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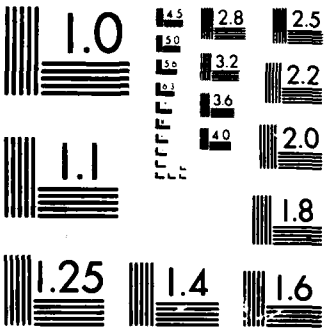
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An Electrochemical and UV-Visible Spectroelectrochemical Investigation of Selectivity of Potentiometric Gas Sensors Based on Polypyrrole

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The sensitivity and stability of polypyrolle as a function of several experimental parameters is discussed.

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AN ELECTROCHEMICAL AND UV-VISIBLE SPECTROELECTROCHEMICAL INVESTIGATION OF SELECTIVITY OF POTENTIOMETRIC GAS SENSORS BASED ON POLYPYRROLE

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It has been shown in previously [1, 2] that a suspended gate field transitor (SGFET) can be used as a general device for sensing of gases and dielectric fluids. The principles of operation of this device is based on chemical modification of the electron work function of a chemically selective layer which is electrochemically deposited within the gate structure of the device.

Electropolymerized polypyrrole (PP), one such layer, can be used as a general matrix into which other chemical functionalities can be incorporated in order to change its selectivity. It has been shown that other organic compounds can be incorporated electrochemically into the bulk of the PP film [3] or that its surface can be covalently modified [4]. Furthermore, PP forms an ohmic junction at noble metal electrodes [5] which is important for the proper operation of the device [1]. In this paper we shall describe the correlation between the spectroelectrochemical characteristics of various types of layers based on PP with their sensitivity and selectivity to some aromatic and hydrogen bonding compounds that interact with the film by hydrogen bonding or through aromatic π-systems.

While pyrrole undergoes slow oxidation at room temperature and atmospheric pressure [6], polypyrrole with BF_4^- anion is remarkably stable after the initial reaction with air . Practically no thermal degradation of the PP has been observed below 130^o C [7]. This means that, if necessary, these devices could be used even at moderately elevated temperatures. In this study the operating temperature of the transistor was only 25^{o}C.

EXPERIMENTAL SECTION

Suspended gate transistors with an approximately 2000Å gap were fabricated and encapsulated as described previously [1]. Encapsulated devices were first etched in solution containing 15 ml (30%) H_2O_2 , 50 ml 0.1M EDTA, and 10 ml conc. NH_4OH for 10 minutes in order to remove traces of residual titanium and tungsten from all surfaces within the gate. Before electrodeposition the Pt gate was conditioned electrochemically by cycling between -0.25 and +1.25 V at 10 V s^{-1} in 1M H_2SO_4 for 10 minutes. Cyclic voltammograms obtained after this pre-treatment were identical with those described by Arvia et.al. [8] . After this step the devices were dried in an oven at 60°C for 12 hours.

The electrodeposition was carried out by applying current pulses supplied from an IBM EC 225 potentiostat operated in the normal pulse mode. The repetition rate was set at 5 seconds, the pulse amplitude was 100 mV, ~~and~~ the scan rate 10 mV/s, the initial and final potentials were +0.6 and +0.9V , respectively unless specified otherwise. The deposition current was integrated with an analog integrator (constructed in these laboratories) until a total charge of 10 μC/gate had been passed. In all experiments the reference electrode was Ag/0.1M $AgNO_3$ in acetonitrile and the basic reaction solution was 0.1 M pyrrole with 0.1M tetraethylammonium tetrafluoroborate (TEAF) as the supporting electrolyte.

Threshold voltage shifts and the basic transistor characteristics were measured with a Hewlett Packard Semiconductor Parameter Analyzer, Model 4145A. Chemical response measurements were made in constant current mode, in saturation (V_{DS} = 4.0V and I_{DS} = 280 - 350 μA).

The test chamber was attached to the outlet of a Perkin Elmer Sigma 2000 gas chromatograph and was maintained at room temperature. The carrier gas was nitrogen (typical flow rate was 25 ml min^{-1}). The output from the SGFET monitor was digitized and stored in a Perkin Elmer 7500

Professional Computer equipped with a LCI-100 Laboratory Integrator.

For the spectroelectrochemical experiments the aforementioned polymers were electrodeposited in the same manner as described above (for Pt wire electrodes) onto 7 mm diameter platinum disc mirror electrodes. These polymer modified electrodes were mounted in a spectrocelectrochemical kinetic cell as described previously [9]. Reflectance spectroelectrochemiical spectra were obtained for the films using the modulated specular reflectance spectroscopic (MSRS) method [9]. The procedure involved pulse modulation between two potentials at which reactions take place at two different rates. The potential pulse modulation at 40 Hz was supplied by a fast rise-time, three-electrode potentiostat and waveform generator (JAS Instruments), ~~was 40 Hz~~. The resulting ac reflectance change was monitored with a phase sensitive detector (Bentham). The wavelength was scanned throughout the UV-visible region using a Xenon arc source (Photon Technology International) and a monochromator (GCA McPherson 300). The resulting difference spectra (detected by a photomultiplier, RCA 31000A) were recorded on a plotter. Negative bands correspond to absorbing species present at the higher potential, while positive bands are indicative of absorbers prevalent at the lower base potential.

An MSRS spectrum of the nitrobenzene radical anion was also recorded for reference. The base potential was first held at a voltage where no faradaic process occurred, and then stepped to a value where nitrobenzene was reduced to its radical anion at a diffusion-limited rate. The difference spectrum was recorded as was previously described for the polymer films.

