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CAMBRIDGE DEPT OF CHEMISTRY J W THACKERAY ET AL.
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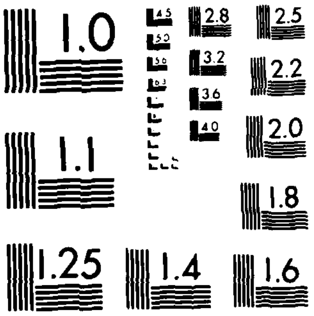

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Abstract

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Microelectrochemical "transistors" can be prepared by connecting two closely spaced (approximately 1.2 micron) Au microelectrodes (0.1 micron thick x 2.4 micron wide x 50 micron long) with anodically grown poly(3-methylthiophene). The amount of poly(3-methylthiophene) used involves about ~~10^{-7}~~ to ~~10^{-6}~~ moles of monomer per ~~cm~~^{2}. The poly(3-methylthiophene) can be platinized by electrochemical reduction of $PtCl_4^{2-}$ at the pair of coated electrodes. The change in conductivity of the poly(3-methylthiophene) with change in redox potential is the basis for amplification of electrical or chemical signals; the conductivity varies by 5 to 6 orders of magnitude upon change in potential from +0.2 (insulating) to +0.7 (conducting) V vs. SCE in aqueous electrolyte. The Pt equilibrates the poly(3-methylthiophene) with the O_2/H_2O or H_2O/H_2 redox couples. [Poly(3-methylthiophene)/Pt]-based transistors are shown to be viable room temperature sensors for O_2 and H_2 in aqueous solution. O_2 reproducibly turns "on" the device, with 1 atm O_2/0.1 M $HClO_4/H_2O$ showing 0.7 mA I_D at a V_D = 0.2 V; H_2 reproducibly turns "off" the device, with 1 atm H_2/0.1 M $HClO_4/H_2O$ showing less than 20 nA I_D at a V_D = 0.2 V, where V_D (drain potential) is the applied potential between the two Au microelectrodes and I_D (drain current) is the current that passes between the two microelectrodes. The turn "on" with O_2 is complete within 2 min and the turn "off" with H_2 is complete within 0.3 min. A platinized microelectrode of a dimension similar to the microelectrochemical transistor shows only 1.0 nA reduction current upon exposure to 1 atm O_2; the current amplification of the transistor is thus a factor greater than ~~10^5~~. The transistor device can also reproducibly respond

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to pH changes in the pH range of 0 to 12, when there is a constant O_2 concentration; there is a reproducible change in I_D to alternate flow of a pH 5.5/pH 6.5 stream for over 10 hrs. The device responds to an injection of 10^{-6} l of 0.1 M $HClO_4$ into an effluent stream of 0.1 M $NaClO_4$ (flowing at 2 ml per min.) within 4 sec. Study of the resistance properties of the [poly(3-methylthiophene)/Pt] vs. potential reveals that the Pt has little effect on the intrinsic conductivity of poly(3-methylthiophene). Rather, the role of Pt is purely as a catalyst to allow equilibration of O_2 and H_2 with the polymer. The amount of Pt used is approximately 10^{-7} mol/cm^2, and microscopy shows the Pt to be present as particles of less than 0.1 micron size.

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Chemically Responsive Microelectrochemical Devices Based on Platinized Poly(3-Methylthiophene): Variation in Conductivity with Variation in Hydrogen, Oxygen, or pH in Aqueous Solution

by

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Prepared for Publication

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CHEMICALLY RESPONSIVE MICROELECTROCHEMICAL DEVICES BASED ON PLATINIZED POLY(3-METHYLTHIOPHENE): VARIATION IN CONDUCTIVITY WITH VARIATION IN HYDROGEN, OXYGEN, OR pH IN AQUEOUS SOLUTION

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Abstract

Microelectrochemical "transistors" can be prepared by connecting two closely spaced (approximately 1.2 micron) Au microelectrodes (0.1 micron thick x 2.4 micron wide x 50 micron long) with anodically grown poly(3-methylthiophene). The amount of poly(3-methylthiophene) used involves about 10^{-7} to 10^{-6} moles of monomer per cm^2. The poly(3-methylthiophene) can be platinized by electrochemical reduction of $PtCl_4^{2-}$ at the pair of coated electrodes. The change in conductivity of the poly(3-methylthiophene) with change in redox potential is the basis for amplification of electrical or chemical signals; the conductivity varies by 5 to 6 orders of magnitude upon change in potential from +0.2 (insulating) to +0.7 (conducting) V vs. SCE in aqueous electrolyte. The Pt equilibrates the poly(3-methylthiophene) with the O_2/H_2O or H_2O/H_2 redox couples. [Poly(3-methylthiophene)/Pt]-based transistors are shown to be viable room temperature sensors for O_2 and H_2 in aqueous solution. O_2 reproducibly turns "on" the device, with 1 atm O_2/0.1 M $HClO_4/H_2O$ showing 0.7 mA I_D at a V_D = 0.2 V; H_2 reproducibly turns "off" the device, with 1 atm H_2/0.1 M $HClO_4/H_2O$ showing less than 20 nA I_D at a V_D = 0.2 V, where V_D (drain potential) is the applied potential between the two Au microelectrodes and I_D (drain current) is the current that passes between the two microelectrodes. The turn "on" with O_2 is complete within 2 min and the turn "off" with H_2 is complete within 0.3 min. A platinized microelectrode of a dimension similar to the microelectrochemical transistor shows only 1.0 nA reduction current upon exposure to 1 atm O_2; the current amplification of the transistor is thus a factor greater than 10^5. The transistor device can also reproducibly respond

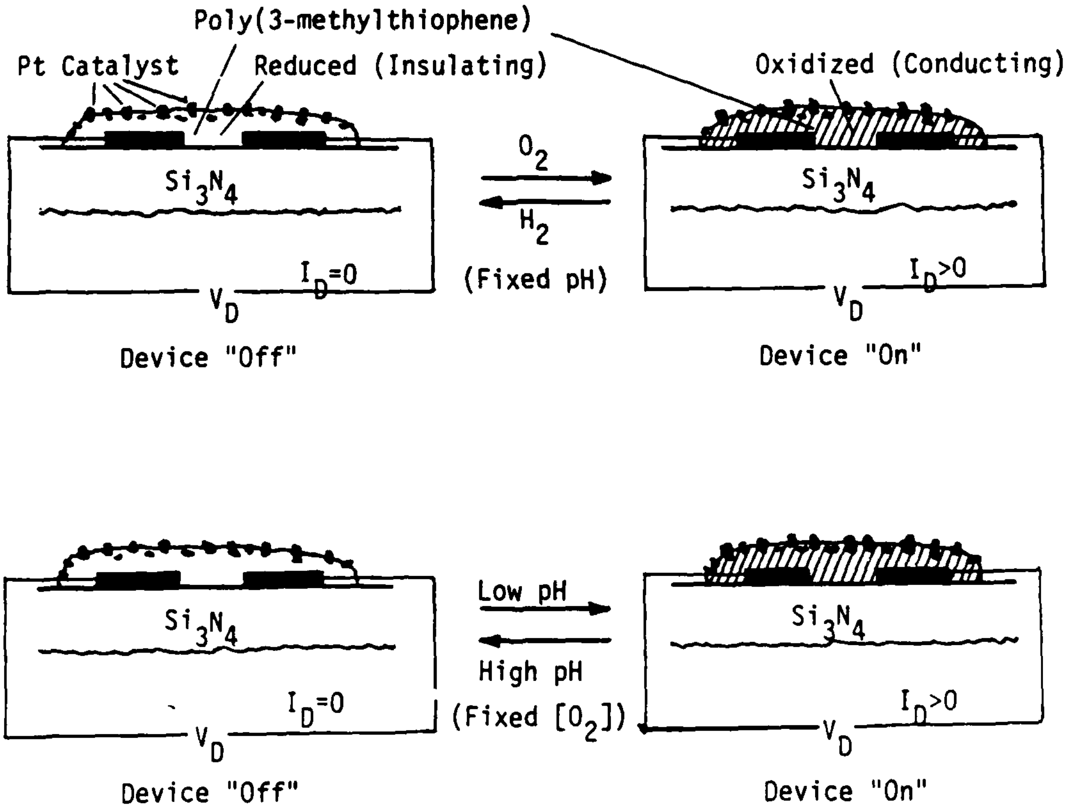
to pH changes in the pH range of 0 to 12, when there is a constant O_2 concentration; there is a reproducible change in I_D to alternate flow of a pH 5.5/pH 6.5 stream for over 10 hrs. The device responds to an injection of 10^{-6} l of 0.1 M $HClO_4$ into an effluent stream of 0.1 M $NaClO_4$ (flowing at 2 ml per min.) within 4 sec. Study of the resistance properties of the [poly(3-methylthiophene)/Pt] vs. potential reveals that the Pt has little effect on the intrinsic conductivity of poly(3-methylthiophene). Rather, the role of Pt is purely as a catalyst to allow equilibration of O_2 and H_2 with the polymer. The amount of Pt used is approximately 10^{-7} mol/cm^2, and microscopy shows the Pt to be present as particles of less than 0.1 micron size.

