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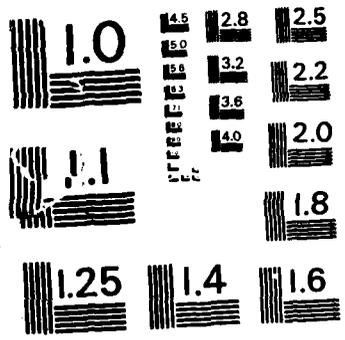
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SEMICONDUCTOR/SOLID ELECTROLYTE JUNCTIONS FOR OPTICAL
INFORMATION STORAGE.
ELECTROCHROMIC EFFECTS ON HEPTYLVILOGEN INCORPORATED WITHIN A
SOLID POLYMER ELECTROLYTE CELL

By

Anthony F. Sammells and Nirupama U. Pujare

Accepted for publication in

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May 15, 1986

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Aurora, IL 60505

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Solid-state electrochromic cells of the configuration $\text{SnO}_2 / \text{poly(AMPS)} / \text{Nafion} / \text{poly(AMPS)} / \text{SnO}_2$ $\text{Glass} / + \text{HV}^{2+} / 117 / + \text{CeCl}_3 / \text{Glass}$ $+ \text{NaPF}_6 / + \text{NaPF}_6$ were prepared. Upon subjecting the (HV ²⁺) working electrode compartment to a cathodic scan, two distinct reduction peaks were observed at respectively -1.74 and -1.90V versus the CeCl ₃ /SnO ₂ reference/counter electrode. This corresponded to the formation		

20: ABSTRACT Continued

of respectively, the radical and diradical cation species of HV^{2+} . This electrochromic cell was found to be highly electrochemically reversible as monitored by a He/Ne laser beam (583nm) transmitted through the bulk of this semi-transparent thin film solid-state cell.

Cells were also prepared using n-TiO₂ as the working electrode in contact with the HV^{2+} compartment. A progressive trend to more negative n-TiO₂ flat band potentials (V_{FB}) was observed between the initially prepared cell and the first and second electrochemically formed HV^{2+} radical cation species.

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EXPERIMENTAL

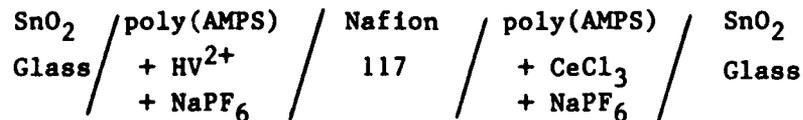
Electrochemical measurements were performed using either a Stonehart Associates BC 1200 or a Wenking LT 78 potentiostat controlled by a BAS Model CV-1B cyclic voltammetry unit. Current-voltage data were recorded on a Houston Instruments Omnigraphic Model 154-046 X-Y recorder.

Single crystal n-TiO₂ was initially heated under hydrogen at 800°C for several hours to enhance its n-doping characteristics. Ohmic contact to the back surface of the crystal was made by the introduction of gallium-indium eutectic into the freshly etched (c.H₂SO₄) surface. Current collection was accomplished with a nichrome wire and silver epoxy (Epoxy Technology, Inc.), and the assembly cured at 150°C for 1 hour. Current collection to the SnO₂ conducting glass was also performed as above. Conductance and capacitance measurements for admittance spectroscopy analysis of the polymer-semiconductor interface from which n-TiO₂ V_{FB} values were obtained were performed using an HP-4276A digital LCZ meter between 100 and 20kHz.

RESULTS AND DISCUSSION

There has been a continuous interest over the last several years to investigate the viologens¹ as the basis for electrochromic alphanumeric displays using both aqueous and non-aqueous liquid electrolytes²⁻⁴. These materials are based upon the alkyl derivatives of 4,4' dipyridyl. Electrochemical reduction of, for example, 1,1' diheptyl-4,4' bipyridyl (heptyl viologen) dibromide in aqueous KBr containing electrolyte, has been shown to result in the formation of insoluble red radical and diradical cation species at the cathode^{5,6}. These processes have been found dependent upon both the anion present in the supporting electrolyte and the cathode material used as a substrate for the reduced heptyl viologen radical species. For example, stable red deposits have been obtained on platinum electrodes in fluoride or sulfate containing electrolytes, whereas no color change is observed when gold is used as the cathode⁵. Electrochromic devices based upon these electrochemically reversible viologen redox couples would greatly benefit by their incorporation within solid-state solid polymer electrolyte (SPE) cells. By this means, relatively thin displays might be feasible compared to their aqueous electrolyte analogs.

