August 31, 1975.

2. Fabrication of the Solid State Electrochromic Devices

The electrochromic device fabricated consisted of a multilayer thin film system shown in Figure I. A brief description of some of the parameters that have been investigated thus far is given below.

2.1 Substrate Preparation

The choice and preparation of the transparent conducting glass substrates have an important role on the device performance. Commercially available NESA glass, a SnO_2 coated conducting glass, and NESATRON (indium oxide) glass were tried but NESA was found to be superior. Although the NESATRON glass has higher conductivity and better optical transmission, it is possible that the diffusion of indium in the device may present a long term stability problem. The SnO_2 glass used in this program was obtained from PPG Industries. The quality of these glasses in terms of the uniformity of optical transmission and sheet resistance was not entirely satisfactory and did present problems in making reproducible devices.

To start with, a thoroughly cleaned substrate is a prerequisite for the preparation of an electrochromic device with reproducible properties. The following procedure was developed for cleaning the glass substrate.

Ultrasonic cleaning for 5 minutes in Klearall (1-1-1 trichloroethane) --- air blow-off --- immersion in chromerge solution for 15 seconds --- tap water rinse --- immersion in ultrasonic bath at 50°C for 5 minutes --- deionized water rinse --- vapor degreasing in isopropyl alcohol vapor for 15 minutes --- preheating the substrate in a high vacuum to 100°C for 15 minutes. The above procedure gave us a reasonably clean substrate for subsequent film deposition. We have also tried gas discharge cleaning but no significant improvement over this method was observed.

3. Deposition of the Electrochromic Layer

3.1 Electrochromic Material

Although several transition metal oxides are known to be electrochromic, only WO_3 and MoO_3 show the effect at room temperature or below to the extent that can be used for display applications. Both of these materials are known to exist in a wide range of substoichiometric composition (MO_{3-x}). These materials evaporate readily in vacuum and during the evaporation process they lose oxygen to form substoichiometric films. Both of these materials have a fairly large band gap (Eg 3.0eV) and are, therefore, completely transparent in the visible. Most of our present work was concentrated on thin

films of MoO_3 and WO_3 , with the emphasis on the later which showed a more pronounced electrochromic effect.

3.2 Deposition Techniques

Most of the standard vacuum evaporation processes can be used for the film preparation resulting in electrochromic devices of varying degrees of sensitivity. We have used two techniques: (i) thermal evaporation and (ii) RF-sputtering from an oxide target. Of these two methods the thermal evaporation by resistive heating has been routinely used because the method is convenient, rapid and under controlled conditions, yields good electrochromic films.

The evaporation was carried out in a standard commercial vacuum system equipped with a 6" oil diffusion pump and a liquid nitrogen trap and capable of maintaining pressure in the range 10^{-6} to 10^{-7} mm. The material used was analytical grade tungstic anhydride obtained from Fisher Scientific Co. The evaporation source was a commercially available tungsten boat obtained from Sylvania Corp. (type S42780). It is also possible to use tantalum and molybdenum boats without changing the film properties.

3.3 Substrate Temperature

The substrate temperature has a profound effect on the adherence, response time and the optical characteristics of the film. A special substrate holder has been designed which permits the substrate temperature to be varied from -50°C to $+250^\circ\text{C}$. The films deposited in the temperature range 25°C to 80°C are strongly adherent and optically clear -- the

degree of adherence increases with increasing temperature. Films deposited at temperatures above 80°C turn blue as a result of thermal reduction in vacuum. However, brief exposure to atmospheric conditions after the film has been evaporated at high temperature ($\geq 100^{\circ}\text{C}$) will remove the blue color and a device fabricated with such a film behaves normally. Attempts to deposit films at -50°C resulted in a cloudy film with very poor adhesion and hence could not be used for the device fabrication. The optimum temperature was chosen to be around 50°C .

3.4 Deposition Rate

The rate of evaporation of the WO_3 film has an effect on the optical quality and the device characteristic such as the response time. The deposition rate was measured by a quartz crystal thickness monitor and was controlled in the range 2 A/sec. to 50 A/sec. The deposition at 2 A/sec. rate resulted in excessive heating of the substrate and the resulting film was blue in color. The fastest rate usually gave better electrochromic films and the optimum rate was chosen to be around 30 A/sec.

3.5 Thickness

The thickness of the electrochromic film has been studied in the range 1500 - 13,500 Å. The rate of coloration and bleaching increases with decreasing thickness. Appreciable coloration can be achieved even in a 1500 Å thick film. The memory of the device, as determined by the length of time the coloration is retained after activation, appears

to increase with increasing thickness of the film. A standard thickness of 5000 Å for the electrochromic layer was chosen for the purpose of optimization of other parameters.

4. Insulating Layer

The chemical nature and the deposition parameters of the insulating layer critically affect the device performance. A comparative study of the device characteristics has been made by using a number of materials, some of which have hitherto not been used before in electrochromic devices. Although a large number of materials have been found which will form an active device, only a few give satisfactory results in terms of optical density and stability. We have concentrated our efforts on two materials, SiO and MgF₂ which appear to give the best results. Of the two materials SiO has been studied previously. It is well known that it is extremely difficult to make SiO films of a defined stoichiometry and reproducible electrical properties. Therefore, to fabricate an electrochromic device with SiO as the insulating layer requires very stringent control of deposition conditions, which makes the fabrication of reproducible devices very difficult.

We have found that the use of MgF₂ gives an order of magnitude improvement over SiO in terms of device reproducibility. However, the long term stability of the device may not be as good as with SiO and this is being investigated now.

Both SiO and MgF_2 can be vacuum deposited over the electrochromic layer and the same considerations apply with regard to the deposition parameters. The resistive heating evaporation is preferred over sputtering particularly for MgF_2 which is difficult to sputter. Both of these materials were evaporated by heating the chemically pure material in a tantalum boat. The substrate temperature was maintained at 50°C . Several film thicknesses in the range 25 Å to 3000 Å have been studied in detail. At very low thickness ($t < 75\text{Å}$) the device showed very little coloration which becomes unstable when the coloration voltage was reduced below the threshold voltage for coloration. The optimum thickness in the case of MgF_2 was found to be between 1000 to 2000 Å. The rate of deposition was not critical and the usual rate was 20 Å/sec.

5. Counter Electrode

Ideally, it is preferable to have a transparent counter electrode of the type SnO_2 or In_2O_3 films but the present day technology of making a conducting film of this type requires high temperature treatment (around 500°C) which is not compatible with the electrochromic device. The alternative is to use a metal film which does not have high transparency ($\sim 60\%$ transmittance) but has sufficient conductivity to have a working device. The preferred material was found to be a thin film of Au. Several other metals besides gold such as Ag and Al were tried but in these cases the diffusion of the metal into the insulating layer presents a

problem. The resistivity of the gold varies a great deal depending upon the substrate used. The thickness of the gold film has been optimized with regard to conductivity, transparency and device performance. The best result is obtained by using a ~ 150 Å thick film deposited at 1 Å/sec. rate on the MgF_2 film at 50°C . Ordinarily, the Au is deposited by thermal evaporation under conditions essentially similar to that described earlier but a sputtered film of Au also works well except that the gold layer has to be relatively thicker. Very thin films of sputtered Au (~ 150 Å) are more resistive than the corresponding evaporated film presumably because Au films may be partially oxidized under the sputtering condition. Several other metals are now being tried.

6. Protective Coating

Thin films of Au evaporated on the MgF_2 or SiO surface have poor scratch resistance and perhaps are sufficiently porous to permit contamination of the device by ambient laboratory environment. It is desirable, therefore, to have some kind of protective coating over the Au surface. We have evaporated a thin film of MgF_2 (~ 150 - 1000 Å) over the gold surface to make the device more scratch resistant. It is difficult to use thicker MgF_2 films (> 1000 Å) because the film has a tendency to craze and lift the underlying gold film because of stress release.

In addition to acting as a protective coating the MgF_2 film has another useful function. It appears to improve the memory of the device, perhaps by keeping away the ambient oxygen or excess moisture.

7. Method for Final Device Fabrication

Initially, most of the devices were made by depositing the layers sequentially, but breaking the vacuum after each evaporation in order to change the source. This raises the question of possible contamination of the layers by adsorbed gases from the ambient laboratory atmosphere. The evaporation method has been modified by introducing four different evaporation sources which enables us to fabricate the entire device by the sequential evaporation of all the component layers without breaking the vacuum in between.

8. Characterization of the Device

The experimental arrangement for the measurement of the dynamic optical and electrical properties of the electrochromic devices such as the current-voltage characteristics, light transmission changes as a function of applied voltage, rate of coloration and bleaching, and the polarization. emf developed in the sample as a result of coloration and bleaching, is schematically shown in Figure 2. The voltage in the shape of a triangle or a square wave-form is applied to the sample from a function generator (Model HP-330A) and a power supply amplifier (HP-6823A). The resulting current through the sample is measured by a digital multimeter. (Keithly Model 160) and is recorded on a X-Y recorder (Model HP-7035B). The monochromatic light from a light emitting diode or a helium-neon laser (emission at 6328 Å) is allowed

to pass through the sample and the transmitted light is monitored by a photo-detector (CdS-type) and recorded on the X-Y recorder. A cryostat has been designed and built to make measurements at temperatures in the range -150°C to $+200^{\circ}\text{C}$ under controlled ambient condition.

