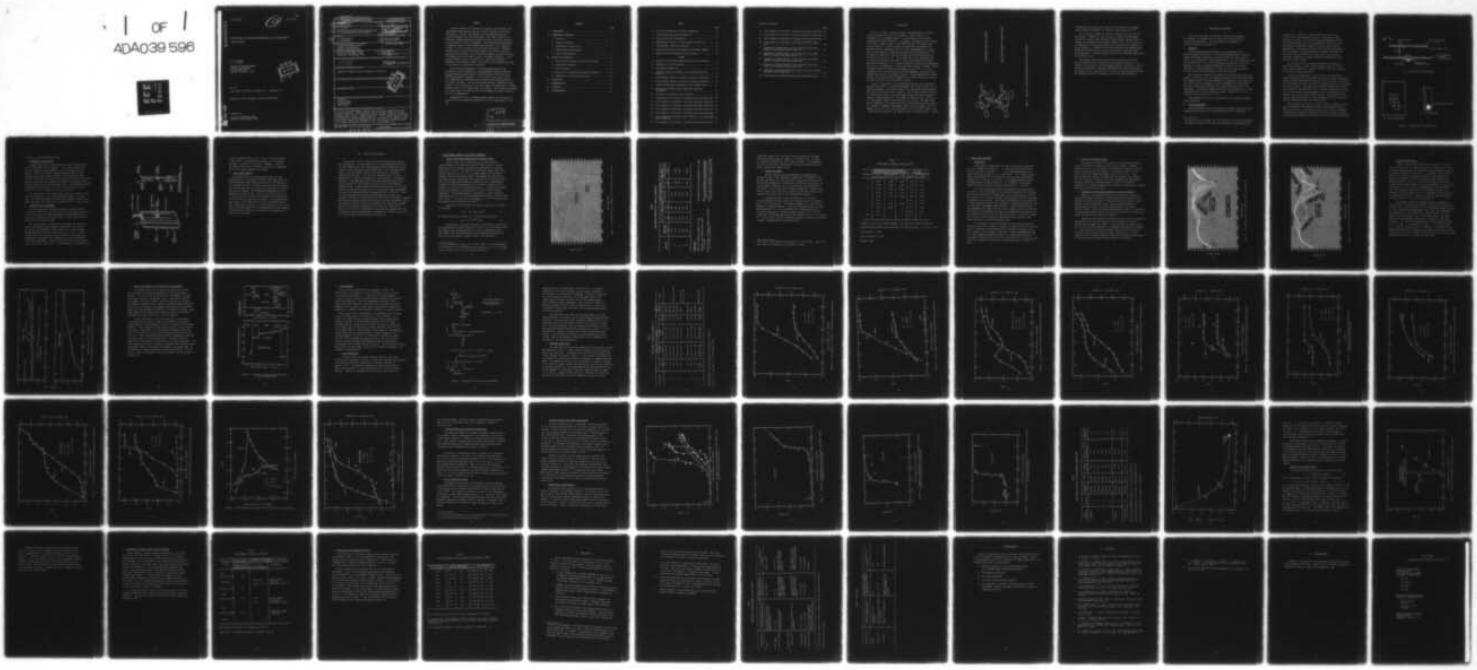
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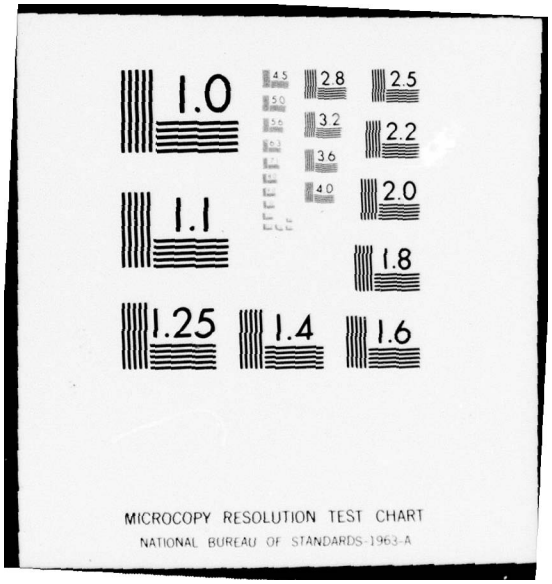
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INVESTIGATION OF LUTETIUM DIPHTHALOCYANINE AS AN ELECTROCHROMIC DISPLAY MATERIAL

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A new type of electrochromic display uses a rare-earth diphthalocyanine as the active material. Characteristics include switching energy of 1 mJ/cm^2, response time of 50 msec, nonvolatile memory, and good visibility in different directions under various lighting conditions. A full spectral range of colors is generated in lutetium diphthalocyanine by variation of the applied voltage. With further research and development, this system should be useful for full color imaging and graphic displays, as well as alphanumerics.

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SUMMARY

Military aircraft of the future will require visual displays with performance characteristics that are not fully satisfied by existing technologies. The new electrochromic system described herein has excellent prospects for such applications. The display material is a rare-earth diphthalocyanine--an organic dye with a molecular structure closely related to that of chlorophyll. The diphthalocyanine undergoes a remarkable series of color changes when subjected to d-c signals up to about 1 V while in contact with an aqueous electrolyte. Operating characteristics include a switching energy of the order of 1 mJ/cm^2, response time of 50 msec or less, nonvolatile memory, and good visibility in different directions under a variety of lighting conditions. A full spectral range of colors is generated in a single dye material by adjustment of the applied voltage. More than a dozen compounds are known in this family of electrochromic materials.

Electro-optical parameters of lutetium diphthalocyanine were determined in this investigation. The experimental approach combined in situ absorption spectroscopy with electrochemical steady-state and pulse potentiostatic techniques. At least four discrete color states were identified and correlated with the potential and charge applied to the display electrode. Colors matched against Munsell standards had high chroma, or color saturation, in red, blue, green, and purple hues. Lighter, somewhat neutral or tan shades were also available. With further development, this system should be useful for full color imaging and graphic displays, as well as alphanumerics.

Recommendations for a continuing program include the evaluation of resolution and low-temperature capabilities, and the improvement of cycle life.

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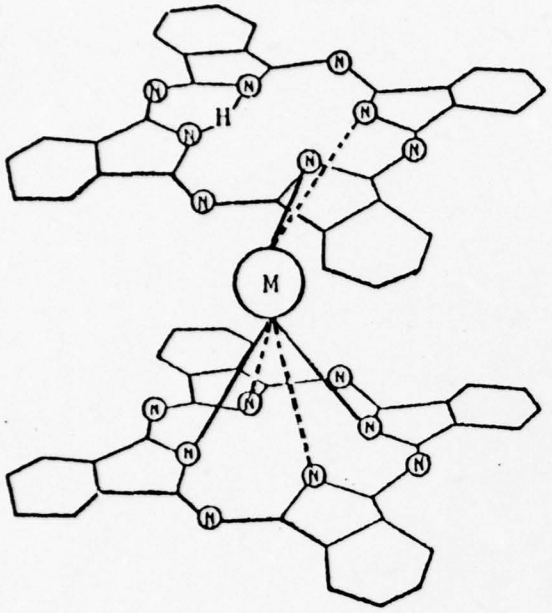
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I. INTRODUCTION

By the late 1980's, military aircraft instrumentation will require cockpit displays with entirely new formats. A great variety of information must be presented rapidly, in minimum space, with low power consumption and high reliability. An example is the Master Monitor Display which forms a central element in the AIMIS system for all-weather Naval attack aircraft.[1] Detailed studies of operational requirements and available display technologies have led to the recommendation of a flat-panel, matrix-addressed liquid-crystal display for this application.[2,3] Low power and legibility in direct sunlight were prime considerations in the choice of liquid crystals. At the same time, it was recognized that a variable-color display would offer a much better approach for coding malfunction information. It is further known that liquid-crystal performance falls off at low temperatures, so that artificial heating is needed to retain an adequate speed of response in environments below -15°C. A low-cost technology that could overcome the color and temperature limitations while meeting other military requirements would be a leading candidate for future displays of the Master Monitor category and for other devices such as map-projection, head-up, and helmet-mounted displays.

Rockwell International is investigating a new type of electrochromic display system which, with further development, may be able to meet all of these requirements. The display material is a rare-earth diphthalocyanine, which has the structure shown in Figure 1. This sandwich molecule consists of a rare-earth ion such as lutetium complexed with two units of phthalocyanine, a common organic dye. The complex is deposited as a colored film on a transparent conductive substrate such as tin oxide. When the filmed plate is immersed in an aqueous electrolyte solution and subjected to small d-c voltages, it undergoes a remarkable series of color changes. The film remains as a solid layer on the electrode in all of its color states. With a low-resistivity substrate, the response time is less than 50 msec. Soviet



M REPRESENTS A RARE-EARTH ELEMENT

LARGE RING STRUCTURE IS HIGHLY COLORED

Figure 1. Structure of Rare-Earth Diphthalocyanine Display Material

investigators have observed this type of electrochromism in diphthalocyanine complexes throughout the lanthanide rare-earth series.[4,5]

This system has a number of excellent characteristics for display applications. Compared to liquid crystals, it offers the advantages of nonvolatile memory, more attractive visual effects, and good off-axis viewing. Its inherently fast response suggests that it will be usable at low temperature if the freezing point of the electrolyte is lowered by a suitable additive. Compared to other electrochromics, the phthalocyanine system has far greater color variety and an order of magnitude lower switching energy. Lifetimes greater than 10^4 cycles have been demonstrated in preliminary tests.

This report describes the first detailed evaluation of electro-optical parameters for a phthalocyanine electrochromic material. The methods of investigation included *in situ* absorption spectroscopy, electrochemical potentiostatic techniques, and quantitative color evaluation by the Munsell system. The results will be useful in making design estimates and guiding the further development of this new display technology.

II. EXPERIMENTAL PROCEDURES

This section describes the materials, fabrication procedures, cell designs, and equipment that were used in the investigation of lutetium diphthalocyanine. The electrochemical methodology is more fully discussed in Section III.

A. MATERIALS

Lutetium diphthalocyanine [$LuH(Pc)_2$] was synthesized by the method of Moskalev and Kirin.[6] Four and six-tenths grams of lutetium acetate from Nucor Corporation were slowly heated in an open container with 12.9 g of Eastman No. 7402 o-phthalonitrile. The solid reaction product, which formed after 3 hr at 300°C, was washed, successively, with acetic anhydride, acetone, and dimethylformamide, and dried in air at room temperature. Further purification occurred in the vacuum sublimation process by which the electrochromic films were prepared.

The transparent conductive substrates for the display electrodes were samples of low-resistivity tin oxide-glass supplied by Corning Glass Works. The conductive layer, which was prepared by a fog process, had a pale gray color and an optical transparency of ~65% throughout the visible range. The sheet resistivity, measured by the 4-point probe method, was 5 to 7 ohms/square. No metallic elements other than tin were detected in electron microprobe analysis of the conductive coating. The glass was 1.5 mm thick and the tin oxide layer, ~1.8 μm.

Other materials used in the investigation were conventional reagent quality chemicals.

B. DISPLAY ELECTRODES*

The electrochromic plates were prepared by thermal sublimation of the diphthalocyanine onto the tin oxide-glass substrate, as illustrated

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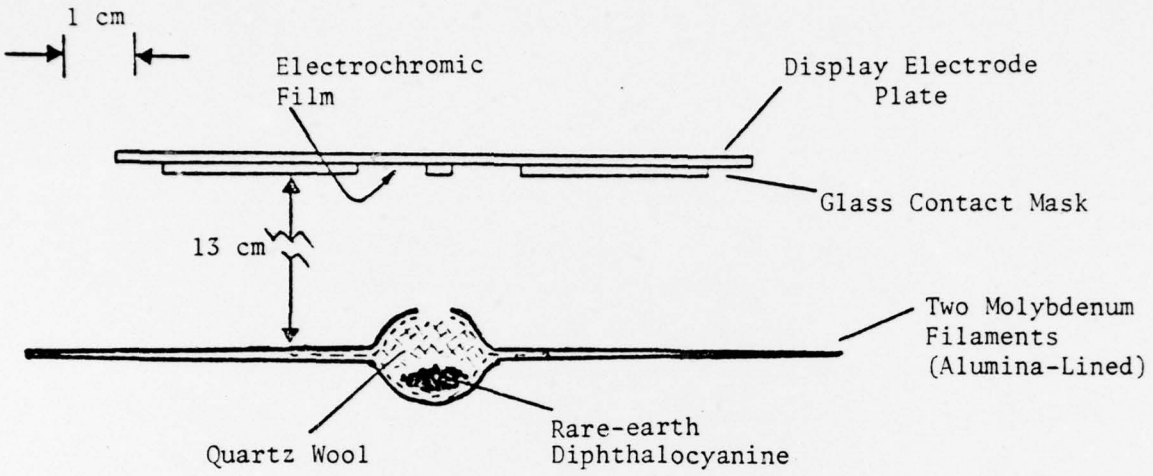
*The terms "display electrode" and "test electrode" are used interchangeably throughout the report to indicate the experimental electrochromic plates.

in Figure 2(a). Before the dye was deposited, the plate was cleaned in an Alconox detergent solution. The pressure during sublimation was $\sim 10^{-5}$ torr, and the filament temperature, $\sim 500^{\circ}C$. The substrate temperature was not independently controlled in the preparation of Electrodes 1 through 10 for the electro-optical measurements. The specimens used in visual color matching against Munsell standards were deposited under an infrared heat lamp that was placed with the surface of the bulb about 2.5 cm above the substrate. Deposition at elevated substrate temperatures usually enhances the color effects.

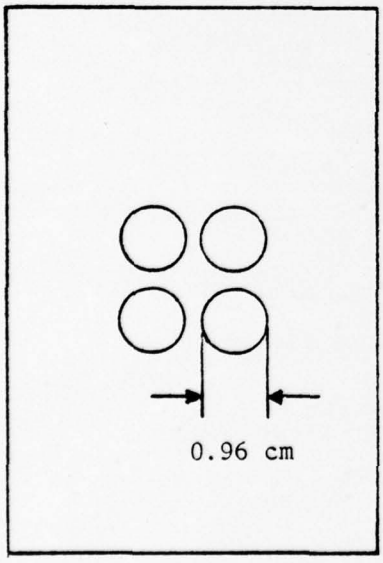
The dye pattern for the numbered electrodes was defined by a glass contact mask with four circular openings, each of 0.713 cm^2 area, shown in Figure 2(b). Deposits of about 3 cm^2 area were used in the color-matching experiments.

Following the deposition of $LuH(Pc)_2$, most of the electrode plates were coated with a transparent collodion (cellulose tetranitrate) binder to improve the adhesion of the dye to the tin oxide. The binder had to be porous and hence, very thin, to permit access of the electroltye solution to the dye. This protective coating was applied with a photo-resist spinner at 4500 RPM from a 4-g/l cellulose tetranitrate solution in a solvent consisting of approximately 4 vol % ethyl ether, 6 vol % methanol, and 90 vol % methyl isobutyl ketone. One milliliter of this solution was dispensed onto the plate containing the four circular dye deposits immediately before the spinning began.

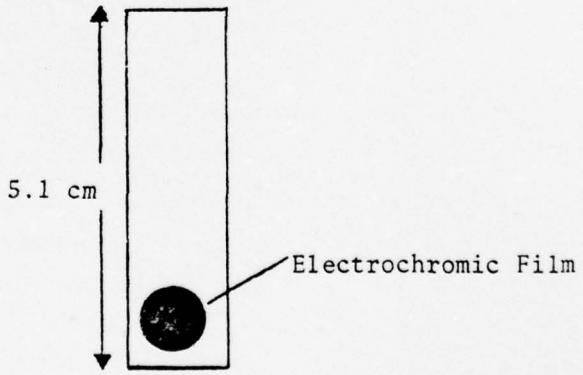
The finished plate was cut into four sections to produce replicate display electrodes, each bearing a circle of electrochromic film, as shown in Figure 2(c). The weight of dye per unit area was determined by measuring the absorption spectrum of the film in the dry state and correlating that maximum optical density with the extinction coefficient



(a) Vacuum Sublimation Technique



(b) Glass Contact Mask



(c) Test Electrode

Figure 2. Preparation of Test Electrodes

of $LuH(Pc)_2$ in dimethylformamide (DMF).

C. EXPERIMENTAL DISPLAY CELLS

In situ electro-optical measurements were made in experimental cells of the design shown in Figure 3. All of this work was done at room temperature in an aqueous 0.1 M KCl electrolyte with air present. Each cell contained a display electrode plate, an open-centered nickel screen counter electrode, which carried the same current as the display electrode, and a silver-silver chloride (Ag/AgCl) reference electrode, which served to establish the potential of the display electrode on the electrochemical scale. The reference electrode was prepared by anodizing a silver wire in the potassium chloride electrolyte to form a surface film of silver chloride.

For unobstructed visual observations of the color changes, simple cells were assembled with the three electrodes resting in a Petri dish. The display electrodes were then viewed against a white filter paper background under conditions described in Part E of this section.

D. ELECTRO-OPTICAL MEASUREMENTS

Absorption spectra of the electrochromic films under applied voltages were obtained by placing a cell of the type shown in Figure 3 in the sample beam of a Perkin Elmer Model 202 Spectrophotometer. A matched cell containing the electrolyte and a blank tin oxide plate was placed in the reference beam.