In this paper we wish to show that metal impregnated conducting polymers can be useful as the active material in microelectrochemical devices that respond to certain chemical changes in aqueous solution. The development of viable chemical microsensors[1,2] is limited by the equilibration of the chemical to be sensed with the microsensor surface. We report here the impregnation of poly(3-methylthiophene) with metallic Pt in order to make the conducting polymer responsive to oxidizing and reducing species, O_2 and H_2, respectively, in a reversible and reproducible manner at room temperature in aqueous solution, as sketched in Scheme I. As recently described, poly(3-methylthiophene)-based "transistors" can be used in aqueous solution to reproducibly respond to a redox signal, e.g. 10^{-16} moles of $IrCl_6^{2-}$ can be detected.[3] In principle, any oxidant capable of oxidizing poly(3-methylthiophene) can be detected. However, only those redox reagents capable of equilibrating with the poly(3-methylthiophene) can be useful in turning the transistor "on" or "off". Since the poly(3-methylthiophene)-based transistor has impressive durability in aqueous solutions, rapid response, and excellent transconductance,[3] this chemically sensitive device is an ideal candidate for microsensor development, provided that it can be made responsive to reagents of interest. Impregnation of the polymer with a noble metal capable of equilibrating with aqueous O_2 and H_2 is our first step in device modification that yields potentially useful functions for the device.

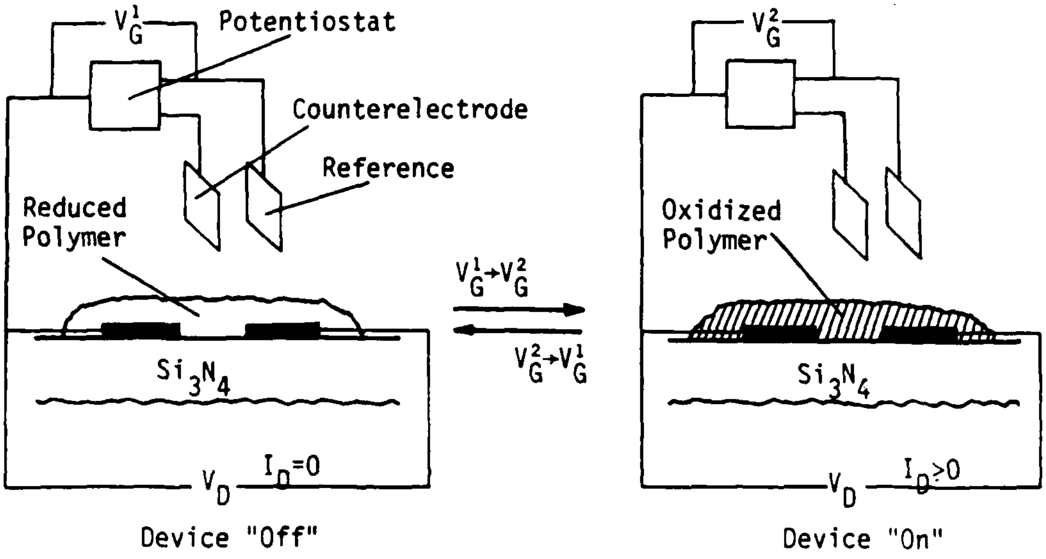
There is considerable precedent for the use of noble metals in redox polymers for the purpose of equilibrating the polymer with the H_2O/H_2 redox couple. The impregnation of viologen-based redox polymers with metallic Pt or Pd has yielded significant advantages in fabricating useful cathodes and photocathodes for H_2 evolution.[4] Recently, Tourillon and Garnier impregnated poly(3-methylthiophene) with Pt and Ag and showed that such polymers on electrodes exhibit high catalytic activity for H_2 formation, with sustained current densities of 200 mA/cm^2.[5] Pt is well known as an active material in electrochemical sensors for O_2.[6] Pd has been used as the chemically sensitive gate on an H_2-sensitive CHEMFET which operates well at elevated temperatures.[7] In this paper, we show that the [poly-3-methylthiophene/Pt]-based transistor, Scheme I, responds reversibly and reproducibly to O_2 and H_2 in aqueous electrolyte at room temperature, and, under aerobic conditions, the transistor responds reproducibly to pH from a range of 0 to 12. The key to the response of the microelctrochemical transistor is that the Pt equilibrates the polymer with the redox couple O_2/H_2O or H_2O/H_2, resulting in a polymer whose conductivity changes dramatically (up to five orders of magnitude) with variation in the pH (at 1 atm O_2) or with change in the atmosphere from O_2 to H_2 at fixed pH.

The ability of poly(3-methylthiophene)-based transistors to amplify electrical signals has already been demonstrated by establishing that the average power needed to turn the device on and off, Scheme II, is much smaller than the average power in the drain circuit at frequencies below 10^3 Hz.[3b,c] Part of the characterization of the [poly(3-methylthiophene)/Pt]-based transistors includes the demonstration that the Pt incorporated does not substantially alter the performance of the device as an electrical signal amplifier. While there is no presently perceived practical use of such a device, such characterization is essential in establishing the ultimate performance of sensors based on microelectrochemical transistors. With respect to their electrical properties, poly(3-methylthiophene)- and the [poly(3-methylthiophene)/Pt]-based transistors are essentially the same. The point is that the Pt in the polymer does not appear to affect the conductivity properties of the polymer at a loading where the Pt is an effective catalyst for the equilibration of the polymer with the O_2/H_2O and H_2O/H_2 redox couples.

Scheme I. Two terminal [poly(3-methylthiophene)/Pt]-based device that can be turned "on" and "off" with O_2 and H_2, respectively, at fixed pH or with pH variation at fixed $[O_2]$.



Scheme II. Representation of a [poly(3-methylthiophene)/Pt]-based transistor that can be turned "on" and "off" by variation in the gate potential, V_G, from $V_G{}^1$ where the polymer is reduced and insulating (device "off", $I_D = 0$) to $V_G{}^2$ where the polymer is oxidized and conducting (device "on", $I_D > 0$).



Experimental Section

Preparation of Microelectrode Arrays. The microelectrode arrays used in this work are those previously described.[8,9] Each chip consists of eight Au microelectrodes with contact leads and pads. The contact pads are symmetrically disposed about the chip, with the array itself occupying 0.01 mm^2. The microelectrode arrays are fabricated on 2" diameter single crystal Si wafers on which is grown a 1 micron SiO_2 layer which is then capped with 0.43 micron Si_3N_4 layer. The Au microelectrodes are deposited on top of the Si_3N_4 and are thus insulated from the Si. The eight Au microelectrodes are 50 micron x 2.4 micron x 0.1 micron thick and are separated by 1.2 micron. After packaging into electrode assemblies the arrays are typically cleaned with an O_2 plasma etch (150 W/2 min.) in order to ash residual photoresist. To insure good electrochemical behavior, the arrays are cycled from 0.0 to about -2.0 V vs. SCE in 0.1 M K_2HPO_4, effecting H_2 evolution at the negative potential. The microelectrodes are then tested by examining their electrochemical behavior in aqueous 0.1 M LiCl/5 mM $Ru(NH_3)_6^{3+}$. A good array shows the same current response for each of the eight microelectrodes: a well-developed current-voltage curve at 50 mV/s for reduction of $Ru(NH_3)_6^{3+}$ characteristic of microelectrodes.[8]

Chemicals. The CH_3CN was HPLC grade and used as obtained from commercial sources. The 3-methylthiophene was obtained commercially and distilled prior to use. The electrolytes were $[n\text{-}Bu_4N]ClO_4$ (Southwestern) for CH_3CN solvent or $HClO_4$, $NaClO_4$, and/or phosphate buffer for H_2O solvent. All gases were obtained from Matheson Gas

Products, including O_2/N_2 mixtures(1% to 10 ppm). Other gas mixtures were made by utilizing a Matheson Gas Proportioner.

Electrochemical Equipment. The equipment included a PAR Model 173/175 Potentiostat/Programmer for the characterization of macroscopic electrodes and a Pine Instruments RDE 4 Bipotentiostat for the characterization of microelectrodes. A Houston X-Y recorder or an oscilloscope was used to record data using the PAR equipment and a Kipp and Zonen BD 91 X-Y-Y'-T recorder was used for recording characteristics of the microelectrodes. In the two terminal sensing experiments, the counter and reference wires on the RDE 4 were shorted in order to allow the bipotentiostat to supply a floating DC bias, V_D, between two microelectrodes connected with poly(3-methylthiophene). A DC battery can also be used to provide V_D and was used in some experiments. The device response to pH, O_2, and H_2 was monitored by plotting drain current, I_D, vs. time.

Derivatization of Microelectrodes. Electrochemical oxidation of 3-methylthiophene at Au microelectrodes is accomplished as described in our previous work.[3] Metallic Pt can be deposited in the polymer film by potentiostatting the polymer at -0.3 V vs. SCE in 1 mM K_2PtCl_4/H_2O[5] for a period sufficient to reduce the desired amount of Pt. In CH_3CN/0.1 M [n-Bu_4N]ClO_4, the cyclic voltammogram of the polymer is the same before and after Pt deposition for Pt deposited at a coverage of about 10^{-7} mol/cm^2. In H_2O/0.1 M $LiClO_4$, the [poly(3-methylthiophene)/Pt] can not be moved positive of about 0.8 V vs. SCE, due to O_2 evolution. Typically, 10^{-7} C is associated with the interconversion of the insulating and conducting form of the poly(3-methylthiophene) and about 2 x 10^{-7} C was used to form Pt necessary to obtain maximum catalytic activity. The typical area of an array covered by a [poly(3-methylthiophene)/Pt]-based transistor is about 5 x 10^{-6} cm^2.