Here we wish to discuss some recent work from our laboratory on solid-state electrochromic cells in which heptyl viologen (HV^{2+}) was initially incorporated within the homopolymer poly-2-acylamido-2-methyl propane sulfonic acid (poly(AMPS)). In this cell, separation between the electrochromic working electrode (HV^{2+} in poly(AMPS)) and the reversible counter electrode ($CeCl_3$ in poly(AMPS)) was achieved by using the insoluble copolymer perfluorosulfonic acid (Nafion). Current collection from each electrode compartment was via the use of SnO_2 conducting glass. The solid-state cell configuration used in this work can be represented by:



These cells were prepared by applying a thin coating (≈ 2 microns) of poly(AMPS) (as a 10% solution) containing 0.04M HV^{2+} and 0.001M $NaPF_6$ as a supporting electrolyte, onto a SnO_2 conducting glass substrate electrode. This electrode was permitted to initially dry for an hour. This was followed

by being directly contacted to an initially Na^+ exchanged Nafion 117 membrane. The counter electrode used in this cell consisted of a similar poly(AMPS) film introduced onto a SnO_2 conducting glass electrode, possessing 0.04M CeCl_3 to maintain redox electrochemistry upon cycling and 0.001M NaPF_6 as a supporting electrolyte.

Both of the above half-cells were pressed together and the resultant solid-state cell permitted to dry a further 30 minutes. This cell was then subjected to cyclic voltammetry (CV) measurements as shown in Figure 1. The logistics associated with these thin SPE cells inhibited the convenient introduction of a reference electrode. As a consequence, electrochromic working electrode potentials were recorded as a function of the CeCl_3 containing SnO_2 conducting glass electrode compartment. Upon subjecting the working electrode compartment to an initial cathodic scan, two distinct reduction peaks were observed at respectively -1.74 and -1.90V versus the $\text{CeCl}_3/\text{SnO}_2$ glass electrode compartment. The initial reduction peak at 1.74V resulted in the appearance of a distinct violet film which became darker at the second reduction potential (-1.9V).

Upon subjecting the electrochromic working electrode to a subsequent anodic scan, two corresponding oxidation peaks were observed at -1.82 and -1.0V resulting in the complete removal of the violet color. The two initial reduction peaks corresponded to the formation of, respectively, the radical and diradical cation species of heptyl viologen resident within the poly(AMPS), presumably located in close proximity to the SnO_2 electrode. Further anodic scan past the initial open-circuit potential (which was typically in the \approx 100mV range) resulted in an oxidation peak at 1.6V. This latter peak was probably associated with the $\text{Ce}^{3+}/\text{Ce}^{+4}$ redox couple within the counter electrode compartment.

The observation by others⁴ that the half-wave potential for HV^{2+} reduction is dependent upon the nature and concentration of anion species within the supporting electrolyte is related to the solubility product of the reduced radical cation species as defined by the product (dipy^+) (X^-). It is precipitation of this red or violet species at or within close proximity of the cathode substrate which is responsible for the observed electrochromic effects in SPE cells discussed here. The initial electrochemical reduction step occurring in this cell leading to the radical cation can be represented

by:



which is followed by chemical formation of the colored reaction product via



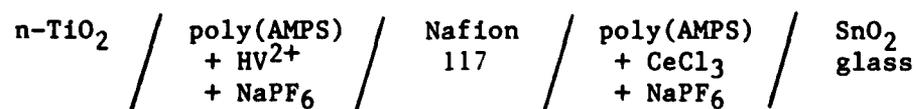
This can, in part, explain the significantly different redox potentials found for HV^{2+} reduction in acetonitrile (where the reduced radical cation is soluble) and water⁷ where in the latter electrolyte, strong association with anionic species can occur leading to precipitation. The second reduction step leading to the formation of the diradical species can be represented by:



The observed more intense electrochromic effect during the second reduction process was probably due to the simultaneous and continuous formation of the initial radical species at this more negative potential region.

The electrochemical reversibility of this electrochromic effect was investigated by monitoring changes in the relative absorption of an initially 1mW He/Ne laser beam (583nm) after being passed directly through this thin SPE cell, as a function of applied potential. The transmitted laser beam intensity was detected using a Hamamatsu PIN photodiode amplified by an RCA 3140 Op. Amp. Figure 2 summarizes the electrochemical cycling characteristics of these electrochromic cells as a function of varying potentiostatted charge/discharge voltages. These were varied between $\pm 0.75\text{V}$ (curve a), $\pm 1.0\text{V}$ (curve b), $\pm 1.25\text{V}$ (curve c), $\pm 1.5\text{V}$ (curve d) and $\pm 2.0\text{V}$ (curve e). Preliminary cells have demonstrated excellent reversibility in excess of a hundred cycles.

To investigate the influence of heptyl viologen and its reduced radical cation species on the $n\text{-TiO}_2/\text{HV}^{2+}$, poly(AMPS) solid-state junction, cells of the general configuration



were prepared. A typical CV from this cell is summarized in Figure 3.