The current-voltage characteristics and the light transmission properties of a typical electrochromic device is shown in Figure 3. Initially, the current rises very slowly; goes through a negative resistance region (not manifested in all cases) followed by a more rapid increase in current. The rise in current is associated with the formation of color-centers and as a consequence the light transmission changes. There is a clearly defined threshold voltage (V_t) below which no coloration would occur. On reversing the polarity, there is a small current-burst which occurs at a voltage (V_B^+) which is slightly lower than or equal to the threshold voltage for coloration. Associated with this current-burst there is a small decrease in coloration density. On reversing the polarity, there is a current-burst associated with complete bleaching of the sample. One can arbitrarily define a voltage (V_B^-) which corresponds to the half-bleaching point, as a parameter to be compared for different samples.

One of the parameters that affects the device performance most critically is the thickness of each of the component layers. Therefore, the characteristics were measured as a function of film thickness in a number of devices and the results are shown in Table I.

Since there is a lack of reproducibility from one sample to another prepared by two consecutive evaporations under apparently identical deposition conditions, the comparison is meaningful to an extent between samples prepared during each evaporation. With our present arrangement we can make up to three devices in any given run and change the thickness of the component layers by suitable masking. It is apparent from Table I that the threshold voltage (V_t) for coloration varies in the range 1.1 to 1.6 Volts but no systematic correlation could be established between V_t and the thickness of any of the component layers. The threshold voltage for the 1st bleaching step which occurs when the sample is still in the coloration mode is related to the threshold voltage for coloration. The potential for the half-bleaching point (V_B) also follows the same trend as V_t and falls in the range 0.25 to 1.1 Volt. With few exceptions the DC-cell resistance (below the threshold voltage) as expected, increases with increasing thickness of the electrochromic and the insulating layer.

8.1 Effect of Electrochromic Layer Thickness

Figure 4 and 5 show the current-voltage characteristic and the light transmission changes in a set of three devices made in a single run; the only difference being the thickness of the electrochromic layer which varies from 1500 to 13,500 Å. It is apparent that the overall shape of the i-v curves and the light transmission changes are essentially similar with some difference in the position of the current peaks, magnitude

of the optical density change (which increases with thickness and decreases again at higher thickness) and the response time for bleaching. In general a film thickness greater than 10,000 Å makes the device slower in response. The optimum thickness is between 5,000 to 11,000 Å.

8.2 Effect of Insulator Layer Thickness

The effect of changing the insulator thickness is shown in Figures 6, 7 and 8. Here again for valid comparison all three devices with varying thicknesses of the MgF_2 layer (50 Å - 1500 Å) were made in a single run under identical conditions. Clearly the best result is obtained with a MgF_2 thickness around 1000 Å. For thicknesses smaller than 75 Å only a slight coloration occurs which corresponds to the first bleaching step. The color-centers are unstable once the voltage is reduced below the threshold voltage (V_B^+). It is also interesting to note that for the 50 Å thick MgF_2 film slight coloration occurs even in the bleached mode. The current density is also considerably higher than the thicker films.

8.3 Effect of Au-Electrode Thickness

The thickness of the counter electrode (Au) has a profound effect on the device characteristics such as i-v curves, rate of coloration and bleaching and more particularly the memory. Figures 9 and 10 show the i-v curves and the light transmission changes for two identical devices with two different thicknesses. Evidently the thicker gold film makes the device more like a diode. The rate of bleaching appears slower in thicker films. Figure 11 shows the effect of gold thickness on the bleaching characteristic. Clearly the

thicker films give a better memory. The gold thickness in the range 170 Å to 2000 Å has been studied and in most cases, with thicker gold film (> 500 Å) a memory of 12 hours or more has been observed. This may imply that the memory of a device may be affected by some diffusing ambient gases such as O₂ or moisture. This is being investigated now.

8.4 Effect of MgF₂ Overcoat on the Au-electrode

The purpose of adding a MgF₂ film overcoat to the device was twofold: (i) to make the gold film more scratch-resistant and (ii) to prevent or slow down the contamination of the device from ambient atmosphere which may have an adverse effect on the stability and performance. MgF₂ was chosen because it is a well known scratch-resistant material which is used for lens coating. As expected from our observation on the Au-film, the MgF₂ layer also has a striking effect on the device characteristics. The result is shown in Table I. The effect on the memory of the device is shown in Figure 12. The thickness of the MgF₂ film has been studied in the range 100 to 1000 Å. The deposition of thicker MgF₂ film (> 1000 Å) on Au film is difficult because the MgF₂ film lifts the Au-film by stress release. Other materials besides MgF₂ are now being studied.

It is to be emphasized that the results presented here on the variation of thickness of different component layers only represents the general trend. The device characteristics are extremely sensitive to evaporation condition which makes the comparison between two samples of identical thickness, but made during separate evaporations, very difficult.

The device characteristics such as response time, memory, i-v curve fall in a wide range even with two films prepared under apparently identical conditions. The reason for this irreproducibility has to be determined before any systematic correlation can be established, and this is being pursued now.

8.5 Voltage Dependence of Coloration and Bleaching

The effect of applied voltage on the rate of coloration and bleaching is shown in Figure 13 (a) and (b). Evidently the rate of coloration and the saturation optical density are voltage dependent. Above 2.5 Volts the coloration density appears to be directly proportional to the number of coulombs that passes through the sample. In the voltage range 1.5 to 2.5 Volts the density is a nonlinear function of the charge passed through the device. The bleaching curves show an induction period which increases with increasing voltage. The induction period is probably associated with an internal polarization field which opposes the external applied field.

8.6 Internal Polarization

Associated with the coloration of the device, an internal polarization emf which has the same polarity as the applied field develops. The polarization emf develops above the threshold voltage and reaches a saturation value of ~ 1.6 Volts when the applied voltage is around 3.0 Volts. Under open circuit condition the emf quickly decreases to a few tenths of a Volt (0.2 to 0.3 Volt) and thereafter decreases more

slowly with simultaneous bleaching of the color-centers. The time required to detect any polarization, emf is around 5 μ sec. above which it increases with increasing time and reaches a steady state value around 50 to 100 m sec. No polarization emf is detected when the device is operated in the bleached mode.

The effect of temperature and different ambient gases are now being investigated in detail. Preliminary results indicate that the ambient gas such as N_2 , O_2 , H_2 and H_2O vapor has a profound effect on the device performance.

9. Super-Ionic Conductors

In all known reversible electrochromic structures, it appears that some sort of ionic motion, such as H^+ ions or oxygen vacancies, is involved in the electrocoloration process. It has been observed ⁽⁴⁾ that by providing an intentional reservoir of ions from a semi-solid ionic electrolyte (source of H^+ , Na^+ etc.), it is possible to greatly improve on the response time and reliability of known electrochromic structures. From a device point of view, a hybrid system comprised of a thin solid film and a semi-solid electrolyte is not satisfactory. The objective of this work is to investigate the possibility of using the recently found super ionic conductors which have high conductivities around room temperature.⁽⁵⁾ Some of these materials, which have appreciable conductivities near room temperature, that could have possible uses in an electrochromic device are listed in Table II.⁽⁶⁾ Most of these materials conduct by Ag^+ ion, which

is not a desirable ion from the electrochromic point of view. In fact, it has been observed that addition of Ag^+ ion in the semi-solid structure has a detrimental effect by trapping the color-center electrons to form metallic silver. However, silver tungsten bronze is well known and therefore, it is perhaps possible to form a silver tungsten bronze by a solid state electrochemical process. Since we initiated this work it has been reported by Green⁽⁷⁾ et al. that an electrochromic device consisting of $\text{SnO}_2\text{-WO}_3\text{-RbAg}_4\text{I}_5\text{-Ag}$ can indeed be made which showed reversible coloration.

9.1 Preparation of RbAg_4I_5 Thin Film Devices

The RbAg_4I_5 is synthesized by taking a stoichiometric mixture of RbI and AgI and heating at 400°C in a sealed glass tube for 6 hours and then annealing the compound at 150°C for 16 hours. The material is then powdered and pressed into a pellet and the conductivity was measured and found to be in close agreement with the reported value.

Thin films of RbAg_4I_5 were prepared by two different techniques - (i) thermal evaporation of the material in a vacuum and (ii) coevaporation of RbI and AgI in their appropriate molecular ratio on a heated substrate ($\approx 100^\circ\text{C}$) to carry out the solid state reaction in situ. The electrical conductivity of the films is continuously monitored during the film formation process and the measured conductivity was found to be $0.27(\Omega\text{-cm})^{-1}$ which is in excellent agreement with the reported value.

compared to the corresponding devices such as $\text{SnO}_2^{\text{II}}\text{-WO}_3^{\text{II}}\text{-SiO-Au}$ which have been studied earlier. Although the lack of reproducibility of the electro-optical characteristics among samples prepared under apparently identical conditions still remains a major enigma, considerable insight has been obtained on various parameters which affect the performance of solid state electrochromics.

The solid state electrochromic devices that are being investigated consist of a multilayer thin film structure. Each of the constituent layers can critically affect the electro-optical characteristics and therefore the major part of the work had to be directed toward the optimization of each layer with respect to parameters such as: substrate preparation, electrochromic material selection, methods of film preparation, control of deposition parameters such as rate of evaporation, substrate temperature, selection of suitable insulating material, development of a transparent counter electrode and the protection of the device against mechanical damage and chemical contamination. A standard method of fabrication has been established and the functional parameters of assembled structures are routinely evaluated.