Electrical Characterization of [Poly(3-methlythiophene)/Pt]-Based Transistors. The resistance between a pair of microelectrodes connected with poly(3-methylthiophene) (before and after Pt deposition) was measured by holding one of the two microelectrodes (designated as the "source") at a potential called the gate potential, V_G, while the potential of the other microelectrode (designated as the "drain") is moved linearly about 20 mV (V_D) around V_G, while monitoring the current, I_D, that passes between the two microelectrodes.[3a,9] The I_D vs. V_G plots in aqueous electrolytes were generated by our previously described methodology.[3,9]

pH Stimulation of a [Poly(3-methylthiophene)/Pt]-based Transistor. The pH was varied at the surface of a device, Scheme I, by utilization of a 1084b Hewlett-Packard High Pressure Liquid Chromatograph. The HPLC was altered by removing the column. The device was placed directly in the path of the effluent stream, which collected in a glass frit. The solvent collected in the glass frit was saturated with air to provide a fixed $[O_2]$. Two methods were used to alter the pH reproducibly. First, we used the gradient programmer to provide alternating compositions of 0.1 $\underline{M}$ NaH_2PO_4/0.1 $\underline{M}$ $NaClO_4$(Solvent A) and 0.05 $\underline{M}$ Na_2HPO_4/0.1 $\underline{M}$ $NaClO_4$(Solvent B). Second, we injected varying amounts of 0.1 $\underline{M}$ $HClO_4$ onto an effluent stream of 0.1 $\underline{M}$ $NaClO_4$. In all such experiments, the flow rate was 2.0 ml/min.

Results and Discussion

Deposition of Pt Onto Poly(3-methylthiophene). Elemental Pt can be electrochemically deposited onto poly(3-methylthiophene) via reduction of $PtCl_4^{2-}$ as described in the Experimental Section. The coverage of Pt was typically about 10^{-7} mol/cm^2 for the experimentation to be described below. A macroscopic Au electrode was first coated with poly(3-methylthiophene) and then with Pt at approximately the same coverage used for the microelectrochemical transistors. Scanning electron microscopy shows that the Pt particles are typically less than 0.1 micron in dimension. Auger spectroscopic investigation of the Au/poly(3-methylthiophene)/Pt electrode shows that the Pt is largely, but not completely confined to the outermost region of the polymer, Figure 1. Such structures have been previously prepared with viologen-based polymers,[4c] but the noble metal can be more cleanly separated from the substrate than demonstrated in Figure 1 for the Au/poly(3-methylthiophene) system. Indeed, it is evident that the Pt can be found throughout the poly(3-methylthiophene). This finding is consistent with the relatively porous, open structure of the poly(3-methylthiophene) compared to the viologen-based systems.[4] The fact that the Pt can be dispersed throughout the poly(3-methylthiophene) represents an advantage in that the polymer/Pt assembly can be regarded as a three dimensional zone of catalytic activity that could yield faster rates of equilibration with sluggish redox couples. The several situations associated with electrocatalysis by polymer coatings on electrodes have been recently discussed.[10]

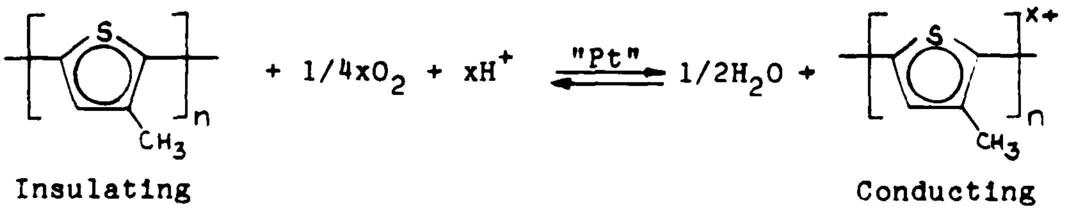
Resistance of [Poly(3-methylthiophene)/Pt] as a Function of Potential. Figure 2 shows the effect of medium, potential, and Pt deposition on the resistance of poly(3-methylthiophene). First, we note that the resistance varies from $>10^{10}$ ohms at 0.0 V vs. SCE to 10^2 ohms at 0.8 V vs. SCE before and after Pt deposition, in CH_3CN/0.1 M [n-Bu_4N]ClO_4. It is interesting that the presence of the metallic Pt has no measurable effect on the potential dependence of the resistance of poly(3-methylthiophene) in CH_3CN. The ability to modulate the conductivity of the polymer is crucial to the sensor function, and it is well-known that metal-filled polymers are good conductors. Thus, it is gratifying to find that the level of Pt required to bring about catalysis (vide infra) of the O_2/H_2O and H_2O/H_2 redox couples does not lead to potential independent, permanent conductivity of the polymer. In aqueous electrolyte, such as H_2O/0.1 M $HClO_4$, Pt deposition leads to a small change in the maximum resistance of the poly(3-methylthiophene) in the reduced state; 8 x 10^7 ohms at -0.3 V vs. SCE prior to Pt deposition to 1 x 10^7 ohms at -0.3 V vs. SCE after Pt deposition. Again the small change in the potential dependence of the resistance of poly(3-methylthiophene) in H_2O upon Pt deposition shows that no shorting of the microelectrodes has occurred, and that the primary role of the noble metal is as a catalyst and not in altering the intrinsic potential dependence of the conductivity of poly(3-methylthiophene). We note that the maximum resistance of the poly(3-methylthiophene) in an aqueous electrolyte is less than in CH_3CN, consistent with previous reports of partial doping of poly(3-methylthiophene) in aqueous medium.[11] Further, the deposition of Pt does lower the maximum resistance by about one order of magnitude. Such lowering of the resistance may be due to the formation of H_2 upon negative potential excursions that can provide a mechanism for transporting charge from one microelectrode to another. Another possibility is that the aqueous environment brings about a structural change that yields a small amount of conductivity due to the deposited Pt. In any event, the resistance of the poly(3-methylthiophene) can still be varied by about five orders of magnitude upon varying the potential, Figure 2, in an aqueous electrolyte.

Characterization of [Poly(3-methylthiophene)/Pt]-Based Microelectrochemical Transistors in Aqueous Electrolyte. As expected from data shown in Figure 2, removal of a small amount of electrical charge from the [poly(3-methylthiophene)/Pt] polymer connecting two microelectrodes increases I_D dramatically, Scheme II and Figure 3. Figure 3 illustrates a typical I_D vs. V_G (fixed V_D) characteristic in aqueous electrolyte. We see a value for the transconductance, g_m, of 120 mS/mm of gate width, similar to that previously reported for the poly(3-methylthiophene)-based transistor characterized in CH_3CN.[3a] As reported earlier,[3a] the [poly(3-methylthiophene)/Pt]-based transistor begins to turn "on" at 0.3 V vs. SCE and I_D achieves a plateau for V_G more positive than about + 0.8 V vs. SCE. The electrochemical characterization of the transistor shows that chemical oxidants, like O_2, and chemical reducing agents, like H_2, could turn the device "on" and "off", respectively, if they are capable of equilibrating with the polymer, because I_D varies strongly in a potential region that is accessible with the O_2/H_2O redox couple.

Note that in an electrically-driven characterization, Scheme II, the poly(3-methylthiophene)-based transistor and the [poly(3-methylthiophene)/Pt]-based transistor show no apparent difference in operation. This point is an important one to make in that the ability to amplify electrical signals with the transistor derived from poly-3-methylthiophene[3b,c] remains intact, while there is an expanded scope of chemicals that can turn on the two terminal device represented by Scheme I, vide infra.

Response of A Two Terminal [Poly(3-methylthiophene)/Pt]-Based Device to O_2 and H_2 Gas. In our earlier work, we showed that a two terminal poly(3-methylthiophene)-based device reproducibly responds to a chemical signal, such as $IrCl_6^{2-}$, to turn on the device because the polymer is oxidized rapidly by the $IrCl_6^{2-}$.[3a] The [poly(3-methylthiophene)/Pt]-based device can be turned on by the O_2/H_2O redox couple, $E^{o\prime} = 0.99$ V vs. SCE at pH = 0, and turned off with the H_2O/H_2 redox couple, $E^{o\prime} = -0.24$ V vs. SCE, Scheme I and Figure 4. Figure 4 shows the response of a [poly(3-methylthiophene)/Pt]-based two terminal device to alternate cycling of oxidizing gas, O_2, and reducing gas, H_2, in H_2O/0.1 M $HClO_4$. Without Pt, the two terminal device is unresponsive to the gases O_2 and H_2: the reduced polymer is not oxidized by O_2 to turn on the device and H_2 does not reduce the oxidized polymer to turn off the device. For the Pt-impregnated device exposure to 1 atm O_2 gives $I_D > 0.7$ mA at $V_D = 0.2$ V. Upon exposure to H_2, the device is shut "off" to $I_D < 20$ nA at $V_D = 0.2$ V. The actual response time of the device to the chemical signals varies somewhat from device to device, but the devices all turn on more slowly with O_2 than they can be turned off with H_2. The faster turn off than turn on is consistent with the fact that the O_2/H_2O redox couple has slower kinetics than the H_2O/H_2 redox couple at Pt.[12] The best devices reach 95% of maximum I_D in <2 min upon exposure to 1 atm O_2, and can be turned off to <5% of the maximum I_D in <0.3 min upon exposure to 1 atm. H_2. Rapid, reproducible response of the [poly(3-methylthiophene)/Pt]-based device to a large number of O_2/H_2 cycles over a several hour time period has been demonstrated without variation in the device properties.