Because of the lower electronic conductivity of $n\text{-TiO}_2$ compared to SnO_2 coated glass, the diradical cation reduction peak is not readily discernable upon initial cathodic sweep. Formation of radical and diradical species become

evident however upon subsequent anodic sweep by a shoulder at $\approx -2.25V$ and a peak at $-1.35V$ vs. the $CeCl_3/SnO_2$, reference/counter electrode. Again, the electrochromic effect at the interface was found to be reversible and distinct as with the previously discussed electrochemical cell. $n-TiO_2$, V_{FB} values were measured from impedance and admittance measurement techniques by use of the appropriate equivalent circuit representative of the $n-TiO_2/HV^{2+}$ interface region. Here parameters measured were based upon resistive or capacitive elements arranged in either series or parallel configurations. The magnitude of these parameters were dependent upon the measurement frequency. This is in comparison to the equivalent circuit elements⁸ which are passive and can be used to gain information on surface-state energies and Faradaic charge transfer rates, etc. As we have discussed previously, a technique has been developed for the measurement of frequency independent Mott-Schottky parameters⁹. This technique was used to obtain Mott-Schottky data from which V_{FB} values for $n-TiO_2$ at its interface with reduced HV^{2+} species could be determined. In this analyses, the double layer capacitance (C_{dl}) was assumed to be much larger than C_{sc} (i.e. $C_{dl} \gg C_{sc}$) although some components of C_{dl} may be present in the measured C_{sc} values. The simplest equivalent circuit configuration of the semiconductor/SPE interface region consists of the space charge capacitance (C_{sc}) connected in series with the bulk conductance G_B ¹¹ (Figure 4). The admittance of this circuit was given by the equation:

$$Y_x = \frac{\omega^2 G_B C_{sc}^2 + j\omega G_B^2 C_{sc}}{G_B^2 + (\omega C_{sc})^2}$$

where ω is the angular frequency ($2\pi f$). The measured parameters, G_p (parallel conductance) and C_p (parallel capacitance) were obtained directly using an HP-4276 LCZ meter. The related admittance was obtained by use of the relationship:⁹

$$Y_z = G_p + j \omega C_p$$

Relating the real and imaginary components of Y_x and Y_z gives:

$$C_p/\omega = \frac{\omega C_{sc}^2 G_B}{G_B^2 + (\omega C_{sc})^2}$$

and

$$\omega C_p = \frac{\omega G_B^2 C_{sc}}{G_B^2 + (\omega C_{sc})^2}$$

Plots of G_p/ω vs. ω and ωC_p vs. ω will exhibit maxima at a frequency $\omega_{\max} = G_B/C_{SC}$ and the desired parameters C_{SC} and G_B can be obtained through the following relationships:

$$G_p/\omega_{\max} = C_{SC}/2$$

and

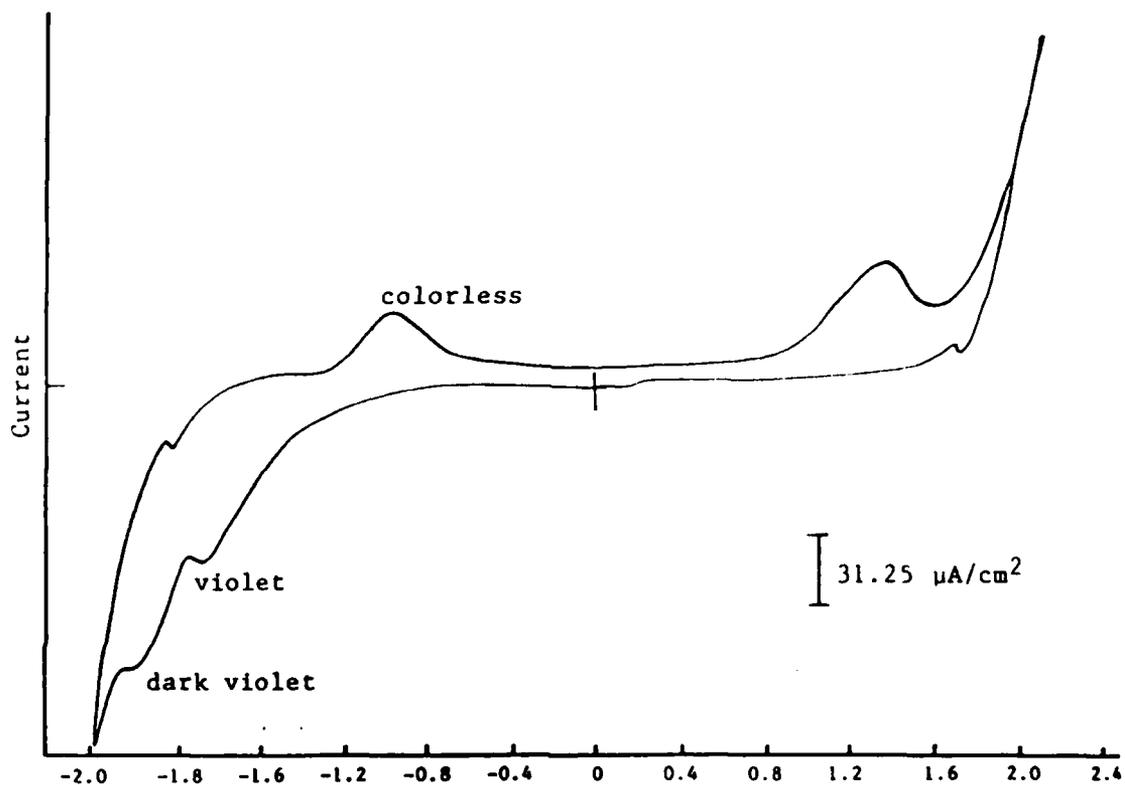
$$\omega C_{p_{\max}} = G_B/2$$

C_{SC} obtained in this manner was frequency independent and thus a plot of C_{SC} values obtained at varying bias voltages yielded frequency independent Mott-Schottky plots for the determination of V_{FB} .

