1.0

1.1

1.25

4.5
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Abstract

Microelectrode arrays consisting of two or eight closely spaced (~ 1 µm) Au or Pt microelectrodes (~ 2 µm wide x ~ 50 µm long x 0.1 µm high) can be modified with a variety of redox active materials in a way that leads to microelectrochemical devices that may be useful as sensors. In general, a pair of microelectrodes connected by a redox active material represents a device, because the current, I_D, passing from one microelectrode (source) to the other (drain) at a fixed potential between them, V_D, can be modulated by electrically- or chemically-induced changes in the state of charge of the redox material. The fundamental issues associated with pH-sensitive devices based on poly(3-methylthiophene), poly(4-vinylpyridine), a viologen-quinone redox polymer, and WO_3 are described to illustrate generic concepts that underlie the development of microelectrochemical sensors.

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MODIFICATION OF MICROELECTRODE ARRAYS: NEW

MICROELECTROCHEMICAL DEVICES FOR SENSOR APPLICATIONS

Page Heading Title: Modification of Microelectrode Arrays

Mark S. Wrighton,* James W. Thackeray, Michael J. Natan, Diane K. Smith,

Gregg A. Lane and Daniel Bélanger

Department of Chemistry

Massachusetts Institute of Technology
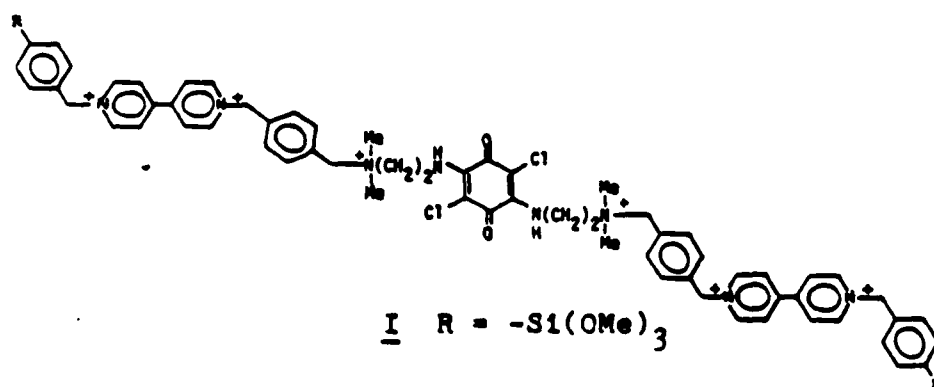
Cambridge, Massachusetts 02139   U.S.A.

*Address correspondence to this author.

Abstract

Microelectrode arrays consisting of two or eight closely spaced ($\sim$1 μm) Au or Pt microelectrodes ($\sim$2 μm wide x $\sim$50 μm long x 0.1 μm high) can be modified with a variety of redox active materials in a way that leads to microelectrochemical devices that may be useful as sensors. In general, a pair of microelectrodes connected by a redox active material represents a device, because the current, I_D, passing from one microelectrode (source) to the other (drain) at a fixed potential between them, V_D, can be modulated by electrically- or chemically-induced changes in the state of charge of the redox material. The fundamental issues associated with pH-sensitive devices based on poly(3-methylthiophene), poly(4-vinylpyridine), a viologen-quinone redox polymer, and WO_3 are described to illustrate generic concepts that underlie the development of microelectrochemical sensors.