The electrochemical responses were determined under essentially steady-state potentiostatic conditions and under 0.1-sec voltage pulses that were separated by longer intervals at lower voltages. A few measurements were made at pulse times up to 0.2 sec. Current-voltage curves were recorded on a pen recorder in the steady-state measurements, and charges were determined on a digital coulometer in the pulse experiments. Detailed conditions of the electrochemical studies are given in Section III. The instrumentation included several

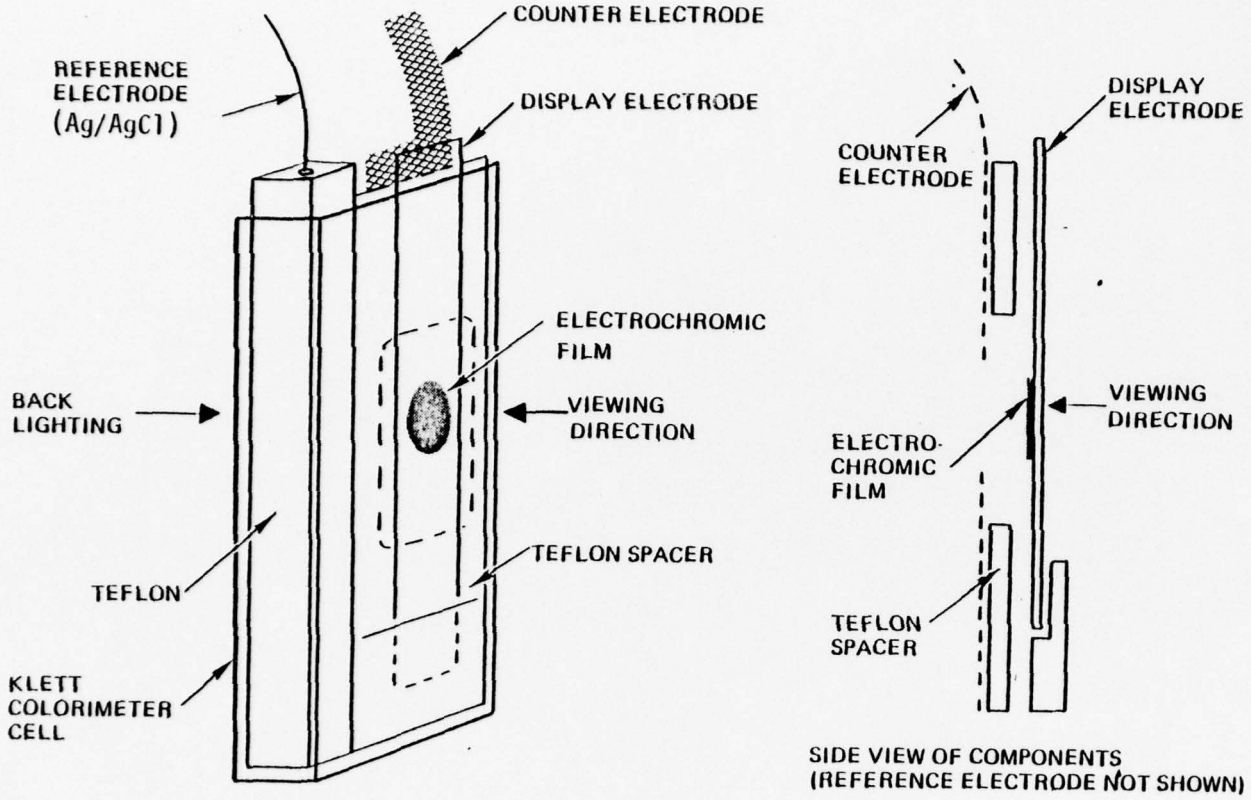


Figure 3. Experimental Display Cell

Princeton Applied Research units: Model 170 Electrochemistry System, Model 173 Potentiostat/Galvanostat with 179 Digital Coulometer, and Model 175 Universal Programmer. A Houston Instruments Series 2000 X-Y recorder, several pulse generators, and an oscilloscope completed the assembly.

E. VISUAL COLOR MATCHING

The display colors at various applied potentials were characterized by the procedure outlined in American Society for Testing Materials (ASTM) Designation D1535-68. The open-dish cell described in Part C of this section was placed in a Macbeth Spectralight Model SPL-75 viewing booth illuminated at the noon-time daylight setting. This lighting corresponded to a color temperature of 7500 $\pm$ 200°K. The test electrode was held at a 45° angle from the horizontal while immersed in the electrolyte, with the filmed side away from the observer. Color matches were made visually with standard color chips in the Munsell Book of Color, Matte Finish Collection. For each display color, the hue, value, and chroma numbers of the corresponding chip were recorded. The matching was considered to be precise to the nearest half steps in the chip array.

III. RESULTS AND DISCUSSION

The discussion in this section follows the chronological steps in the investigation. Uniform composition of the vacuum-deposited $LuH(Pc)_2$ was first demonstrated, and a spectroscopic method for measuring the dye content of each electrode film was established. An initial green color state of the electrochromic material was selected as a reference condition for the study. This state was characterized by the film's spectrum and its open-circuit potential in the cell prior to electrical excitation. Electrochromic spectra were then determined under steady-state conditions in closely spaced intervals on the electrochemical potential scale. Several abrupt spectral shifts were noted. The current drawn by the dye during steady-state or slow potential-sweep measurements was barely distinguishable from the background level in the cell. Under a 4-level pulse routine simulating display operation, however, the electrical response of the dye stood out clearly from the background response, and pronounced threshold effects were found in the charge-potential curves. The uptake of charge by the dye was correlated with the spectral changes and the film thickness and examined on the basis of a model circuit. Finally, the colors of a representative electrochromic specimen were characterized by visual matching against a standard set of Munsell color chips. All of these results are discussed in detail below.

A. ELECTROCHROMIC MATERIAL AND DISPLAY ELECTRODES

1. Spectra and Uniform Composition of Sublimed $LuH(Pc)_2$

Figure 4 shows typical absorption spectra for lutetium diphthalocyanine in the dry-film state and in DMF solution. Uniform composition of the sublimed dye material is indicated by the spectroscopic data in Table 1. The ratio of solution peak heights $(OD)_1 / (OD)_2$ remained constant at 2.05 $\pm$ 0.02 as a powder sample was fractionally sublimed. The solution optical density (absorbance) per unit area of film dissolved was related under these conditions to the dry-film value $(OD)_f$ by an average proportionality constant of 0.153. Approximately one-third of the powder preparation was nonvolatile, remaining in the filament at the end of the sublimation process. Some of this residue may have been produced by polymerization of the dye at the filament temperature. From another Rockwell investigation, a molar extinction coefficient* of 1.27×10^5 has been determined for $LuH(Pc)_2$ at the 615-nm peak in DMF.[7] This value may be compared with 1.42×10^5 estimated from the graphical data of Moskalev and Kirin.[8]

From the dry-film spectrum, the weight of dye per unit area may be calculated:

$$Wt/A = 14.5\ (OD)_f\ \mu g/cm^2 \qquad (1)$$

The number of molecules per cm^2, N_f, is then given by Equation 2.

$$N_f = 7.25 \times 10^{15}\ (OD)_f \qquad (2)$$

Alternatively, the weight and number of molecules in the film can be determined by dissolving a known area of film in a known volume of DMF and measuring the solution spectrum in a cell of appropriate optical path length. The electrodes containing the binder were characterized from the dry-film spectra, however, since it was found that a

---

*ε in the equation $OD = \log_{10} (I^o/I) = \varepsilon c \ell$, where c is the concentration in moles/liter and ℓ is the optical path length in cm; I^o is the incident light intensity, and I is the transmitted intensity.

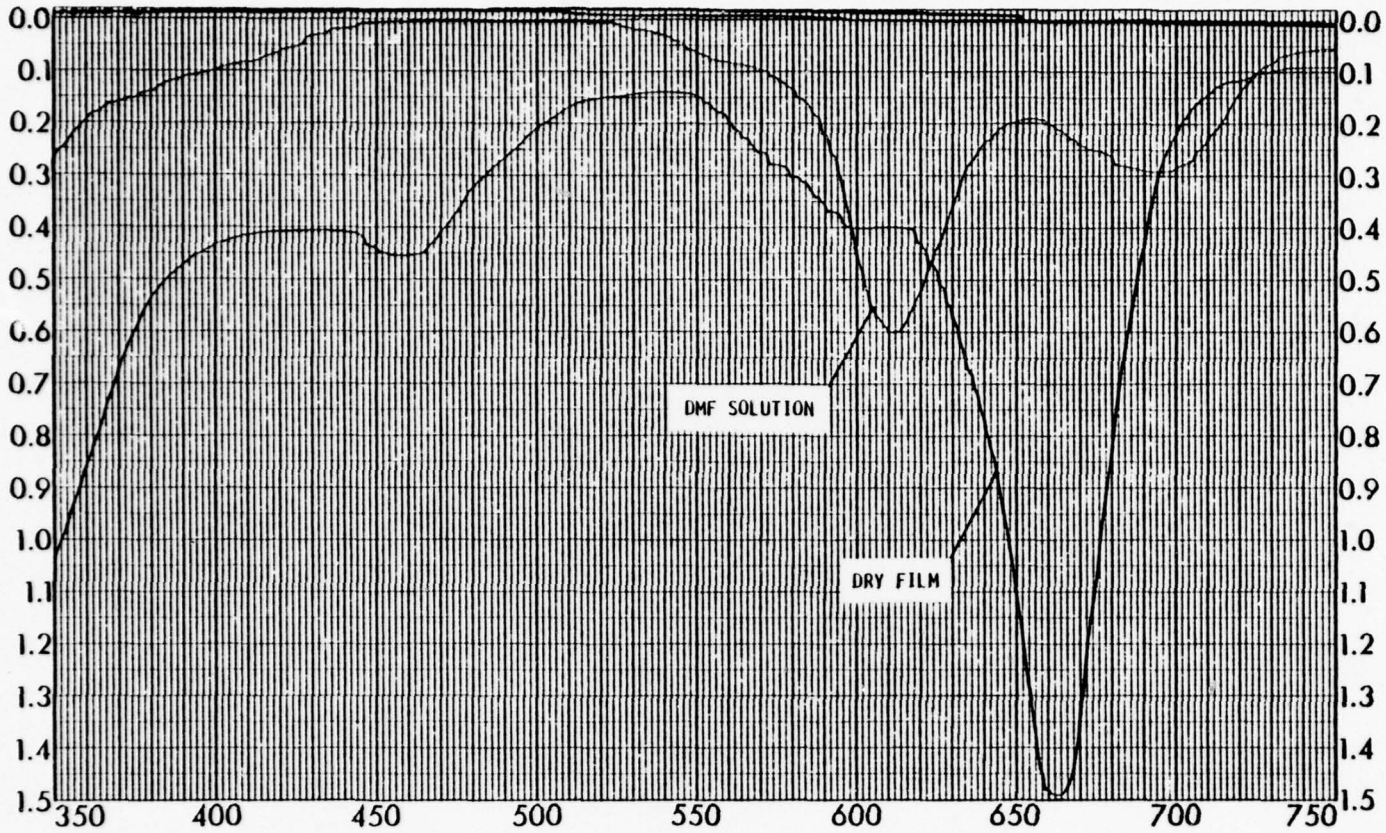


Figure 4. Absorption Spectra of $LuH(Pc)_2$ in a Dry Film and in DMF Solution

TABLE 1

FRACTIONAL SUBLIMATION OF $LuH(Pc)_2$ PREPARATION

Fraction	Cumulative Wt Loss (%)	Spectroscopic Data: DMF Solution λ_1 (nm)	DMF Solution λ_2 (nm)	DMF Solution $(OD)_1/(OD)_2$	Dry Film λ_f (nm)	Dry Film $(OD)_1/\lvert A(OD)_f \rvert$ (cm^{-2})
1	32.0	615	694	2.10	--	--
2	37.8	614	696	2.00	666	0.148
3	47.1	612	694	2.05	663	0.158
4	64.1	615	694	2.05	--	--
5[a]	66.7	616	694	2.06	662	0.154

Conditions:

Initial wt $LuH(Pc)_2$ powder: 54.7 mg.

Substrate: Microscope slide without tin oxide.

Heater Current: 10.0 Amp initially; increased to 10.5 Amp for Fraction 5.

[a]No additional material sublimed at 10.5 Amp.

DMF solution prepared by dissolving measured area A (2 to 3 cm^2) of film in 10 ml DMF.

Solution spectra recorded in 1-cm cell (except Fraction 5 in 4-cm cell; converted to 1 cm).

significant amount of dye was swept across the surface of the plate during the spinning step and trapped in the binder layer. Although this trapped dye showed only very slight electrical or electrochromic activity, it would have contributed to the solution spectrum when the entire electrode was exposed to DMF.

2. Display Electrodes

Optical densities and corresponding film characteristics are given in Table 2 for Electrodes 1 through 10.* In addition to the dry-film spectrum in air, the open-circuit spectrum was recorded with the electrode immersed in 0.1M KCl prior to electrical excitation. An "initial green" spectrum at -0.15V vs Ag/AgCl was also determined in most cases. It is evident from the spectra summarized in Table 2 that the dry, open-circuit, and -0.15-V conditions were quite similar; they represent the initial state of the electrochromic material.

A typical film with an optical density of 0.7 at 668 nm contained 10 $\mu g/cm^2$ of dye, based on the projected area of the deposit, and 5×10^{15} molecules/cm^2. The surface roughness of the tin oxide is neglected in these evaluations. From x-ray diffraction studies on metal phthalocyanines,[9] it may be estimated that a phthalocyanine ring structure lying flat on a substrate surface occupies 1.30×10^{-14} cm^2. A monolayer of diphthalocyanine would then consist of 0.77×10^{14} molecules/cm^2. On this basis, the film containing 10 $\mu g/cm^2$ of $LuH(Pc)_2$ would have a thickness of approximately 65 molecular layers.

*The Munsell color matches are reported for a film with OD = 0.940 in the dry state; this specimen is not included in Table 2.

TABLE 2

ELECTROCHROMIC SPECIMEN CHARACTERISTICS[a]

Electrode	OD Before Electrical Measurements			Dye Film Thickness[b]	
	668 ± 3 nm	666 ± 6 nm	663 ± 9 nm		
	$(OD)_f$ Dry in Air	Open Circuit 0.1 M KCl	-0.15V 0.1 M KCl	($\mu g/cm^2$)	(molecules/cm^2 x 10^{-15})
1	0.280	0.288	0.288	4.05	2.03
2	0.290	0.265	0.295	4.19	2.10
3[c]	0.495	0.555	0.563	7.16	3.59
4	0.510	0.437	0.463	7.37	3.70
5	0.550	0.480	0.490	7.95	3.99
6	0.775	---	---	11.2	5.62
7	0.805	0.790	0.850	11.6	5.84
8	0.860	0.835	---	12.4	6.24
9	1.09	---	---	15.8	7.90
10[d]	1.55	---	---	22.4	11.2

[a] $LuH(Pc)_2$ on tin oxide; circular deposit, 0.713 cm^2 area (except Electrode 3); collodion binder present (except Electrode 10). Replicate sets: 1-2, 3-5, 6-8, 9-10.

[b] From Equations 1 and 2.

[c] Area of deposit 2.52 cm^2.

[d] Without binder.

B. STEADY-STATE RESPONSES

1. Methodology

Three types of measurements were made on the display electrodes at or near steady-state conditions: (a) The open-circuit potential of the test electrode in contact with 0.1 M KCl was measured against the Ag/AgCl reference through an electrometer circuit. (b) Current-voltage curves were recorded with the display electrode potential continuously changing at the slow rate of 10 mV/sec. (c) In situ absorption spectra were determined at fixed potentials in 0.1-V intervals. The changes between the fixed potentials were made automatically at 10 mV/sec.

All of the controlled-potential measurements were done potentiostatically, so that any changes at the counter electrode did not influence the results and the effect of ohmic drop in the electrolyte was minimized. This method is one of several standard electrochemical half-cell techniques. Its operation is as follows: The potential between the test electrode and a stable reference electrode such as Ag/AgCl is compared continuously with a voltage from a programmed signal generator. Small deviations between the programmed input signal and that actually applied to the test electrode are sensed by an electrometer and fed into the amplifier that supplies the cell current between the test and counter electrodes. In this way, enough cell current is always supplied to maintain the test electrode at the desired potential on the electrochemical scale.

If the counter electrode were made of a well-stabilized electrochemical system such as Ag/AgCl or $Pb/PbCl_2$ in contact with the KCl electrolyte, it could function simultaneously as a reference electrode, and the drive circuitry could be greatly simplified. Such an arrangement was used in a battery-operated demonstration model of a phthalocyanine display.[7] The present investigation was done with 3-electrode cells, in order to fully resolve the response of the display electrode from that of the cell as a whole.

2. Choice of Initial Color State

As expected, the open-circuit potential of the display electrode prior to electrical excitation was not very well defined. Readings between zero and -0.35 V *vs* Ag/AgCl were obtained on a group of tin oxide plates with and without dye deposits. It was noted in Part A of this section that the dye spectrum changed very little at -0.15 V. The green condition of $LuH(Pc)_2$ occurring near this potential was therefore used as a reference or initial color state throughout the investigation. The other colors were then characterized in terms of the applied potentials or the input charge densities required to bring about the various transitions from the green state.

3. Dependence of the Absorption Spectrum on Applied Potential

Changes in the absorption spectra of the rare-earth diphthalocyanines with applied potential in aqueous potassium chloride were first reported by Moskalev and Kirin.[8] The spectra shown in Figures 5 and 6 document these electrochromic effects for the lutetium compound in greater detail and extend the data to higher positive and negative potential ranges. They also include some additional colors. In particular, the Russian investigators did not indicate the very dark blue, violet, and bright red that we have observed with $LuH(Pc)_2$.

Pronounced color changes are evident in Figures 5 and 6, which were obtained on a film with the relatively low dye content of 12 $\mu g/cm^2$. Optical density changes of at least 0.4 unit occurred, for example, near 520, 630 and 670 nm on application of potential differences not exceeding 2 V. The subtraction of these wavelengths from white light results in transmitted colors of red, blue, and green, respectively. The color capability of the lutetium compound is more fully described and correlated with the electrical variables in later sections of the report.