Figures 5-7 compare Mott-Schottky data obtained using this technique for the $n\text{-TiO}_2/\text{HV}^{2+}$, poly(AMPS) interface region for respectively the as made junctions (Figure 5), after electrochemical reduction of HV^{2+} to the radical cation by potentiostatting at -1.35V (Figure 6), and after reduction to the diradical cation at -2.25V . All potentials were measured versus the $\text{CeCl}_3/\text{poly(AMPS)}$ counter/reference electrode. As can be seen from this data, there is a progressive trend to more negative V_{FB} values for $n\text{-TiO}_2$ as HV^{2+} is reduced. Similar observations are found with liquid-junction PEC cells using $n\text{-TiO}_2$ as an electrode.

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Electrode voltage (volts) vs. SnO₂ conducting glass. Reference/counter electrode.

Figure 1. CV of cell

Polyamps + 0.04M Heptyl viologen
+ 0.001M NaPF₆ on
SnO₂ conducting glass

Nafion 117
membrane
Na⁺

Polyamps + 0.04M CeCl₃
+ 0.001M NaPF₆ on
SnO₂ conducting glass

Sweep rate - 50mV/sec

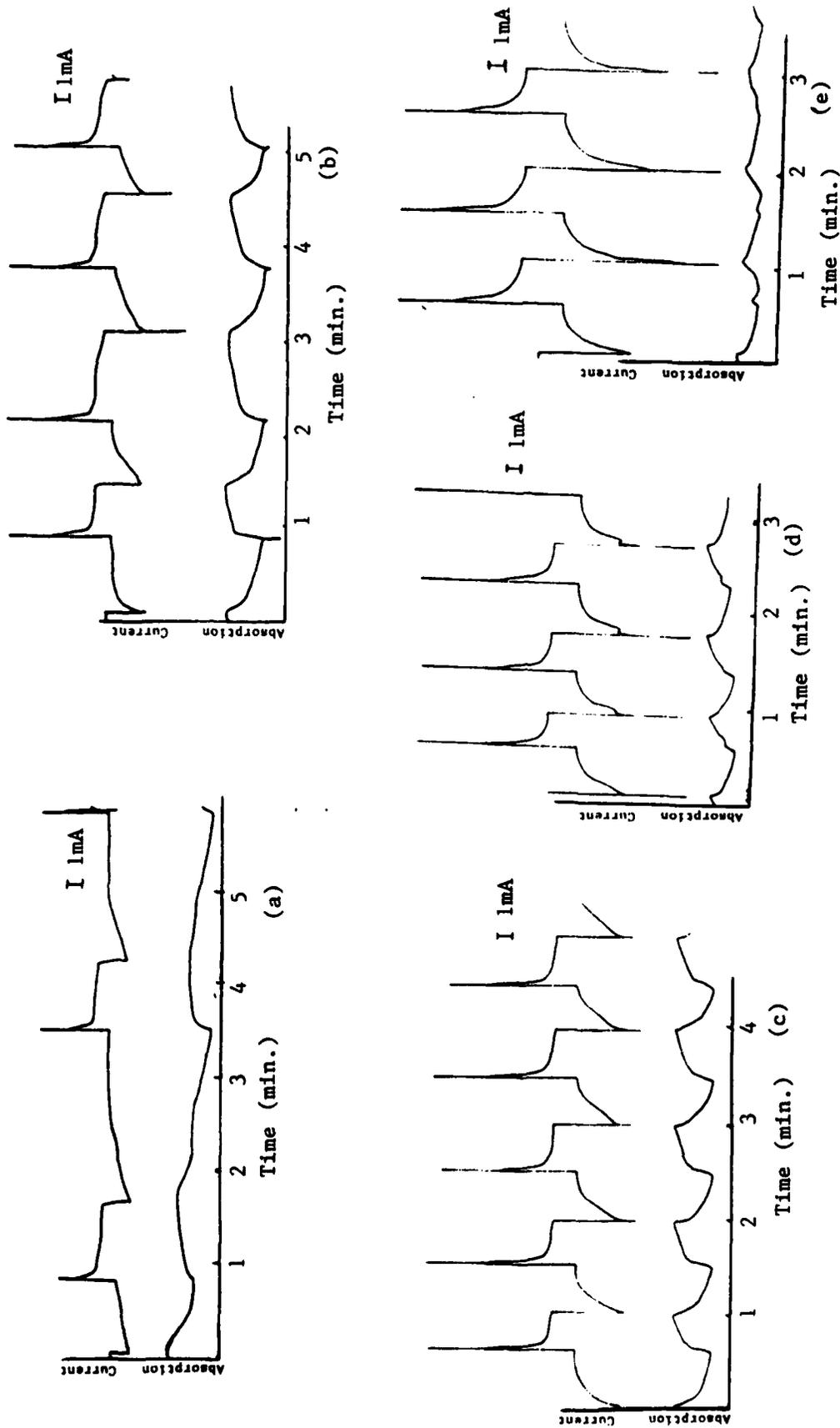
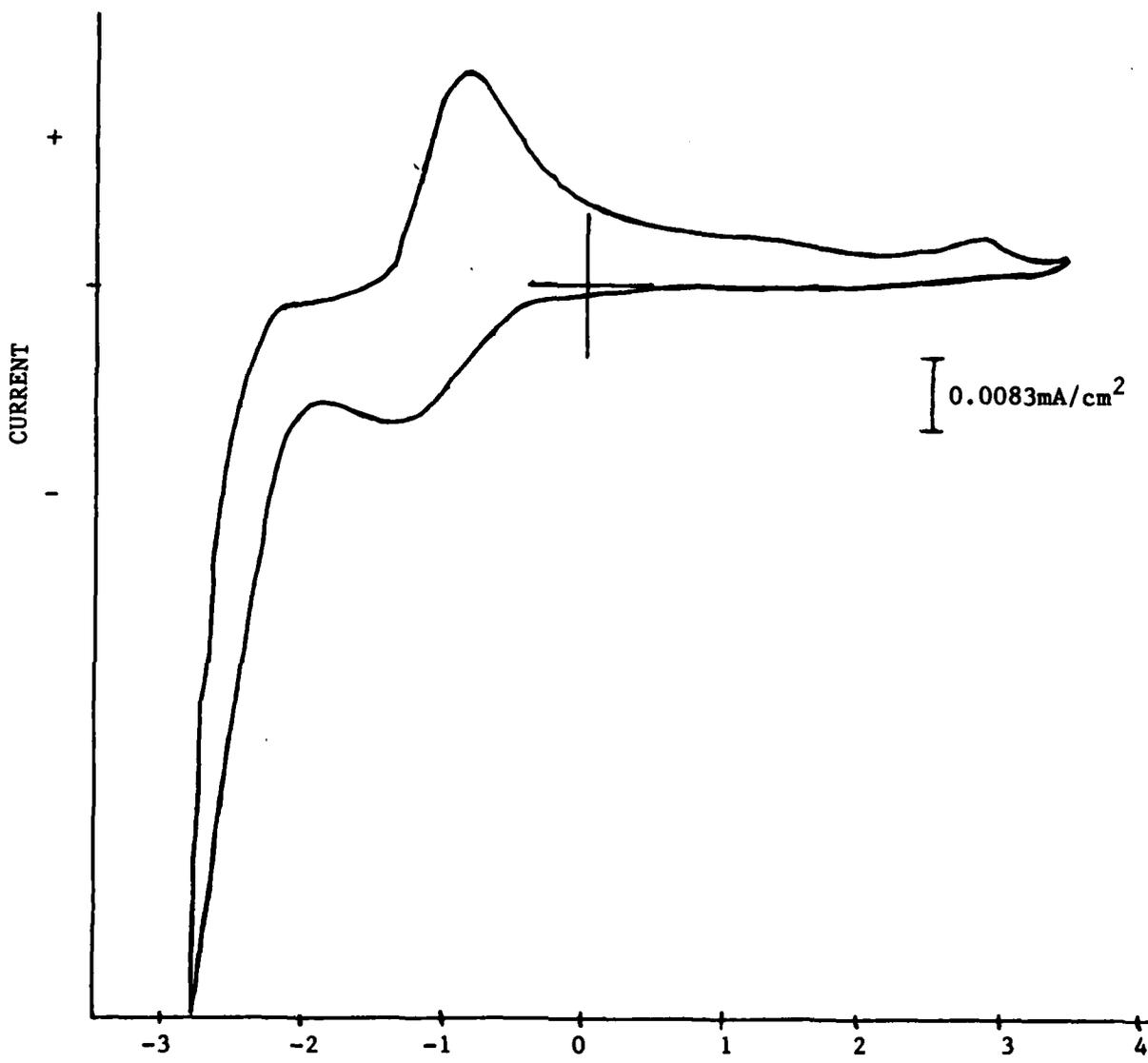


Figure 2.

Charge/light absorption characteristics for the cell

SnO₂ cond. glass/0.04M Heptyl Viologen in / Nafion 117 / 0.04 M CeCl₃ in polyamps/SnO₂ cond. glass
 polyamps + 0.001 M NaPF₆ membrane + 0.001 M NaPF₆

Illumination source: He/Ne laser at 583 nm; Beam intensity: 1 mW. Potentiostatted at
 a) $\pm 0.75V$, b) $\pm 1.0V$, c) $\pm 1.25V$, d) $\pm 1.5V$, and e) $\pm 2.0V$ upon cycling.