Thin films of superionic conductors such as RbAg_4I_5 have been prepared by different techniques - (i) direct evaporation of the compound and (ii) by co-evaporation of RbI and AgI in the appropriate molar ratio and by synthesis of the compound in situ by solid state reaction. Electrochromic devices have been fabricated by incorporating this material into the standard solid state structure. The characteristics of such devices are being evaluated. Attempts are also being made to synthesize thin films of β -alumina for this purpose.

The literature survey on the preparation and properties of transition metal oxides to be used in conjunction with known electrochromic materials has been completed and efforts are beginning to fabricate an electrochromic structure based on this novel concept.

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A device consisting of $\text{SnO}_2\text{-WO}_3\text{-RbAg}_4\text{I}_5\text{-Ag}$ or Au was fabricated by using this technique. However, no coloration was observed in such a device when Ag or Au is used as the electrode, however the sample colored when the Ag is replaced by a graphite electrode. A special kind of flexible graphite electrode (graphite powder dispersed in a polymer) was pressed against the film and the device colored under the pressure contact when the SnO_2 electrode was made negative. However, no bleaching was observed on reversing the polarity. The color-center thus formed bleached slowly under ambient condition. Devices made with KAg_4I_5 also behaved likewise. We are continuing our efforts in this area.

9.2 Thin Film Devices with β -alumina

Beta alumina has been the subject of considerable interest in recent primarily because of its high ionic conductivity and its applicability in solid state batteries^(8,9). It is a crystalline, non-stoichiometric compound having the composition $\text{AM}_{11}\text{O}_{17}$ where A may be Li, Na, K, Rb or Ag and M may be Al, Fe or Ga. This type of solids, can be classified as super ionic conductors. The mobile ions (Li, Na etc.) are statistically distributed among a magnitude of nearly equivalent sites in widely separated planes perpendicular to the hexagonal axis and two dimensional ionic conduction occurs from the interchange of ions between sites in these planes.

In order to have high ionic conductivity in thin films it is desirable to have a highly crystalline film. To our knowledge, thin films of β -alumina have not been made. Our initial attempt to make thin films of this material by

sputtering in oxygen resulted in a highly insulating Al_2O_3 thin film. We are presently investigating an alternative method of making thin films of conducting β -alumina, and the use of pressed discs.

10. Multilayer Transition Metal Oxide Structure

In this phase of our work attempts are being made to fabricate an electrochromic device consisting of:

Glass - SnO_2 / EC_1 / EC_2 / Metal

where EC_1 is a known electrochromic material such as WO_3 or MoO_3 and EC_2 is a film of transition metal oxide (NiO , FeO etc.) which is not in its highest oxidation state. Such a device would operate by the oxidation of the EC_2 layer (hole injection) and reduction of the EC_1 layer (electron injection). The literature survey on the preparation and properties of the relevant transition metal oxides has been completed and we are starting to fabricate an electrochromic device by incorporating these oxide layers.

11. Accomplishments

We have successfully made a number of solid state electrochromic devices and evaluated their performance characteristics to optimize the functional parameters. The optimization process turned out to be quite difficult primarily because of poor reproducibility of the device fabrication process. In spite of this limitation we have made some significant advances in optimizing the fabrication parameters. We have reached a state where we can make some good electrochromic devices for final characterization.

Table I

Some Characteristics of an Electrochromic Device - $\text{SnO}_2\text{-WO}_3\text{-MgF}_2\text{-Au-MgF}_2$
With Variations in Thickness of Component Layers

Sample No.	WO_3	Thickness in A		Top Coat (MgF_2)	Characteristics			
		MgF_2	Au		V_t (Volts)	V_B^+ (Volts)	V_B^- (Volts)	R (ohms) D.C.
104-17	3000	1040	154	120	1.33	1.10	0.80	46
	5000	1040	154	120	1.15	1.00	1.00	43
	10,000	1040	154	120	1.30	1.30	0.80	39
104-18	4513	1010	157	126	1.20	0.55	0.75	133
	1500	1010	157	126	1.30	1.00	0.25	89
	1500	1003	135	136	1.43	1.25	0.25	75
104-19	7500	1003	135	136	1.20	none	0.80	200
	13,450	1003	135	135	1.30	none	----	2083
	5026	250	160	120	1.20	1.00	none	----
104-22	5026	500	160	120	1.00	0.90	0.65	100
	5026	1026	160	120	1.10	1.00	0.75	150
	5020	50	160	118	1.10	1.50	none	50
104-23	5020	750	160	118	1.23	0.90	0.80	109
	5020	1482	160	118	1.10	1.20	1.10	833
	5042	25	157	120	1.20	1.20	none	48
104-24	5042	1000	157	120	----	----	----	----
	5042	2000	157	120	1.12	1.10	0.80	172

Table I (page 2)

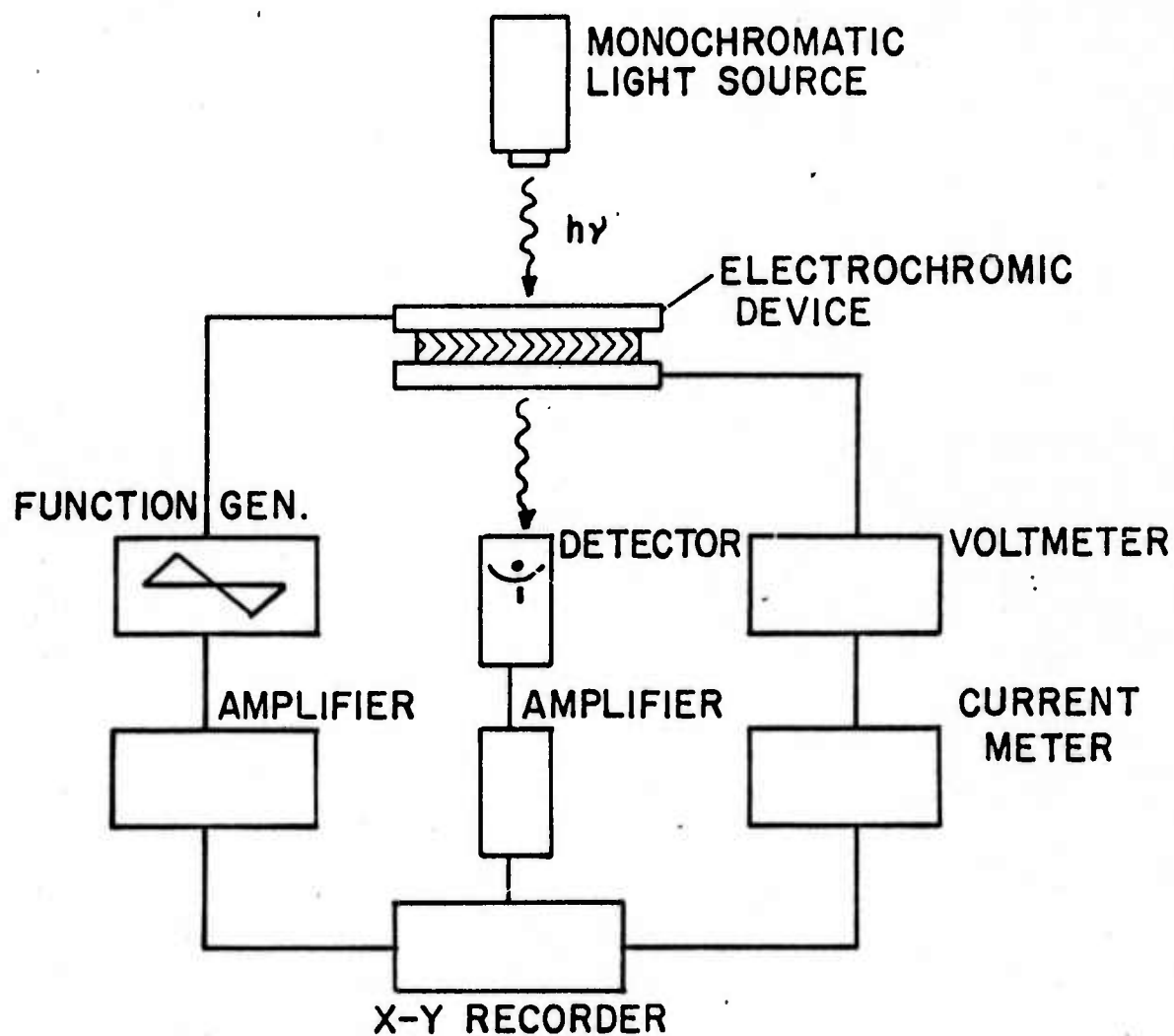
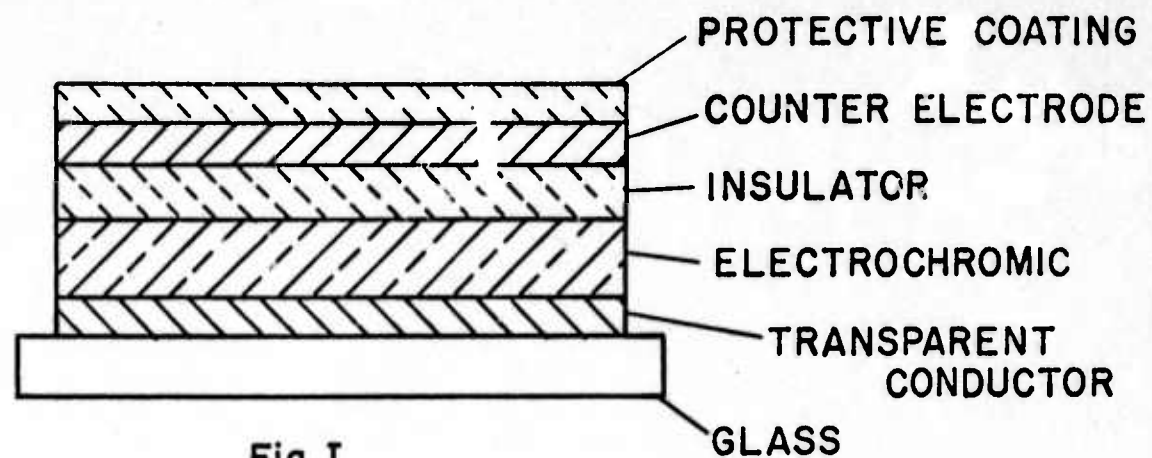
Sample No.	WO ₃	Thickness in A		Top Coat (MgF ₂)	V _t (Volts)	Characteristics		
		MgF ₂	Au			V _B ⁺ (Volts)	V _B ⁻ (Volts)	R (ohms) D.C.
104-28	5046	75	158	120	1.20	1.10	0.80	28
	5046	1500	158	120	1.20	1.20	1.10	1920
	5046	2485	158	120	----	----	----	----
104-29	5082	100	155	125	1.10	1.20	0.70	40
	5082	1000	155	125	1.60	none	1.00	250
104-84	5046	1130	150	120	1.40	1.40	1.40	63
	5046	1130	250	120	1.40	1.20	----	----
	5046	1130	500	120	1.60	----	1.30	1000
104-83	5078	1050	150	118	1.25	1.20	1.20	100
	5078	1050	250	118	1.25	1.10	1.20	100
	5078	1050	500	118	1.55	----	1.25	83
104-58	5000	1000	155	500	2.00	1.50	1.40	140
	5000	1000	155	1000	1.80	none	2.00	120
104-57	5035	1006	160	130	1.30	0.80	1.00	100
	5035	1006	160	300	1.30	1.10	0.80	62
	5035	1006	160	600	1.35	1.40	1.10	95