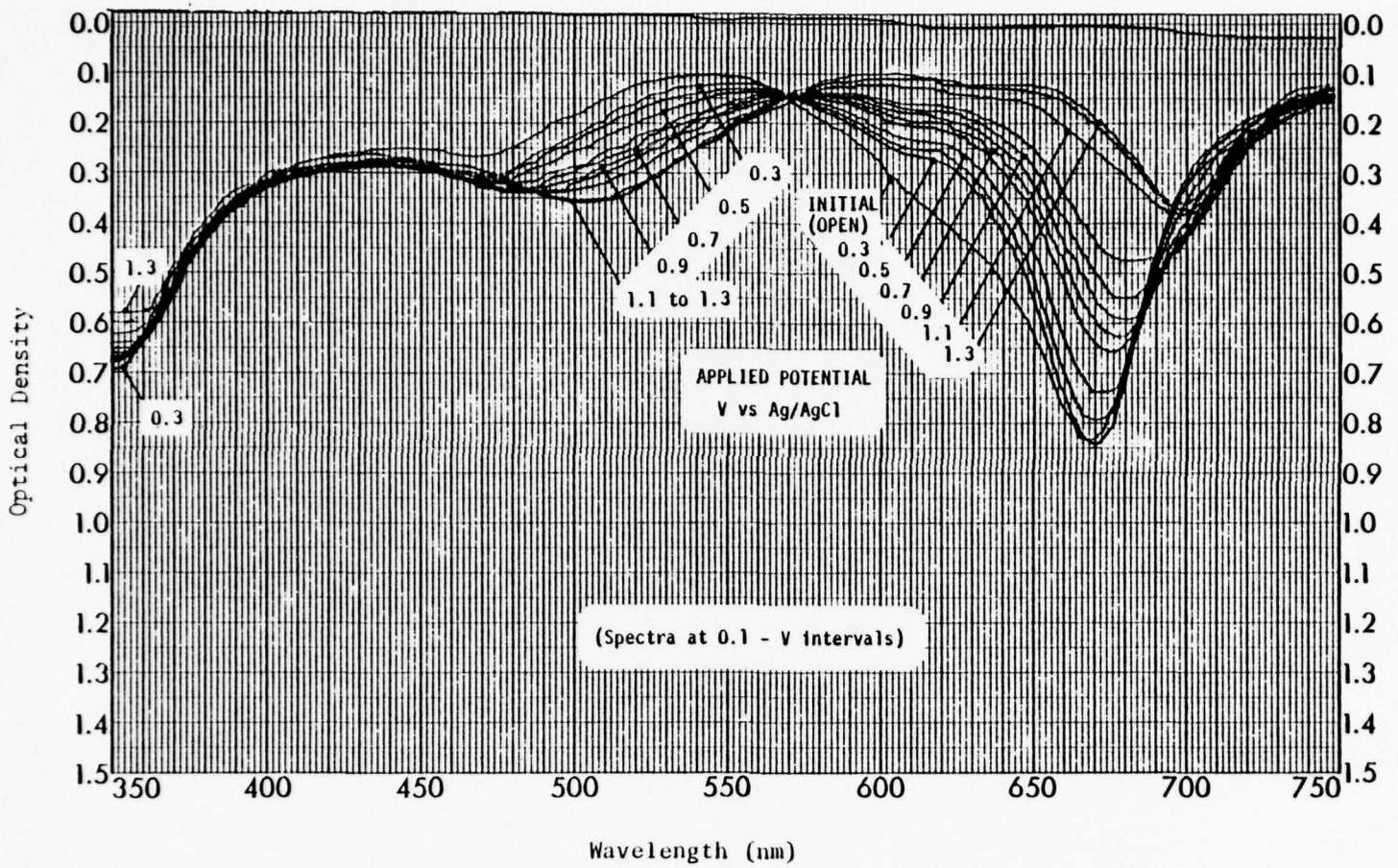


Figure 5. Electrochromic Spectra of LuII$(Pc)_2$ at Positive Potentials

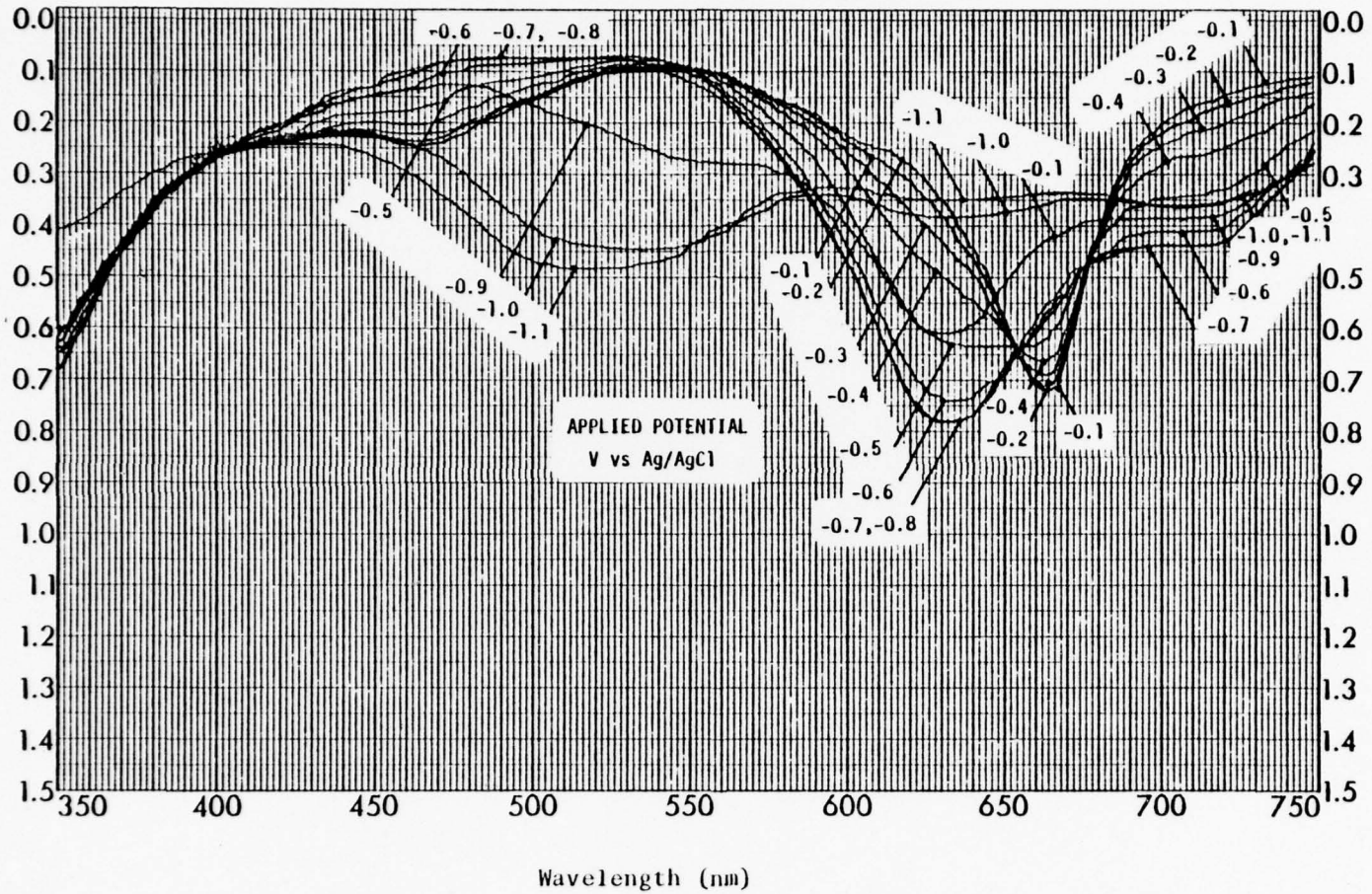


Figure 6. Electrochromic Spectra of LuH$(Pc)_2$ at Negative Potentials

4. Current-Voltage Curves

Figure 7 shows current-voltage curves recorded at 10 mV/sec for the electrode used to obtain the spectra in Figures 5 and 6. The blank recordings were made by inverting the same electrode so that the dye deposit was above the liquid level. In contrast to the spectral behavior, the electrical responses under these conditions had few distinctive features. With the dye present, a small current peak appeared between 0.6 and 0.7 V in the positive scan, and a slowly-rising current occurred beyond -0.4 V in the negative. In the case of Electrode 10, the 0.63-V peak was accompanied by a definite yellow color. The cathodic current beyond -0.4 V probably was due to the reduction of dissolved oxygen which, for experimental convenience, was not removed from the cells. With sealed cells and improved designs, extraneous effects of this kind can be minimized.

Some further comment on background currents is appropriate at this point. The total potential range in any aqueous system will be limited by electrolytic reactions such as hydrogen and oxygen evolution. It will be recalled from thermodynamics that water should decompose on the application of 1.23 V between the anode and cathode. When the electrode is a semiconductor such as tin oxide, however, the useful range is often considerably greater than it would be on most metal electrodes. The electrolyte decomposition processes apparently began near +1.1 V and -1.1 V *vs* Ag/AgCl in Figure 7. A net working range of 2.2 V may be estimated from this information. Any problem due to background current in the display cell is greatly mitigated by the fact that the various colors are stable on open circuit; the excitation signal therefore does not have to be applied continuously.

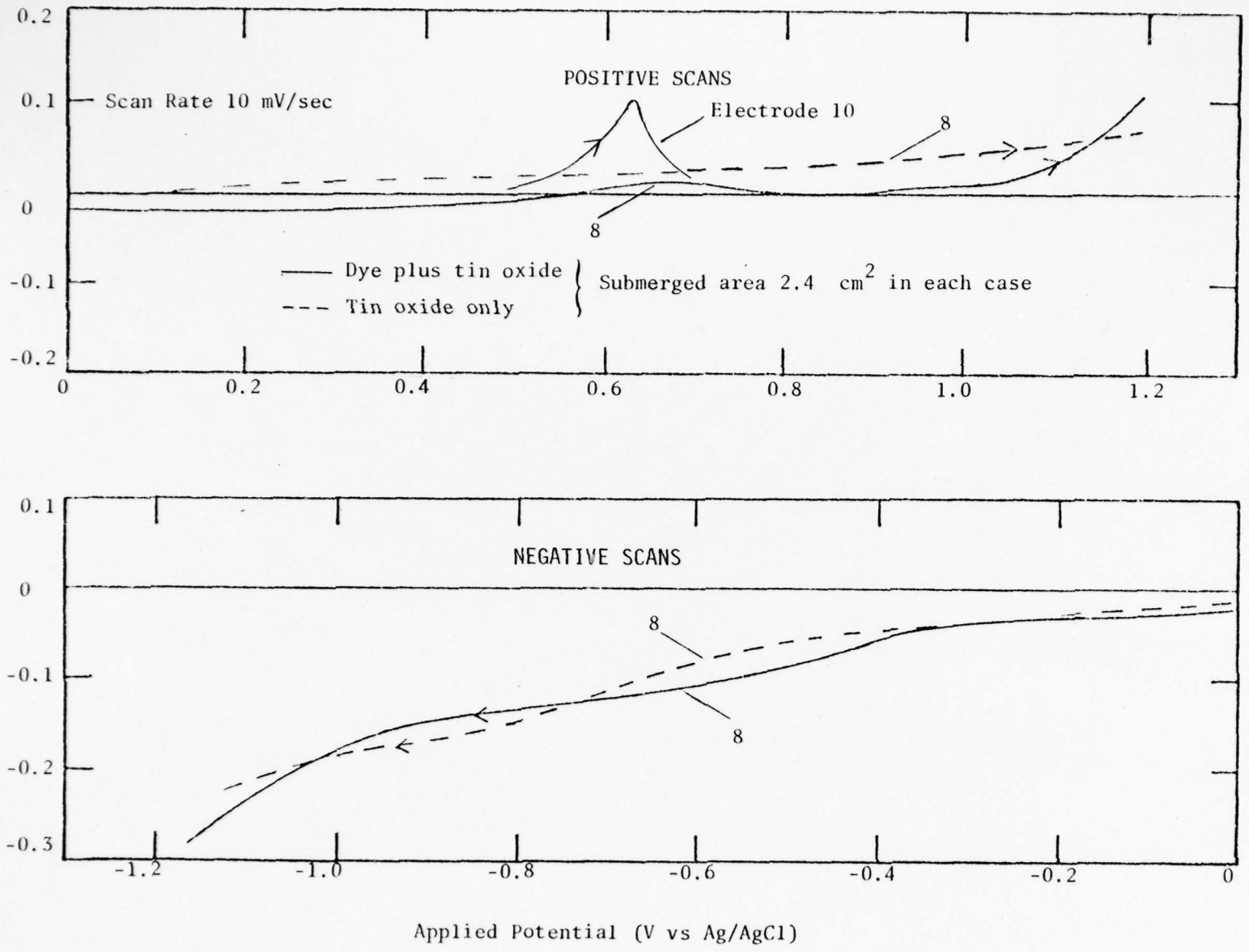


Figure 7. Current-Voltage Curves Recorded in Slow Potential Scans

5. Transition Potentials from Steady-State Measurements

The spectral data could be analyzed in several ways to show the occurrence of discrete transformations in the electrochromic material. One of these was the observation of isosbestic, or common intersection, points in the spectral curves. Such points occurred, for example, at 570 nm in Figure 5 and at 654 and 676 nm in Figure 6. This behavior indicated that the number of absorbing centers (molecules or ions) was not changing, even though the positions of the absorption maxima were shifting under the influence of the applied potential. Some points where two species had equal absorption peaks at two different wavelengths also may be seen, as at -0.5 V in Figure 6.

A much clearer view of the color transitions is presented by the lower section of Figure 8, where the wavelength of the highest absorption peak in each spectrum is plotted as a function of the applied potential. Pairs of points are shown where two peaks of equal heights were found. Abrupt shifts in the predominant wavelength occurred at -0.95, -0.50, and +1.05 V, and a less pronounced inflection was noted at +0.50 V. These transition potentials mark the boundaries of the five color zones noted on the steady-state plot. The upper section of Figure 8 will be discussed in connection with the pulse experiments. The color changes are not quite as abrupt as one might infer from this figure. Intermediate shades of blue-violet, blue-green, yellow-green, etc. can be selected by a simple adjustment of the applied potential. A set of $LuH(Pc)_2$ colors is described in terms of the Munsell and CIE systems in Section III-E.

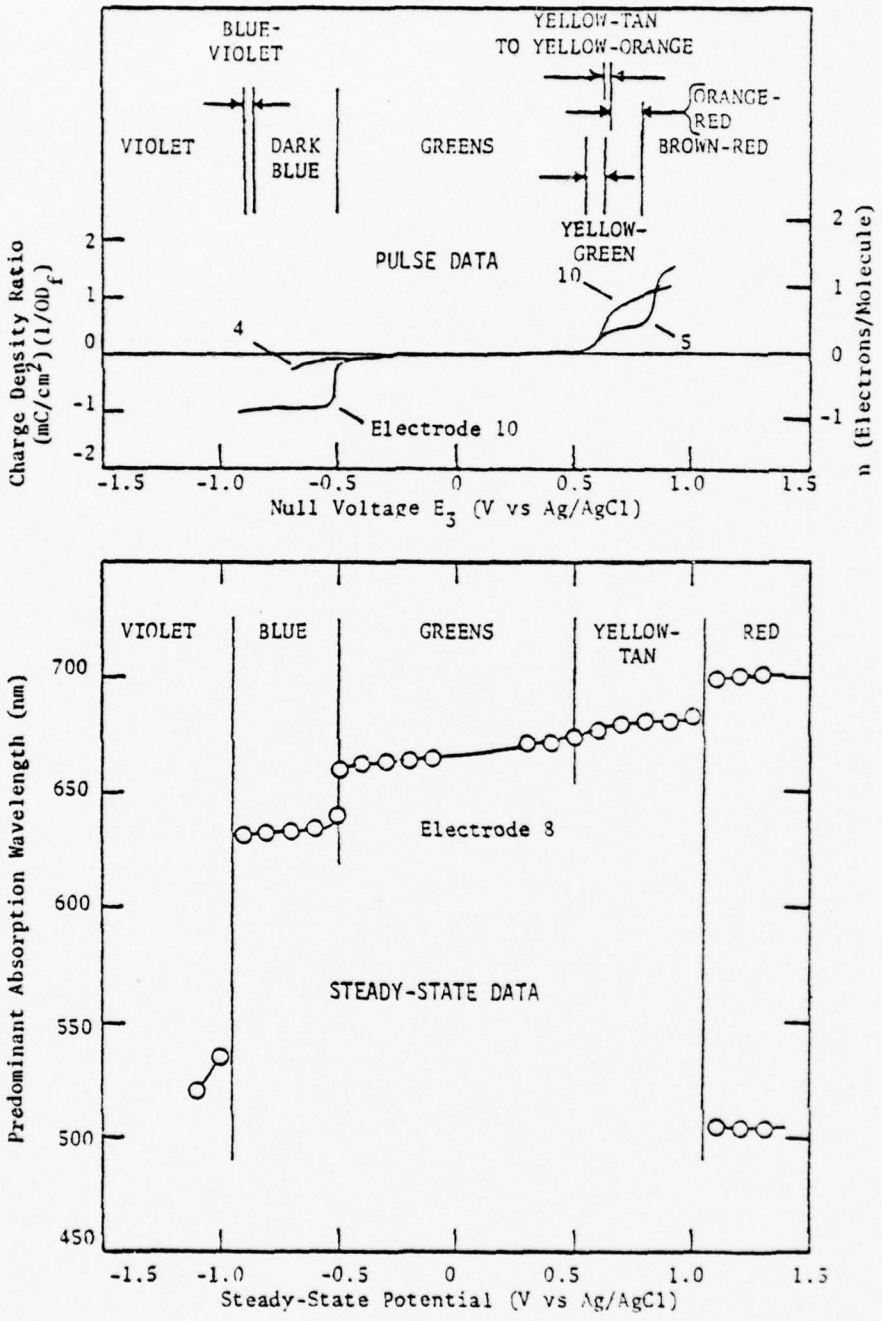


Figure 8. Correlation of Results from Steady-State and Pulse Measurements

C. PULSE RESPONSES

In the practical operation of an alphanumeric display, the characters must be switched on or off in 200 msec or less to achieve a satisfying visual effect. It is essential for design purposes to know the input voltages and charge densities required for switching under these conditions. The pulse measurements discussed in this section were made to provide a correlated set of electrical and optical parameters for the $LuH(Pc)_2$ system under conditions that simulate the operation of a segment or other geometric element in a display character.