This article describes several molecule-based microelectrochemical devices that respond to pH. The details of microelectrochemical devices based on platinized poly(3-methylthiophene), (Thackeray, 1986 and Thackeray and Wrighton, 1986) poly(4-vinylpyridine), (Bélanger and Wrighton, 1986) the polymer derived from I, $[(BV-Q-BV^{6+}]_n$, (Smith et al., 1986a & b), and WO_3, (Natan, 1986 and Natan et al., 1986b) in connection with response to variation
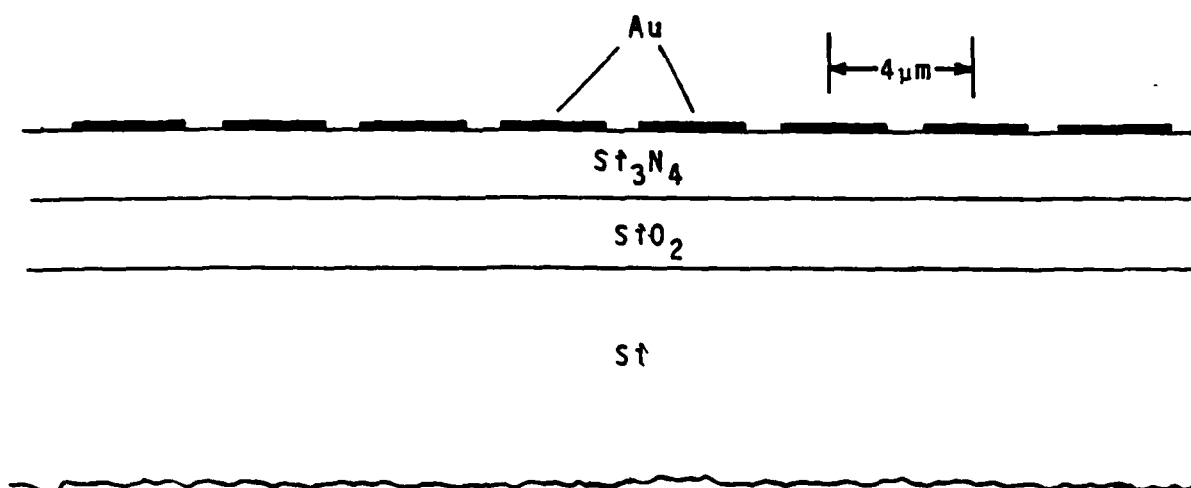

I R = -Si(OMe)$_3$

in pH, have been elaborated elsewhere. An interesting overview of new kinds of electronic devices based on macromolecular materials has also appeared (Chidsey and Murray, 1986). The aim of this article is to provide a summary of some approaches to the development of small, sensitive, and specific sensors of biological and chemical substances that stem from modification of microelectrode arrays. Results from the four systems mentioned above will be used to illustrate concepts of generic significance to the development of new kinds of sensors.

Research on molecule-based microelectrochemical "devices" in the Wrighton group has been inspired by developments in chemistry, biology, and microfabrication technology (Wrighton, 1985). The ability to carry out solid state microfabrication in the micron size regime makes it possible to exploit synthetic and naturally occurring molecular materials to achieve

device-like "functions" that depend on the properties of the molecular material(s) which comprise the device. Recent research has demonstrated that molecule-based transistors (Kittlesen et al., 1984; White et al., 1984; Paul et al., 1985; Thackeray et al., 1985) and diodes (Kittlesen et al., 1985; Kittlesen and Wrighton, 1986) can be fabricated with crucial dimensions of significantly less than 1 μm. Though a polyaniline-based transistor has been shown to amplify power up to a frequency of 1 kHz (Lofton et al., 1986), the near term applications of molecule-based transistors are not likely to be in conventional electronics systems where solid state semiconductor devices are presently used. Rather, molecule-based devices will likely find use in those situations where the properties of the molecular material are crucial to the desired function. Applications for molecule-based devices as sensors are, therefore, a realistic practical opportunity.
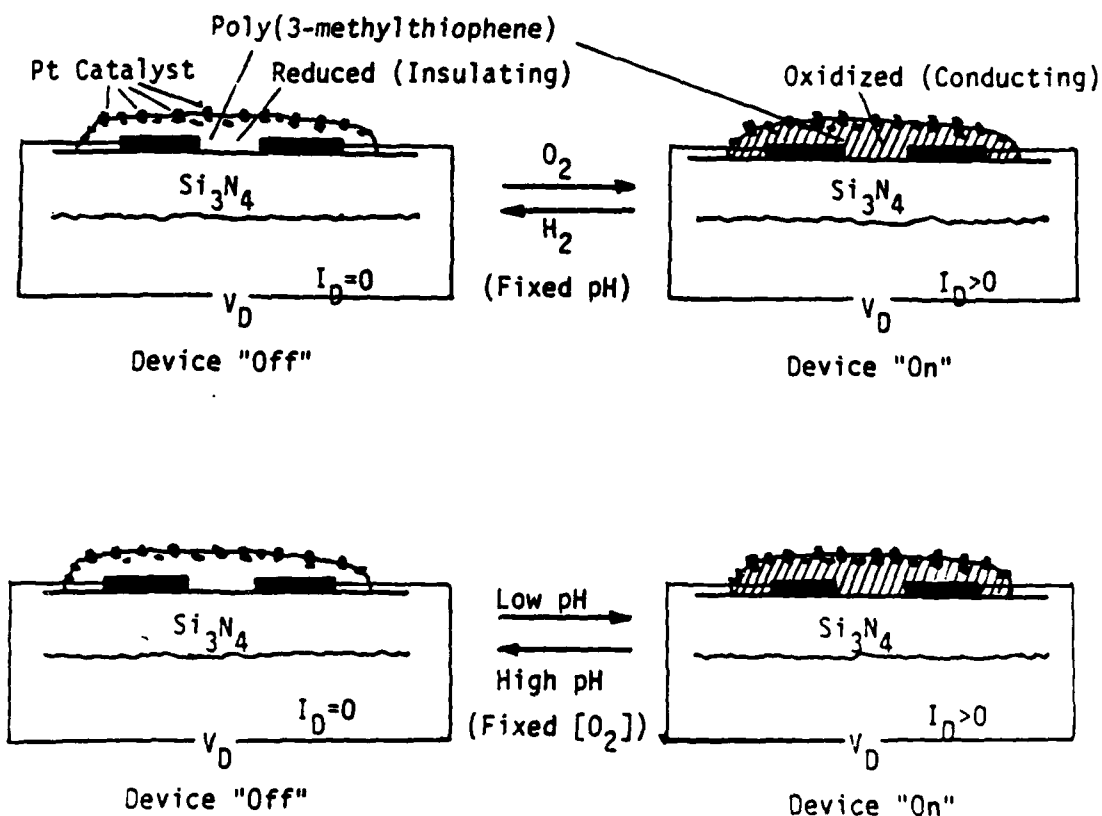
Microelectrode Arrays. Conventional microfabrication techniques used in the manufacture of microelectronic devices (Elliott, 1982) can be used to prepare microelectrode arrays. Scheme I shows a cross sectional view of a typical array fabricated and used by the Wrighton group, and Figure 1 shows photograph of a typical "chip" consisting of an eight-electrode array and contact pads. Basically, the array consists of eight, individually addressable, closely-spaced electrodes, each of which can be regarded as a "microelectrode," since the width of each electrode is only about 2 μm. Recently, there has been much interest in microelectrodes (Howell and Wightman, 1984). Our focus has been on the exploitation of electrode modification techniques leading to the connection of two or more closely-spaced microelectrodes to achieve microelectrochemical devices which have functions analogous to solid state diodes or transistors. Details concerning microfabrication of microelectrode arrays have been published