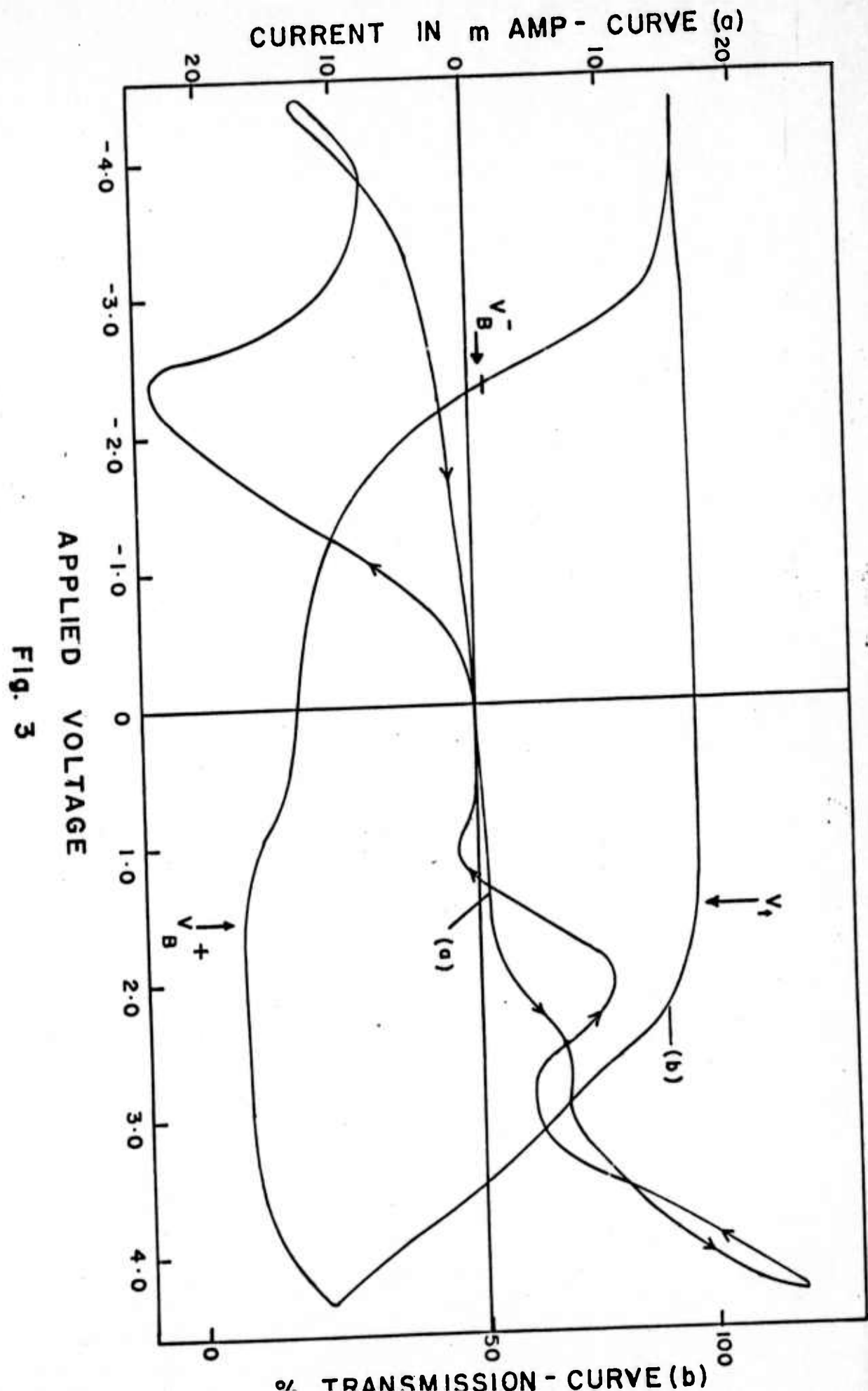
Table II
Ionic Conduction Properties of a few Solid Electrolytes
Near Room Temperature (6)

Material	Temp. °C	Conductivity (ohm ⁻¹ cm ⁻¹)	Mobile Ion
RbAg ₄ I ₅	20	2.7x10 ⁻¹	Ag ⁺
KAg ₄ I ₅	38	6.7x10 ⁻²	Ag ⁺
NH ₄ As ₄ I ₅	20	2.0x10 ⁻¹	Ag ⁺
Ag ₇ I ₄ PO ₄	25	1.9x10 ⁻²	Ag ⁺
B-Ag ₃ SI	25	1.0x10 ⁻²	Ag ⁺
Ag ₄ RbI ₄ CN	25	1.8x10 ⁻¹	Ag ⁺
Na ₂ O.11Al ₂ O ₃	25	3.0x10 ⁻²	Na ⁺
BCu ₂ HgI ₄	25	7.6x10 ⁻⁷	Cu ⁺
ZrO(H ₂ PO ₄) ₂ .3H ₂ O	25	2.0x10 ⁻³	H ⁺

REFERENCES

- (1) S. K. Deb, Appl. Optics Suppl. 3, 192 (1969); Phil. Mag., 27, 801 (1973); U. S. Patent No. 3,829,196 (1974); Proc. Electronics Comp. Conference, Washington, D.C. (1974) p11.
- (2) S. K. Deb and R. F. Shaw, U. S. Patent No. 3,521,941 (1970).
- (3) S. K. Deb, Proc. Roy. Soc. (London), A306, 211 (1968).
- (4) H. Witzke and S. E. Schnatterly, U. S. Patent No. 3,840,287 (1974).
- (5) Wiedersich, H. & Geller, S., "The Chemistry of Extended Defects in Non-Metallic Solids", L. Eyring & M. O'Keefe, eds., North Holland, (1970) p.629.
- (6) F. Chen, "Properties and Uses of Silver Solid Electrolyte" Ph. D. Thesis, (1972) University of California, Santa Barbara, p. 3.
- (7) M. Green and D. Richman, Thin Solid Films, 24, 545 (1974).
- (8) Yao, Y. & Kummer, F., J. Inorg. Nucl. Chem. 29, 2453 (1971).
- (9) Kummer, J. T., Progr. Sol. St. Chem., 7, 141 (1972).