While a detailed study has not been made, the data in Figure 4 show that the device turns on to a smaller extent at a partial pressure of O_2 that is significantly less than 1 atm. Figure 5 shows additional data in this regard and also establishes that H_2 is not needed to turn off the device. The value of I_D for the two terminal device is clearly affected by simply changing the partial pressure of O_2 between 1 and 10^{-2} atm, more or less consistent with the equilibrium indicated in equation (1). Experiments on macroelectrodes provide additional insight into the catalytic role of Pt in poly(3-methylthiophene). The potential of a [poly(3-methylthiophene)/Pt] macroelectrode is only +0.60 V vs. SCE in 1 atm O_2/ 0.1 M $HClO_4/H_2O$, and a potential of -0.30 V vs. SCE in 1 atm H_2/0.1 M $HClO_4/H_2O$. The potential difference, 0.9 V, is smaller than that expected ideally, 1.23 V. All of the voltage loss, 0.33 V, is associated with the O_2/H_2O couple ($E^{o\prime}$ = 0.93 V vs. SCE, at pH 1.0). However, the voltage loss is also seen at similarly platinized Pt and platinized Au macroelectrodes. Therefore, the catalytic Pt in poly(3-methylthiophene) appears to be as effective as Pt itself, and the non-



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ideal behavior of Pt in equilibrating with O_2 explains the voltage loss.[12] The inability to achieve the O_2/H_2O potential is likely associated with achieving a mixed potential arising from the O_2/H_2O_2 redox couple, $E^{o\prime} = +0.44$ V vs. SCE at pH = 0. Incidentally, small amounts of H_2O_2 in aqueous electrolyte do not turn on a non-platinized poly(3-methylthiophene)-based two terminal device, whereas the platinized device is responsive.

The two terminal device illustrated in Scheme I obviously turns on with O_2 in $HClO_4$. The device can also be turned on in the presence of other acids including pH = 1 solutions of HNO_3, HBF_4, and H_2SO_4. For a given device there is about a factor of two lower value of I_D at 1 atm O_2 for the H_2SO_4, but the other acids give the same maximum value of I_D within experimental error. It is known that there is variation in the conductivity of conducting polymers depending on the charge compensating anion, but it has been suggested that poly(3-methylthiophene) is somewhat less sensitive to anion than other polymers, e.g. polypyrrole,[13] because of its more open structure.[11]

It is possible to establish that a kind of amplification of the chemical signal can be realized with a [poly(3-methylthiophene)/Pt] device. A pair of "naked" Au microelectrodes with the same amount of Pt deposited on their surface can be held at 0.0 V vs. SCE and the reduction current for the reduction of O_2 in H_2O can be monitored. For the pair of "naked" microelectrodes, the largest reduction current was 1.0 nA, in a situation where $I_D > 0.7$ mA is found upon turn on with O_2 of a two terminal [poly(3-methylthiophene)/Pt] device. The ratio of I_D to the reduction current at the pair of naked microelectrodes is thus greater than $7 \times 10^5 : 1$. The point is that the charge needed to turn on the transistor results in a large flow of charge in the drain circuit of the device and represents a larger signal than can be achieved by a conventional amperometric detection of the O_2 in solution. Thus, smaller O_2 signals should be detectable at the transistor device.

The "naked" microelectrodes for amperometric detection showed switching times similar to those for O_2/H_2 cycling as found for the [poly(3-methylthiophene)/Pt] transistor; i.e. 2 min to show 95% of maximum reduction current for O_2, and 0.3 min to show 95% of maximum oxidation current for H_2. The similar turn "on" and turn "off" times for the platinized microelectrodes and the [poly(3-methylthiophene)/Pt]-based device indicate that the Pt on the polymer is as effective catalytically as on a "naked" Au surface. However, it should be noted that the surface area associated with the polymer supported Pt may be much greater than for the smooth Au surface. In previous work it was found that the catalytic activity per unit mass of noble metal is lower on the viologen-based polymers than on the surface of solid electrode materials.[14]

Response of Two Terminal [Poly(3-methylthiophene)/Pt]-Based Devices to Variation of pH. Figure 6 shows I_D of a two terminal [poly(3-methylthiophene)/Pt] device vs. pH for an O_2-saturated aqueous electrolyte. The oxidizing power of the O_2/H_2O couple is reduced by 60 mV/pH upon moving to more basic conditions. Thus, the drain current is reduced dramatically in shifting from pH 1 to pH 12.0. Above pH 12, the device shows no response to O_2-saturated solutions. At pH 12 (0.1 $\underline{M}$ Na_3PO_4/0.1 $\underline{M}$ $NaClO_4$), we measure a lower limit variation of I_D of 50 nA upon O_2/H_2 cycling. Operationally, the device shows the largest, most easily detectable response in acidic solutions, but reproducible response can also be achieved in neutral and basic solutions. It is important to note that I_D does not vary linearly with pH, Figure 6, as expected from the transistor characteristic shown in Figure 2. Variation in pH at fixed $[O_2]$ is expected to result in a 59 mV/pH shift in the potential, and this is approximately the case. However, as noted above the Pt catalyst does not bring the polymer to the standard potential for the O_2/H_2O redox couple. Accordingly, the characteristic in Figure 2 does not predict the pH response shown in Figure 6. The data in Figure 2 would lead to the expectation that the two terminal device would show the maximum slope in the I_D vs. pH plot at a pH of about 7 where $E^{o\prime}(O_2/H_2O) =$ +0.57 V vs. SCE. In fact, the maximum slope in the I_D vs. pH plot, Figure 6, occurs near pH 4, because the Pt does not bring the polymer to the reversible O_2/H_2O potential. Thus, as for response to O_2 at fixed pH, the response of the two terminal device in Scheme I to pH variation at fixed $[O_2]$ is not that predicted from the electrical characteristic of the transistor in Scheme II, because the Pt is not an ideal catalyst for the O_2/H_2O redox couple.

The two terminal [poly(3-methylthiophene)/Pt] device shows reproducible response to pH variation at fixed $[O_2]$ for a long period of time. Figure 7 shows I_D vs. time while changing the pH repetitively between 5.5 and 6.5 at V_D = 0.2 V. The pH change was accomplished by using the gradient programmer of an HPLC, where solvent A contained pH 5.5, 0.1 $\underline{M}$ NaH_2PO_4/0.1 $\underline{M}$ $NaClO_4$, and solvent B contained pH 8.6, 0.05 $\underline{M}$ Na_2HPO_4/0.1 $\underline{M}$ $NaClO_4$. By programming the

HPLC, a reproducible pH variation could be delivered to the two terminal device for ~10 h.

Data in Figure 7 demonstrate drift-free and constant response to pH variation for the entire experiment. It should be emphasized that the experiment does not demonstrate the lifetime of useful function. Rather, the data shown establish that the lifetime is at least 10 h. In fact, the device used to collect the data in Figure 7 also responded, drift-free, for another 6 h to a pH variation between 5.5 and 3.5 with a reversible, reproducible change in I_D of 3.0 microamps (larger I_D at lower pH). An impressive feature of the long term experiments involving pH variation at fixed $[O_2]$ is that the devices can operate with negligible drift. This is surprising because it is well known that Pt is easily poisoned; under the carefully controlled conditions used in the experimentation the overall function of the device is constant. This information does not prove that practical applications will emerge, but the data do show that the activity of the catalyst and the properties of the conducting polymer are intrinsically sufficiently persistent to achieve useful functions. Considering that the Pt probably leads to the creation of some H_2O_2, vide supra, the long term constant operation in experiments like that summarized by Figure 7 suggests that the [poly(3-methylthiophene)/Pt] system is oxidatively durable. One final point should be made concerning durability. In an experiment like that in Figure 7 there is a constant current passing from one microelectrode to another and in one direction. During the experiment $>10^5$ C/cm^2 pass through each microelectrode/polymer interface at a current density of >3 A/cm^2. In practical applications there is probably merit in considering the use of periodic variation in the sign of V_D. At least this would minimize the migration of the Pt catalyst. In the experiments carried out thus far we have not found problems from catalyst migration, but it is a problem that is likely to be encountered in long term operation of such devices.

Figure 7 does not establish the response time of the device to pH change. In Figure 7 the response of the device follows the variation of pH. A rapid change in pH could be delivered by direct injection of a pulse of 0.1 $\underline{M}$ $HClO_4$ into an effluent stream of 0.1 $\underline{M}$ $NaClO_4$. The detection of such a pH "jump" is illustrated in Figure 8. There is a fast, reproducible response to a change in pH when 1.0 microliter of 0.1 $\underline{M}$ $HClO_4$ (1×10^{-7} moles H^+) is injected. We see a change in I_D of 1.0 microamp at $V_D = 0.1$ V. Again, the change in I_D is reproducible over many injections, and the speed of response is constant. The turn "on" time is <4 s.