This display had been investigated in a preliminary study by using a 2-level voltage pulse to switch from one color to another. As a result, the system was known to behave somewhat like a capacitor and resistor in series. It was suspected, moreover, that the 2-level switching used more charge than was actually necessary to achieve the color change; i.e., the electrode was being overdriven toward the end of the pulse period in order to obtain a fast response at the beginning. Excess charge input is undesirable from an energy standpoint, and it can cause damage to the cell if it brings about extraneous electrode reactions such as hydrogen and oxygen evolution. The 4-level pulse routine used here minimized the background processes and permitted determination of the charge taken up by the dye. It also provided virtually open-circuit, but controlled, conditions for recording the spectra. This technique is explained below.

1. Pulse Methodology

Voltage, current, and charge functions for the 4-level pulse technique are illustrated in Figure 9. The display electrode was controlled in the pulsing mode by the potentiostatic principle described in Section III-B-1. The transient responses are based on the simple RC model, which represents a first approximation to the display electrode behavior. Some of the resistance R was in the tin oxide, while the

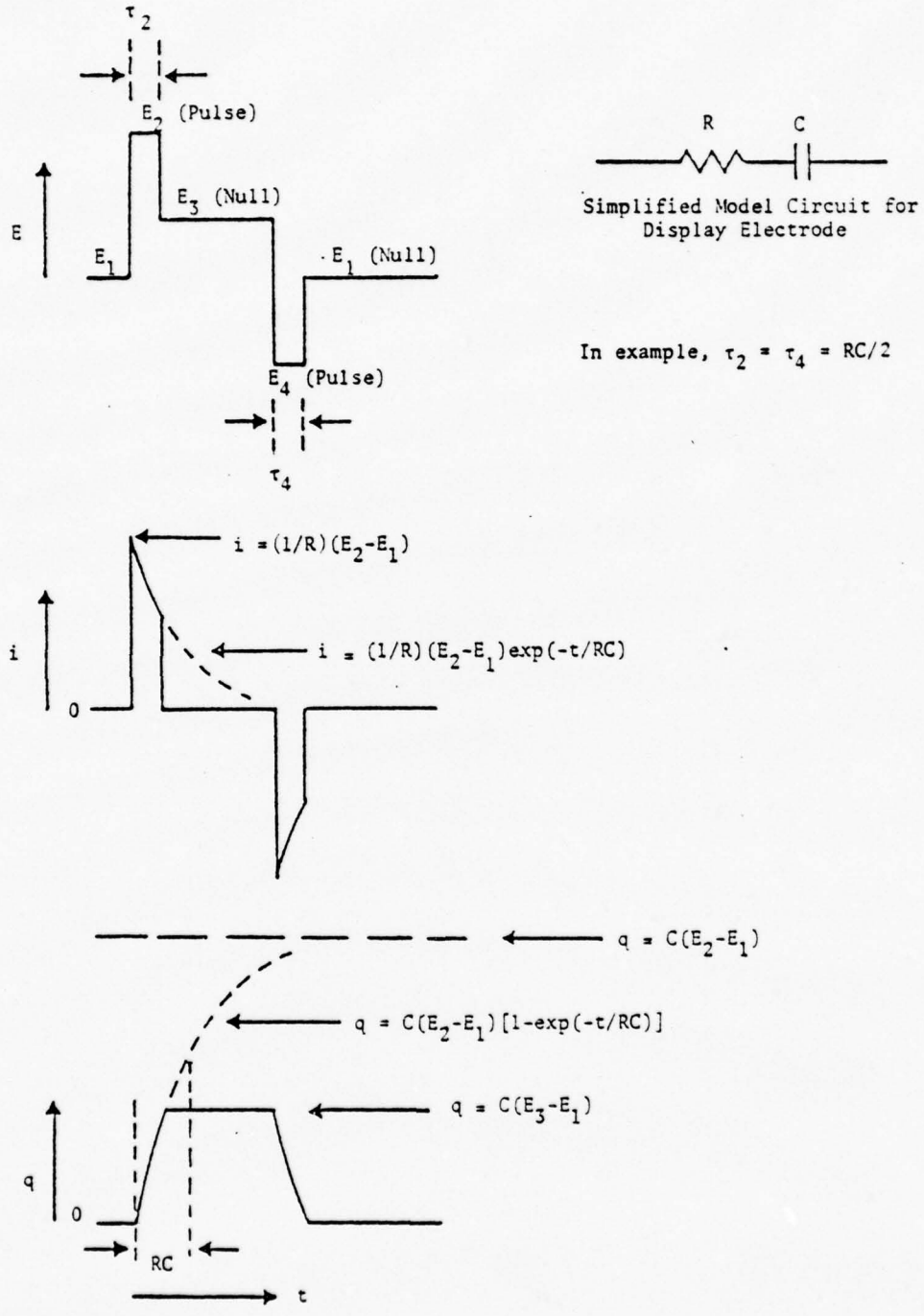


Figure 9. Principles of Four-Level Pulse Technique

capacitance C was a characteristic of the dye film. It should be emphasized that C was not constant over the range of potentials investigated. In a more detailed treatment, it could be represented as a step function of potential, with large capacitances at the abrupt color transitions, and small ones in the broader regions where individual colors predominate. Other notations in Figure 9 include E_1 through E_4 for the applied voltage levels, τ_2 and τ_4 for the respective pulse times, and i and q for the current and charge at the display electrode.

The potential E_1 was taken at the initial green color state under essentially zero current, and the input charge was measured from this point. E_2 was varied in small increments toward the red or blue condition, and E_3 was adjusted each time by trial to attain a current null. With this procedure, visual and spectral observations could be made under substantially open-circuit conditions at E_1 and E_3. If the electrode had a tendency to deviate from either of these potentials, however, it was prevented from doing so by the potentiostatic control circuit. After a time (usually several min) at E_3, the potential was returned to E_1 by pulsing through E_4.

2. Four-Level Pulse Data

The conditions of the pulse measurements for nine display electrodes are summarized in Table 3. Some of the null potentials were reproducible within a few millivolts. The current-time trace on the oscilloscope then closely resembed that shown in Figure 9. A less perfect but readable null was obtained as E_2 approached the end of the positive or negative potential range. The complete set of pulse data is presented in Figures 10 through 20, in which the charge q and the null potential E_3 are plotted as functions of the pulse potential E_2. The background charges were much smaller than the dye charges, as illustrated by the blank curves included in Figures 11, 18, and 20. In analyzing the pulse data, therefore, no corrections were made for the portions of the electrodes not covered by the dye.

TABLE 3

CONDITIONS OF PULSE MEASUREMENTS [a,b]

Electrode	Potentials (V vs Ag/AgCl)				Optical Data at E_1 and E_3	Notes
	E_1 Null	E_2 Range Pulse	E_3 Range Null	E_4 Pulse		
1	-0.15	0.70 to 1.60	0.52 to 1.04	-0.30	Spectral	--
2	-0.15	0.70 to 1.70	0.53 to 1.05	-0.30	Spectral	--
3	-0.15	0.70 to 1.80	0.56 to 0.85	-0.30	Spectral	Film area 2.52 cm^2
5	-0.15	0.70 to 1.70	0.62 to 0.90	-0.30	Spectral	--
6	-0.15	0.60 to 1.70	0.32 to 0.72	-0.30	Visual	τ_2 varied from 0.1 to 0.2 sec.
7	-0.15	1.00 to 1.70	0.54 to 0.74	-0.30	Spectral	--
9	-0.22	-0.70 to -2.10	-0.33 to -0.54	0.40	Visual	--
4	-0.15	-0.40 to -1.40	-0.31 to -0.67	-0.30	Spectral	--
10	-0.26 0.00	0.30 to 1.70 -0.70 to -2.90	0.26 to 0.89 -0.47 to -0.89	-0.30 0.40	Visual Visual	Without binder

[a] Pulse potential and time notations are indicated on Figure 9.

[b] $\tau_2 = \tau_4 = 0.1$ sec and A = 0.713 cm^2 unless noted.

