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Charge Transport in Oxidation Product of
Lutetium Diphthalocyanine

by

M. M. Nicholson and F. A. Pizzarello

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CHARGE TRANSPORT IN OXIDATION PRODUCT OF LUTETIUM DIPHthalOCYANINE

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ABSTRACT

A red/green anodic-reaction boundary was propagated in a lutetium diphthalocyanine film by application of a constant current through a metallic and an electrolytic contact. From the boundary velocity and the electric field in the red phase, the oxidation product was found to contain a charge carrier with a concentration approximately twice that of the dye molecules and a mobility of $4 \times 10^{-6} \text{ cm}^2/\text{V-sec}$. These results and the charge compensation requirement of the boundary process suggested that the red oxidation product was a solid anion conductor. The estimated bulk resistivity of the red material at room temperature was 1600 ohm-cm.

*Electrochemical Society Active Member

Key words: Diphthalocyanines, charge transport, electrochromism

The lanthanide elements form dipthalocyanines with the proposed molecular structure shown in Fig. 1. When the metal is trivalent, one labile hydrogen remains in the complex. Hence, the formula may be abbreviated $MH(Pc)_2$, where M denotes a lanthanide ion and Pc represents the divalent group $C_{32}H_{16}N_8^{-2}$. Soviet investigators have published a number of papers on this series of compounds since 1965 (1-9)*. The electrochemistry is unusual. Moskalev and Kirin found that the absorption spectrum of a lutetium dipthalocyanine film on a tin oxide electrode in aqueous potassium chloride underwent major, essentially reversible, changes as the applied potential was varied from -0.8 to 1.0 V vs Ag/AgCl (3,6). Different mechanisms were proposed for the changes at cathodic and anodic potentials. The film was initially green. A shift toward blue-green at negative potentials was attributed to field-induced ionization of the solid dye material, and a "cinnamon" color, produced anodically, was thought due to complexing with oxygen or water. Although these steps may be involved, they do not fully account for the responses of this system observed subsequently in our laboratory (10,11).

We found deep blue and violet forms at more negative potentials and several shades of red in the positive region. Preliminary charge-density measurements indicated the

*Only a partial bibliography is given.

occurrence of at least one cathodic and one anodic faradaic process (10). The reactions were surprisingly fast at film thicknesses of about 50 molecular layers. All color changes occurred in less than 50 msec under potentiostatic pulses, even though the reactants and products remained on the electrode as an insoluble film. The color variety and fast responses persisted at -50° in a 30 wt % CaCl_2 electrolyte. Because of this behavior, the rare-earth diphthalocyanines are of special interest for electrochromic display applications (10,11).

The fast electrode kinetics led us to postulate solid-state conduction in all color states of the dye material; a non-conductive product formed at any stage would tend to block the reaction. Neodymium diphthalocyanine was already known to be an electronic semiconductor with a bulk resistivity of 23 ohm-cm at 25° in pressed-powder form (2). This paper reports an investigation of charge transport in the red oxidation product of lutetium diphthalocyanine by a solid-state moving-boundary technique. The carrier concentration and mobility were evaluated on the basis of a one-carrier model. Although the mobile species has not yet been identified, the results suggest that the red material is a solid anion conductor with a room-temperature resistivity of 1600 ohm-cm.

Experimental

Lutetium diphthalocyanine was synthesized from lutetium acetate and *o*-phthalonitrile by the method of Moskalev and Kirin (4). The dye films were prepared by vacuum sublimation from a small heated source onto a stationary alumina substrate at $\sim 10^{-5}$ torr. Details of the synthesis and film deposition procedures are given in Reference 10. The color density of the film provided a visual estimate of its thickness during evaporation. The dye concentration in the finished film was determined from its optical density (OD) at the 668-nm absorption peak, measured on a Perkin Elmer Model 202 dual-beam spectrometer. It was established previously (10) that the film concentration in molecules/cm² was given by $c_0 = 7.25 \times 10^{15} \times (\text{OD})$. The optical density ranged from 0.4 to 1.2 in the present work.

For investigation of transport processes in the dye material, the films were deposited on an insulator instead of tin oxide. The substrates were laser-cut strips of single-crystal Czochralski-grown sapphire, 1.25 cm wide and approximately 4.5 cm long. The (01 $\bar{1}$ 2) crystallographic plane was exposed to the dye, and the long edges of the strips were oriented in the [201] direction. A gold contact 4 mm wide was sputtered across one end of the specimen, on top of the dye. The other end dipped into an air-

saturated aqueous electrolyte, either 1 M KCl or 1 M Na_2SO_4 .

The cell arrangement and instrumentation are indicated in Fig. 2. The dye specimen on the sapphire strip was attached to an interior wall of a Klett colorimeter cell with a small amount of soft wax. The counter and reference electrodes were Ag/AgCl in the KCl electrolyte and Pb/PbSO₄ in the Na_2SO_4 . Agar salt bridges were used to separate these electrodes from the main cell compartment in the sulfate solution. A constant anodic current was supplied by a Princeton Applied Research 173 galvanostat, and the total voltage between the reference and test electrodes was monitored with a Keithley 610C electrometer and strip chart recorder.