RESULTS

Electrochemistry

Suspended gate field effect transistors (SGFET) coated with polypyrroles (PP) prepared under different conditions have shown markedly different selectivities to various gases, and a large variation in the threshold voltage shift DV_T which is related to the change in the electron work function of the polypyrrole layer [1]. The threshold voltage shifts for SGFETs with various PP layers measured with respect to bare, cleaned Pt in air at room temperature are summarized in Table I together with a qualitative description of their selectivity. In order to characterize these films, we have used both cyclic voltammetry and spectroelectrochemistry. The cyclic voltammograms for PP co-deposited with 4-nitrotoluene, and with nitrobenzene are shown in Fig.1. It is interesting to note that the voltammetry corresponding to the reduction/oxidation of the nitro group can be seen in nitrotoluenes (only 4-nitrotoluene is shown in Fig. 1A) even after repeated cycling between the reduced and oxidized form of PP. The results are similar to the reduction of poly(N--p-nitrophenyl pyrrole) investigated by Diaz et.al. [4]. The V_T shifts of PP/nitrotoluenes are strongly positive (~ + 8V) indicating a substantially increased electron affinity of this material as compared with ordinary PP. On the other hand the V_T shift for the PP/nitrobenzene is only moderately positive and the redox pattern of the nitro group in PP/nitrobenzene can be seen only if the cycling is limited to between 0 and -2.5V (Fig. 1Ba). When the PP is oxidized the nitro group redox pattern is lost after only a few cycles (Fig. 1Bb).

Spectroelectrochemistry

MSRS spectra for the five films are shown in Figure 2; These spectra were taken in 0.1M TBAF/acetonitrile. In each case the recording with reference to a pulse sequence -0.60V to -2.40V

(vs. Ag(Ag+)), secondly -0.60V to +1.20V, and thirdly -0.60V to -2.40V, again. This sequence was chosen in an effort to determine differences in the films caused by film oxidation. First the films were reduced, and difference spectra at 40 Hz modulation were recorded. The spectra for the oxidations were then recorded. Finally, the spectra for the reductions were again obtained, and any changes in bands due to film alteration caused by oxidation were noted.

The difference spectrum resulting from the reduction of PP/nitrobenzene film (Figure 2a) differs from those obtained for the other four films; a negative peak at 395 nm appears in the nitrobenzene/polypyrrole spectrum. The difference spectra for the oxidations of the five films are all quite similar (Figure 2b). Subsequent to oxidation, spectra for reductions were again recorded (Figure 2c). The spectra for the five films then appeared similar. The negative peak at 395 nm in the nitrobenzene/polypyrrole film has disappeared as a consequence of the oxidation excursions undergone during the recording of the spectrum in Figure 2b.

The MSRS spectrum of nitrobenzene radical anion is shown in Figure 2 (insert). A single negative Lorentzian shaped peak is seen with a maximum in acetonitrite at 447 nm, somewhat shifted from the maxima seen in DMF [10] and sulfolane [11], where peaks due to nitrobenzene anion radical were observed at 464 and 465 nm, respectively. Neutral nitrobenzene does not absorb in this wavelength region.

Chemical Response

The overall response of the SGFET coated with PP or nitroarene modified polypyrroles parallels the electrochemical observations; All transitors with PP matrix respond to alcohols and to acetonitrile. However, the polarity of the response to acetonitrile as well as its amplitude varies for different PP (Fig.3). The response to methanol is always higher than to acetonitrile; however.the response is somewhat affected by the solvent used for the electrodeposition (Fig.4). For PP deposited from acetonitrile the ratio of response to methanol/acetonitrile mixture is 5.2 whereas for

PP deposited from methanol this ratio is 8.0. The effect of nitroarene co-deposition on selectivity to aromatic compounds is pronounced (Fig.5). While there is no sensitivity to toluene from PP deposited from methanol, acetonitrile, or acetonitrile/1M toluene solutions, both 2-nitro- and 4-nitrotoluene PP give a strong, reversible response, while PP/3-nitrotoluene yields only a weak, irreversible response.

Response of SGFET coated with PP/nitrobenzene depend on the electrochemical history of this material. The PP/nitrobenzene deposited with the final potential at $\pm$ 0 V (Fig. 6A) yields a response to water, alcohols, and to the aromatics. Reduced material (Fig. 6B,C) shows a much lower response to aromatics and a lower and inverted response to water. This behavior can be explained by the loss of nitrobenzene from the PP matrix upon reduction of the nitro group. As expected none of the tested coatings listed in Table I responded to aliphatic hydrocarbons or to cyclohexane.