Electrode voltage (volts) vs. SnO₂ conducting glass reference/counter electrode.

Figure 3. Cyclic voltammogram of cell

n-TiO ₂	0.04 M heptyl viologen in poly-AMPS + 0.001 M NaPF ₆	Nafion 117 membrane Na ⁺	0.04 M CeCl ₃ in poly-AMPS + 0.001 M NaPF ₆	SnO ₂ conducting glass
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Sweep rate: - 50 mv/sec.

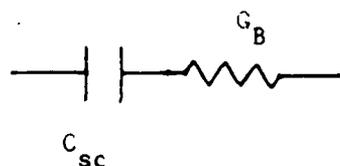
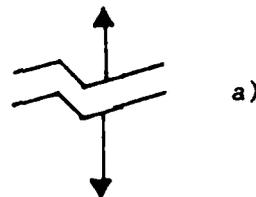
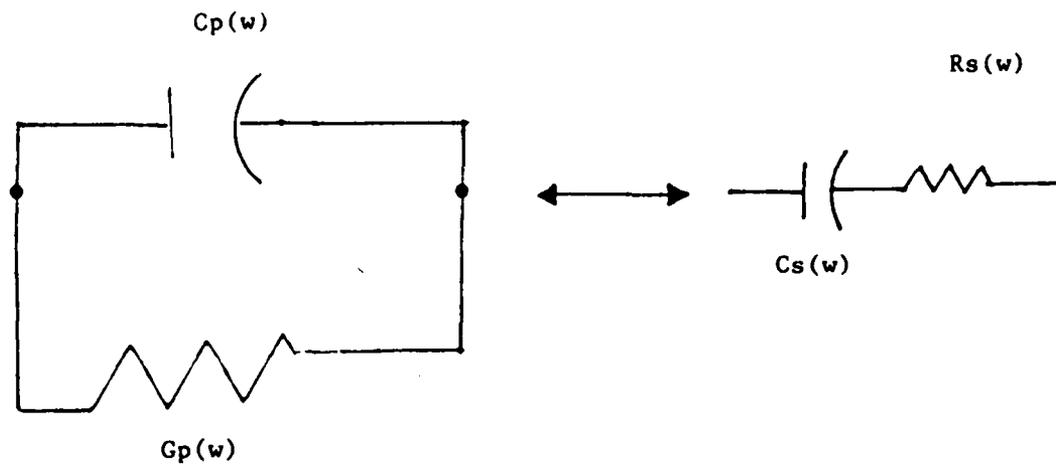


Figure 4. Passive element network for C_{sc} measurement in Mott-Schottky analyses.

- a) This transformation is performed by a successive reduction in the equivalent circuit representation of the semiconductor/SPE interface¹⁰.