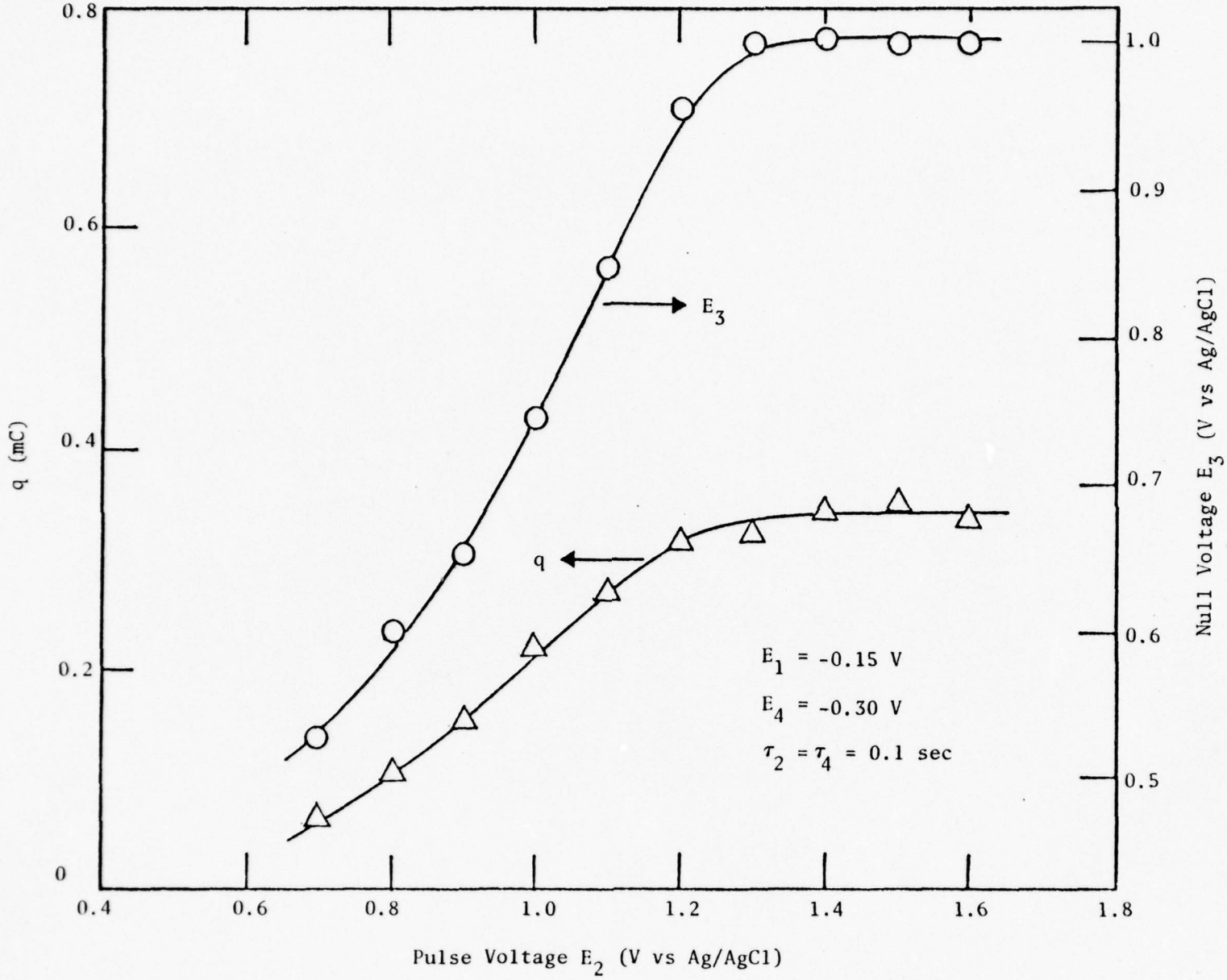


Figure 10. Pulse Response of Electrode 1 Switching from Green toward Red

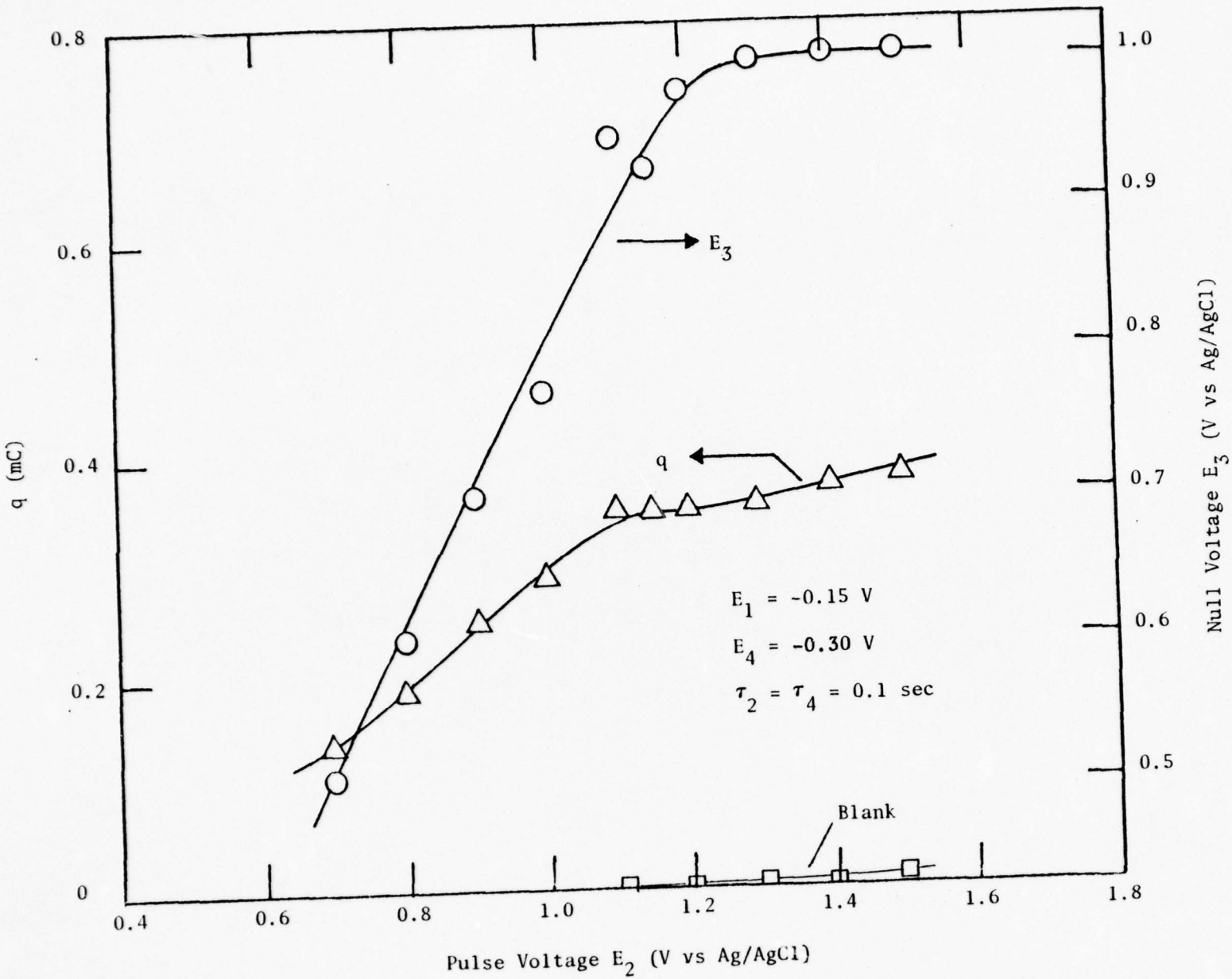


Figure 11. Pulse Response of Electrode 2 Switching from Green toward Red

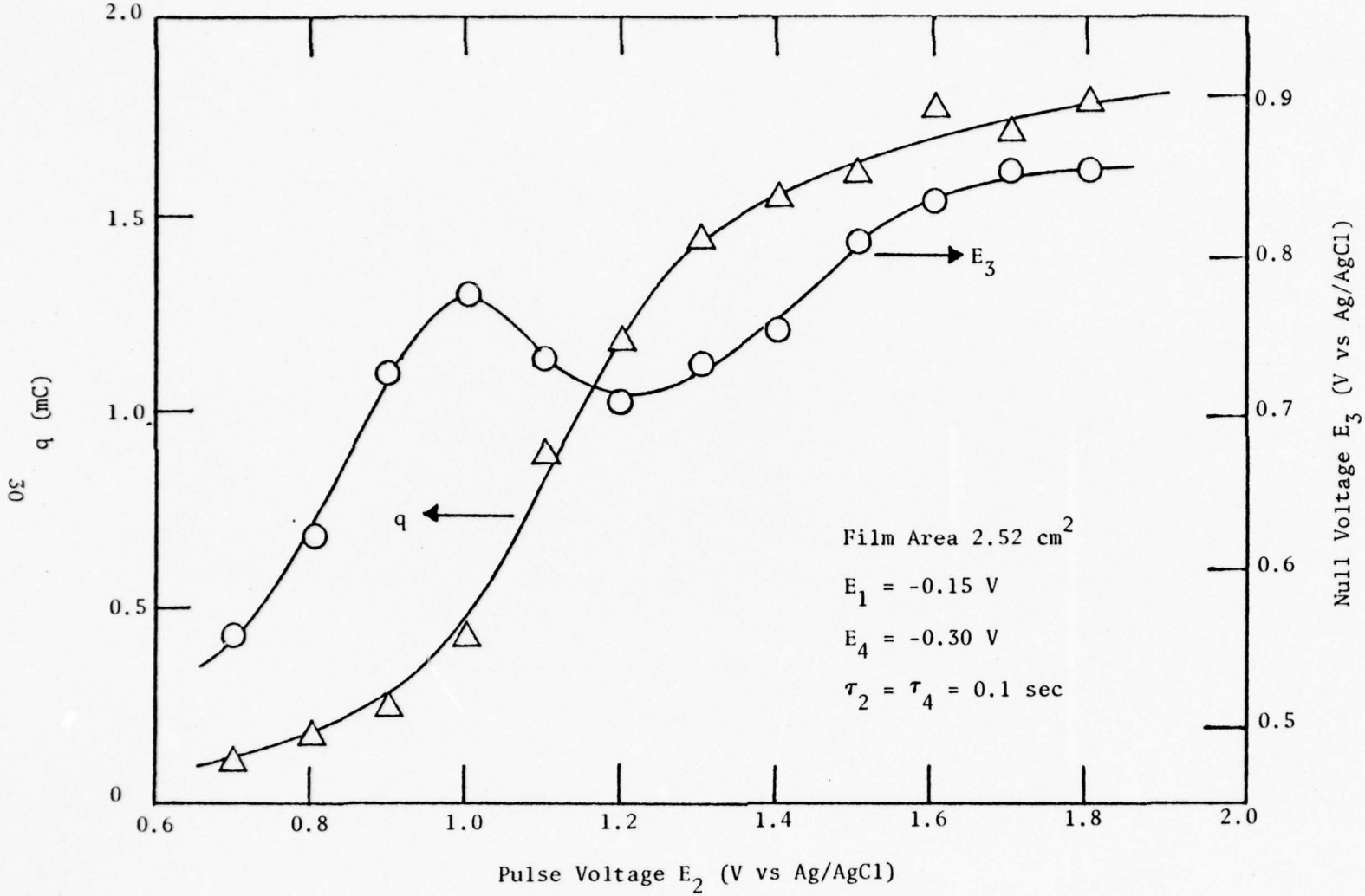


Figure 12. Pulse Response of Electrode 3 Switching from Green toward Red

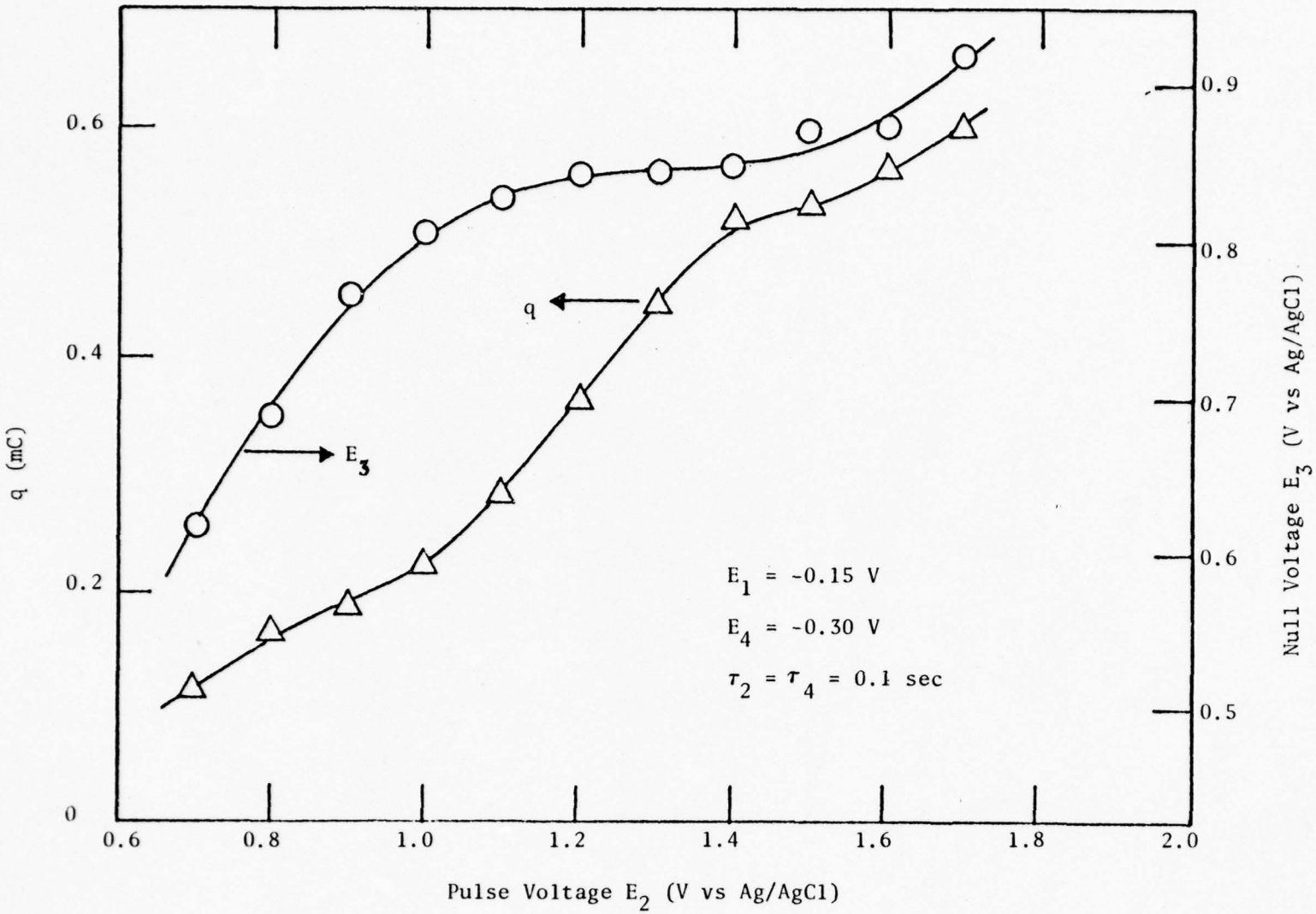


Figure 13. Pulse Response of Electrode 5 Switching from Green toward Red

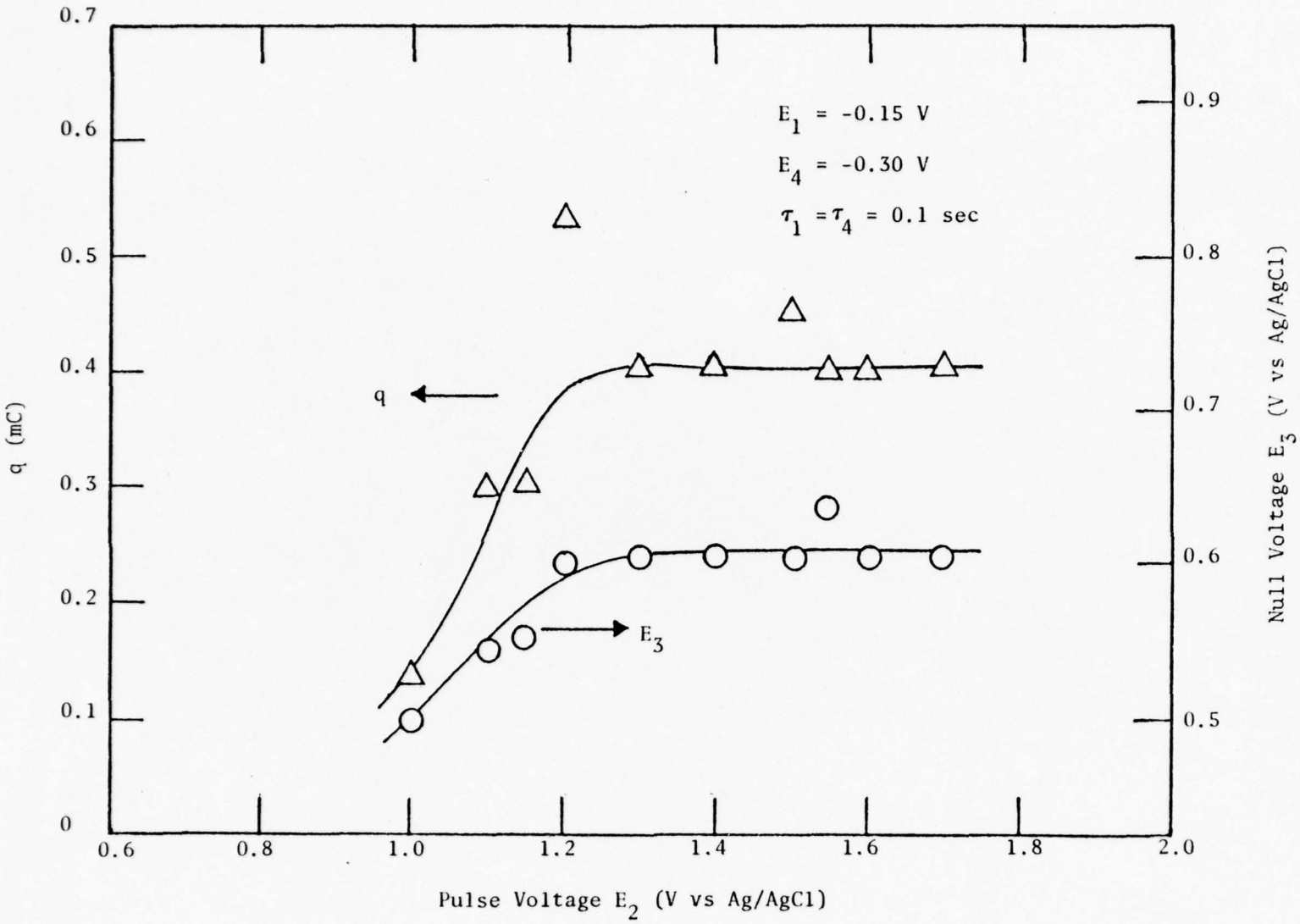


Figure 14. Pulse Response of Electrode 6 Switching from Green toward Red

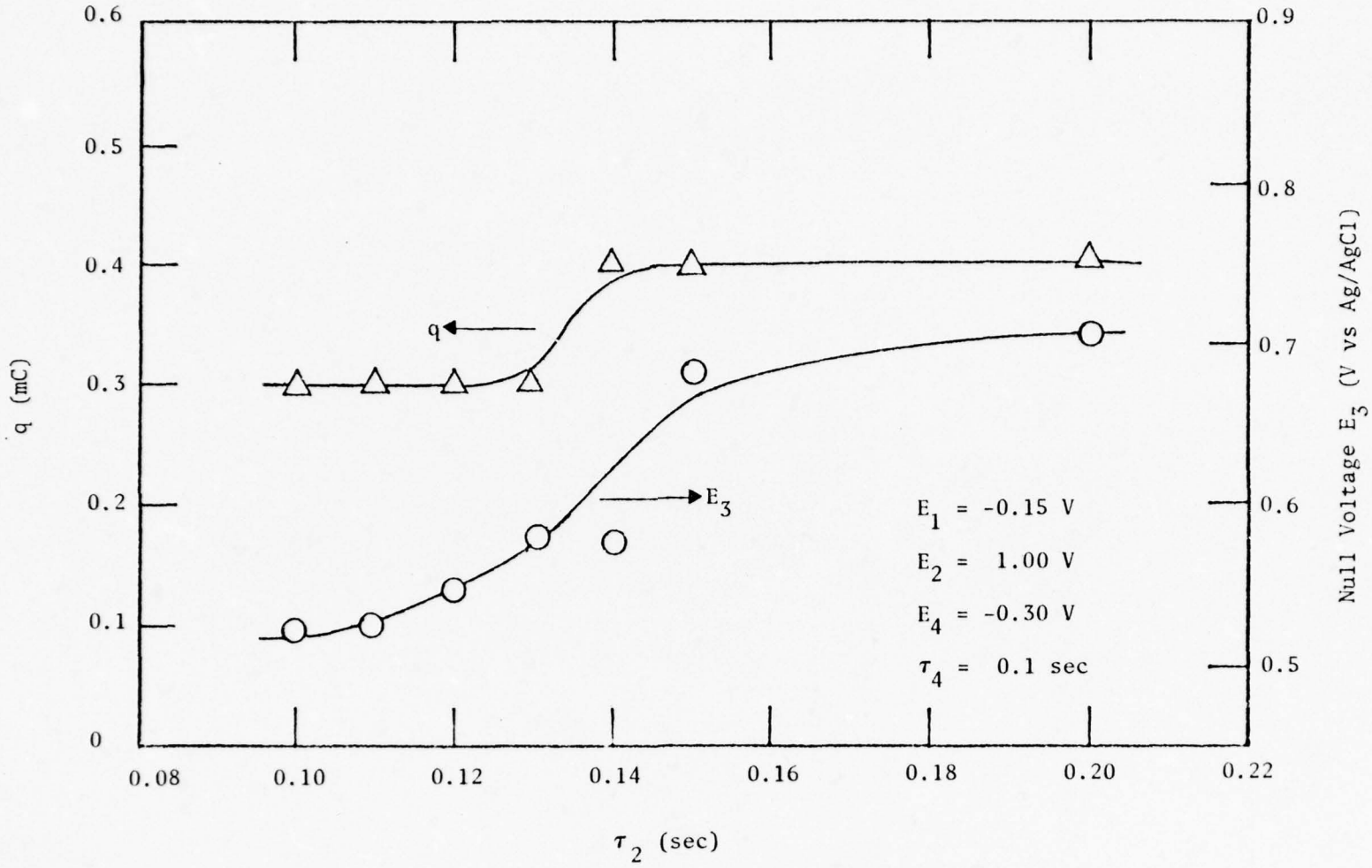


Figure 15. Pulse Response of Electrode 6 with Variable τ_2, Switching from Green toward Red