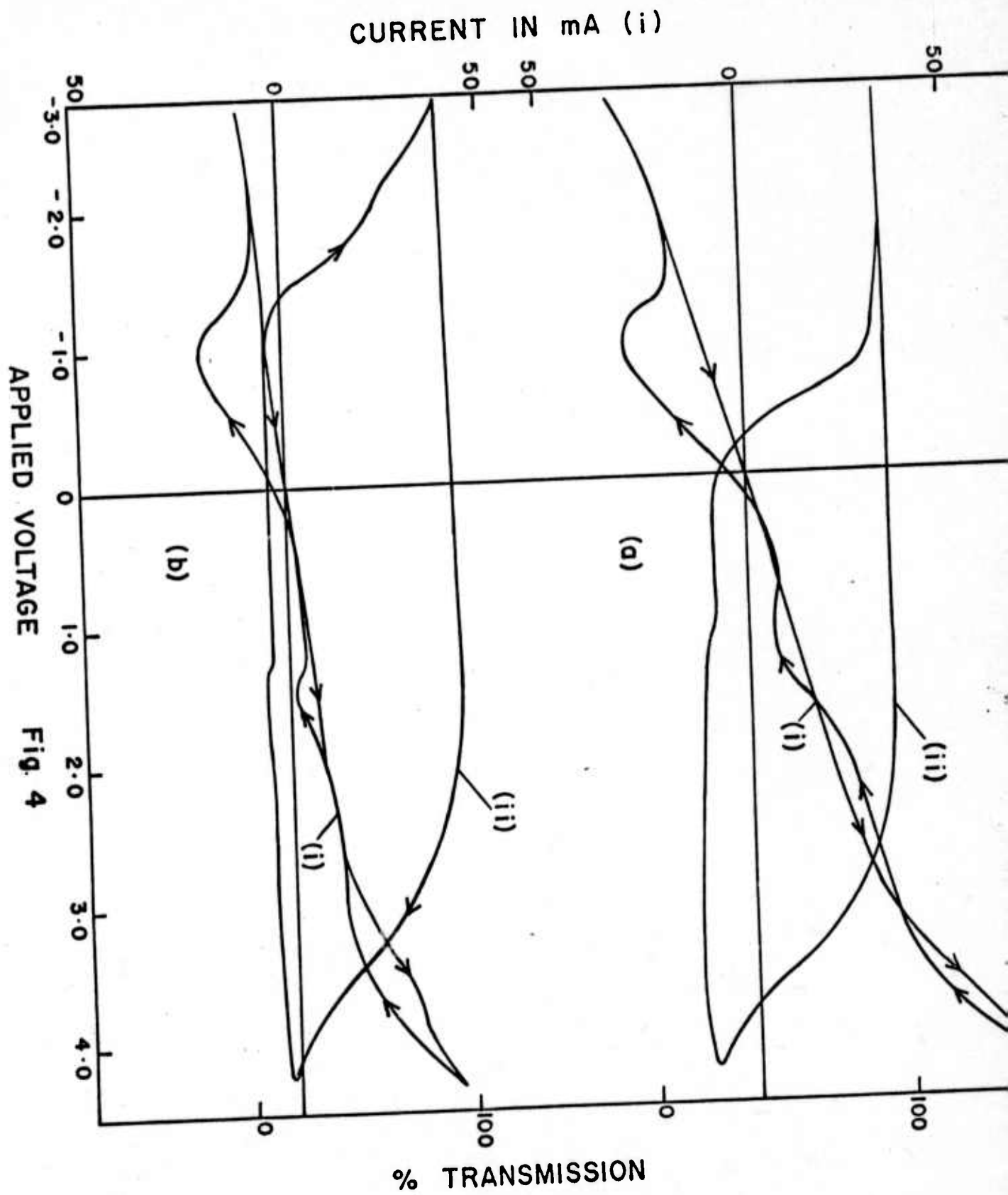


Fig. 4

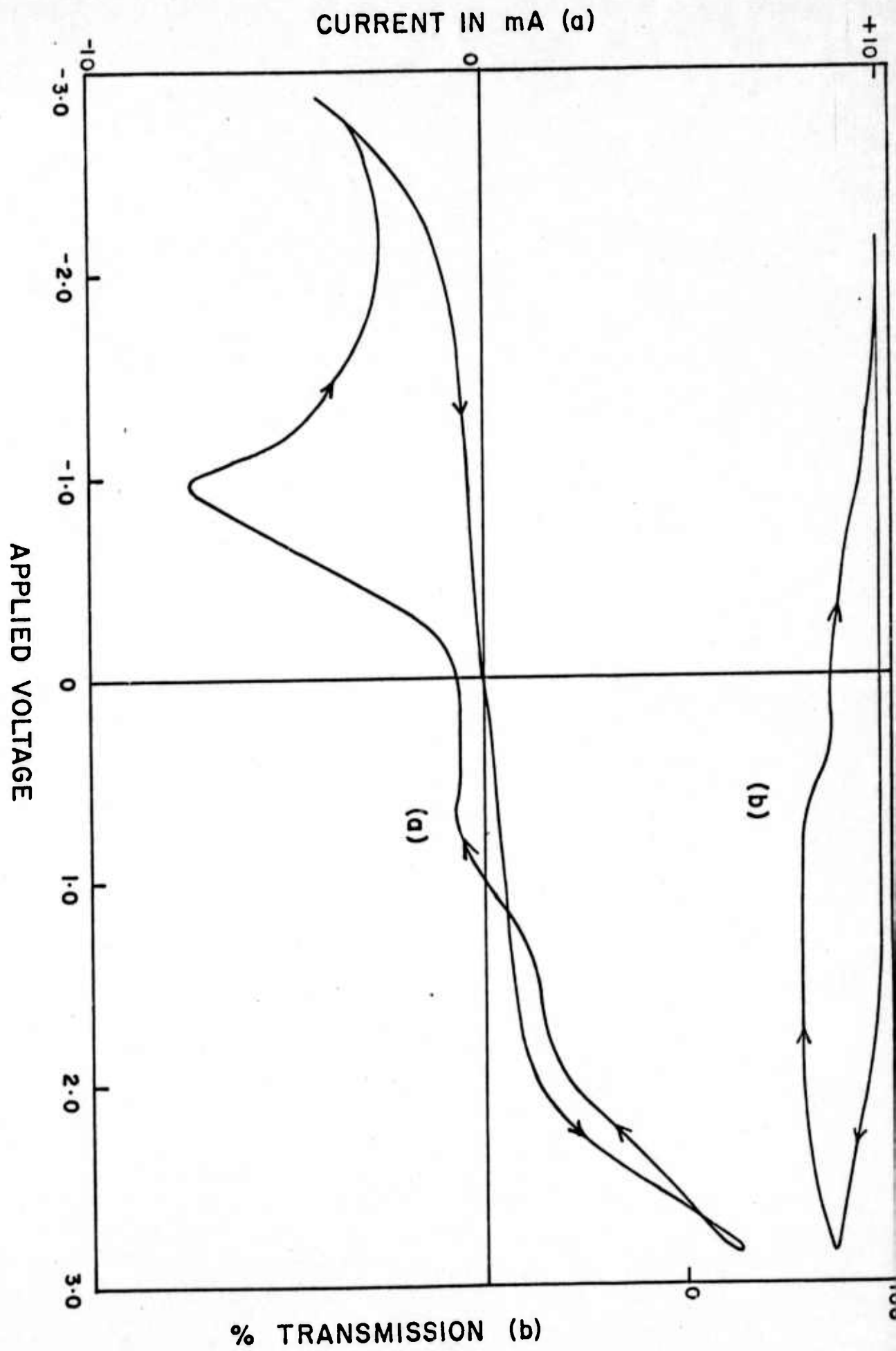


Fig. 5

NOTICES

Disclaimers

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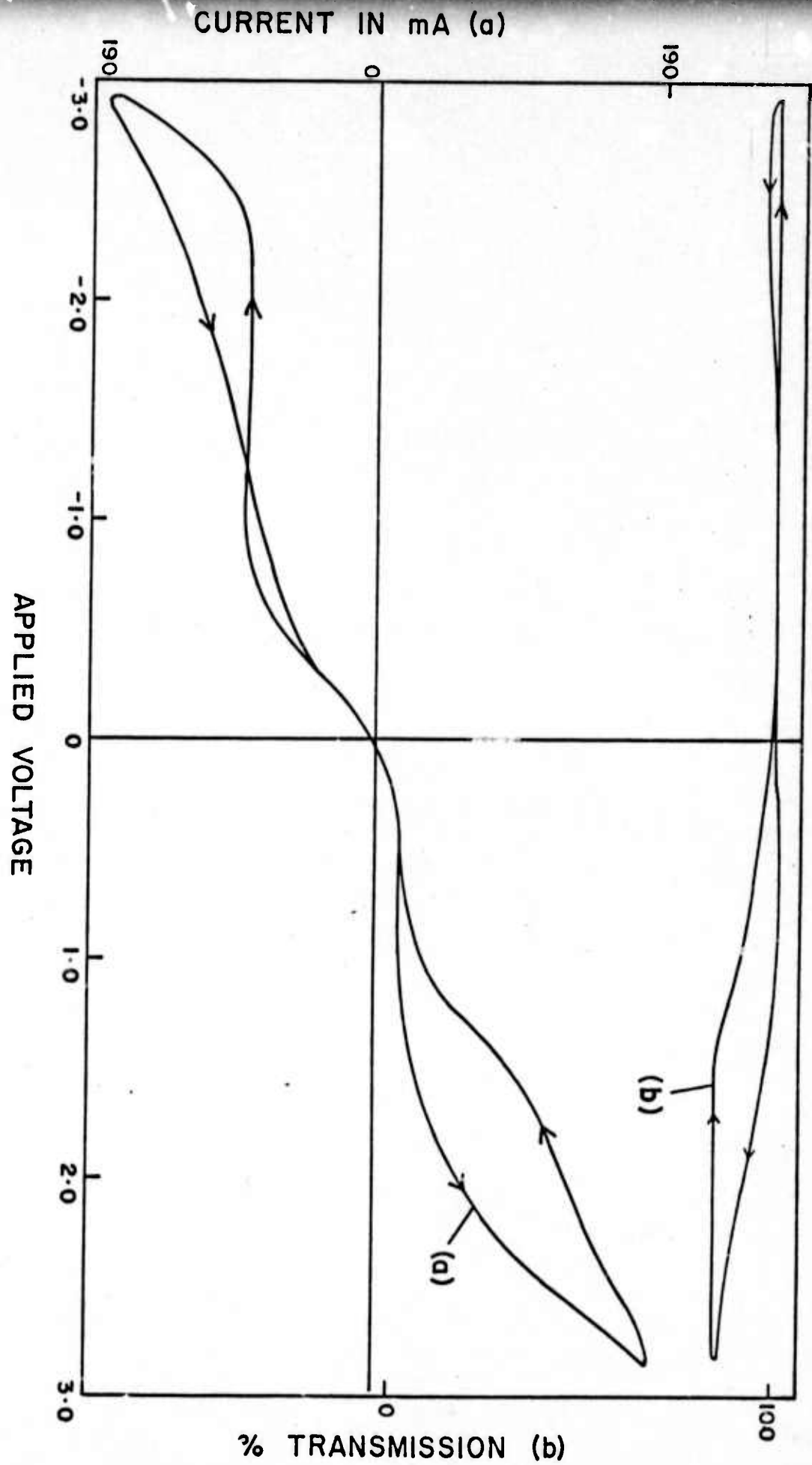