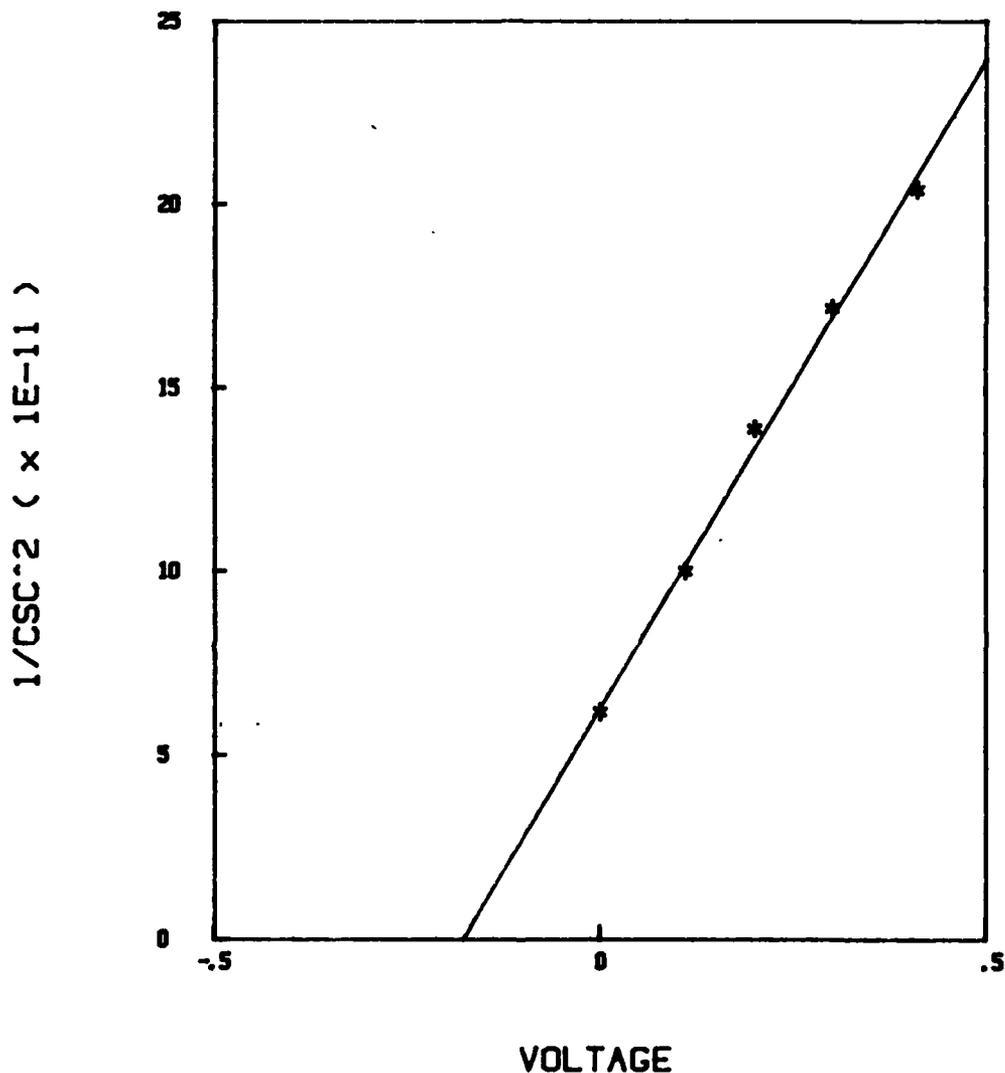


Figure 5. Mott-Schottky Plot of the cell.



Before being subjected to electrochemical reduction V_{FB} for n-TiO₂ = -0.1801 V.

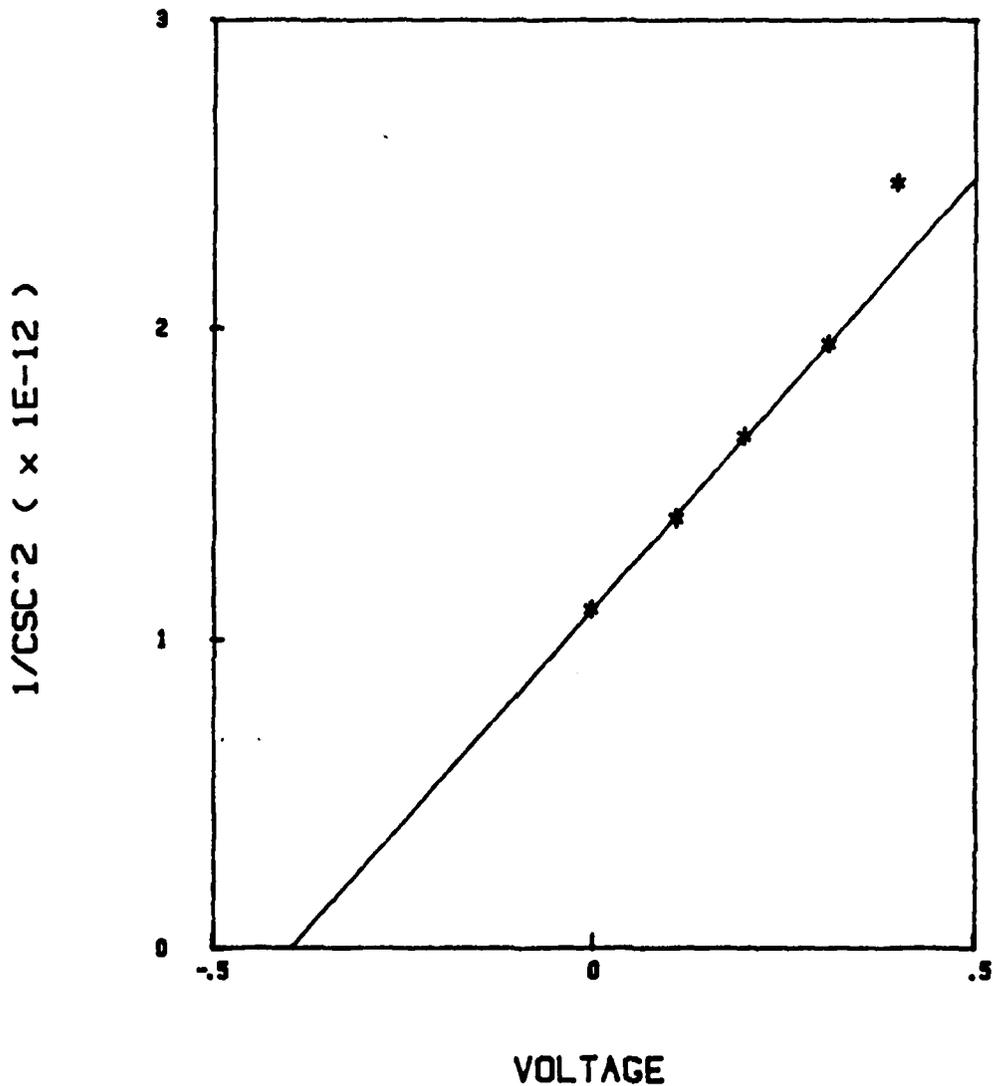


Figure 6. Mott-Schottky plot of the cell

n-TiO ₂	0.04M heptyl viologen in poly-AMPS + 0.001 M NaPF ₆	Nafion 117 membrane Na ⁺	0.04M CeCl ₃ in poly-AMPS + 0.001 M NaPF ₆	SnO ₂ Conducting Glass
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After being reduced at -1.35V corresponding to the radical cation.