Before the experiment began, a line was engraved across the lower end of the specimen with a diamond scribe. Electrolyte was added to the cell until the level was approximately 1 mm above the scribe line. This line defined the lower end of the electrical path in the film. It also acted to nucleate a uniform boundary in the potassium chloride solution. The color change began at the liquid level instead of the scribe line in sodium sulfate.

For observation of the moving red/green boundary, the cell was inserted in a commercial table-top color-slide viewer, which provided back illumination and approximately 2X magnification. A piece of millimeter graph paper was taped on the back of the

Klett cell to locate the boundary position. The propagation distance of the red region was determined at frequent intervals, either by direct reading or by counting the number of red millimeter squares and dividing by the film width. The latter method, yielding an average distance, was preferred in the case of a slightly irregular boundary.

The voltage distribution in the red film was of primary interest. Since small electrolytic or electronic probes could not be attached to the film with the cell arrangement used, an "electrolyte probe" technique was devised. After the boundary had advanced about 10 mm, the electrolyte level was raised in successive increments of ~ 1 mm, with the current still applied. This effectively shorted the portion of the red film below the liquid surface, and a corresponding abrupt drop in the total voltage occurred. Meanwhile, the green-film resistance was unchanged. The voltage distribution throughout the red region was determined in this way.

Results and Discussion

Observations.--Under constant anodic current, the red color was propagated upward from the liquid electrolyte. The red/green boundary was quite sharp, and the region below it had a uniform red color. The transport properties reported herein are for this red film, unwetted by the electrolyte.

Experimentally, both the boundary velocity and the electric field in the red phase were found to be constant for a given applied current. These simple results made it possible to calculate a carrier concentration and mobility for the red material. Sheet resistivities of the red and green films were also found, and bulk resistivities were estimated from those values and the apparent film thickness based on the initial optical density.

In Fig. 3 and 4, propagation distances for the KCl and Na_2SO_4 electrolytes are shown as functions of time at several constant currents. The points fell on straight lines passing through the origin, with slopes essentially proportional to the current density. Hence, for a given film the coloring process required a constant number of charges per unit area, or per molecule of dye.

Figures 5(a) and 6(a) show total voltage measured during boundary propagation. In a typical experiment, that voltage

increased linearly with both time and propagation distance for an extended period. Eventually, it tended to rise more rapidly, although the distance-time function remained linear. Some results obtained with the electrolyte-probe technique are shown in Fig. 5(b) and 6(b).

Transport Model.--One-dimensional transport of a charged species i in an electric field is governed by Eq. 1

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial}{\partial x} \left[\frac{\partial c_i}{\partial x} + \frac{zF}{RT} c_i \frac{\partial E}{\partial x} \right] \quad [1]$$

where c_i is the concentration of the mobile species with charge z , and D_i is its diffusion coefficient; t is time, x is distance, E is potential, and the term F/RT has its usual meaning (12). In a multi-carrier system, the different mobile species generate a set of simultaneous equations in this form, and the treatment can be complicated. However, many solids conduct predominantly by one mobile species with a transference number near unity. A single equation as in [1] then suffices. The transport data for the red dye material were analyzed on the basis of a one-carrier model.

Although the color boundary continued to advance, the red region behind it was in a steady state, indicated by constancy of the boundary velocity at constant applied current. Then

$\partial c_i / \partial t$ was zero, and Eq. [1] could be integrated to obtain an expression for the carrier flux f_i .

$$f_i = D_i \frac{\partial c_i}{\partial x} + D_i \frac{zF}{RT} c_i \frac{\partial E}{\partial x} \quad [2]$$

The first term on the right side of Eq. [2] is the diffusion flux, and the second term is the flux due to migration in the electric field.

It is easily deduced that the diffusion term was negligible in the moving-boundary experiments: With constant current density, the total flux was constant. Under steady-state conditions, the concentration gradient also was constant in time, though not necessarily zero at any point in space. It was found experimentally, however, that the electric field was constant in time and independent of distance. With constant values of f_i , $\partial c_i / \partial x$, and $\partial E / \partial x$ in both time and space, it is evident from Eq. [2] that c_i must have been constant. Then $\partial c_i / \partial x = 0$, and the diffusion flux was zero.

The carrier mobility then could be calculated from the electric field \mathcal{E} and the carrier velocity $\partial x / \partial t$, which was the same as the velocity of the boundary:

$$\mu_i = \frac{1}{\mathcal{E}} \frac{\partial x}{\partial t} \quad (\mathcal{E} \equiv \frac{\partial E}{\partial x}) \quad [3]$$

The product zc_i was related to the current density I and the velocity through Eq. [4]

$$I = \frac{i}{w\delta} = zc_i F \frac{\partial x}{\partial t} \quad [4]$$

where c_i is the bulk concentration, i is the total current, w is the width of the film, and δ is its thickness. Since δ was not accurately known, it was appropriate to use a surface or film concentration $c_{i(s)}$, which may be expressed in moles per unit area.