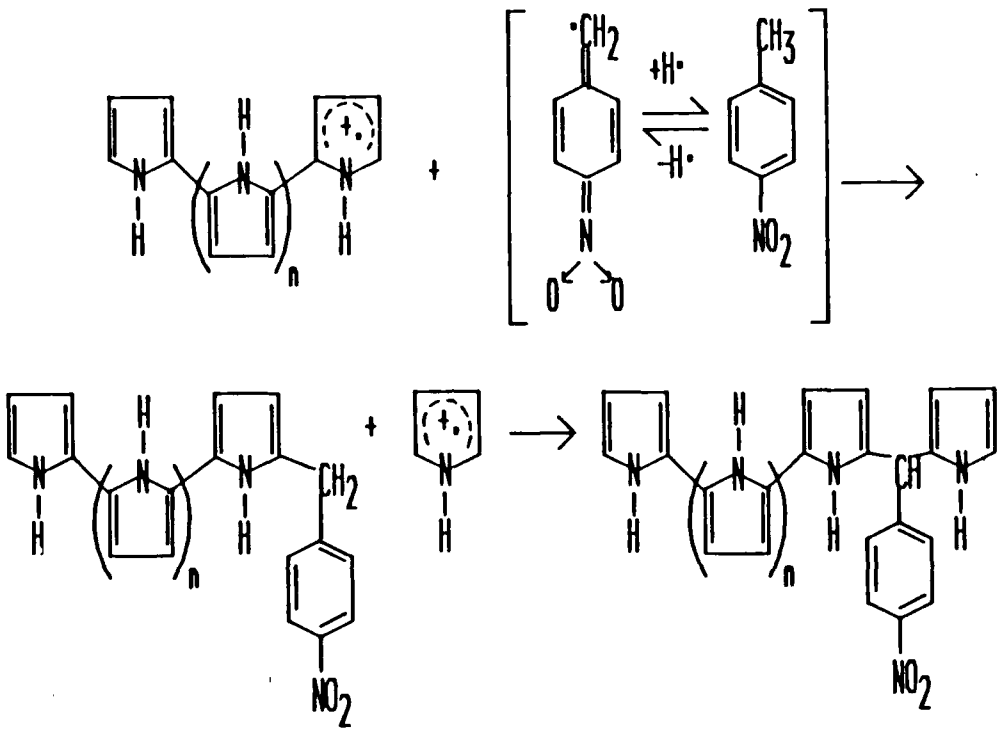
DISCUSSION

The most striking feature of the transistors modified with PP/nitrotoluenes is the large (+6.5 to +8.7V) shift of the threshold voltage (Table I)which indicates a large increase in the electron work function due to the presence of the covalently bound nitroarene moiety. Because of the complex geometry of the transistor gate (Pt mesh) and the resulting non-homogeneous electric field in the gap , no absolute equilibrium measurements have been attempted in this work. However, the rapid return of the signal to the baseline (Figures 3-6) following the passage of the concentration impulse is a clear indication of the reversibility of these interactions. The exception seems to be the response of PP/3-nitrotoluene to toluene which is irreversible (curve c in Fig. 5).

In this group of sensors, PP is used only as a binding matrix, but we see that the chemical selectivity is achieved by incorporation of additional functional groups. As has been observed previously, SGFETs with PP layers respond to alcohols and water. This selectivity is undoubtedly related to the tendency of pyrrole to hydrogen bond [12]. Not surprisingly, all transistors investigated in this study have shown a response to aliphatic alcohols and to water. The fact that the response to water was stronger when the electrodeposition of PP was carried out from methanol rather than from acetonitrile (Fig.4) indicates that solvation during the polymerization may have left the final polymer with "solvent footprints" which made it an entropically more favorable binder for the organic substrate of similar shape. This may be termed a solvent-induced template effect similar to one proposed for example by Shea and Dougherty [13] for template-mediated synthesis. In this context the PP may not be an optimum matrix because of its high crystallinity [14]. The negative shift of V_T to addition of acetonitrile vapor is consistent with the negative DV_T of PP deposited from acetonitrile solution (relative to PP deposited from methanol). The origin of this shift is again presumably in the π-π or π-H interactions between acetonitrile and PP.

The co-polymerization of PP with nitrotoluenes produced a remarkably strong shift in the threshold voltage of the final material as compared to the plain PP (+ 6.787 V for 2-nitrotoluene, +

8.984 V for 3-nitrotoluene and + 7.784 V for 4-nitrotoluene). Such large shifts can be explained only by copolymerization of pyrrole with nitrotoluene and formation of a susbstantially different material with much higher electron affinity. The likely mechanism for this reaction involves the nitrotoluyl radical, analogous to the reaction between pyrrole and benzyl radical [15]:



The presence of incorporated nitroarene has been confirmed by cyclic voltammetry (Fig.1) and by spectroelectrochemistry (Fig.2). On the other hand nitrobenzene, which cannot readily co-polymerize with PP, was found to bind only loosely, presumably as a charge transfer complex with the neutral PP. Upon oxidation of the matrix the nitrobenzene is rapidly lost by diffusion with concommittant loss of sensitivity to aromatic analytes (Fig.6). The sensitivity to aromatic hydrocarbons and the total lack of sensitivity to cyclohexane is due to the π-π interactions of the former with the nitroarene moiety within the PP/nitrotoluene copolymer. The polarity of the response, i.e. induced increase or decrease of the electron affinity, is difficult to explain at present, and is the subject of further study.

The electropolymerization of PP is a convenient yet chemically complicated process in which different materials are formed depending on the current density and on the solvent and anion present in the solution during electrolysis [16]. Unfortunately the mesh structure of our suspended gate transistor does not allow us to control the current density such that the exact PP film thickness or a film of uniform chemical composition could be produced. These studies as well as the equilibrium response measurements will be done on SGFET with a parallel plate configuration of the suspended gate.