Fig. 6

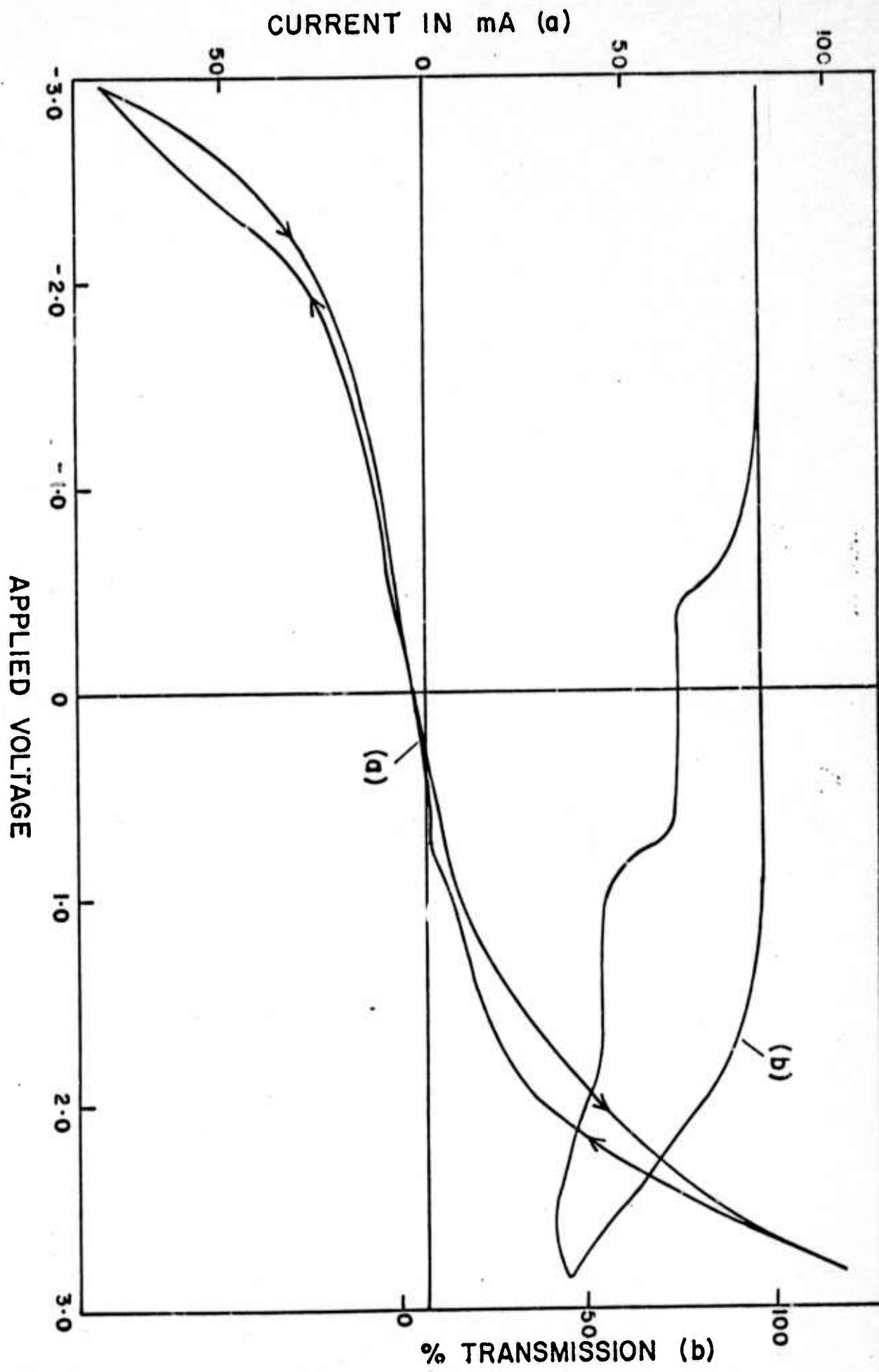


Fig. 7

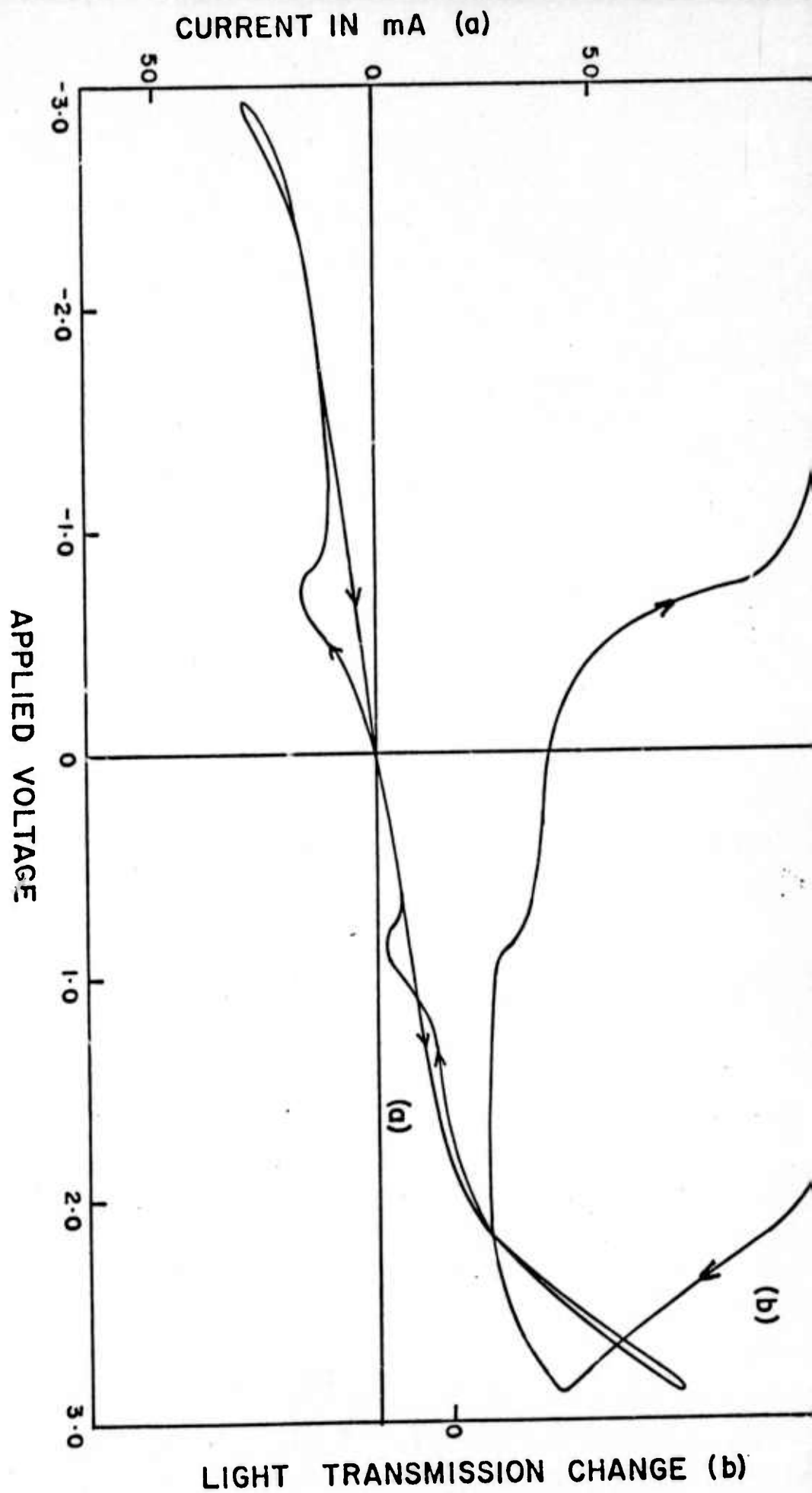
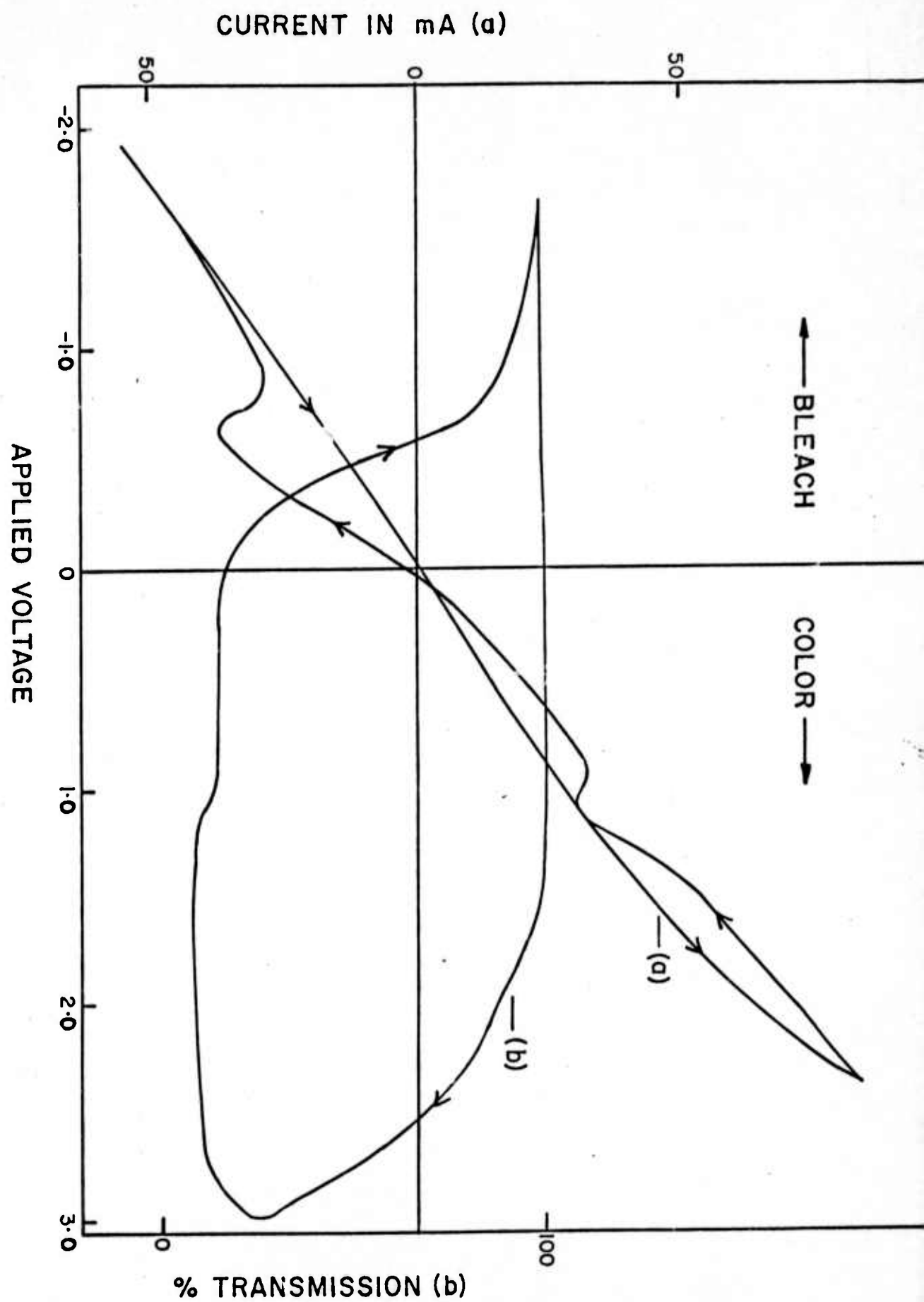