$$c_{i(s)} = \delta c_i \quad [5]$$

Then, from Eq. [4],

$$zc_{i(s)} = \frac{i}{wF(\partial x/\partial t)} \quad [6]$$

Evaluation of Resistivities.--The total voltage measured with respect to the reference electrode was the sum of three boundary potentials and an ohmic term:

$$E_{total} = E_s + E_b + E_m + i(R_r + R_g) \quad [7]$$

In Eq. [7], E_s is the potential difference at the red film/solution interface, E_b is the potential difference at the red/green boundary, E_m is the potential difference at the green film/metal boundary,

and R_r and R_g are the total resistances of the red and green sections. Although the interfacial potentials were not individually known, they should have remained constant at a given current density, once the propagation was established. The film resistances were related to the sheet resistivities $\rho_r(s)$ and $\rho_g(s)$ (ohms/square) through Eq. [8]

$$R_r + R_g = [\rho_r(s) - \rho_g(s)] (x/w) + \rho_g(s) l/w \quad [8]$$

where l represents the total length of the film specimen. The resistivities are treated here as constants independent of distance within the respective phases. From Eq. [7] and [8], it is evident that

$$\partial E_{\text{total}} / \partial x = (i/w) [\rho_r(s) - \rho_g(s)] \quad [9]$$

Hence, the difference in sheet resistivities was obtained from the slope of a plot of E_{total} vs x , as in Fig. 5(a) and 6(a). The sheet resistivity of the red film was determined separately by the electrolyte probe technique. Since this was a relatively fast procedure, R_g remained constant. Hence, $\rho_r(s)$ could be found from a plot of the type in Fig. 5(b) and 6(b).

$$\rho_r(s) = \frac{\partial E}{\partial x} \frac{w}{i} \quad (R_g = \text{constant}) \quad [10]$$

Table 1 gives the measured sheet resistivities of the red and green films and the corresponding bulk resistivities calculated from film thicknesses based on the approximate crystal density of 1.58 g/cm^3 for LuH(Pc)_2 . This density was estimated from that of U(Pc)_2 (13), with the assumption that the two compounds have the same crystal structure and unit-cell dimensions. The average bulk resistivity of the red product was 1300 ohm-cm in the KCl experiments and 2000 ohm-cm in the Na_2SO_4 . In all cases, the red film was more resistive than the green, which is an electronic conductor (2). The variations in bulk resistivities observed among the different specimens were not surprising, since the film-deposition process was not precisely controlled.

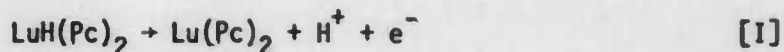
Interpretations.--Table 2 summarizes results of the transport experiments. Although the applied currents were at the micro-ampere level, the estimated current densities through the cross sections of the films ranged from 15 to 150 mA/cm^2 , as noted in Table 1. The carrier concentration term $zc_i(s)$, from Eq. [6], was approximately twice the concentration c_0 of the dye molecules. This carrier concentration is unusually high for an organic solid without metallic character. It was not surprising to find that the color conversion may occur by a 2-electron faradaic process. A reaction product containing two units of

mobile charge per molecule was not anticipated, however. The small integral ratio of carriers to dye molecules strongly suggests that the red material is an ionic conductor with one divalent or two monovalent mobile ions per molecular unit.

The mobility calculated from Eq. [3] was of the order of $4 \times 10^{-6} \text{ cm}^2/\text{V-sec}$. This magnitude is more typical of an ion in a stoichiometric solid electrolyte than of an electronic charge carrier. It is comparable to $8 \times 10^{-6} \text{ cm}^2/\text{V-sec}$ for H^+ in polycrystalline hydrogen uranyl phosphate (14) and $1.2 \times 10^{-5} \text{ cm}^2/\text{V-sec}$ for Ag^+ in single-crystal silver beta alumina (15), both at 25° . The concept of mobile ions in lutetium diphthalocyanine is consistent with the open crystal structures of $\text{Th}(\text{Pc})_2$ and $\text{U}(\text{Pc})_2$ (7,13).

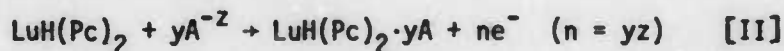
Ionic conduction is also quite acceptable in terms of reaction mechanisms. Electrons are removed from the dye molecules at the color boundary and transported through the green film to the external circuit. The red oxidation product is a neutral material with a different chemical composition. These conditions require a compensation process involving both charge and material transport in the red phase. Such compensation could occur by loss of cations or gain of anions at the solution boundary.

Since $\text{LuH}(\text{Pc})_2$ should contain one labile hydrogen, proton loss with formation of Lu(IV) may be considered:

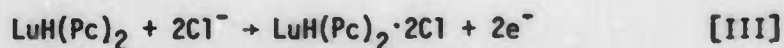


This reaction would correspond to $n = 1$, however, and the moving-boundary experiments yielded n values closer to 2. Moreover, the product Lu(Pc)_2 provides no obvious path for continuing transport of protons from their source at the reaction boundary, through the red film, to the electrolyte solution. If such transport did occur, the boundary velocity should decrease with propagation distance; this was not observed. Hence, the cation mechanism seems improbable.