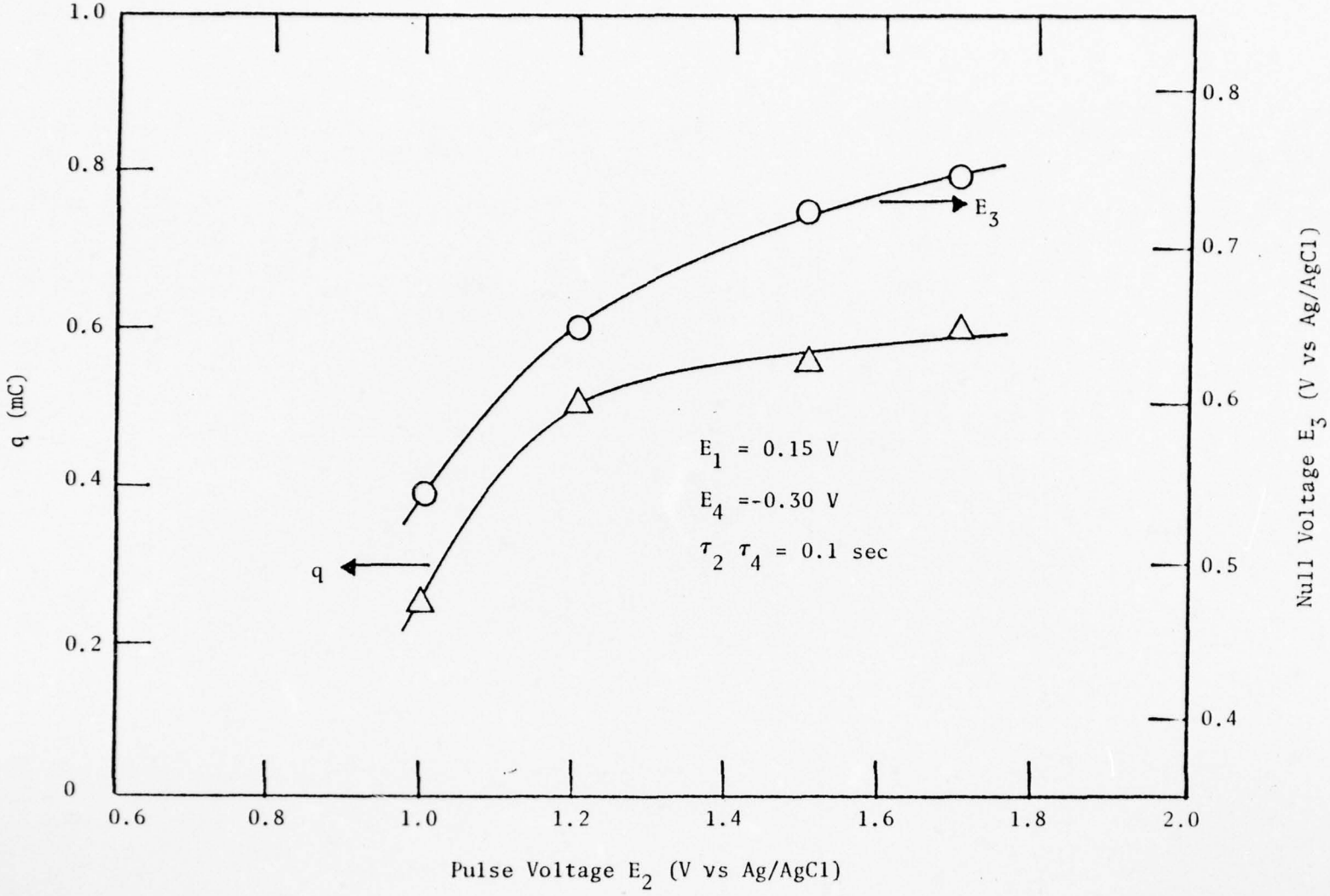


Figure 16. Pulse Response of Electrode 7 Switching from Green toward Red

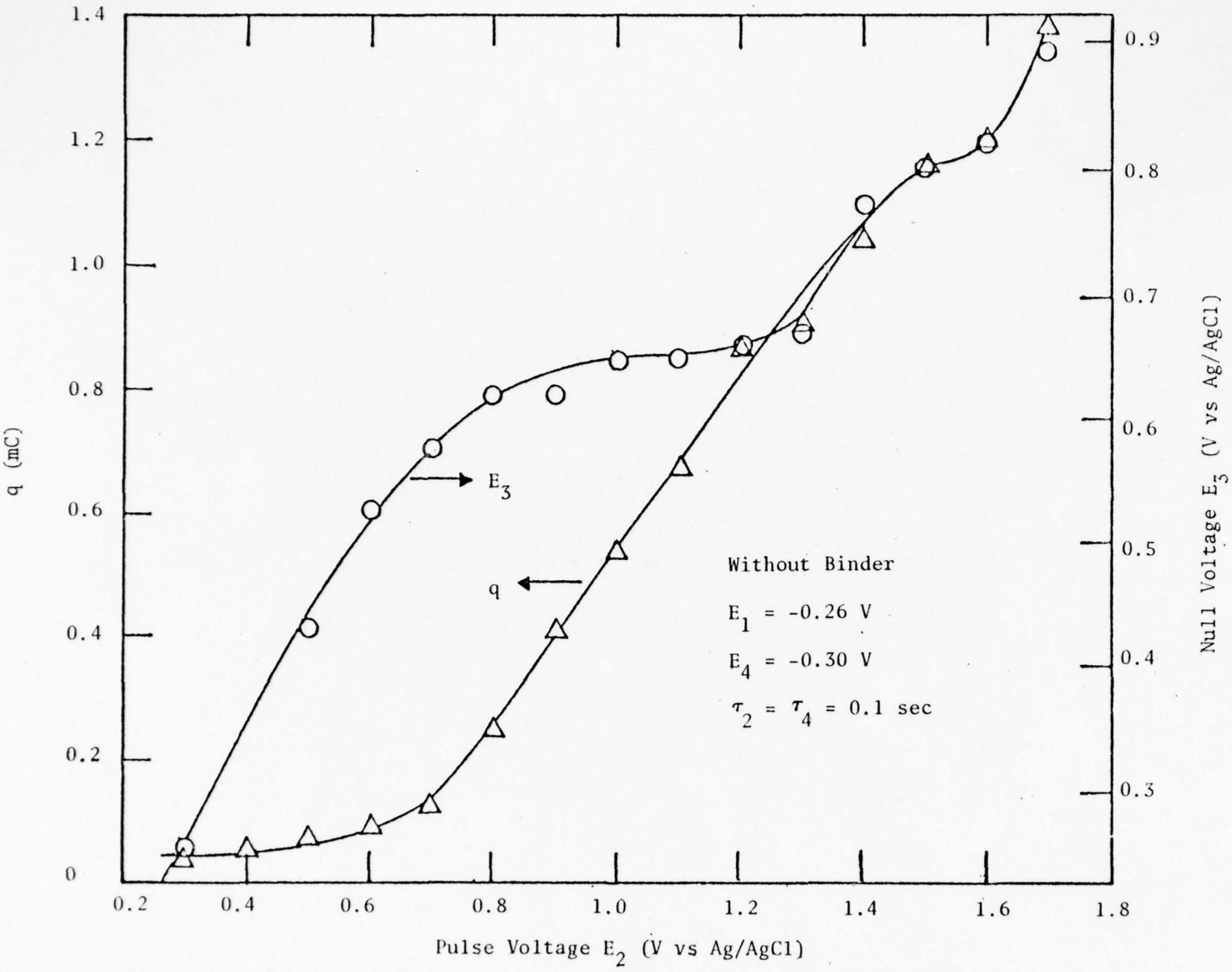


Figure 17. Pulse Response of Electrode 10 Switching from Green toward Red

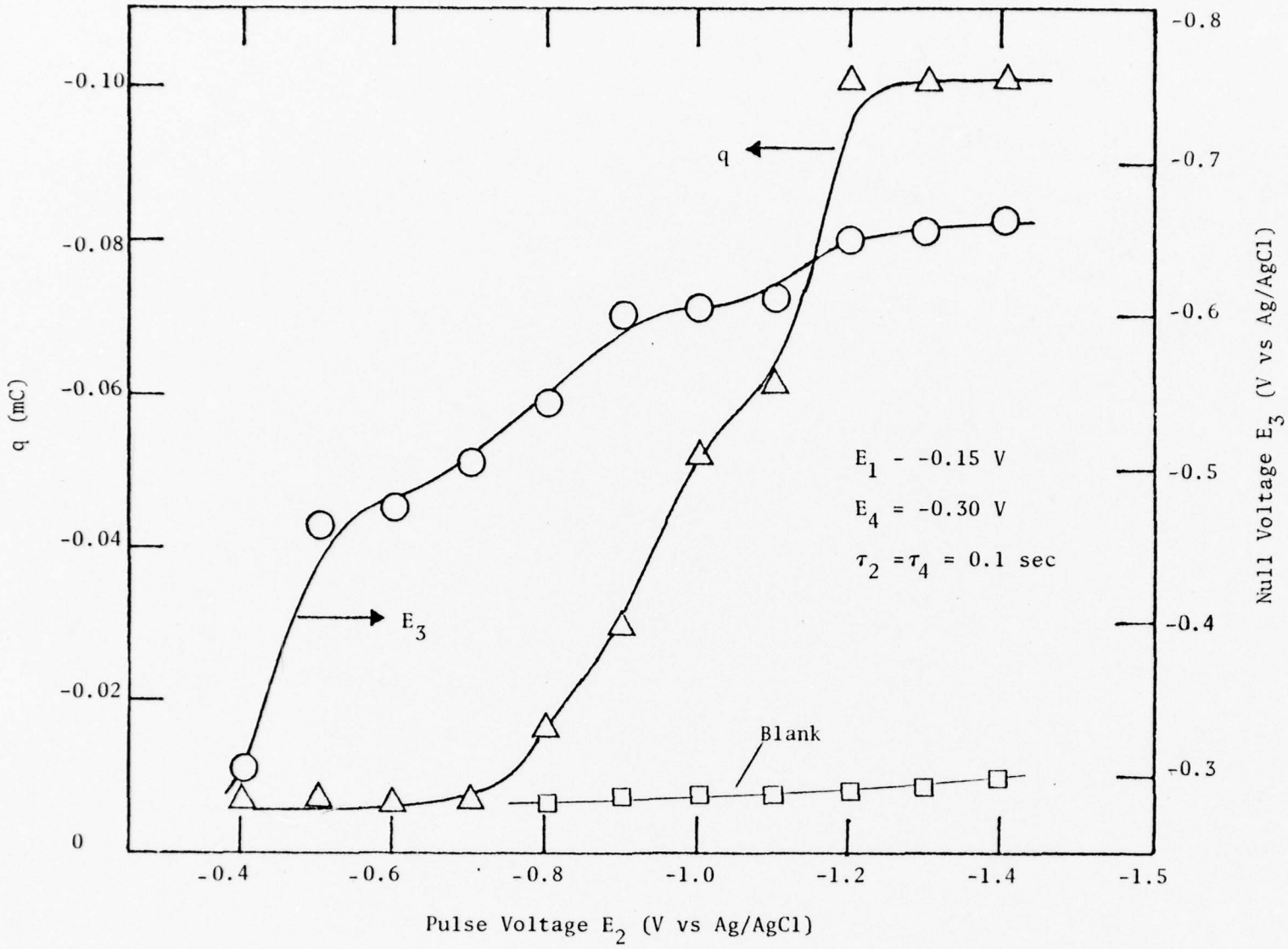


Figure 18. Pulse Response of Electrode 4 Switching from Green toward Blue

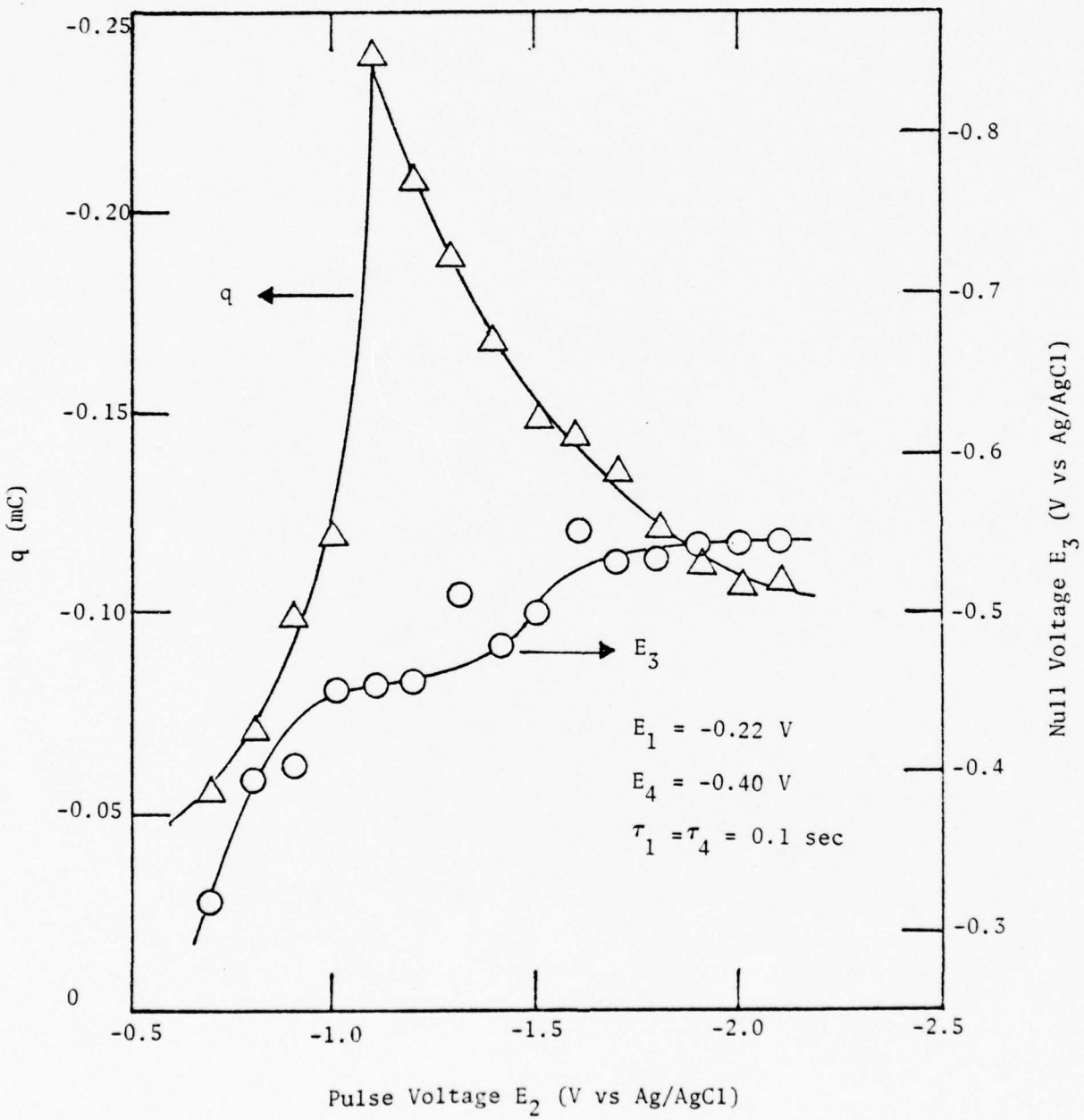


Figure 19. Pulse Response of Electrode 9 Switching from Green toward Blue

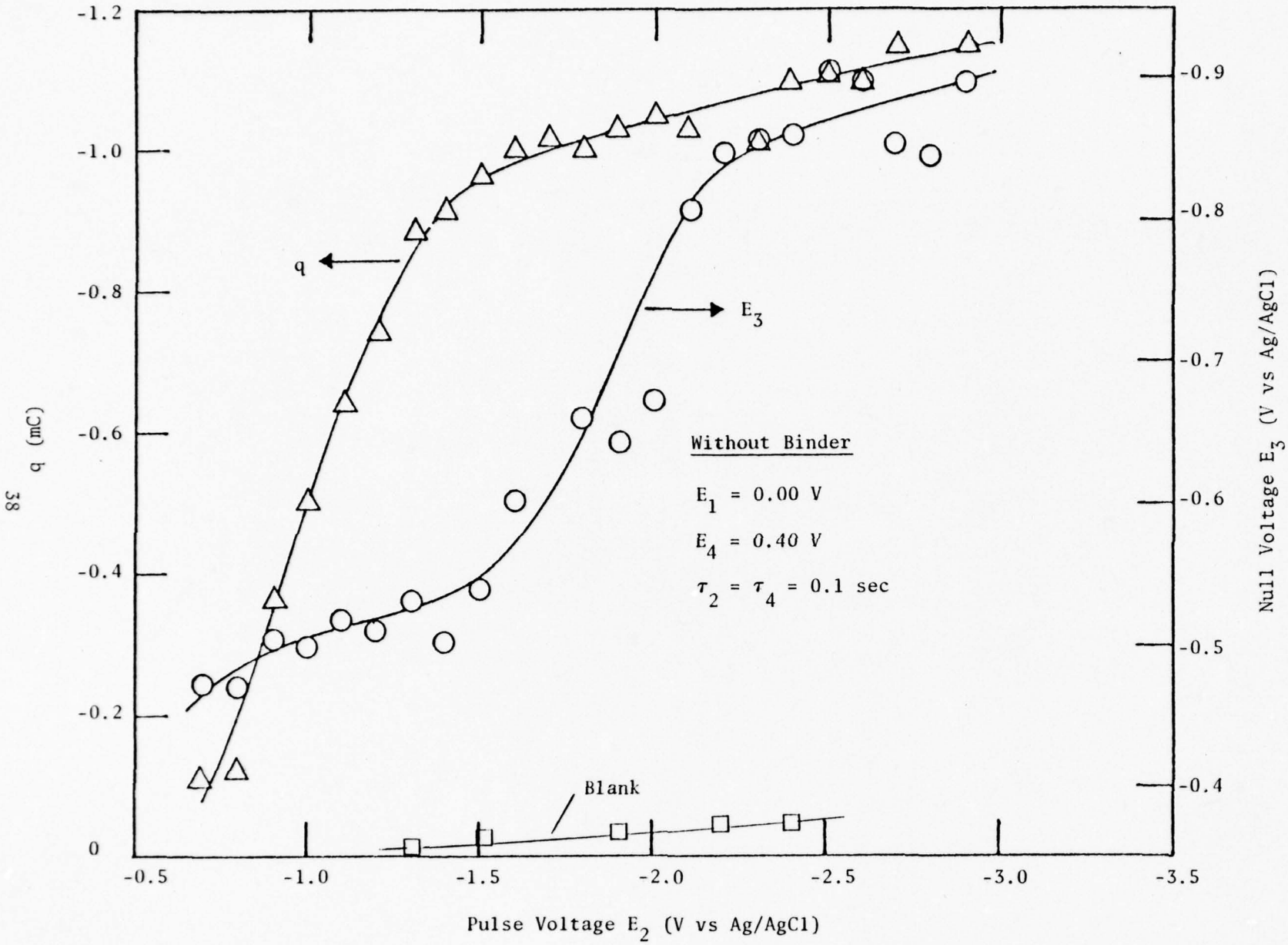


Figure 20. Pulse Response of Electrode 10 Switching from Green toward Blue

The pulse measurements revealed a number of interesting characteristics that were not evident under steady-state conditions. These are discussed below.

3. Limiting Charges and Limiting Null Potentials

The charge transferred in switching the display electrode from E_1 to E_2 tended to reach a limiting value as E_2 increased in the positive or the negative direction. Plateaus also occurred in the null potential plots. This behavior, coupled with the spectral observations, indicated that definite charges and corresponding open-circuit potentials were associated with the different color states of the dye.

The effect of varying pulse time was examined in the experiment represented by Figure 15. The time τ_2 was varied in this case from 0.1 to 0.2 sec, while E_2 was held constant at +1.0 V. The charge for the green-to-red transition increased from 0.3 to 0.4 mC near τ_2 = 0.14 sec and remained constant thereafter. Figure 14 for the same electrode indicates that the same limit of 0.4 mC was reached in 0.1 sec with $E_2 > 1.3$ V. Since the positive pulse ranges for the other electrodes extended to at least 1.6 V, it may be assumed that the correct limiting charges were attained within the usual τ_2 interval of 0.1 sec.

4. Use of Transparent Binder

The negative (blue) region of the potential scale was explored less extensively than the positive (red) because there was some difficulty in maintaining contact between the dye and the tin oxide in the blue and violet states.* This problem is reflected in Figure 19, for Electrode 9. A decrease in charge began suddenly near E_2 = -1.1 V, and the color change was incomplete. The film usually was more adherent when the tin oxide was carefully cleaned and an organic binder was applied. Electrodes 4 and 10 behaved satisfactorily in the blue region, although the latter had no binder.

*In a more recent investigation, this problem appears to have been solved by the use of an improved film deposition process.