Fig. 8



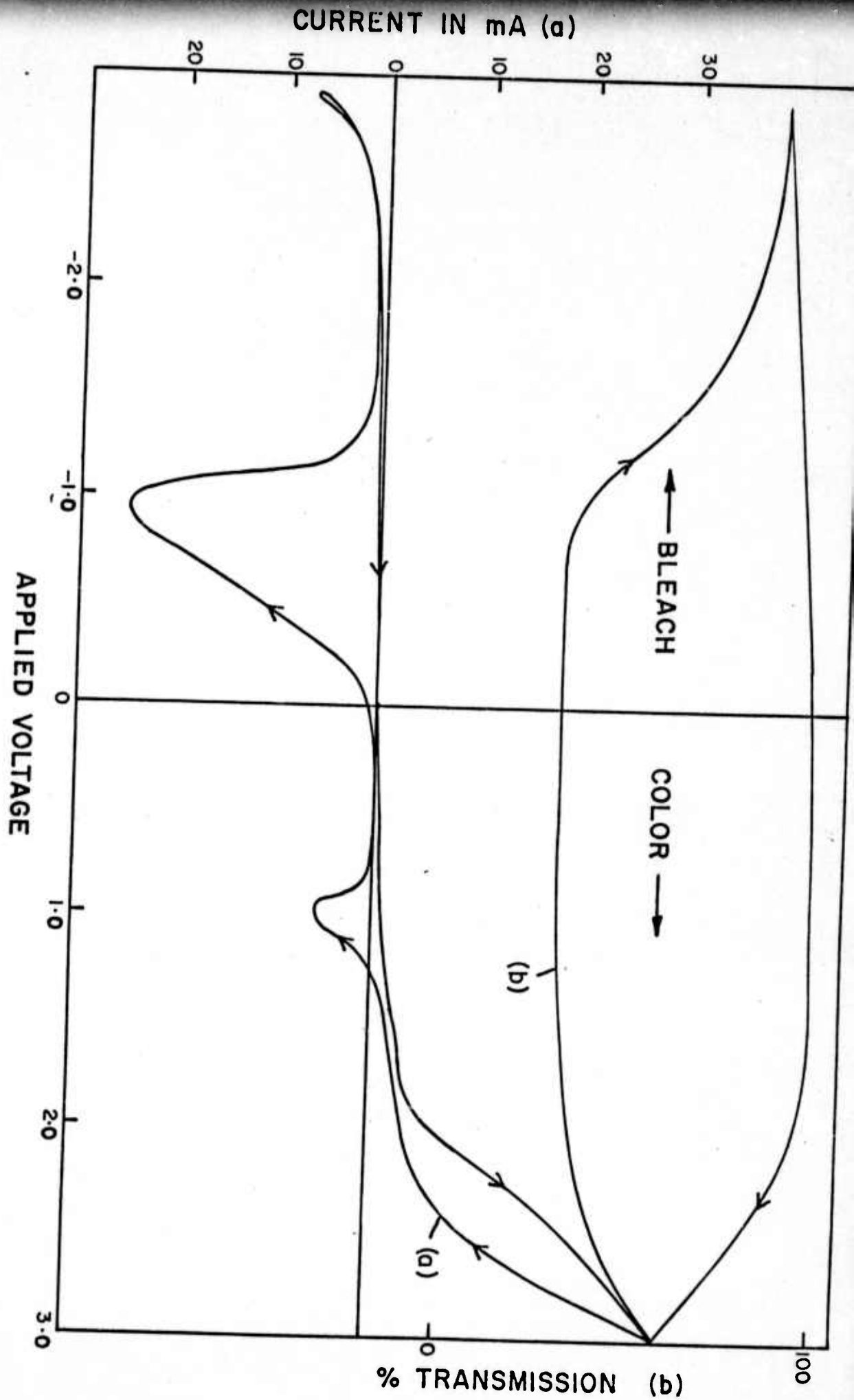


Fig. 10

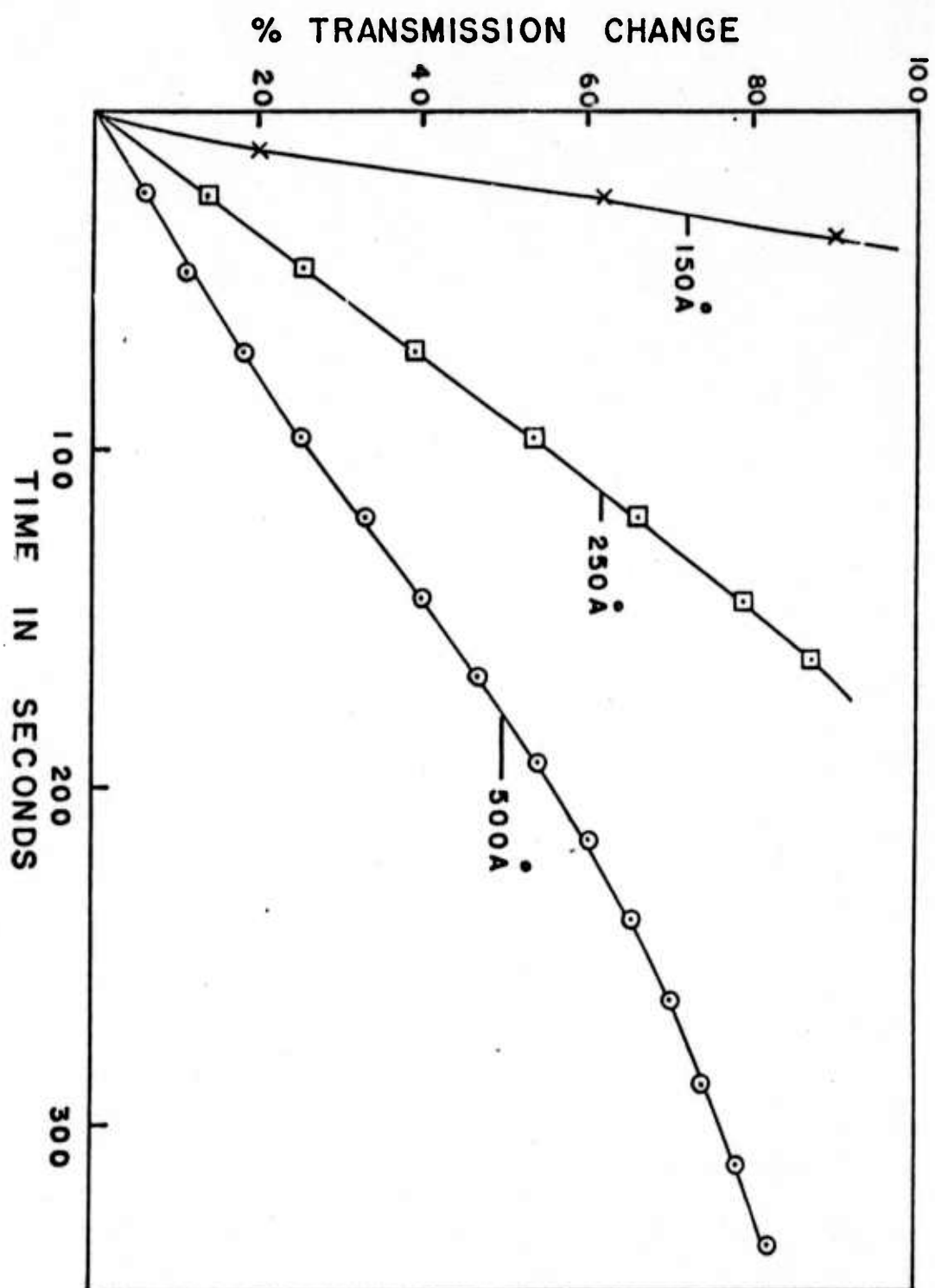


Fig. 11