The anion mechanism can be represented by



The product would consist of the mobile anions A^{-z} in an immobile organic cation lattice. With a chloride electrolyte, the reaction could be



Anodic formation of a halogen complex is consistent with results of tracer studies by Moskalev and Kirina, which showed that a lutetium diphthalocyanine anode can remove traces of iodine, originally present as I_2^- from a supporting electrolyte

solution (9). The anion A^{-2} in the case of the sulfate solution might be OH^{-} , or possibly HO_2^{-} or $SO_4^{=}$.

The mobility measurements were not precise enough to distinguish between the different anions in the red film. However, the average experimental n was 2.5 for the chloride electrolyte and 1.8 for the sulfate; it is possible that the n values actually are different for the faradaic reactions in the two electrolytes. Experimental deviation from an integral value of n could be due to several factors, including electrolytic side reactions and some inaccuracy in determining the surface concentration of the dye (10).

Transport properties of the rare-earth diphthalocyanines are important in electrochromic display applications. Faughnan, Crandall, and Lampert found, for example, that a space-charge-limited proton current controlled the bleaching rate in the tungsten oxide electrochromic system (16). The calculated proton mobility in the blue cathodically formed tungsten bronze was $8 \times 10^{-7} \text{ cm}^2/\text{V-sec}$. The mobilities reported here for the charge carrier in oxidized lutetium diphthalocyanine are about five times larger. This factor must contribute to its faster electrochromic response. Investigations of electrode reactions and transport mechanisms in the diphthalocyanines are continuing.

Acknowledgments

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R. V. Galiardi performed qualitative experiments on the moving boundary technique and suggested use of the color-slide viewer for the quantitative work.

SYMBOLS

c_i	concentration of species i , moles/cm ³
$c_{i(s)}$	surface concentration of species i , moles/cm ² or molecules/cm ²
c_o	surface concentration of dye, molecules/cm ²
D_i	diffusion coefficient of species i , cm ² /sec
E	electrical potential, volts
E_b	potential difference at reaction boundary, volts
E_m	potential difference at green film/metal interface, volts
E_s	potential difference at red film/solution interface, volts
E_{total}	potential difference between metal contact and reference electrode, volts
\mathcal{E}	electric field in red film, V/cm
F	faraday constant, 96,494 C/g-equiv
f_i	flux of species i , moles/cm ² -sec
I	current density, A/cm ² or mA/cm ²
i	total current, A or μ A
L	total length of film specimen, cm
n	electrons lost per molecule of dye in color conversion process
OD	optical density
R	gas constant, 8.314 joules/deg-mole
R_g	total resistance in green film, ohms
R_r	total resistance in red film, ohms

T	absolute temperature, °K
t	time, sec or min
w	width of film specimen, cm
x	distance, cm
y	anions utilized per molecule of dye in color conversion process
z	number of charges on species i
δ	thickness of dye film, cm
μ_i	mobility of species i , $\text{cm}^2/\text{V-sec}$
ρ_g	bulk resistivity of green dye, ohm-cm
ρ_r	bulk resistivity of red dye, ohm-cm
$\rho_g(s)$	sheet resistivity of green dye, ohms/square
$\rho_r(s)$	sheet resistivity of red dye, ohms/square

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Table 1. Film Resistivities of Lutetium Diphthalocyanine and its Red Oxidation Product*

Specimen	Initial OD At 670 nm	Current Density** (mA/cm ²)	$\rho_g(s)$ (ohms/square) $\times 10^{-8}$	$\rho_r(s)$ (ohms/square) $\times 10^{-8}$	ρ_g (ohm-cm) $\times 10^{-3}$	ρ_r (ohm-cm) $\times 10^{-3}$
1 M KCl Electrolyte ⁺						
1	0.48	14 37 145	1.3 0.2 0.93	1.8 1.4 4.2	0.52 0.09 0.41	0.72 1.3 2.1
2	0.88	50	0.56	1.1	0.45 Avg 0.37	0.91 Avg 1.3
1 M Na ₂ SO ₄ Electrolyte ⁺						
4	0.89	50	0.68	1.1	0.55	0.88
5	1.00	87	0.24	0.69	0.22	0.63
6	1.20	22 37 73	2.1 -- 0.78	4.0 2.6 1.2	2.3 -- 0.86 Avg 0.98	4.4 2.9 1.3 Avg 2.0
Two Gold Contacts Without Electrolyte						
8	0.89	10	1.3	--	1.1	--

*Green-film conduction is electronic; red-film conduction probably is ionic.

**Based on film thickness estimated from crystal density.

+Air-saturated.

Table 2. Charge Transport Properties in Oxidation Product of Lutetium Diphthalocyanine

Specimen*	Current (A) $\times 10^7$	$\partial x / \partial t$ (cm/sec) $\times 10^4$	\bar{E} (V/cm)	$z_{ci}(s)$ (molecules/cm ²) $\times 10^{-16}$	n ($z_{ci}(s)/c_0$)	μ_i (cm ² /V-sec) $\times 10^6$
1 M KCl Electrolyte**						
1	1	0.55	14	0.91	2.6	3.9
	2	1.00	23	1.00	2.8	4.3
	8	4.5	300	0.89	2.6	1.9
2	5	2.5	45	1.28	2.0	5.9
3*	3	0.83	--	1.81	2.3	--
					Avg 2.5	Avg 4.0
1 M Na ₂ SO ₄ Electrolyte**						
4	5	3.3	43	0.75	1.2	6.6
	5	2.9	85	0.87	1.3	3.3
5	10	3.7	55	1.36	1.9	6.6
6	2	0.63	--	1.60	1.8	--
	3	0.87	96	1.70	1.9	3.8
	5	1.53	104	1.60	1.8	1.5
	10	3.65	95	1.30	1.5	0.9
7*	1	0.160	--	3.10	3.4	--
					Avg 1.8	Avg 4.3

*00 was 1.20 for Specimen 3 and 1.24 for Specimen 7; given for others in Table 1.