$$V_{FB} \text{ for } n\text{-TiO}_2 = -0.3951\text{V}$$

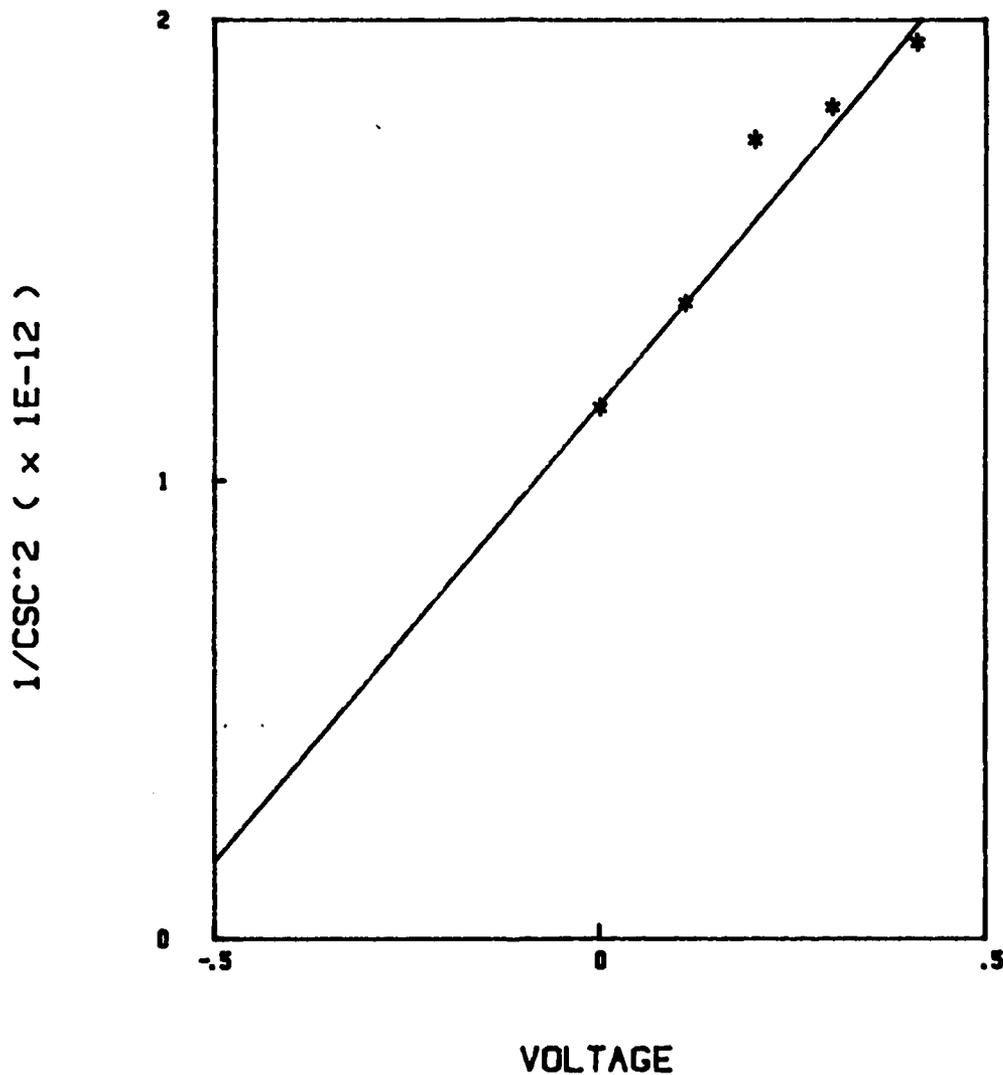
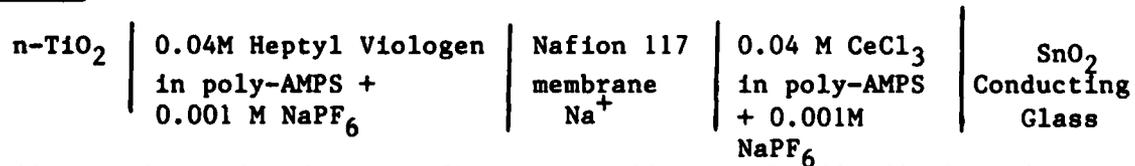


Figure 7. Mott-Schottky plot of the cell



After being reduced at -2.25V corresponding to the diradical cation.

$$V_{FB} \text{ for } n\text{-TiO}_2 = -0.5916V$$

END

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