The MSRS spectra clearly indicate the incorporation of nitrotoluenes into polypolypyrrole. The difference spectra of the three nitrotoluene/polypyrrole aggregates resemble the spectra obtained from polypyrrole electrodeposited in the absence of any nitroarene (Figure 2). As a result of the initial film reduction (Figure 2a), a positive peak at 440 nm, corresponding to the interband transition in neutral polypyrrole [7], appears in the difference spectra of the three nitrotoluene/polypyrrole films as well as in the spectrum of the polypyrrole film itself. Also, a broad negative peak at around 550 nm, due to the reduced form of the polymer, is seen for all five films. During film oxidation, a very broad positive peak with a maximum near 600 nm is observed for all five films, along with a shoulder near 430 nm. The shoulder corresponds to interband transitions seen above during film reduction. The broad, humped peak with its maximum around 600 nm, is due to transitions in the neutral polymer matrix as well, and probably owes its broadness and structure to the presence of oligomers of varying chain length. Spectral dependence on chain length has been noted before for polypyrrole [17] and in poly-paraphenylene [18]

The magnitude of the peak at 600 nm (Figure 2b) larger then expected is due to the fact that the oxidized form of the polymer is conductive and therefore acts optically more like a metal. Since what is recorded is a difference spectrum, the small absorbances in the visible range due to the neutral species translate into bands of large magnitude when compared with the near zero absorbance occurring at the electrode surface of the oxidized form of the film. The 430-440 nm band is depressed

relative to the 580-620 nm band since the oxidized form of the polymer absorbs to some extent at these higher energies [17] . This is indicated in the difference spectra. No peak due to the oxidized form appears at any wavelength. However, a small contribution to the absorbance in the violet cut-off region due to transitions in the oxidized species cancels to some extent the band due to the neutral form of PP in the 430-440 region.

The difference spectrum obtained during the initial reduction of PP/ nitrobenzene (recorded prior to any oxidation) shows the only optical anomaly (Figure 2a); A negative peak around 400 nm is observed, with the positive peak due to the neutral form of the polymer matrix is absent. No such phenomena appears in the MSRS spectra of the other four polymer films. The spectrum of nitrobenzene radical anion in acetonitrite (Figure 2a-insert) shows a broad peak with a maximum near where the interband transition in the neutral form of PP occurs. It is presumed that the signal due to nitrobenzene radical anion formed during the reduction of surface adsorbed nitrobenzene overwhelms the absorbance due to the interband transition, which is opposite in sign. This accounts for the apparent negative peak at 345 nm and the absence of a positive peak at 440 nm; both nitrobenzene radical and neutral PP absorb in the same wavelength region, and a competition is established which results in the more complex difference spectrum (Figure 2c). The second reduction (Figure 2c) following oxidation (Figure 2b) results in the disappearance of the nitrobenzene anion radical peak, with the appearance of some positive $\Delta R/R$ contribution from the 430-440 nm interband transition band of the neutral species. The spectrum from PP/nitrobenzene is now similar in appearance to the spectra obtained for the other four films. This is evidence that the charge-transfer complex between nitrobenzene and PP postulated previously is probably destroyed when the film is oxidized. Here, spectral information complements voltammetric data (Figure 1) suggesting that nitrobenzene is not incorporated into the polymer during electropolymerization, whereas the three nitrotoluene species do indeed co-polymerize with pyrrole to form the PP matrix.

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FIGURE LEGENDS

Fig. 1 Electrochemical behavior of PP/nitroarene layers prepared on Pt disc electrode (3 cm^2) from 1M nitroarene, 0.1M pyrrole, 0.1M TEA TFB acetonitrile solution. After deposition the electrode was rinsed and transferred to fresh 0.1M TEA TFB actonitrile solution. The scan rate was 0.5 V s^{-1}.

A: PP/ 4-nitrotoluene; B: PP/nitrobenzene cycled first (Fig.1 Ba) between $\pm$ 0 and - 2.4 V, then (Fig. 1Bb) between 0 and +1.3 V; C: The first cycle between +1.3 and -2.4 V for PP/nitrobenzene. The scan direction is indicated by arrows.

Fig. 2 MSRS spectra resulting from reductive and oxidative pulsing for ----- PP, ····· PP/2-nitrotoluene; - · - · - · PP/3-nitrotoluene; - ·· - ·· - PP/4-nitrotoluene, and ——— PP/nitrobenzene. Spectrum "nb" is that of solution nitrobenzene radical anion.(a), initial reduction; base potential: -0.60 V, pulse height: -1.80 V. (b), oxidation; base potential: -0.60 V, pulse height: +1.80 V. (c), reduction spectra recorded after film oxidation; base potential -0.60 V, pulse height: -1.80 V. Sensitivity in (a) and (c) is five times that of (b). Other parameters are given in the text.

Fig. 3 Response to acetonitrile of SGFET coated with various PP. a- PP/4-nitrotoluene; b- PP/2-nitrotoluene; c- PP/3-nitrotoluene; d- PP from acetonitrile; e- PP from methanol; f- PP/nitrobenzene; g- PP/toluene

Fig. 4 Response of polypyrrole deposited from : A - methanol, B - acetonitrile, to injection of 5 µL of methanol: acetonitrile mixture (1:10 molar ratio). Nitrogen flow was 24 mL min^{-1}; V_{DS} = 4.0V; I_{DS} = 350 µA

Fig. 5 Response to toluene of SGFET coated with various PP. a- PP/4-nitrotoluene; b- PP/2-nitrotoluene; c- PP/3-nitrotoluene; d- PP from acetonitrile; e- PP from methanol; f- PP/nitrobenzene; g- PP/toluene

Fig. 6 Response of SGFET coated with PP/nitrobenzene in acetonitrile to injection of 0.5 μL of : 1 - acetonitrile; 2 - benzene; 3 - toluene; 4 - methanol; 5 - 0.1 μL of water.

A: Final deposition potential ± O V

B: After reduction at -1.0 V for 10 min

C: After repeated cycling between ± 0 and - 2.5 V

ABSTRACT

It is shown that electrochemical incorporation of nitrotoluenes into the the polypyrrole matrix changes profoundly the electron work function of ~~this material~~ as compared with plain polypyrrole. Simultaneously this material exhibits selective sensitivity to aromatic compounds. The presence of the nitroarenes in the polypyrrole matrix has been confirmed spectroelectrochemically.