Specimen width w was 1.25 cm in all cases.

**Air-saturated.

Illustrations

1. Structural Formula of Rare-Earth Diphthalocyanine
2. Experimental Arrangement for Moving-Boundary Measurements
3. Dependence of Boundary Propagation Distance on Time with
1 M KCl Electrolyte
4. Dependence of Boundary Propagation Distance on Time with
1 M Na₂SO₄ Electrolyte
5. Voltage-Distance Relationships with 1 M KCl Electrolyte
6. Voltage-Distance Relationships with 1 M Na₂SO₄ Electrolyte

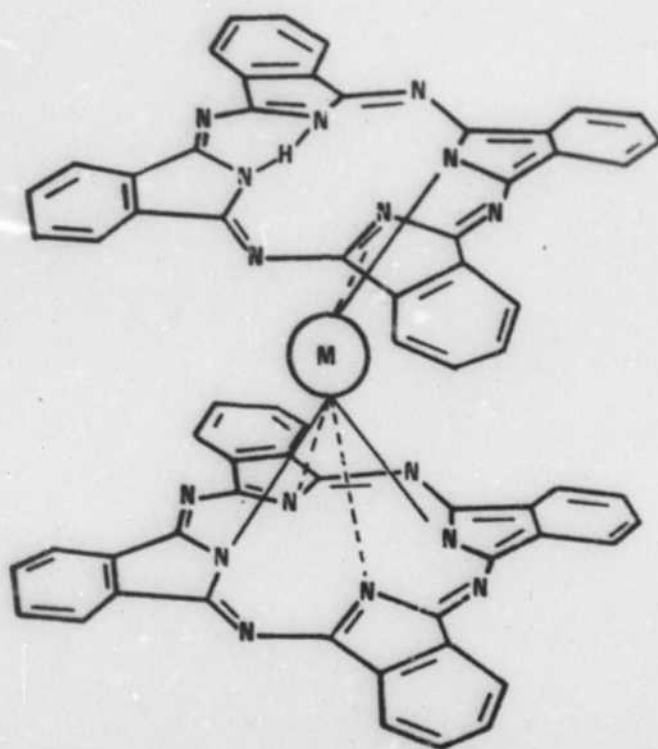


Fig. 1

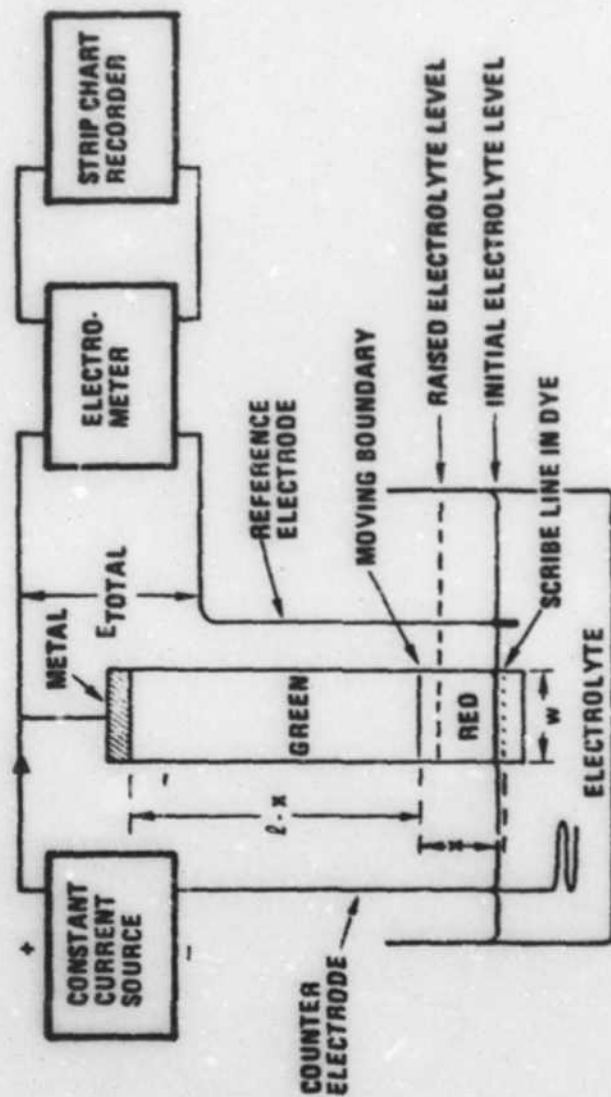


Fig. 2

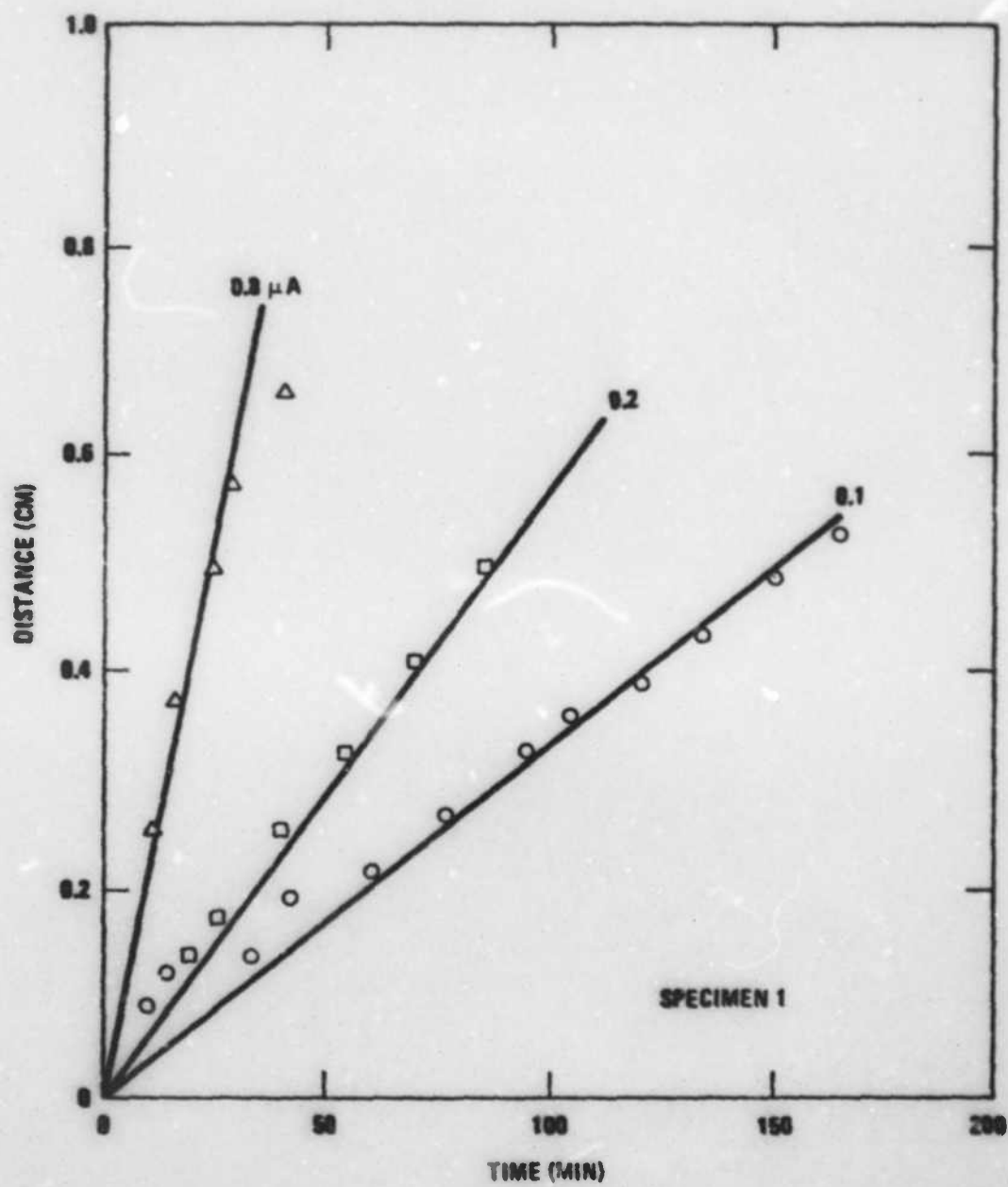


Fig. 3