Conclusions

The characterization of the [poly(3-methylthiophene)/Pt]-based devices sketched in Schemes I and II show that the Pt can be deposited in an amount that will allow the polymer to be equilibrated with the O_2/H_2O and H_2O/H_2 redox couples without significantly altering the essential potential dependence of the conductivity of the polymer. Thus the [poly(3-methylthiophene/Pt] composite material is chemically sensitive in a way that allows the demonstration of microelectrochemical devices responsive to H_2 and O_2 at fixed pH and to pH at fixed $[O_2]$. The Pt catalyst is nearly ideal for the H_2O/H_2 redox couple in that rapid response can be achieved and the polymer can be equilibrated to the standard potential. The Pt catalyst is less effective for the O_2/H_2O redox couple; the response is slower and the standard potential is not achieved with the Pt-impregnated polymer. The catalytic activity of Pt in the poly(3-methylthiophene) parallels its behavior in other situations.[12]

The interesting property of the [poly(3-methylthiophene)/Pt] material is that the conductivity can be varied by five orders of magnitude in acid solution by changing the atmosphere from H_2 to O_2. This suggests that there may be useful applications as a sensor, but there are at least two problems that should be mentioned. First, the two terminal device is a "floating" device without a reference electrode and operates as a system that responds to the potential of the medium at a rate that is dependent on having active catalyst. The catalyst is a noble metal known to be easily deactivated. Second, the conductivity of the polymer is likely to be somewhat electrolyte dependent, for a given potential. More elaborate characterization of the electrolyte dependence is required to assess whether the device is practical. As a pH sensor at fixed [O_2] the device also has some possible shortcomings related to the issues mentioned above. However, the demonstration of reproducible response under laboratory conditions, Figure 7, provides evidence that there is not an intrinsic materials limitation that rules out useful devices.

It should be emphasized that the electrical characteristics of the device in Scheme II are essentially the same with and without the Pt in the polymer. The point is that the data in Figure 3 are the same as would be obtained without the Pt catalyst. There are electroactive materials that have an intrinsic pH dependence that can be useful in demonstrating devices that are responsive to pH variation where the device is operated as in an ISFET,[1] where V_G and V_D are fixed. In this regard research in the Wrighton group[15] has been directed toward characterization of microelectrochemical transistors based on a quinone-containing polymer,[16,17] polyvinylpyridine,[18] or metal oxides.[19,20] Unlike the poly(3-methylthiophene) these materials have an intrinsic pH dependence that yields pH-dependent transistor characteristics. However, a significant disadvantage of such materials compared to the [poly(3-methylthiophene)/Pt] composite is that the devices have maximum value of I_D that is substantially lower. Research in the Wrighton group is now directed toward the synthesis of intrinsically chemically sensitive redox polymers that have high maximum conductivity.

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Figure Captions

Figure 1. Auger signal intensities as a function of Ar ion sputtering time for a macroscopic Au electrode first modified with poly(3-methylthiophene) and then with elemental Pt as outlined in the Experimental Section.

Figure 2. Resistance between two poly(3-methylthiophene)-connected microelectrodes as a function of V_G in (A) CH_3CN/0.1 M [n-Bu_4N]ClO_4, before and after Pt deposition and in (B) H_2O/0.1 M $HClO_4$ before Pt deposition and in (C) H_2O/0.1 M $HClO_4$ after Pt deposition.

Figure 3. Drain Current, I_D, vs. gate potential, V_G, at fixed V_D = 0.200 V, for a [poly(3-methylthiophene)/Pt]-based transistor in H_2O/0.1 M $HClO_4$ as in Scheme II.

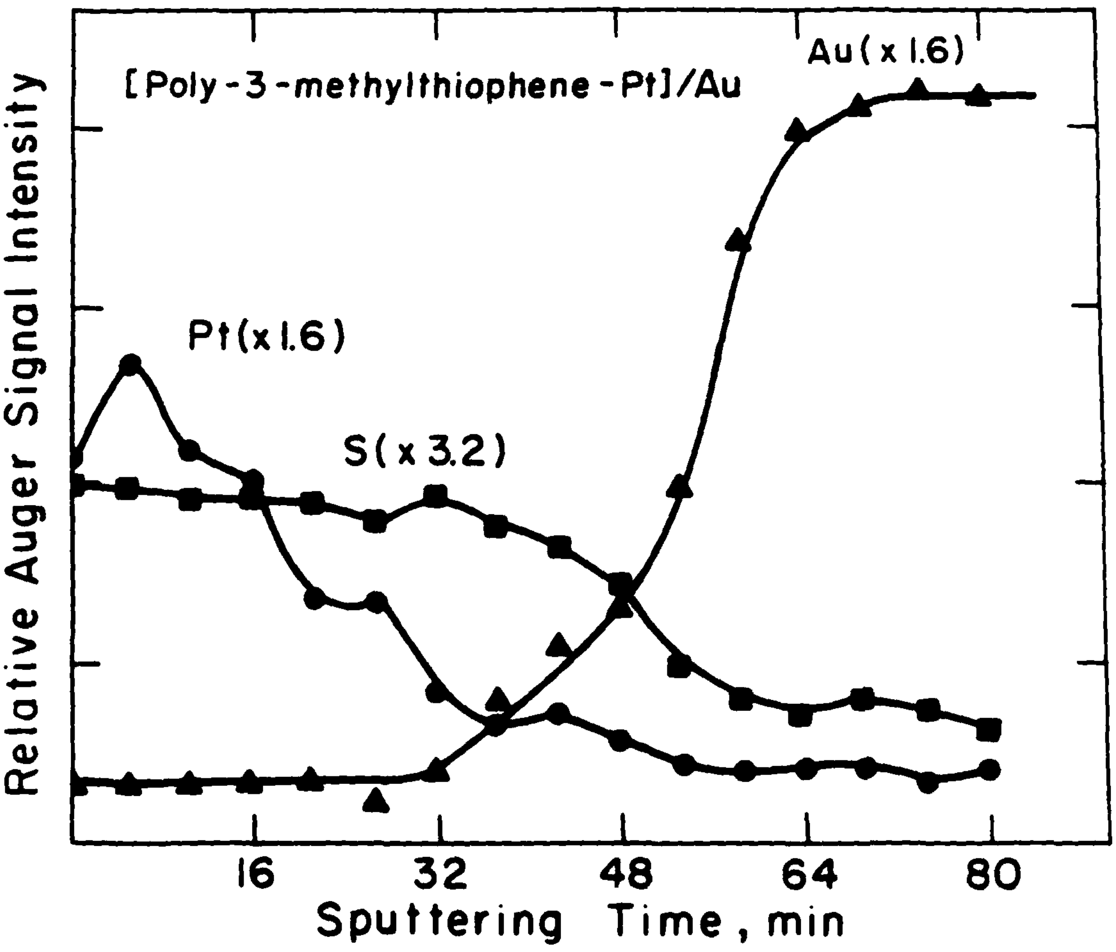
Figure 4. I_D vs. time for a two terminal [poly(3-methylthiophene)/Pt]-based device, Scheme I, upon exposure to O_2 and H_2 gas in 0.1 M $HClO_4/H_2O$. In all cases the total pressure is 1 atm, with N_2 as a diluent for the 10^{-2} atm O_2 signal.

Figure 5. Response of a two terminal [poly(3-methylthiophene)/Pt]-based device to variation in O_2 partial pressure (total pressure 1 atm) to show that the device does not require H_2 to be turned off, consistent with the equilibrium represented by equation (1).

Figure 6. I_D vs. pH for a [poly(3-methylthiophene)/Pt]-based device, Scheme I, exposed to 1 atm O_2/0.1 M $NaClO_4/H_2O$, $V_D = 0.200$ V.

Figure 7. I_D vs. time for a two terminal [poly(3-methylthiophene)/Pt]-based device upon periodic alternation between pH 5.5 and 6.5 at $V_D = 0.200$ V.

Figure 8. I_D vs. time for a two terminal [poly(3-methylthiophene)/Pt]-based device upon injection of 1 microliter of 0.1 M $HClO_4$ into an unbuffered, pH 6.0, 0.1 M $NaClO_4$ effluent stream at $V_D = 0.200$ V.