5. Voltage Thresholds from Pulse Measurements

The pulse potential E_2 is an operational variable that depends on the switching time requirement and the series resistance that must be overcome. The null potential E_3 is a more basic parameter of the system. It is the switching voltage for the limiting case of zero resistance or very long switching time. By plotting the charge against E_3, one obtains a function corrected for the instantaneous IR drop at the end of the time τ_2. Charge density plots of this type are given in Figures 21 through 24. In accordance with convention, the negative charges, due to electrons flowing into the electrode from the external circuit, are plotted downward on these four figures, and the increasingly negative, or cathodic potentials are plotted toward the left.

Threshold potentials for the charge injection processes were found in the q vs E_2 curves (Figures 10 through 20). They were more sharply revealed, however, by the steep S-shaped plots of q/A vs E_3 in Figures 21 through 24. These curves have important implications, since a threshold response is very desirable in the operation of a matrix display through multiplexed circuitry.[10] Although the question of matrix addressing for phthalocyanine displays will require further investigation, it is now clear that the electrical thresholds are very pronounced. Correlations of the charges with the color transitions are discussed in Section III-D.

6. Charge Density Relationships

The limiting charge densities $(q/A)_{lim}$ read from the curves in Figures 21 through 24 are recorded in Table 4. Also given for each film are the ratio of the limiting charge density to the initial optical density $(OD)_f$ in the dry state, and the corresponding number of electrons per molecule. In Figure 25, the limiting charge density ratio for the green-to-red transition is shown as a function of $(OD)_f$, which is proportional to the film thickness. Several interesting observations can be made from

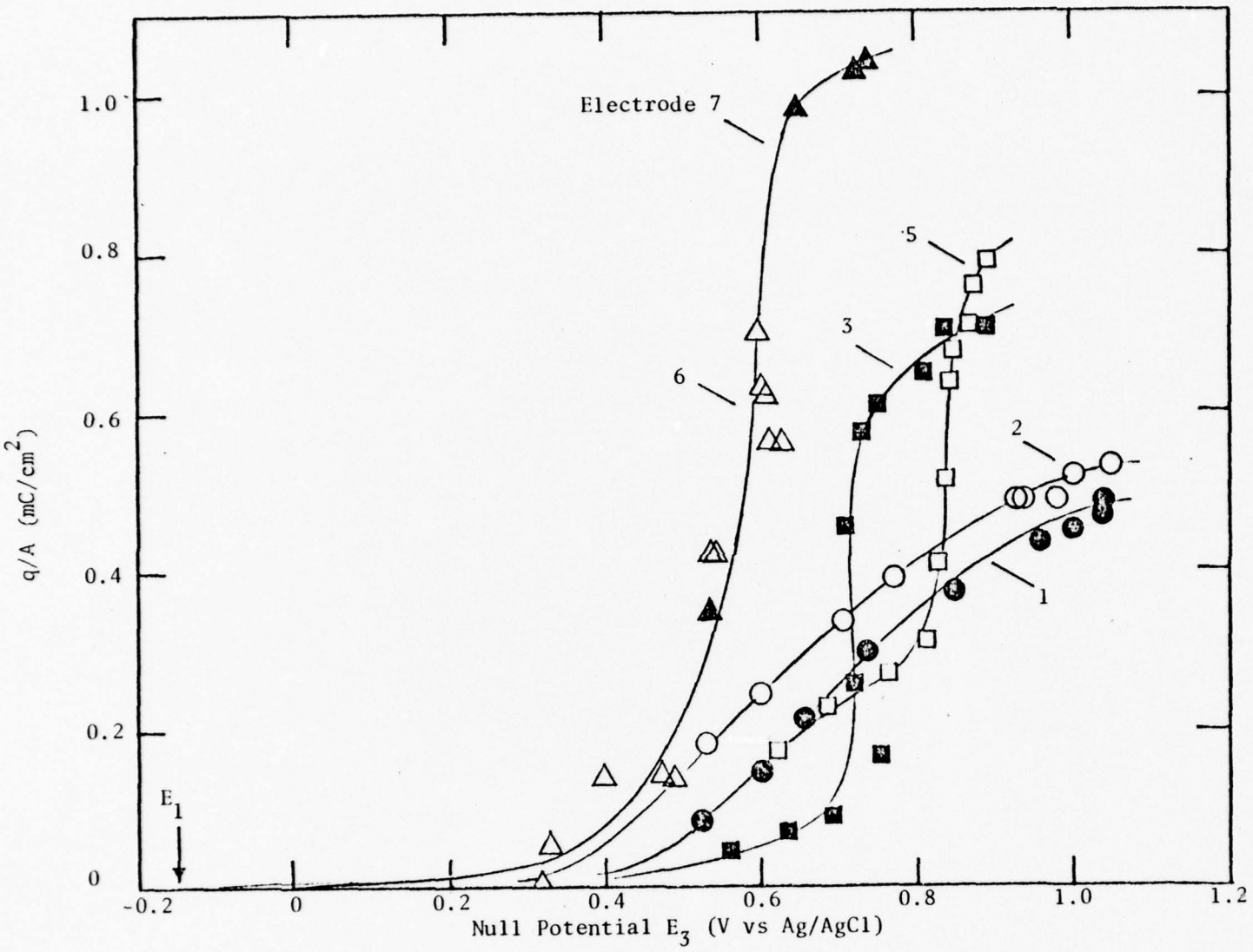


Figure 21. Dependence of Charge Density on Null Potential with Binder Present, Switching from Green toward Red

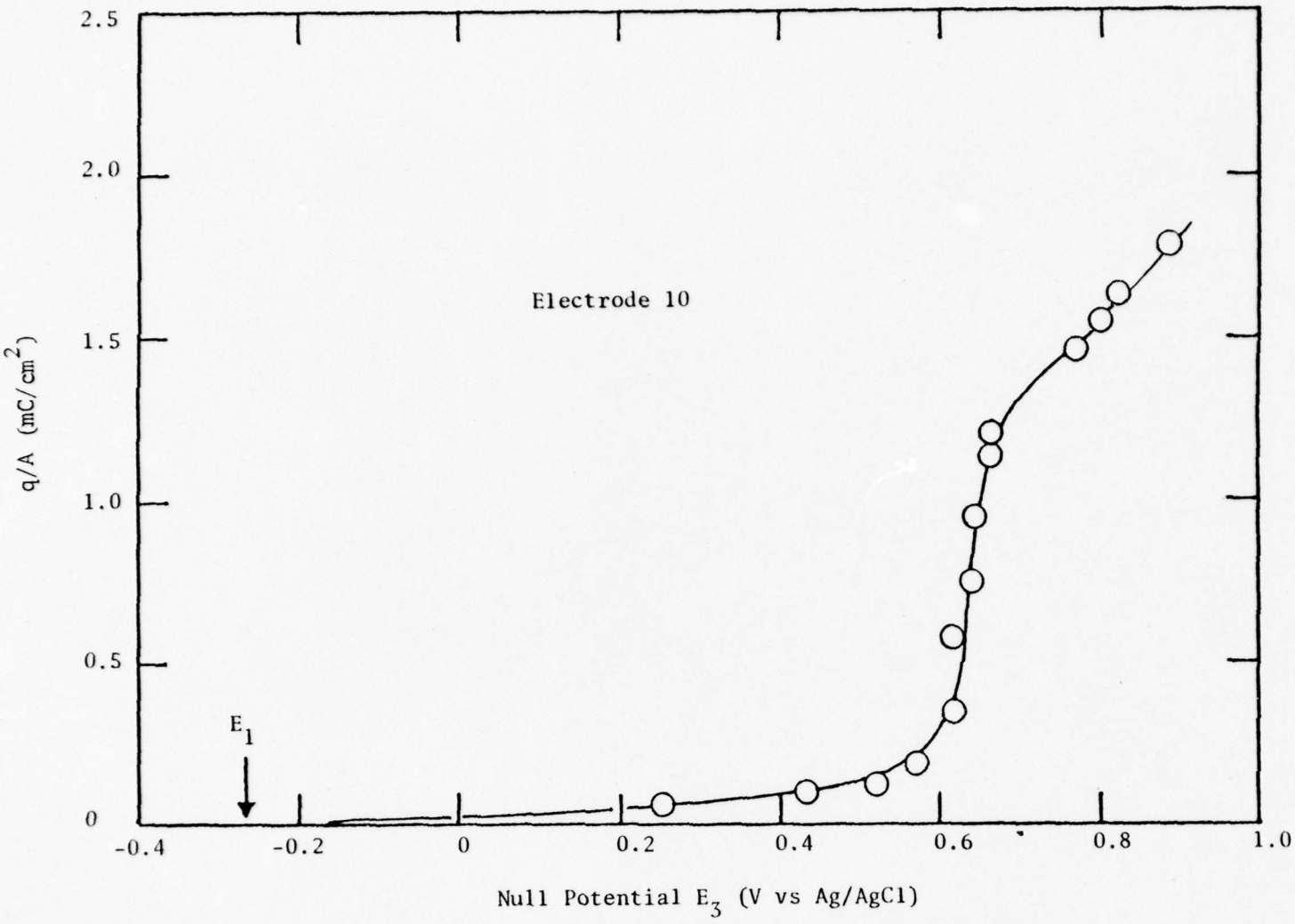


Figure 22. Dependence of Charge Density on Null Potential with Binder Absent, Switching from Green toward Red

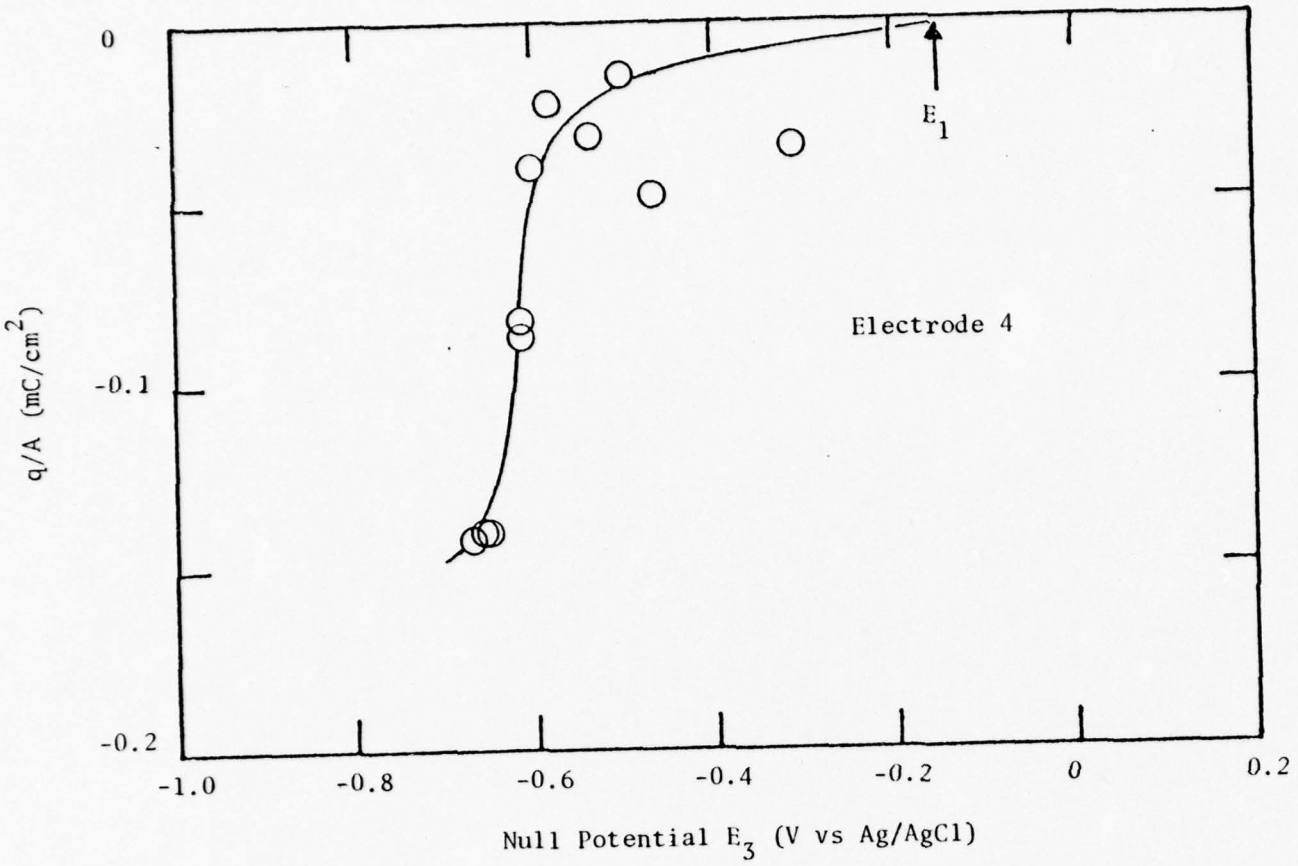


Figure 23. Dependence of Charge Density on Null Potential with Binder Present, Switching from Green toward Blue

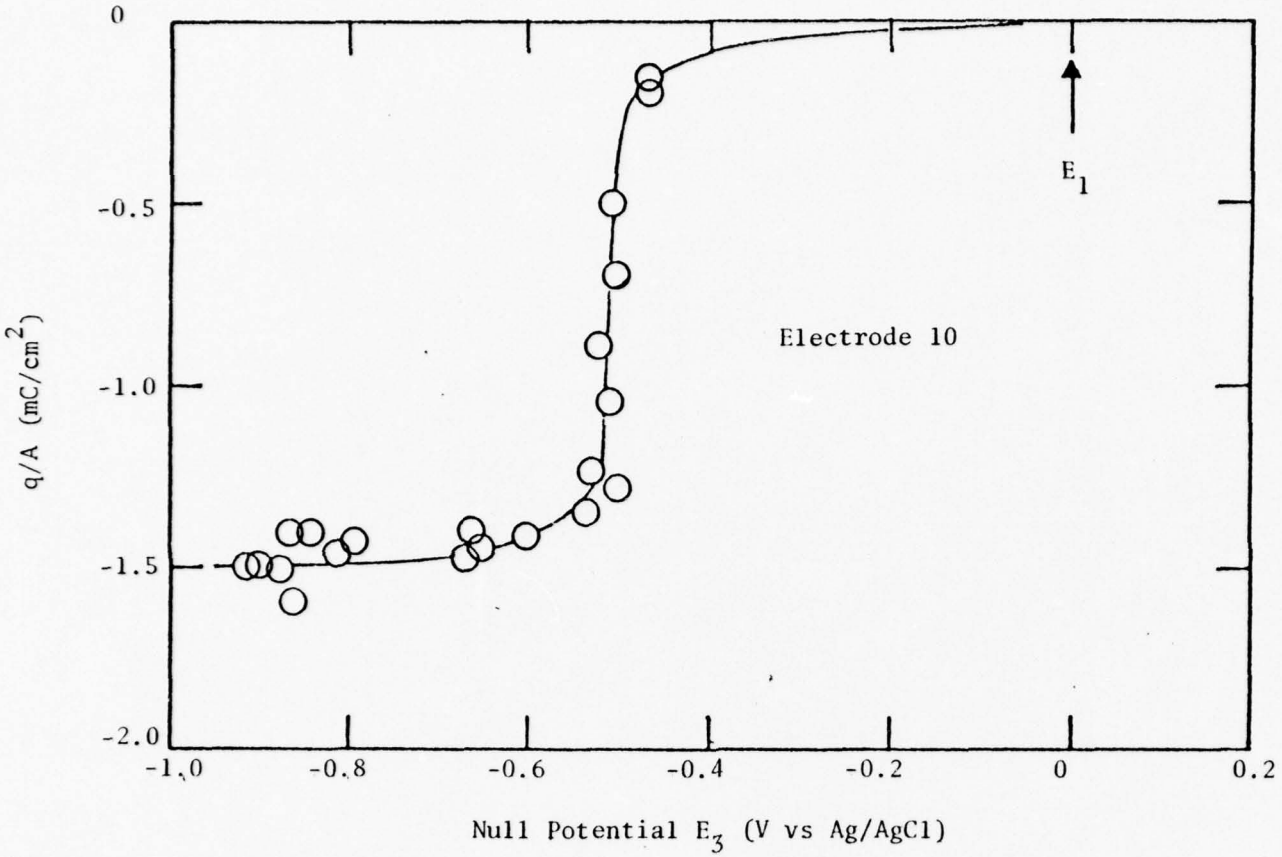


Figure 24. Dependence of Charge Density on Null Potential with Binder Absent, Switching from Green toward Blue

TABLE 4

CHARGE DENSITY CHANGES IN ELECTROCHROMIC TRANSITIONS[a]

Color Transition	Electrode	Collodion Binder	$(OD)_f$[b]	$(q/A)_{lim}$[c] (mC/cm^2)	$(q/A)_{lim} \times (1/OD)_f$ (mC/cm^2)(1/OD)	n (electrons/ molecule)
Green/Red	1	Present	0.280	0.48	1.71	1.5
	2	Present	0.290	0.53	1.83	1.6
	3	Present	0.495	0.70	1.41	1.2
	5	Present	0.550	0.79	1.44	1.2
	7	Present	0.805	1.04	1.29	1.1
	10	Absent	1.55	1.40	0.90	0.8
Green/Blue	4	Present	0.510	-0.140	-0.274	0.24
	10	Absent	1.55	-1.24	-0.80	0.7
Green/Violet	10	Absent	1.55	-1.48	-0.95	0.8

[a] From pulse measurements; taking q = 0 in the green state at E_1.

[b] Initial optical density of dry film at 668-nm absorption peak.

[c] Limiting charge density from Figures 21 through 24.