BRIEF

Selectivity of suspended gate field effect transistors to aromatic compounds, acetonitrile, alcohols, and water can be modified by electrochemical incorporation of different compounds into the polypyrrole layer within the transistor structure.

Threshold voltage shifts and Responses of SGFETs With Polypyrrole Film Deposited Under Different Conditions

Deposition Conditions	V_T Shift	Response
acetonitrile (Ac)	- 0.284	Ac (-)
methanol	+ 0.776	Ac (-)
1M toluene (T), Ac	+ 0.275	Ac (+)
1M nitrobenzene, Ac	+ 0.712	Ac (++)
1M 2-nitrotoluene, Ac	+ 6.503	Ac (++), T (++++)
1M 3-nitrotoluene, Ac	+ 8.700	Ac (++), T(+)
1M 4-nitrotoluene, Ac	+ 7.500	Ac (----), T (---)

Table 1

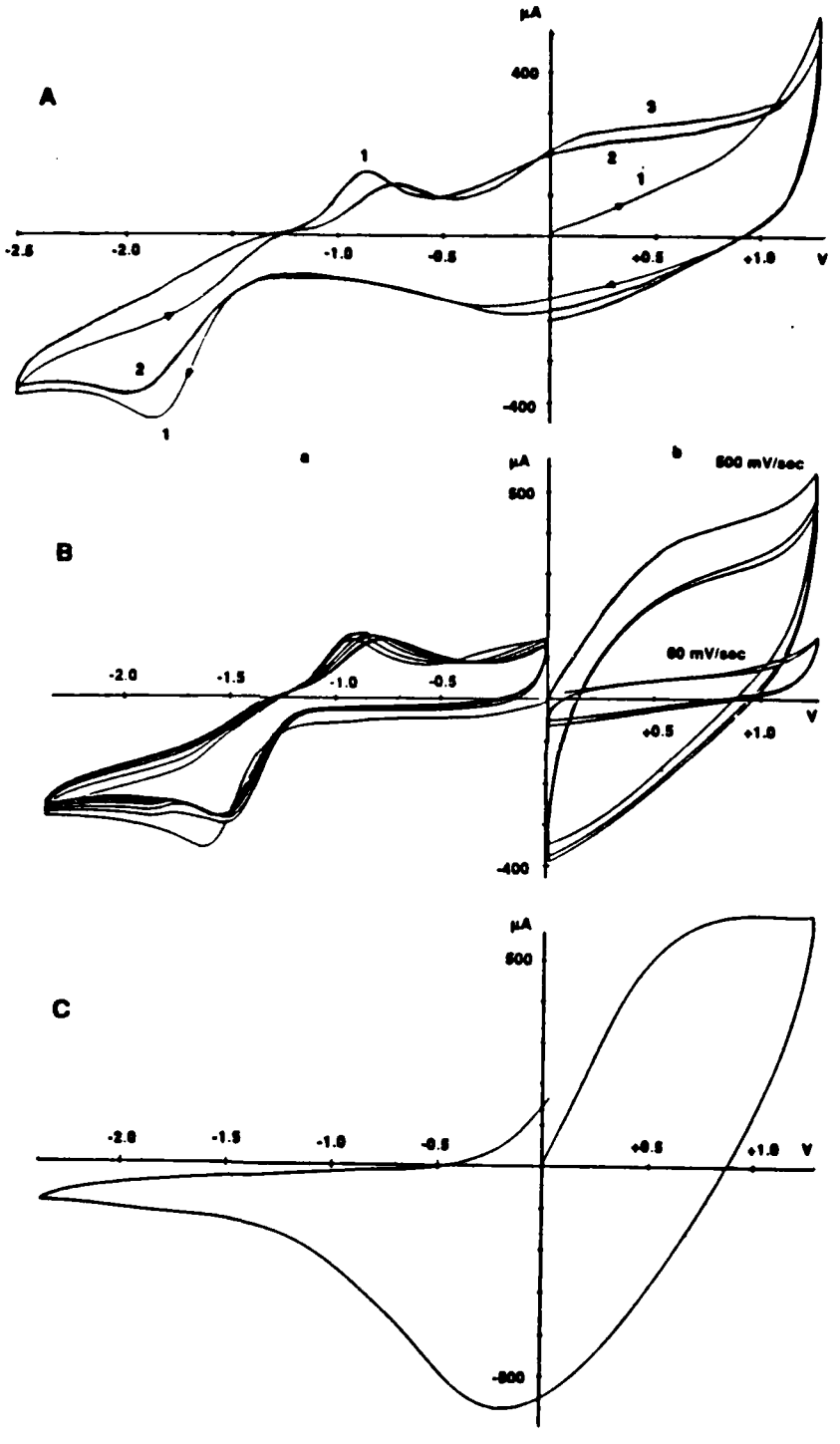
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Fig. 1