[Poly-3-methylthiophene-Pt]/Au
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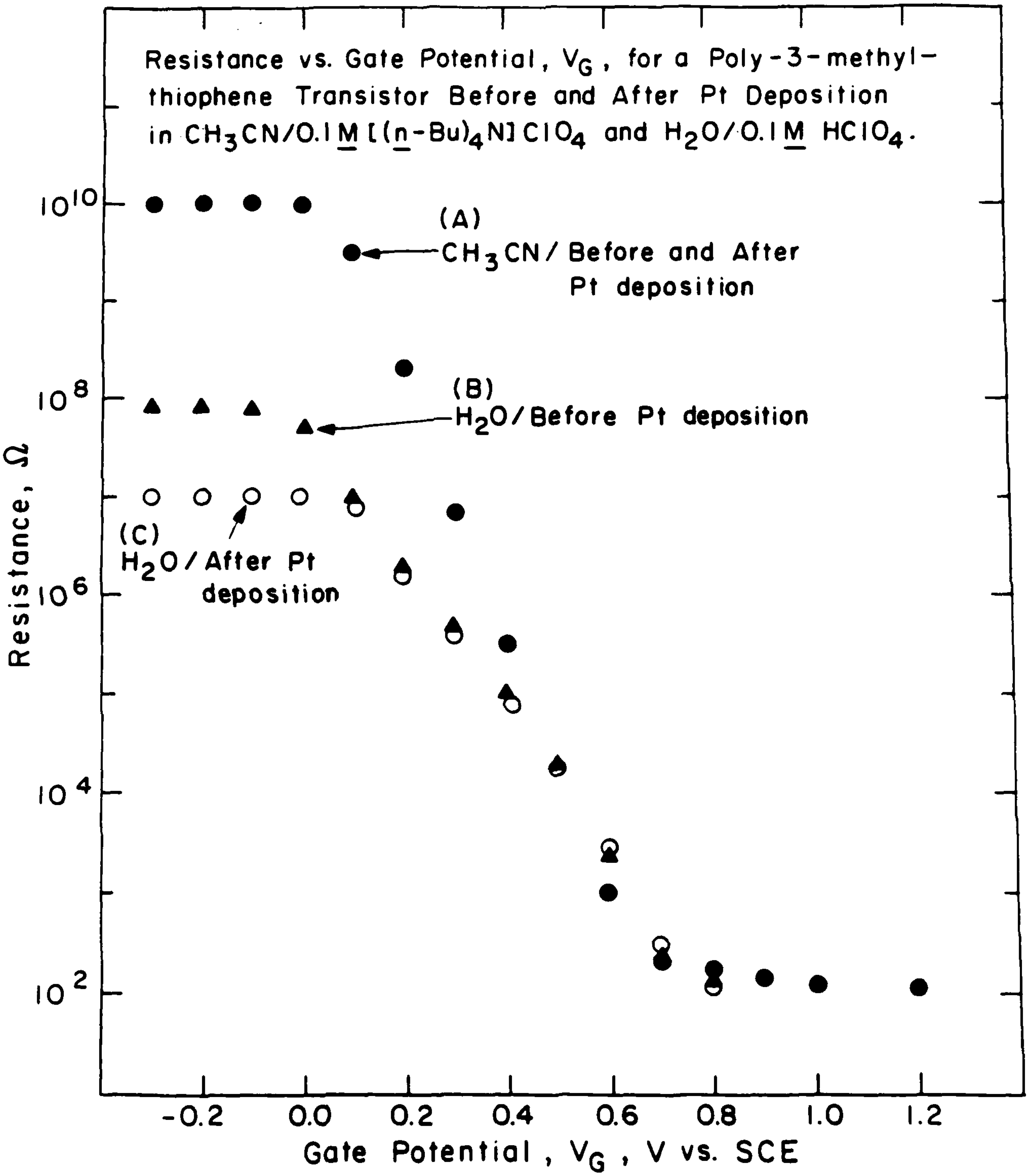
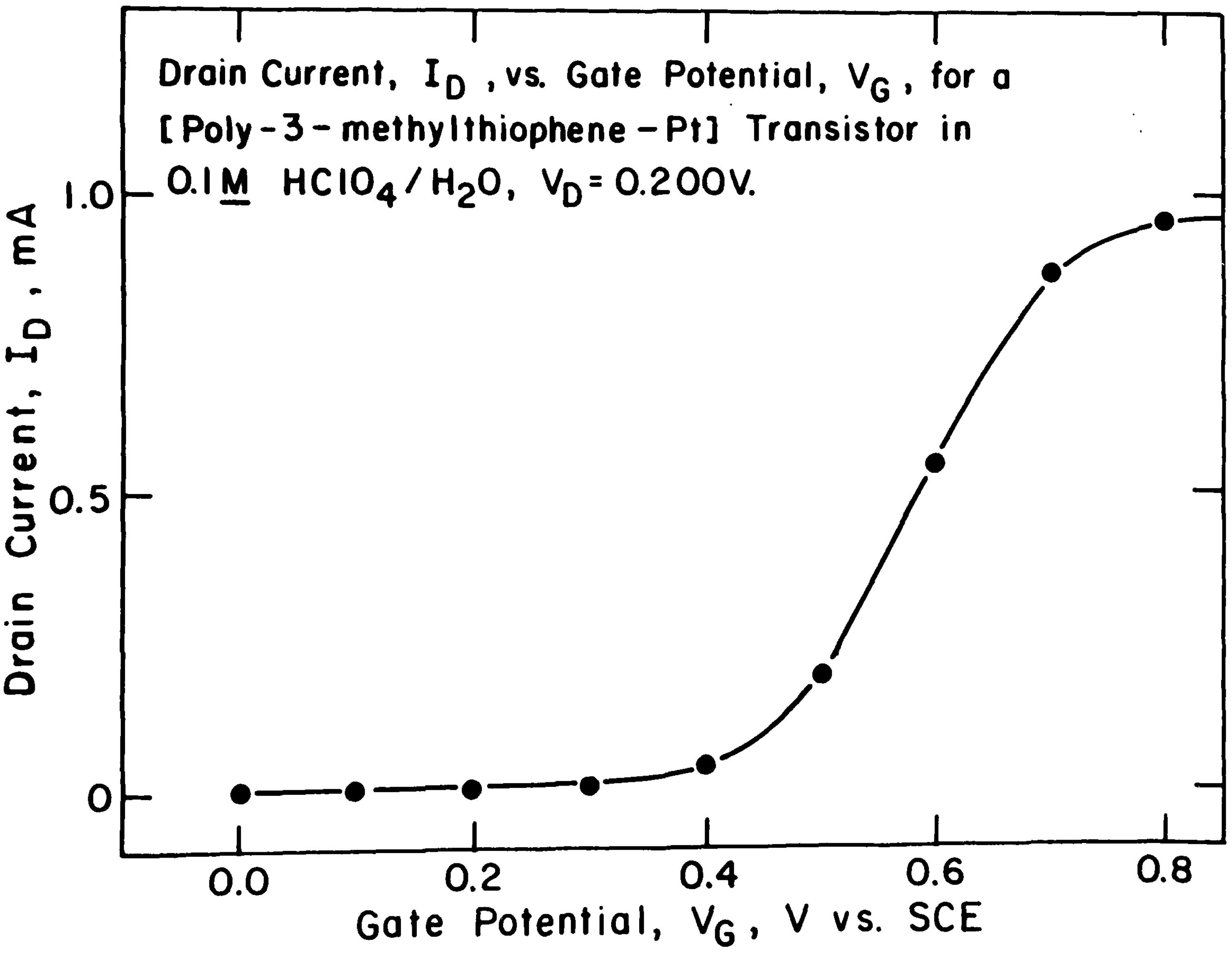