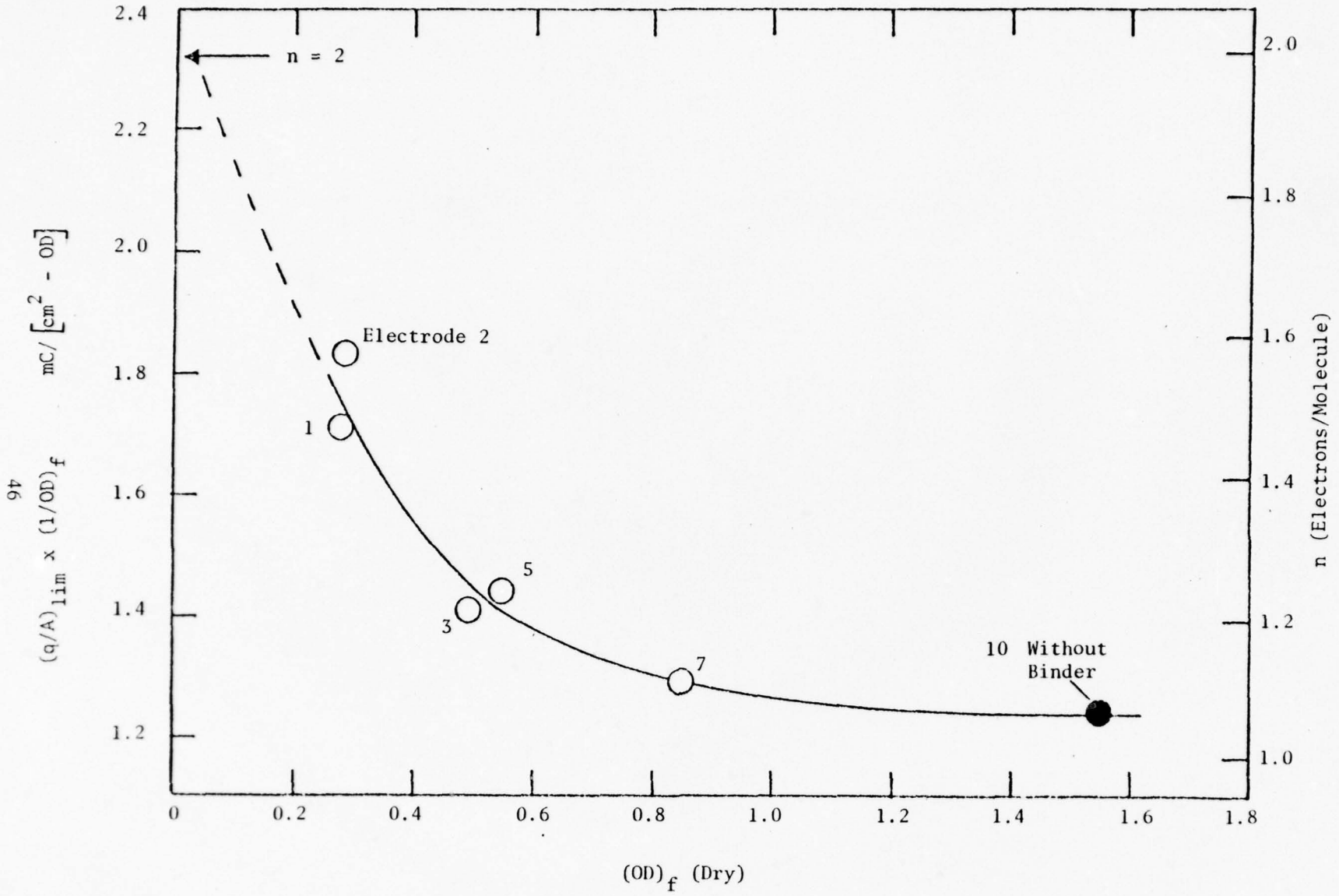


Figure 25. Dependence of Limiting Charge Density Ratio on Film Thickness for Green-to-Red Transition

this plot: (a) The point for Electrode 10, without the binder, appears to fall on a smooth curve with those for electrodes containing the binder. (b) Electrode 3, with a larger film area, also fits on this curve. (c) Extrapolation to zero film thickness suggests a limiting charge of two electrons per molecule, while for the thicker films the charge approaches n = 1.

The green-to-blue transition required an apparent 0.7 electron per molecule in Electrode 10, which was a rather thick film, and the corresponding green-to-red value was 0.8. In contrast, the blue-to-violet transition for the same electrode involved only an incremental 0.1 electron per molecule. The binder may have decreased the charge uptake at negative potentials (compare Electrodes 4 and 10), but more data are needed to verify this point. An investigation of the electrochromic mechanisms in the diphthalocyanines is planned under another program.

7. Comparison with Model Circuit

A time constant RC may be calculated from the relationship

$$RC = \tau_2 / \ell n \left[(E_2 - E_1) / (E_2 - E_3) \right] \qquad (3)$$

which is derived for the model circuit in Figure 9 by noting that

$$q = C(E_2 - E_1) \left[1 - \exp(-\tau_2 / RC) \right] = C(E_3 - E_1). \qquad (t = \tau_2) \quad (4)$$

It is obvious from the shapes of the curves in Figures 21 through 24 that the capacitor model is a rough approximation. The charge does not rise linearly with potential, as in a true capacitor, but follows, instead, an S-shaped curve through the transition region. Analysis of the pulse data for Electrode 2 according to Equation 3 yielded the plot shown in Figure 26. The four time constant values in the interval from $E_2 = 0.2$ to $E_2 = 0.7$ averaged 62 msec. As expected, the points beyond the red-to-tan transition fell on a different curve, since the effective capacitance then was much lower. This model would be more appropriate on a differential basis, with smaller intervals between E_1 and E_2.

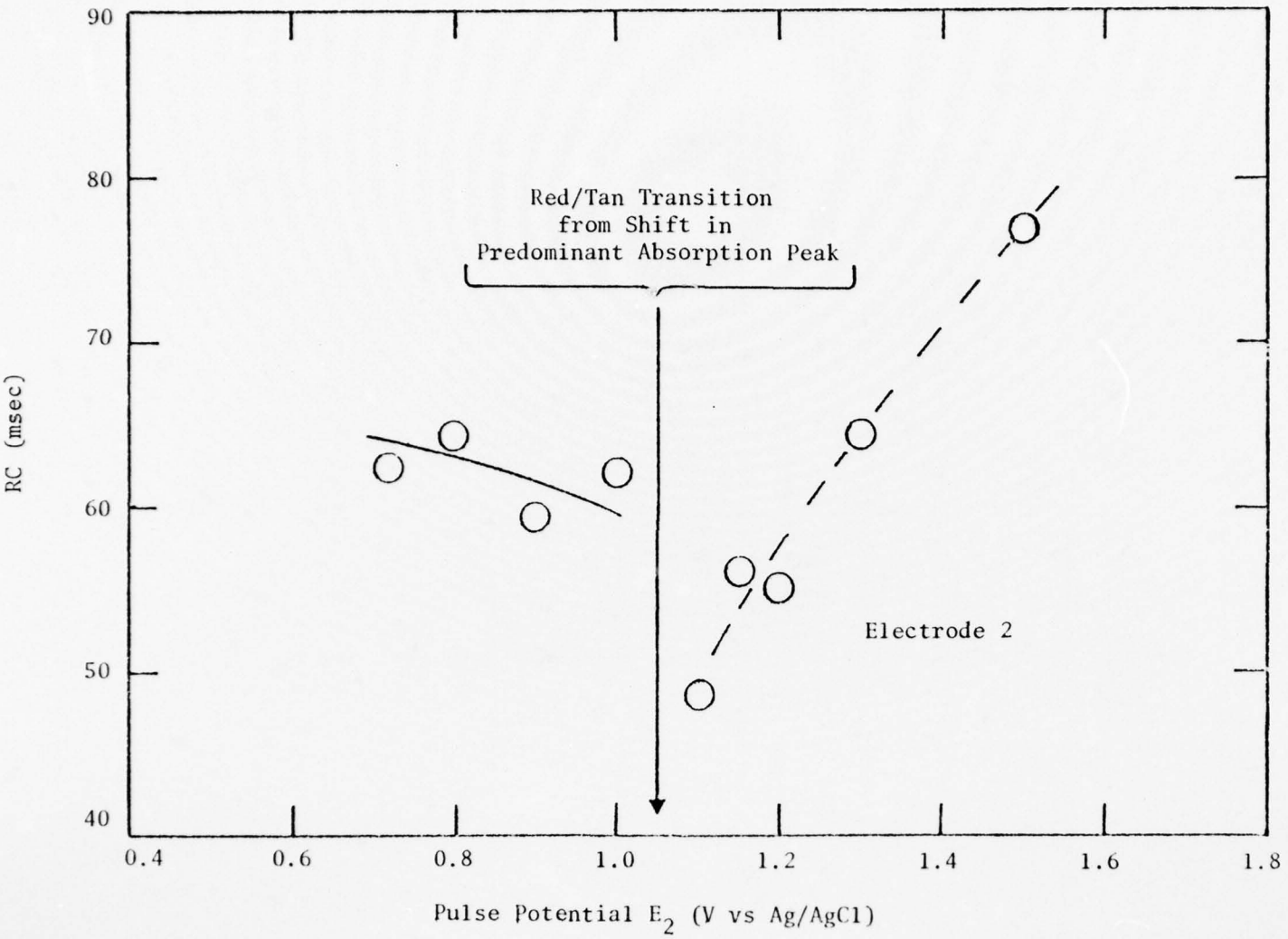


Figure 26. Time Constant Calculated from Resistance-Capacitance Model

Apparent capacitance values may also be estimated from the plots of q/A vs E_3, taking $\Delta(q/A)/\Delta E_3$ along the rising part of the curve. A capacitance of 610 $\mu f/cm^2$ was estimated in this way for Electrode 2. Such high capacities are not unusual in electrochemical systems. For the time constant of 62 msec, the corresponding series resistance (considering the area of the circular deposit) would be about 140 ohms. The tin oxide plate could account for about 30 ohms in series with the dye film. Further study will be needed to develop a more detailed electrical model.

D. CORRELATION OF STEADY-STATE AND PULSE RESPONSES

Figure 8 presents a general scheme for correlation of the steady-state, pulse, and optical data. The upper section of this figure contains plots of the charge density ratio against the null potential for Electrodes 4 and 5 (replicates), with the binder, and Electrode 10, without the binder. The colors noted in the upper section were observed visually for Electrode 10. This rather dense film displayed more definite yellow shades than most of the specimens examined, and the yellow was accompanied by a small, but definite, peak in the current-voltage curve (Figure 7). These observations suggest that clear yellows could be produced consistently by more careful structuring of the $LuH(Pc)_2$ film. Tan shades resembling manila paper, which are noted in the lower section of the figure, are more typical of the lutetium system in its present stage of development.

It is clear from Figure 8 that the charge transitions in the pulse responses coincide with the spectral shifts observed under steady-state conditions. The transition potentials obtained by the two methods are compared in Table 5.

TABLE 5

ELECTROCHROMIC TRANSITION POTENTIALS

Predominant Color[a]	Method of Evaluation		
	Steady State	Pulse	
	Spectral Shift[b]	q/A vs E_3	Conditions
	Transition Potential (V vs Ag/AgCl)		
Red			
→	1.05		
Yellow-Tan		0.64, 0.84	Without binder (Fig. 22)
		0.58 to 0.84	With binder (Fig. 21)
→	0.50		
Green			
→	-0.50	-0.51	Without binder (Fig. 24)
		-0.61	With binder (Fig. 23)
Blue			
→	-0.95	--	Incremental charge very small
Violet			

[a]For further color details, see Figure 8 and Table 6.

[b]From shift of predominant absorption wavelength, Figure 8.

E. QUANTITATIVE COLOR CHARACTERIZATIONS

Colors matched with the Munsell standards under daylight conditions are recorded in Table 6. The corresponding CIE designations were obtained from the conversion table in Reference 11. These colors are representative of lutetium diphthalocyanine, but they do not include all of the shades available with that compound.

The visual effects are outstanding, even at this early stage of development. Green, blue, and purple were found at high saturation levels (chroma of 10) on the respective Munsell charts. The red (5 R 6/8) was not as pure a color in this film. Clearer, saturated reds approaching 5 R 6/12 have been produced on other occasions, however. The variations in the reds may be associated with the morphology of the dye film or the substrate. These intense colors are all well balanced against one another with respect to their visual effects, and they produce pleasing dark-on-light contrasts with the more neutral shades represented here by 2.5 GY 7/2. This relatively light color contained a significant gray component from the tin oxide. It should be possible to avoid the gray effect through the use of improved transparent substrates.

TABLE 6

DISPLAY ELECTRODE COLORS EVALUATED BY THE MUNSELL SYSTEM[a]

Applied Potential V vs Ag/AgCl	Munsell Notation[b]		CIE Notation[c]		
	Hue	Value/Chroma	Y	x	y
1.15	5 R	6/8	0.3005	0.418	0.325
0.60	7.5 R	6/4	0.3005	0.363	0.329
0.40	2.5 GY	7/2	0.4306	0.333	0.357
0.00	5 G	7/6	0.4306	0.280	0.372
-0.40	5 BG	7/8	0.4306	0.235	0.333
-0.60	2.5 BG	6/10	0.3005	0.215	0.358
-0.80	10 BG	7/8	0.4306	0.223	0.301
-0.90	5 PB	5/10	0.1977	0.208	0.204
-1.00	5 PB	4/10	0.1200	0.192	0.184
-1.20	2.5 P	5/10	0.1977	0.266	0.208

[a] OD = 0.940 for dry film at 680 nm; colors observed on 2.9 cm^2 area.

[b] Hue includes color abbreviations R (red), G (green), Y (yellow), B (blue), P (purple); high value corresponds to a light color; high chroma represents high saturation.

[c] Y is luminous reflectance; x and y are chromaticity coordinates.

IV. CONCLUSIONS

Lutetium diphthalocyanine is compared with other electrochromics in Table 7. Previous research[7] had shown this system to have multicolor capability, fast response, nonvolatile memory, and the prospect of long cycle life. The present investigation led to the following conclusions:

1. It was confirmed that a complete spectrum of visual colors is produced in lutetium diphthalocyanine by the application of d-c signals ranging from +1.3 to -1.3 V.* Several of these colors reach a chroma of 10 on the Munsell scale.

2. Steady-state electro-optical data revealed a series of spectrally distinct states in the electrochromic material. Transformations between these states occur at characteristic electrochemical potentials.

3. Pulse responses showed that definite charge increments are associated with the spectral shifts. Pronounced thresholds were found in the plots of charge density versus potential.

4. For a given color transition, the switching charge density is a nonlinear function of the dye-film thickness. In green-to-red switching, the charge can approach 2 electrons per molecule for films containing less than 4 $\mu g/cm^2$ of dye, and 1 electron per

---

*Potentials corresponding to the various colors are reported with reference to the Ag/AgCl electrode in 0.1 M KCl. When the display electrode is at zero on this scale, it is green. A display cell can be arranged so that the total input voltage is the difference between the potential for the background color and that for the contrasting color of the character.

molecule for films containing more than 20 $\mu g/cm^2$. Some transformations producing good color contrast, such as tan to blue-green, are attainable with about 0.5 electron per molecule.

5. As a first approach to an equivalent circuit model, the display electrode can be represented by a resistor and a large capacitor in series. The time of the optical response is controlled by the rate at which the capacitor is charged or discharged. A typical switching time in present experimental cells is 50 msec.

6. Display potentialities of this system include imaging and graphic projections based on combinations of intense colors such as red, blue, green, and purple, as well as alphanumeric panels with dark-on-light contrasts such as dark blue on tan.

7. Further research and development work on the diphthalocyanine electrochromics is strongly recommended.

TABLE 7

COMPARISON OF ELECTROCHROMIC DISPLAY SYSTEMS

Characteristic	Electrochromic Material		
	Lutetium Diphthalocyanine[a]	Tungsten Oxide[12,14]	Viologen[12,13]
Colors	Wide range of colors with a single material by varying applied voltage.[b]	Blue on white	Purple on white
Input Signal	<1.5 V d-c	~1 V d-c	1 to 2 V d-c
Transient Behavior	Self-limiting response; resembles capacitor	Progressive darkening under applied signal; color centers eventually saturate.	Progressive darkening until film resistance builds up.
Writing or Erasure:			
Time Near 25°C	<50 msec; minimum time not yet determined.	~0.2 sec (H^+ type)[14] Inherently slow due to solid-state diffusion process.	10 to 100 msec at 25°C; liquid-diffusion limited; slower at low temperatures.
Charge Density	~0.5 to 1 mC/cm^2	5 to 20 mC/cm^2	5 to 10 mC/cm^2
Energy Density	~0.5 to 1.5 mJ/cm^2	5 to 20 mJ/cm^2	5 to 20 mJ/cm^2
Temperature Range	5° to 63°C without apparent change in speed; ~40°C expected with further development	--	(Aqueous)

[a]Electrical characteristics of $LuH(Pc)_2$ depend on the color combination selected.

[b]Can be front or back lighted.

(TABLE 7. Continued)

Characteristic	Electrochromic Material		
	Lutetium Diphthalocyanine	Tungsten Oxide[12,14]	Viologen[12,13]
Memory	Several hr; not yet optimized.	Yes	1 Mo
Cycle Life	$>10^4$ in early tests; improvement in progress.	2×10^6 [14]	$>10^5$
Electrolyte	Aqueous KCl (Nonhazardous)	Usually H_2SO_4 gel (corrosive; hazardous on contact).	Aqueous KBr (Nonhazardous).

V. RECOMMENDATIONS

Rockwell International plans to undertake a basic mechanism study on the electrochromic diphthalocyanines in the near future. In continuing development of this new technology for display applications, the following areas should be investigated:

1. Resolution capability for line arrays and matrices; cell responses under multiplexing conditions.
2. Low-temperature operation.
3. Cycle-life improvement.
4. Additional diphthalocyanine compounds.
5. Cell components, including electrode substrates of high transparency, counter electrodes, electrolytes, and optical background materials.

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