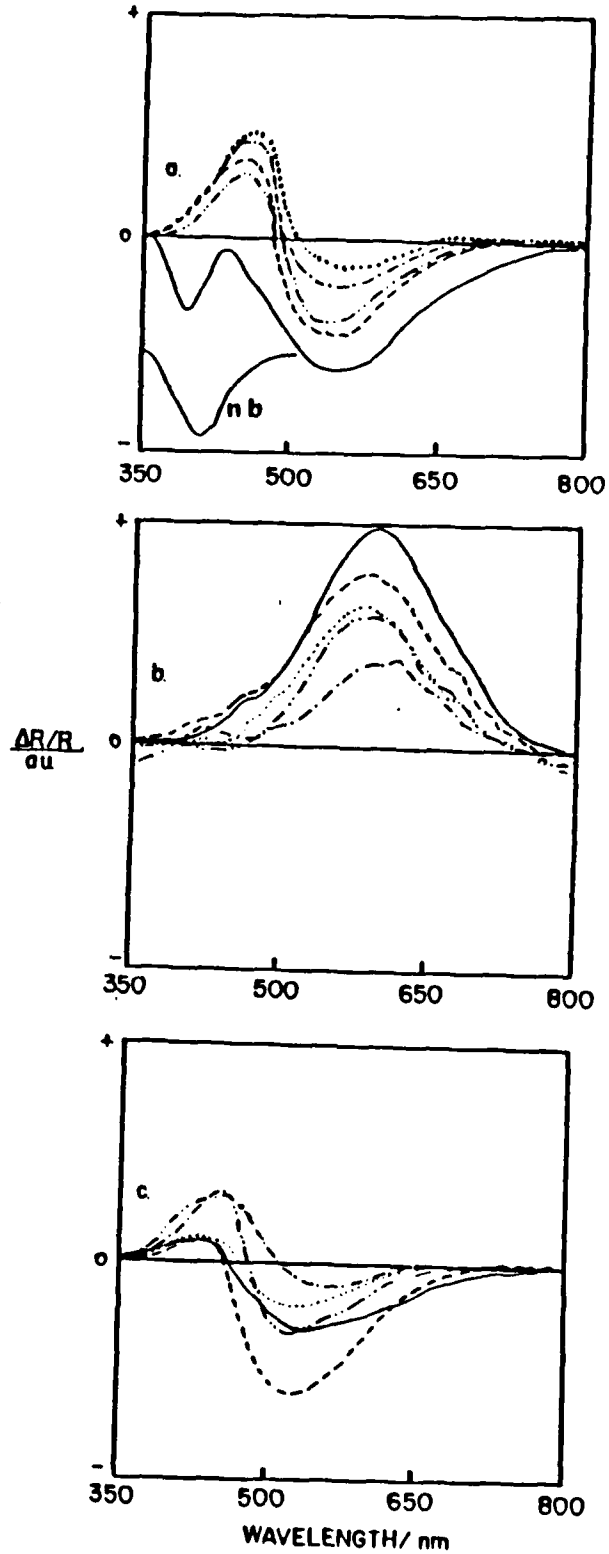

Fig. 2

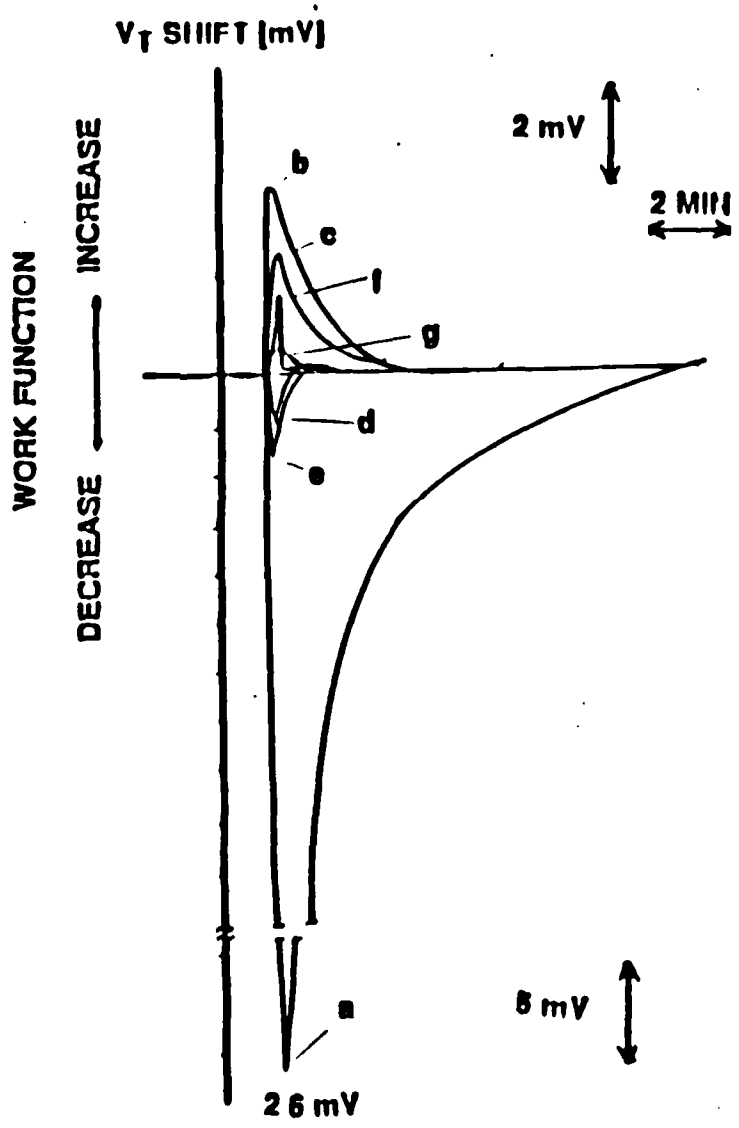
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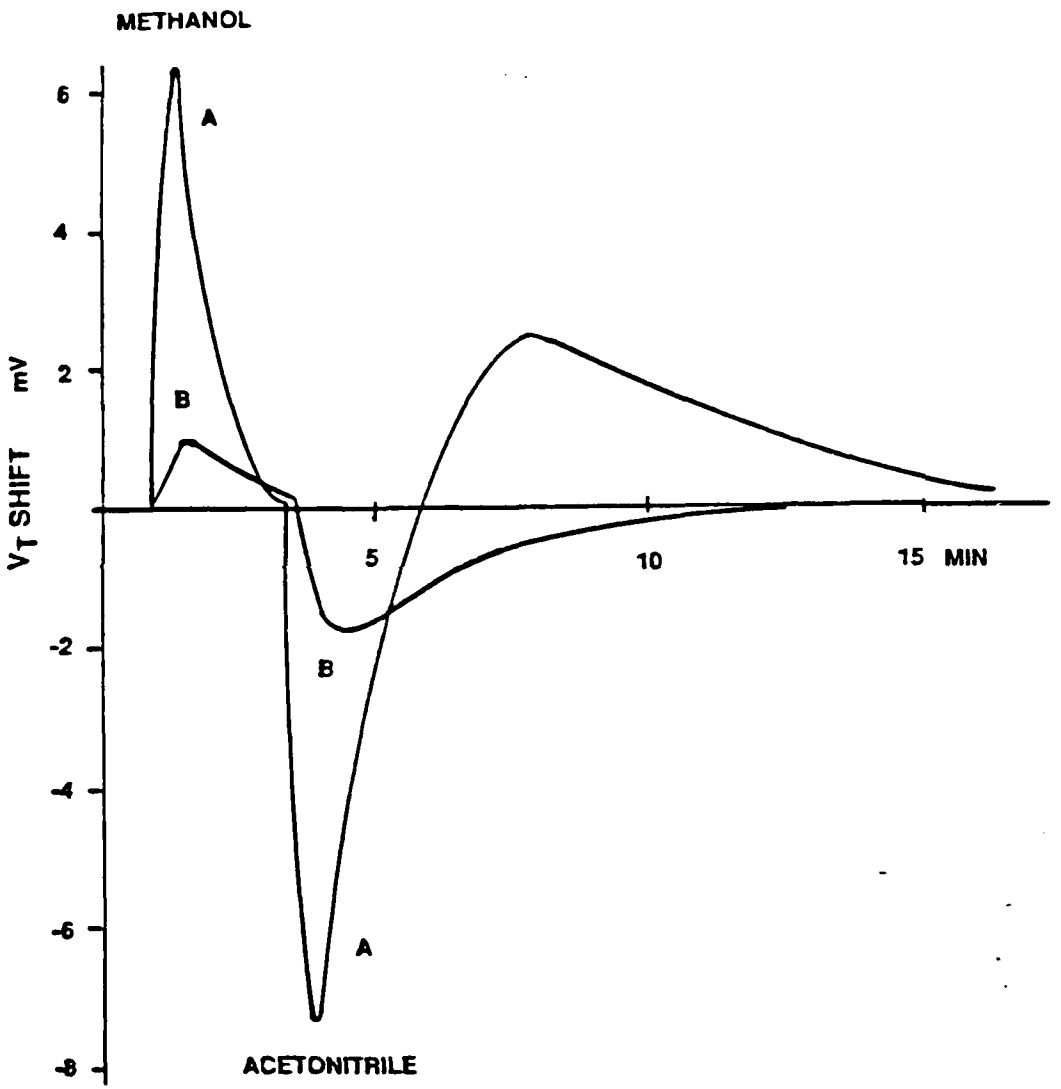