Scheme I. Cross-sectional view of a typical eight-electrode microelectrode
array used in the demonstration of microelectrochemical devices
described in the text. Cf. Figure 1 for a micrograph of an actual
eight-electrode device.

(Kittlesen, 1985, and Kittlesen, et. al, 1985). The small size of the individual electrodes is important, but the close spacing between them is crucial to making microelectrochemical devices. The small spacing between the microelectrodes is the crucial dimension because the magnitude of the current that passes between two microelectrodes connected with electroactive material is inversely proportional to their separation. All of the devices to be described in the following sections involve the use of electroactive materials, having modest maximum conductivity, to connect two microelectrodes. Accordingly, smaller electrode spacings would be desirable to increase the signal derived from the device and to improve the response time. These issues will be of greatest concern for devices based on conventional redox materials, as opposed to so-called conducting polymers, as will be developed below. Technology exists to fabricate microelectrodes arrays with electrodes spaced closer than the ~1 μm employed so far.
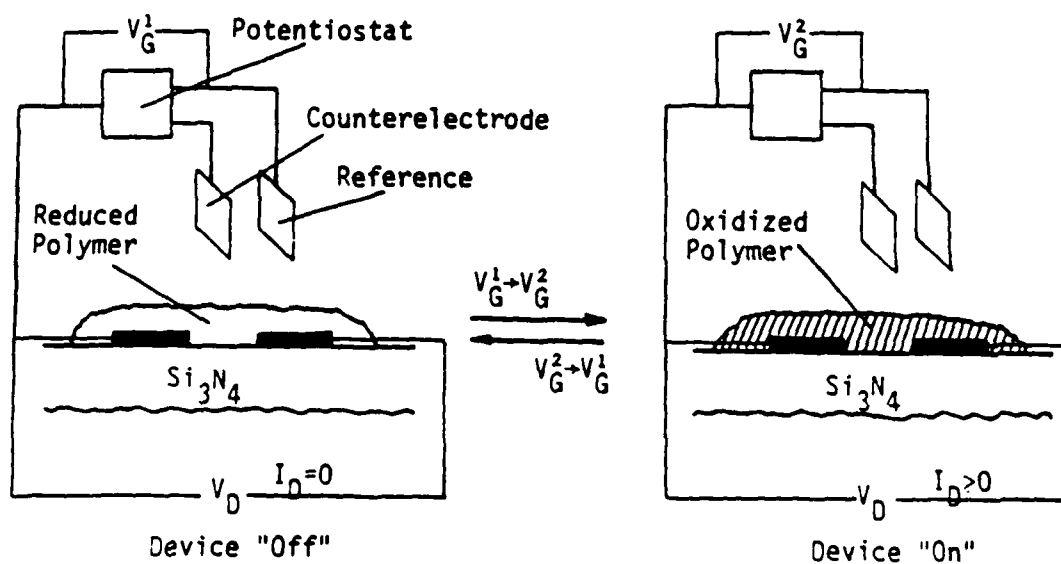
Catalysis: A Key to Specificity, Speed, and Sensitivity. Scheme II illustrates a two-terminal poly(3-methylthiophene)-based device that has recently been described (Thackeray, 1986; Thackeray and Wrighton, 1986). The device is responsive to variation in O_2, H_2, and pH. There are several important features that lead to the response. First, poly(3-methylthiophene) (Tourillon and Garnier, 1982) undergoes a dramatic change in conductivity when it is cycled between its reduced (insulating) and oxidized (conducting) form (Thackeray et. al., 1985). Second, a Pt catalyst will equilibrate the poly(3-methylthiophene) with H_2O/H_2 and O_2/H_2O redox couples and is effective at a loading sufficiently low that the poly(3-methylthiophene) still undergoes a dramatic change in conductivity upon oxidation/reduction (Tourillon and Garnier, 1984; Thackeray, 1986; Thackeray and Wrighton, 1986). Finally, the changes in conductivity of the poly(3-methylthiophene) are sharpest in a range