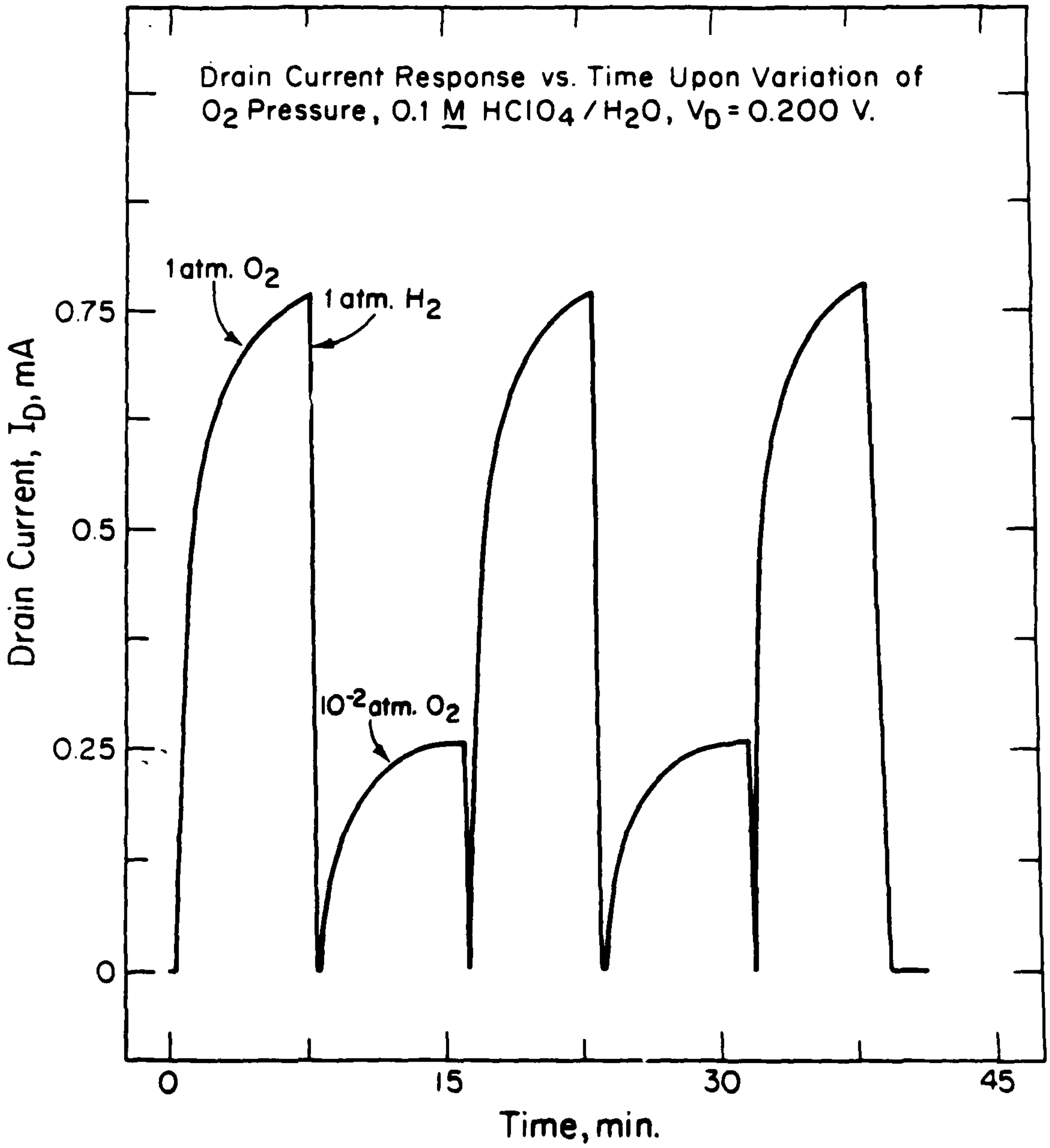
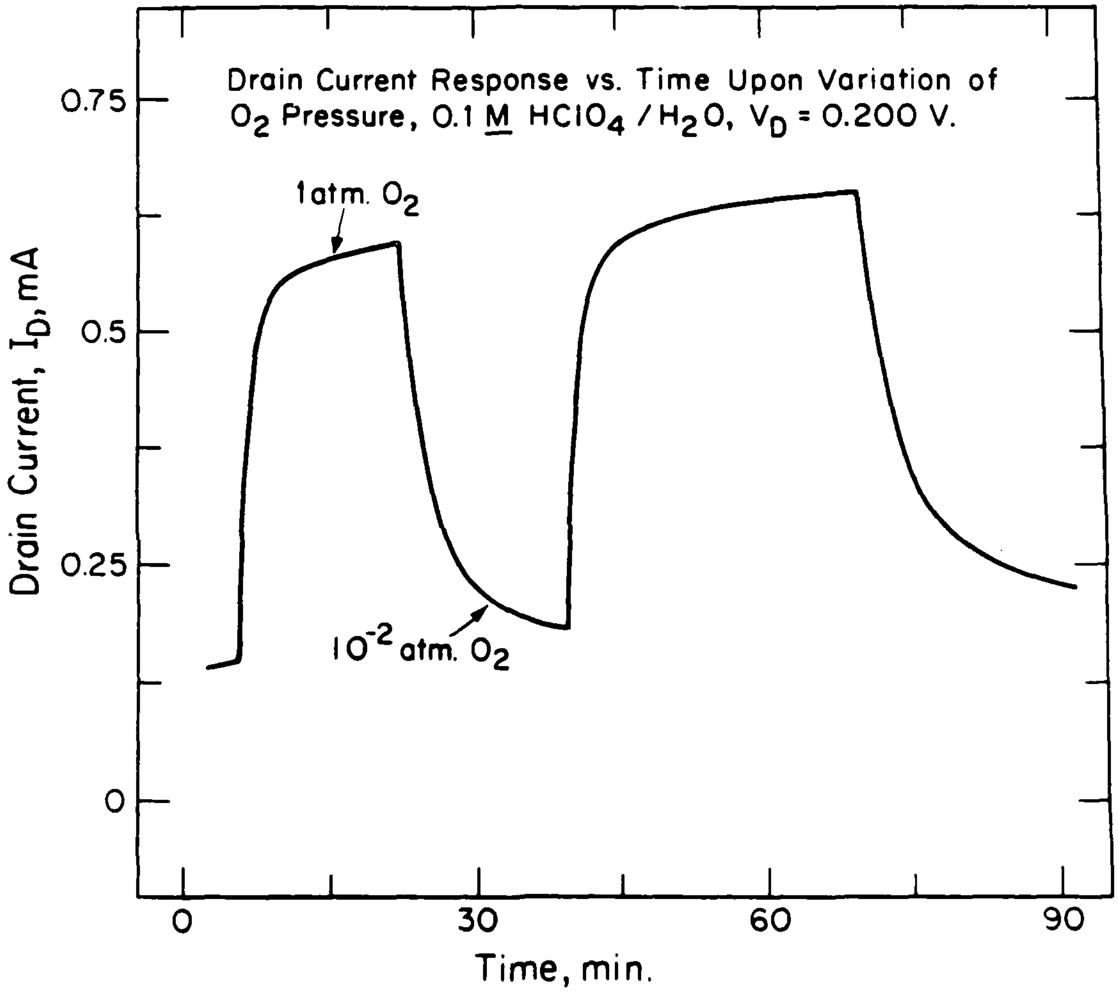
Pt(x1.6)
S(x3.2)
Relative Auger Signal Intensity
16
32
48
64
80
Sputtering Time, min