Fig. 3



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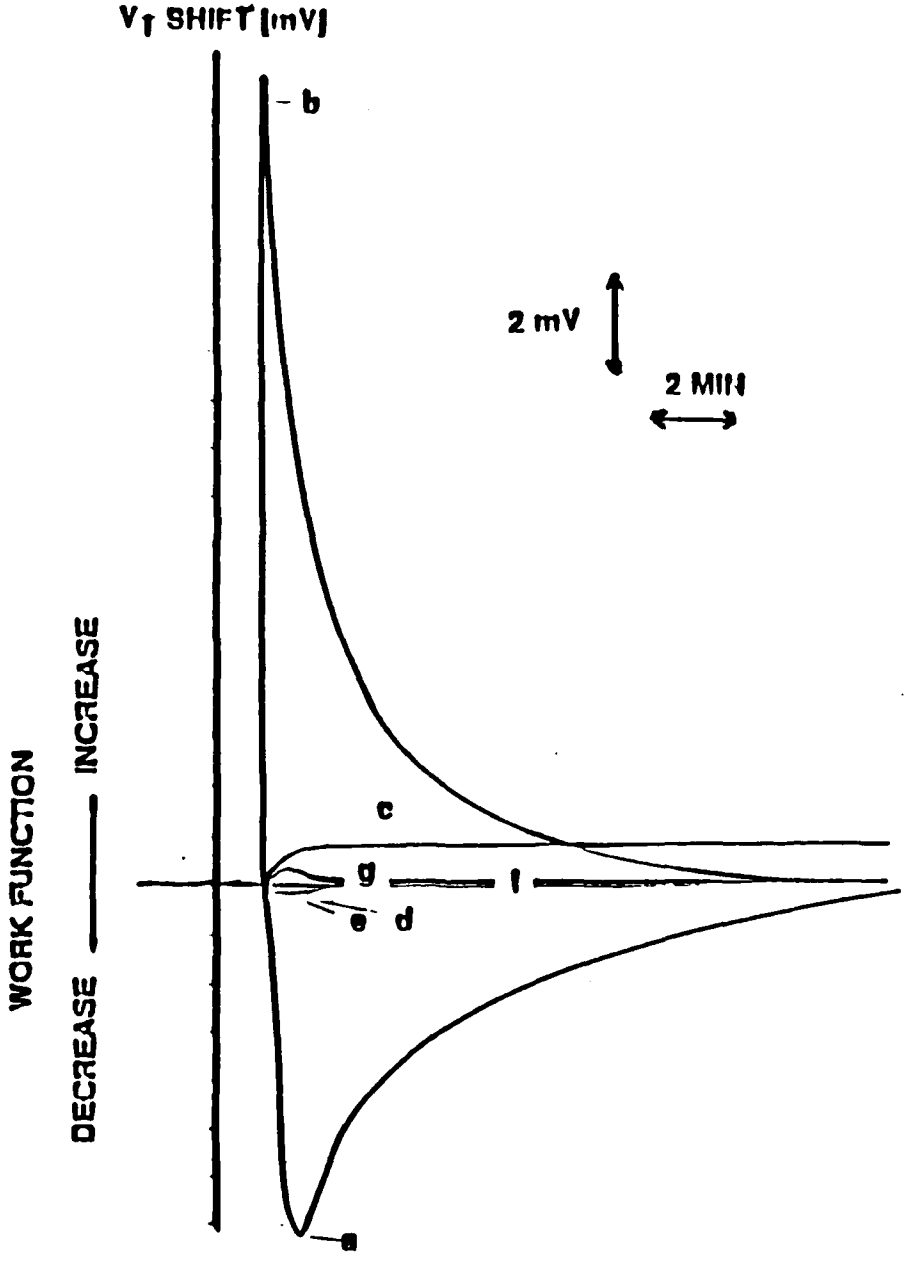
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Fig. 5