Poly(3-methylthiophene)

Pt Catalyst / Reduced (Insulating) Oxidized (Conducting)

Si_3N_4 O_2 ⇌ H_2 (Fixed pH) Si_3N_4

$I_D=0$ $I_D>0$

V_D V_D

Device "Off"   Device "On"

Si_3N_4 Low pH → ← High pH (Fixed $[O_2]$) Si_3N_4

$I_D=0$ $I_D>0$

V_D V_D

Device "Off"   Device "On"

Scheme II.   Two-terminal poly(3-methylthiophene)/Pt-based device for response
to O_2 and H_2 (at fixed pH) or pH (at fixed O_2 concentration). The
Pt serves as a catalyst to equilibrate the redox polymer with the
O_2/H_2O and H_2O/H_2 redox couples yielding a device that turns on
($I_D>0$) when the polymer is oxidized (Thackeray, 1986; Thackeray and
Wrighton, 1986). Cf. Figure 2 for an illustration of the response
of the poly(3-methylthiophene)/Pt) device to O_2 and H_2 at fixed pH.

of electrochemical potentials accessible by variation in the O_2 or H_2 concentration (at fixed pH) or by variation in pH (at fixed O_2 concentration).

Properties of the poly(3-methylthiophene)-based device of importance in the sensor function can be established by measurements of the electrical characteristics of the microelectrochemical transistor illustrated in Scheme III (Thackeray et al., 1985). The range of electrochemical potentials where variation in drain current, I_D, can be achieved is established by measuring I_D (at fixed drain potential, V_D) as a function of the gate potential, V_G. The I_D-V_G characteristic stems from intrinsic properties of the molecular material: the shape of the curve, the region of significant I_D, and the maximum and minimum values of I_D all depend on the molecular material. Thus, in principle, the I_D-V_G characteristic can be manipulated by purposeful alteration of the molecular material. The electrical characteristics of the poly(3-methylthiophene) are such that the device begins to turn on at $V_G \approx +$ 0.4 V vs. SCE and is completely on at $V_G \approx +$ 0.9 V vs. SCE. The resistance between the "source" and "drain", Scheme III, can be altered from $>10^{10}$ Ω to $\sim 10^2$ Ω in CH_3CN /0.1 M [n-Bu$_4$N]ClO$_4$ for a source-drain separation of ~ 1 μm and a polymer coverage of $\sim 10^{-7}$ mol/cm^2. The exposed area of such a device is $\sim 10^{-6}$ cm^2. In H_2O/electrolyte electrical characteristics similar to those in CH_3CN/electrolyte are found. The devices are typically durable in a pH range from 0 to 12 and a V_G range from -0.1 to +0.8 V vs. SCE and show similar electrical characteristics in all media. The poly(3-methylthiophene)-based transistor can be rapidly switched on and off by cycling V_G between a potential where the polymer is reduced (and insulating) and a potential where the polymer is oxidized (and conducting): the time required to turn on to >90% of the steady state I_D value is <50 ms and the time required to turn off the