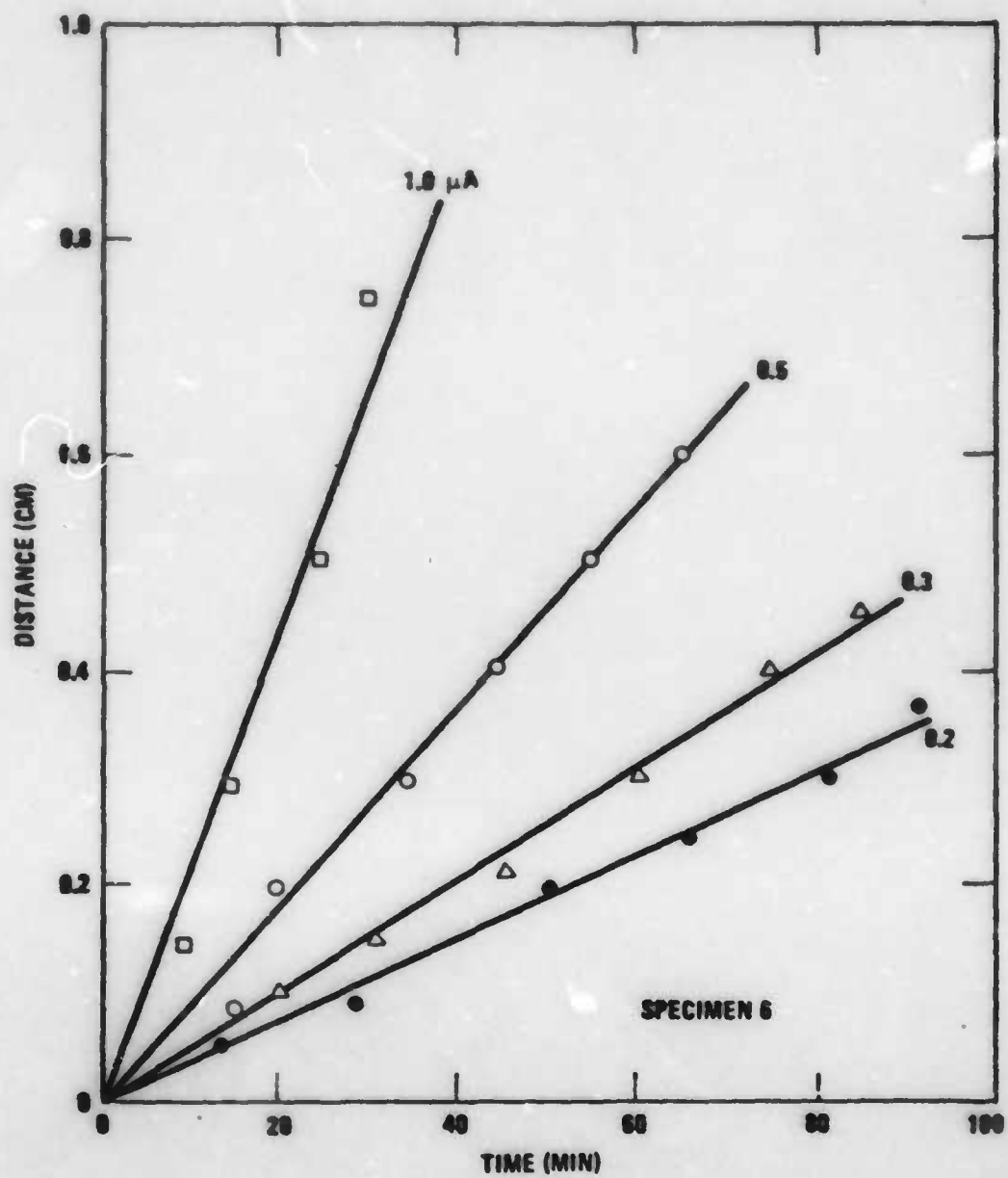


Fig. 4

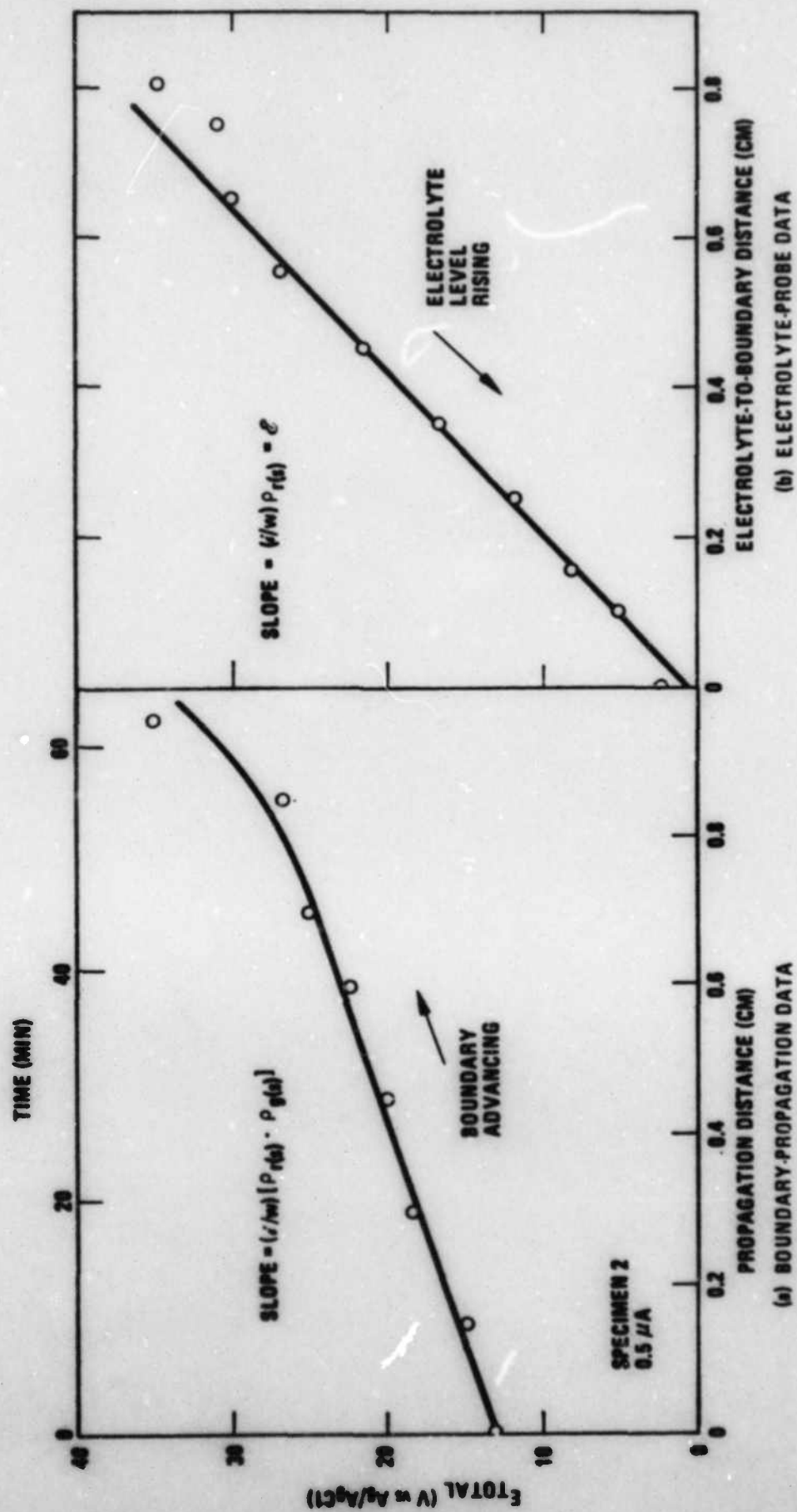


Fig. 5

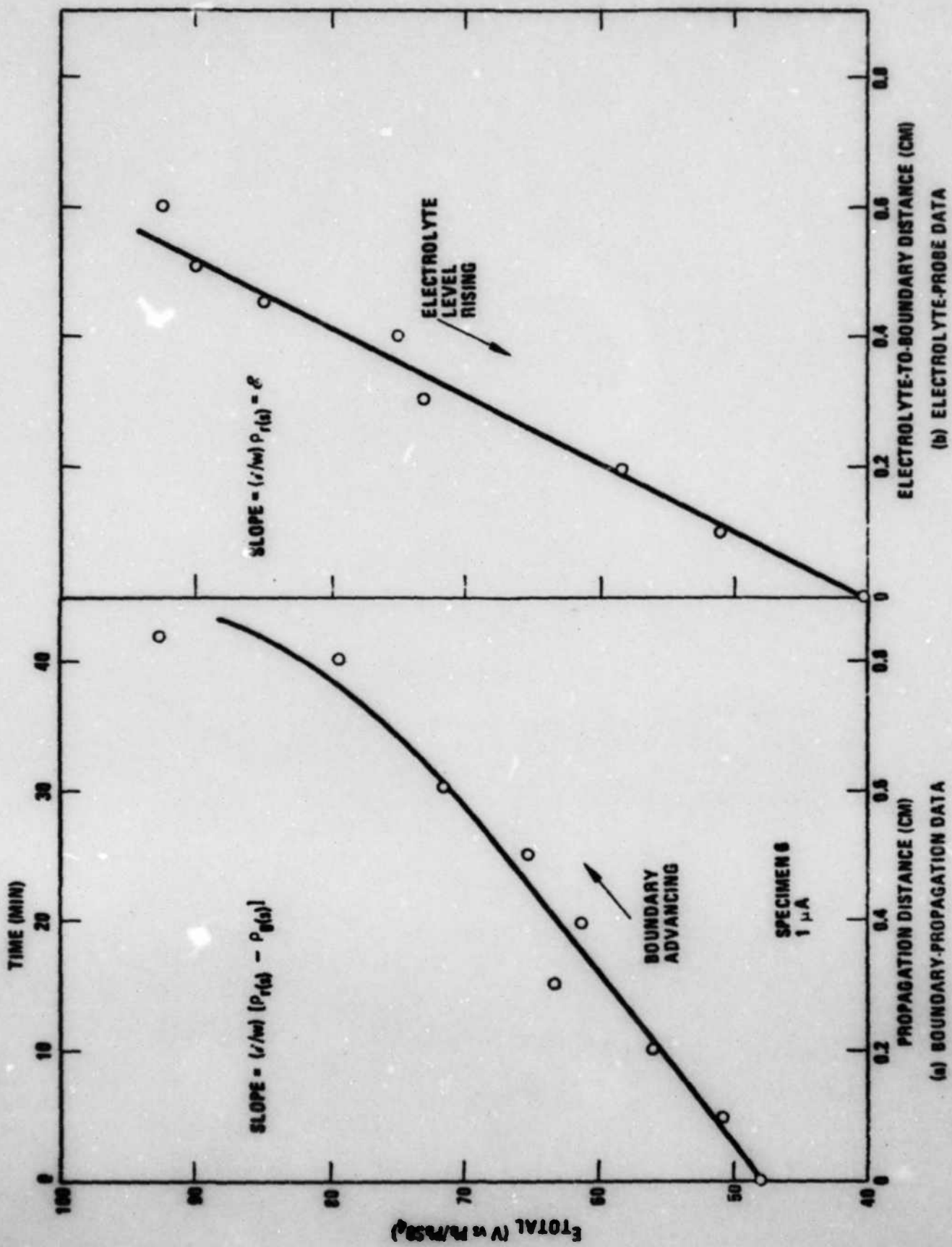


Fig. 6

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