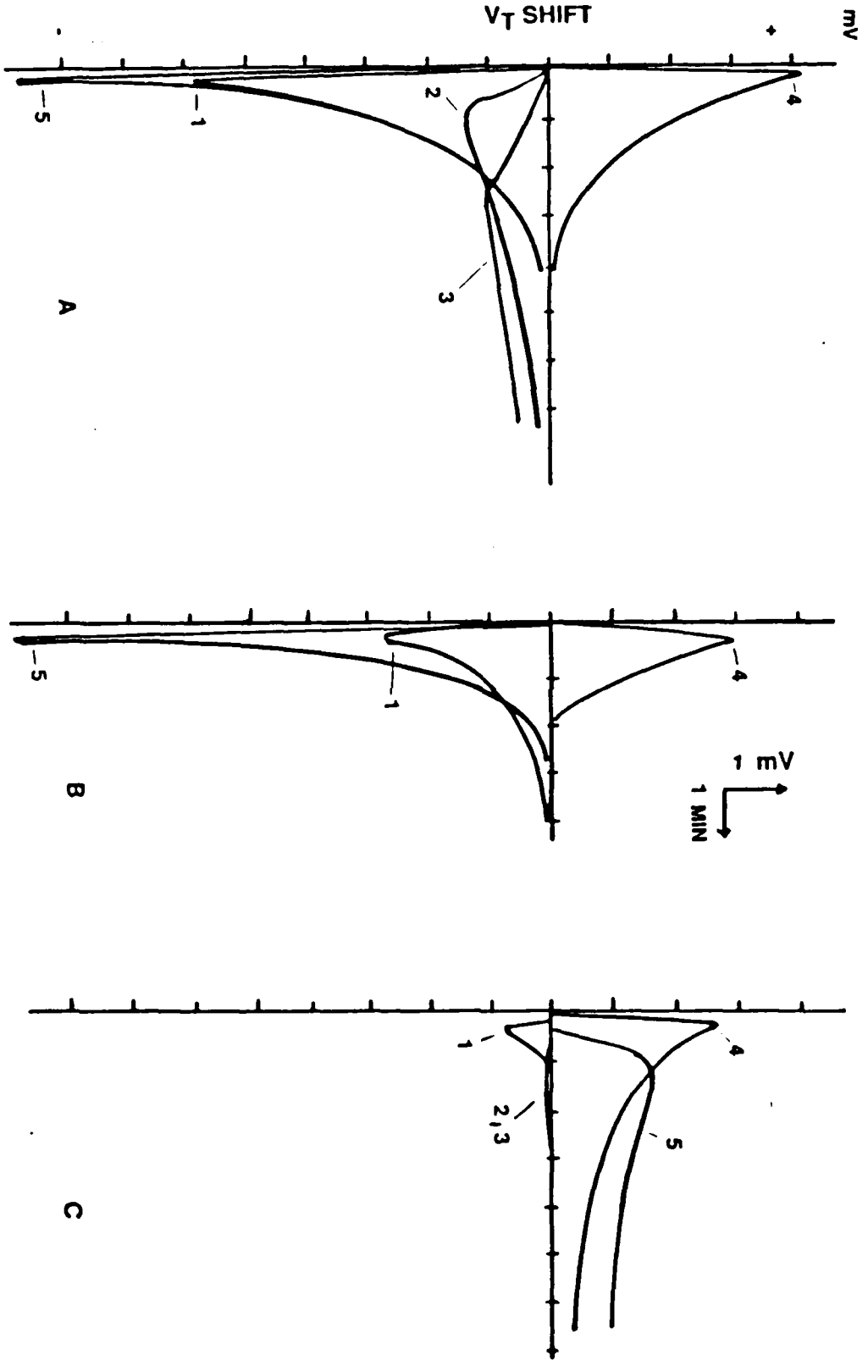

Fig. 6

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