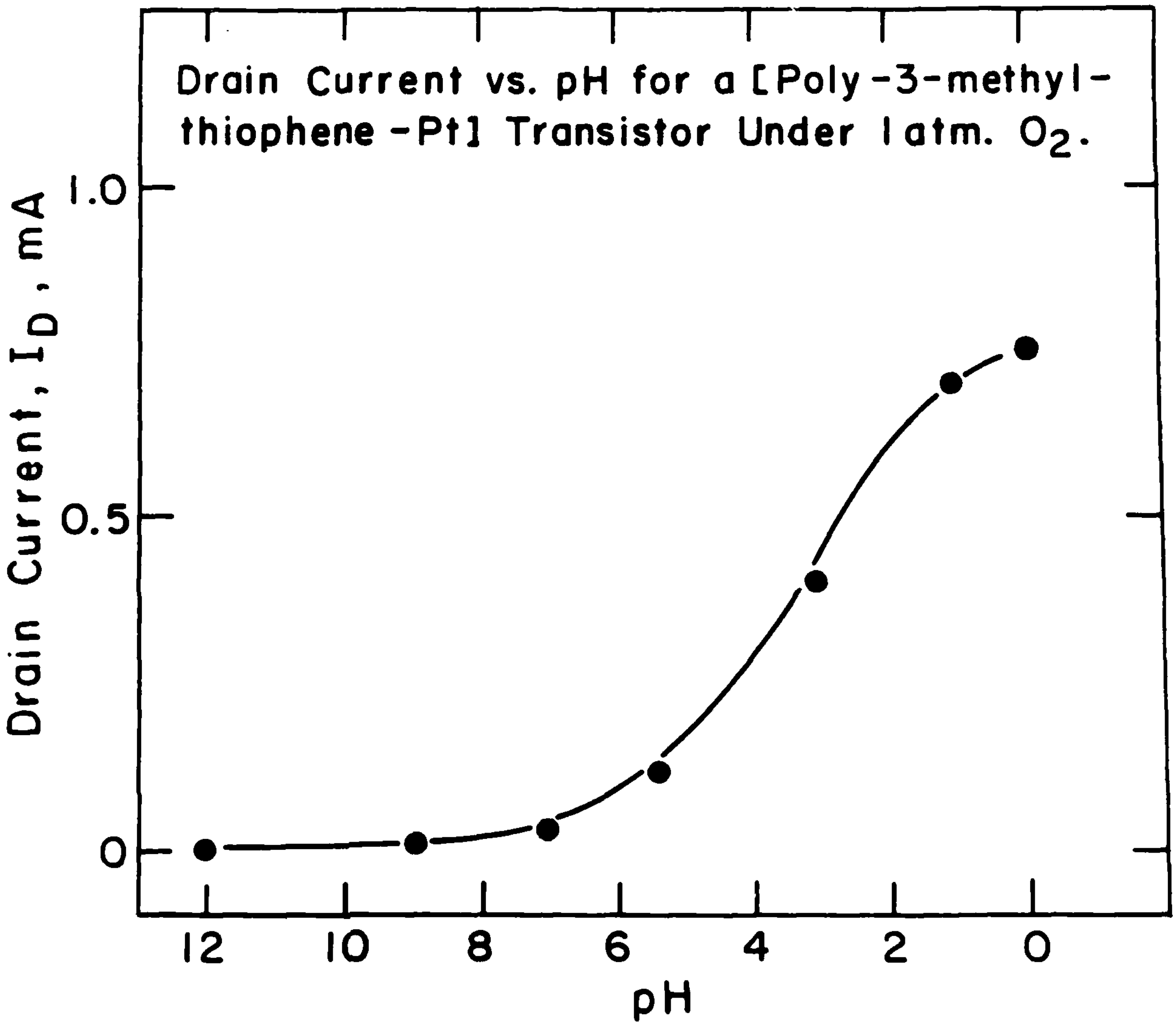


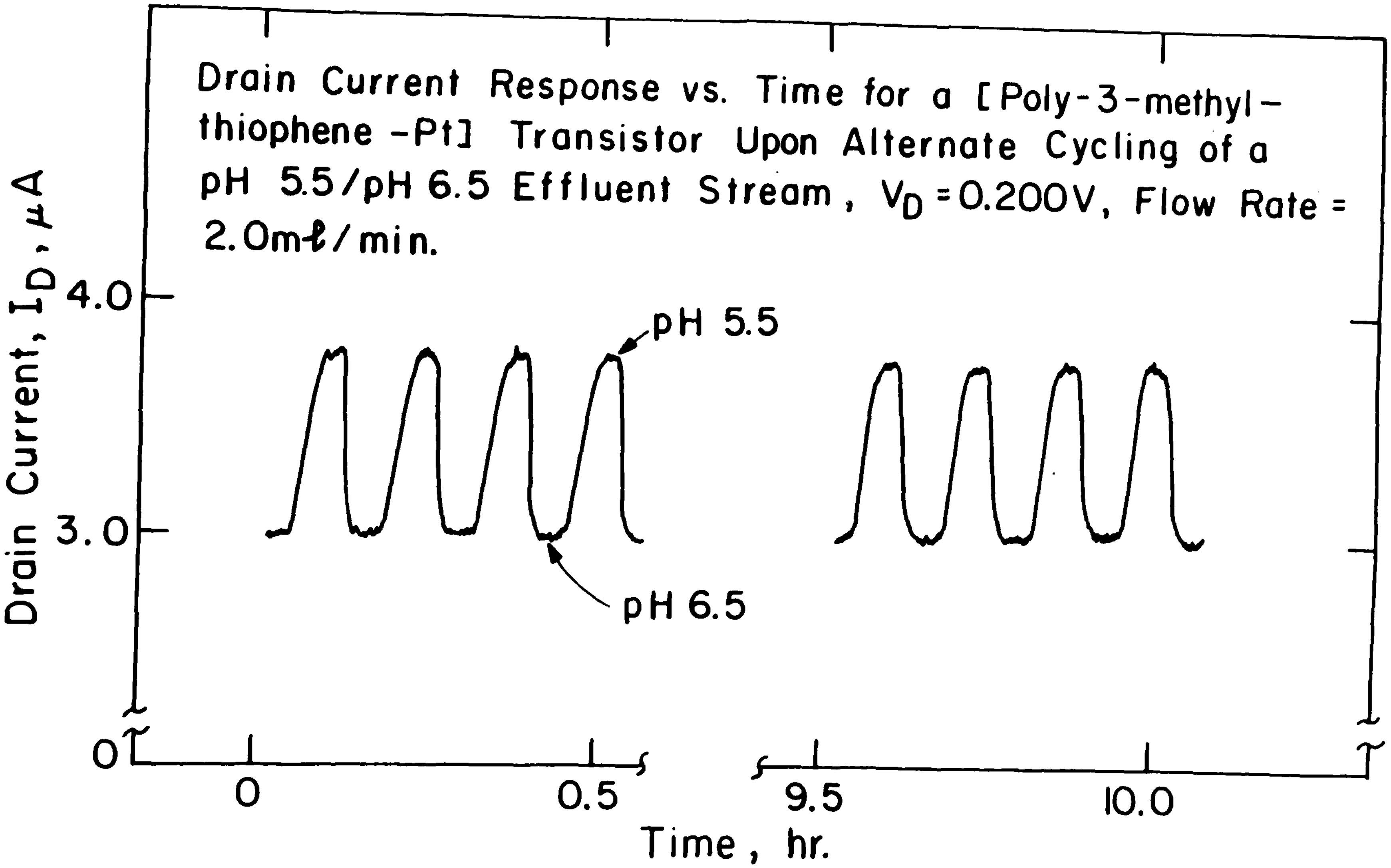
Resistance vs. Gate Potential, V_G, for a Poly-3-methylthiophene Transistor Before and After Pt Deposition in $CH_3CN/0.1\,\underline{M}\,[(\underline{n}\text{-Bu})_4N]ClO_4$ and $H_2O/0.1\,\underline{M}\,HClO_4$.


Drain Current, I_D, vs. Gate Potential, V_G, for a [Poly-3-methylthiophene-Pt] Transistor in 0.1M $HClO_4/H_2O$, $V_D = 0.200V$.

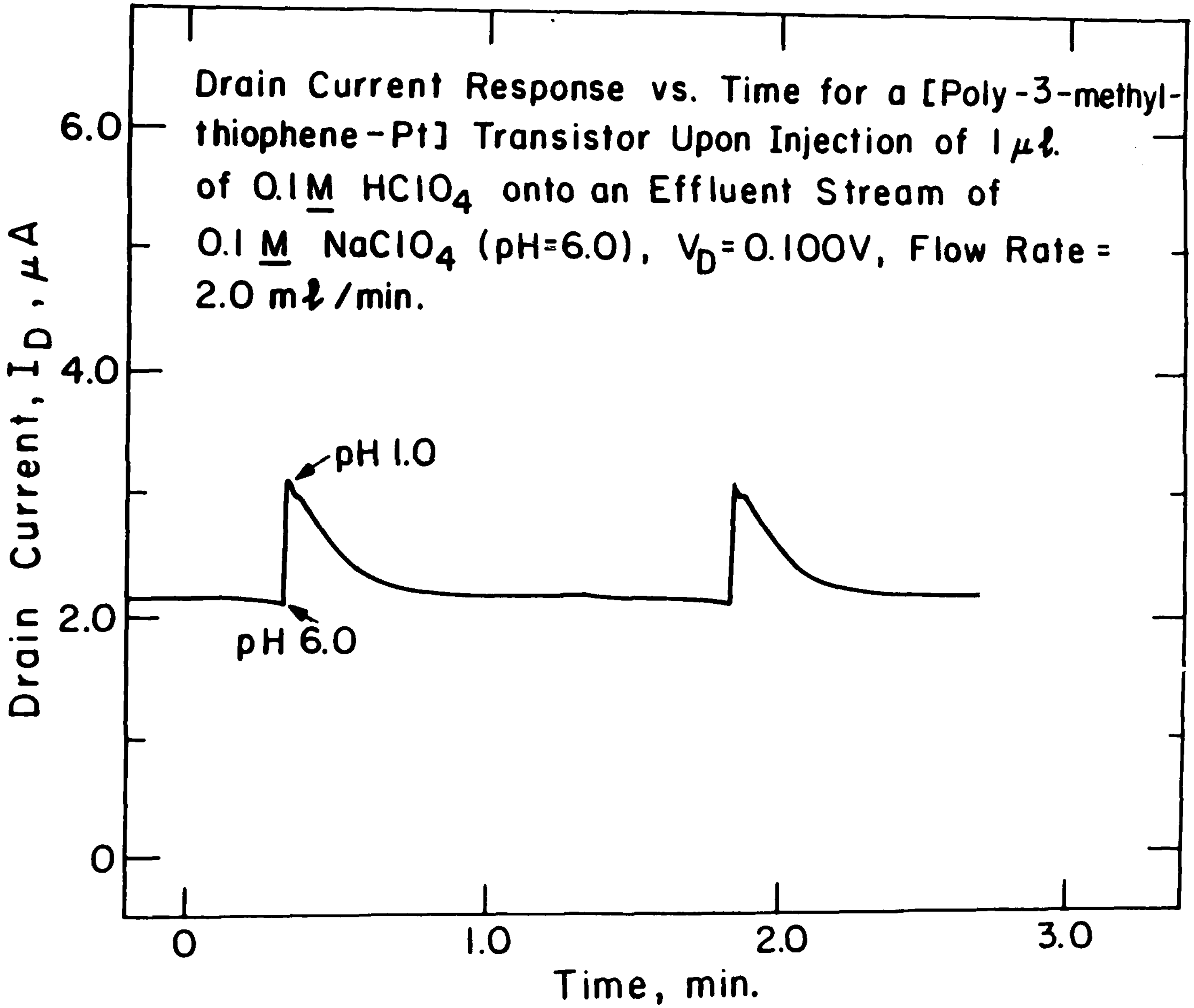

Drain Current Response vs. Time Upon Variation of
O_2 Pressure, 0.1 M $HClO_4/H_2O$, V_D = 0.200 V.
1 atm. O_2
1 atm. H_2
10^{-2} atm. O_2
Drain Current, I_D, mA
0.75
0.5
0.25
0
0
15
30
45
Time, min.


Drain Current Response vs. Time Upon Variation of
O_2 Pressure, 0.1 M $HClO_4/H_2O$, V_D = 0.200 V.
1 atm. O_2
10^{-2} atm. O_2
Drain Current, I_D, mA
0.75
0.5
0.25
0
0
30
60
90
Time, min.


Drain Current vs. pH for a [Poly-3-methyl-thiophene-Pt] Transistor Under 1 atm. O_2.
Drain Current, I_D, mA
1.0
0.5
0
12
10
8
6
4
2
0
pH



Drain Current Response vs. Time for a [Poly-3-methylthiophene -Pt] Transistor Upon Alternate Cycling of a pH 5.5/pH 6.5 Effluent Stream, $V_D = 0.200V$, Flow Rate = 2.0mℓ/min.



Drain Current Response vs. Time for a [Poly-3-methylthiophene-Pt] Transistor Upon Injection of 1 μℓ. of 0.1 M HClO$_4$ onto an Effluent Stream of 0.1 M NaClO$_4$ (pH=6.0), V_D=0.100V, Flow Rate = 2.0 mℓ/min.

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