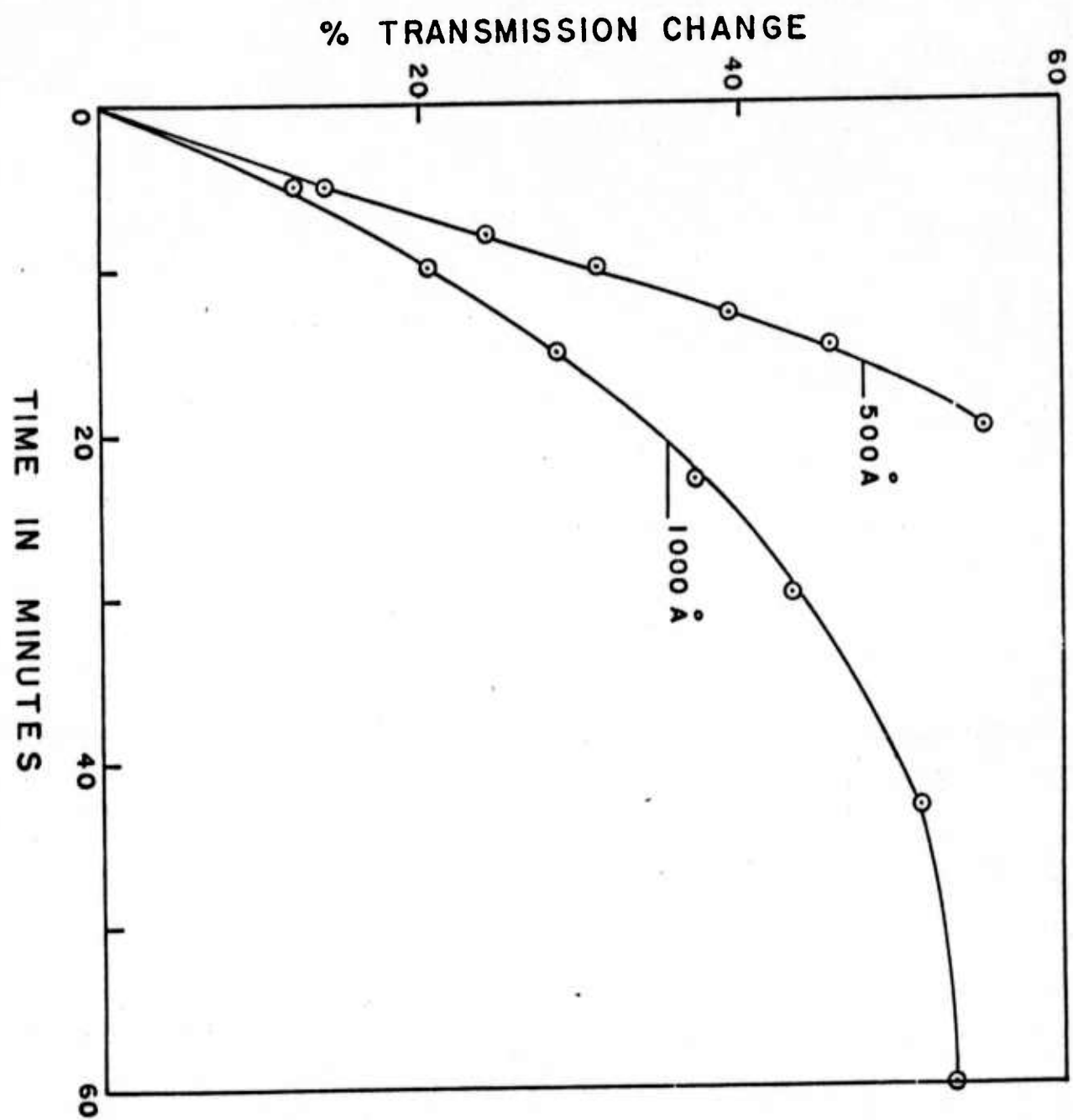
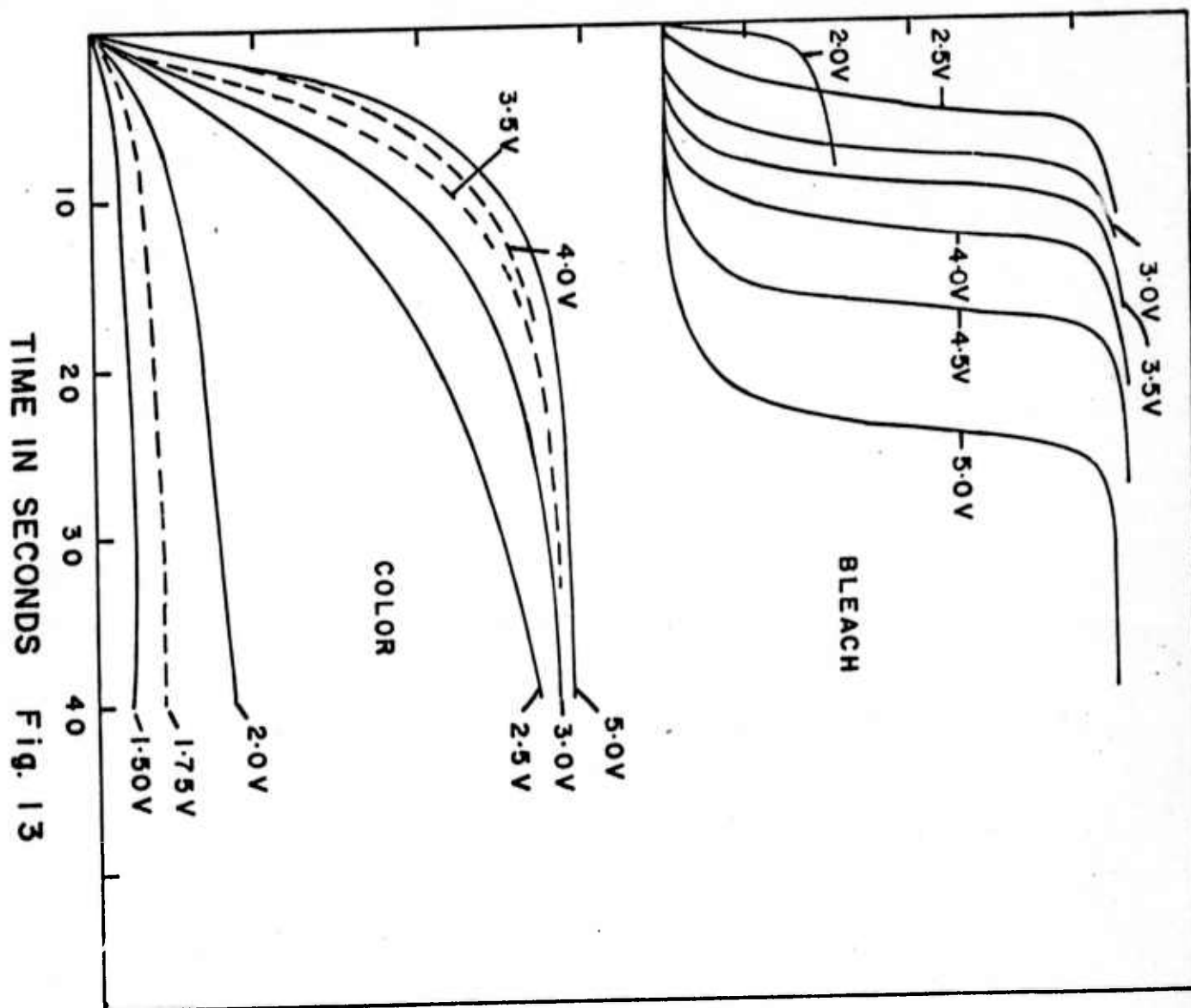


Fig. 12

OPTICAL DENSITY CHANGE



TIME IN SECONDS Fig. 13