Scheme III. A microelectrochemical transistor based on poly(3-methylthiophene). Variation in V_G from V_G^1 to V_G^2 causes the polymer to be switched from its reduced and insulating state to its oxidized and conducting state (Thackeray, et. al., 1985).

device to <10% of the maximum steady state I_D value is <50 ms. The electrical characteristics of the device in Scheme III suggest that a good redox sensor can be achieved: there is a large change in I_D in a useful potential range, the response is rapid, and the active material is durable over a wide range of conditions.

A poly(3-methylthiophene)-based redox sensor can be based on the dramatic change in conductivity of the polymer that can be brought about chemically. Any chemical system, comprising a signal, that equilibrates with the redox polymer can, in principle, be "detected" by virtue of the change in I_D (at fixed V_D) in a two-terminal configuration as illustrated in Scheme II. However, large changes in I_D will occur only when the chemical signal is in the redox potential regime established (by electrical characterization) to give large I_D variation. For poly(3-methylthiophene)-based devices the I_D-V_G characteristic shows dramatic change between +0.4 and +0.9 V vs SCE. Since the electrical characteristics of the poly(3-methylthiophene)-based device are essentially independent of the medium in which it operates, any chemical oxidant capable of oxidizing the reduced poly(3-methylthiophene) will be detected as an increase in I_D (turn on), and any reductant capable of reducing oxidized poly(3-methylthiophene) will be detected as a decrease in I_D (turn off), equation (1). Thus, the I_D-V_G characteristic, which stems from the redox

$$\text{[Insulating]} \quad - xe^- \quad \rightleftharpoons \quad \text{[Conducting]} \qquad (1)$$

properties of the molecular material, is the basis for an important degree of specificity. For example, the strong oxidant $[Fe(\eta^5-C_5H_5)_2]^+$ ($E^{\circ\prime}$ = 0.307 vs. SCE) (Bard and Faulkner, 1980) would turn on a two-terminal

poly(3-methylthiophene) device, but the weak oxidant $[Co(\eta^5\text{-}C_5H_5)_2]^+$ ($E^{\circ\prime}$ = -0.90) (Sheats, 1979) would not, owing to the ability of the former, but not the latter, to serve as an oxidant for the chemistry represented by equation (1).

While the $I_D\text{-}V_G$ characteristic of the device in Scheme III does provide an important and useful degree of specificity, two oxidants of the same oxidizing power will, in principle, both be detected. However, differences in the kinetics of the redox processes represented by equation (1) for two different oxidants can provide a basis for specificity. For example, the oxidant $IrCl_6^{2-}$ in H_2O will turn on the two-terminal poly(3-methylthiophene) -based device, but O_2 will not (Thackeray, 1986 and Thackeray et. al., 1985). Similarly, $Fe(CN)_6^{4-}$ will turn off the device, but H_2 will not. The point is that O_2 is thermodynamically capable of serving as an oxidant and H_2 as a reductant for the redox processes represented in equation (1), but the kinetics are poor. The kinetics for the O_2 oxidation and H_2 reduction can be improved dramatically by using a catalyst: Pt electrochemically deposited onto the polymer, Scheme II, will equilibrate the polymer with the O_2/H_2O or the H_2O/H_2 redox couples to yield a device which can be turned on with O_2 and off with H_2, Figure 2. Further, since $E^{\circ\prime}(O_2/H_2O)$ depends on pH, the device can be turned off and on by variation in pH at fixed O_2 concentration. The Pt catalyst serves the function of improving rate of equilibration with O_2/H_2O and H_2O/H_2, but does not alter the essential $I_D\text{-}V_G$ (electrical) characteristic of the device. The catalyst provides a mechanism to improve the specificity of the sensor system by rapidly equilibrating the active device material with the chemical signal of interest. A simple example would be to distinguish between O_2 and $IrCl_6^{2-}$ by having two poly(3-methylthiophene)-based devices on a chip with one device made responsive to O_2 by selective deposition of a Pt catalyst. Exposure of the two devices to $IrCl_6^{2-}$ would turn on both devices, whereas O_2 would only
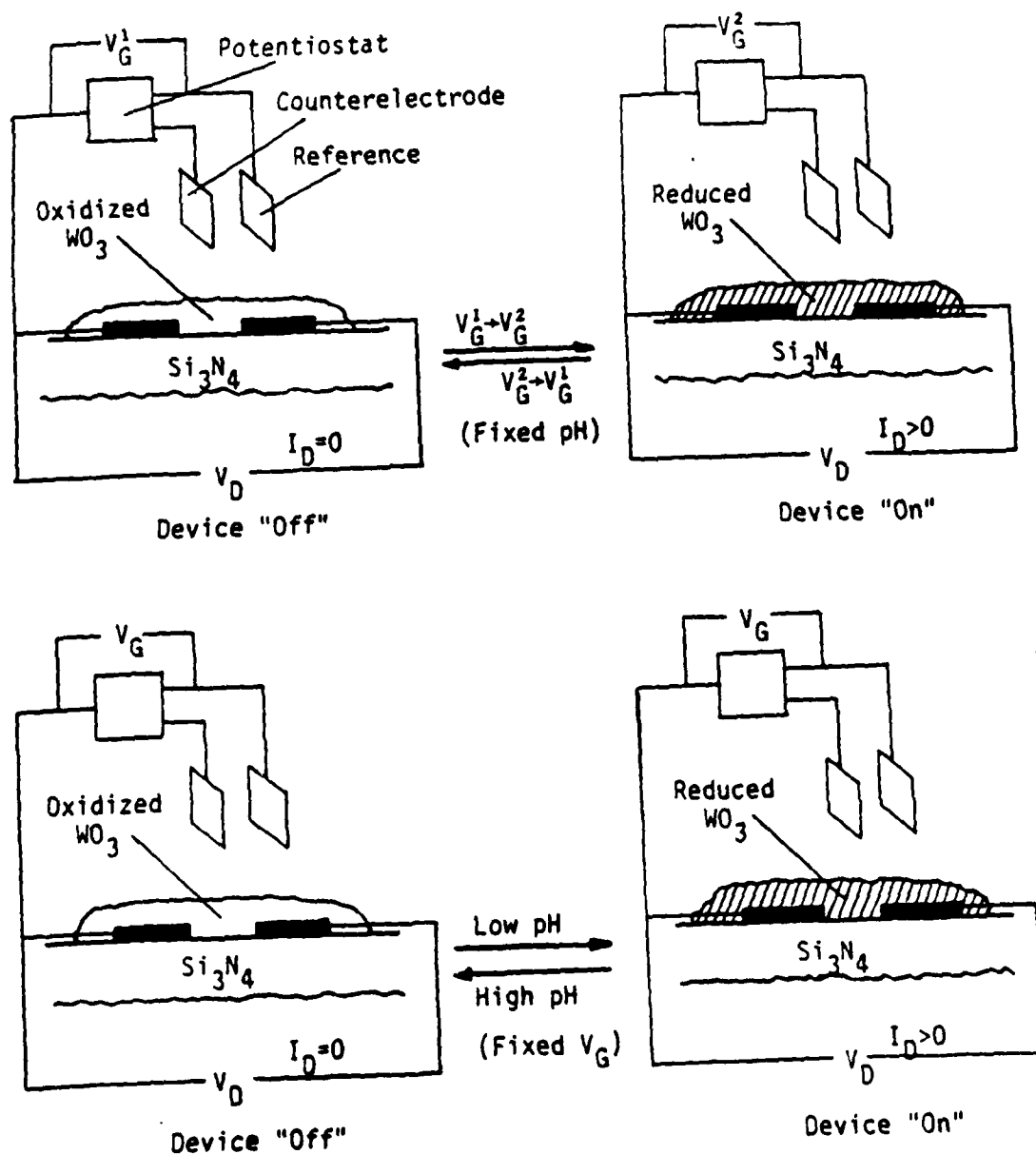
turn on the device with Pt. The deposition of Pt onto poly(3-methylthiophene) establishes that catalysis can be useful in bringing about a response at a microelectrochemical device that is unresponsive without the catalyst. Owing to the catalytic activity of Pt, the poly(3-methylthiophene)/Pt "composite " material system in H_2O has a conductivity that is reproducibly dependent on the O_2 concentration at fixed pH or on the pH at fixed O_2 concentrations.

A two-terminal device that can be turned on by a chemical, as in the turn on of the poly(3-methylthiophene)/Pt device by O_2 illustrated in Figure 2, can be regarded as an amplifier of the chemical signal, in one sense. The amount of charge transferred in effecting the turn on can be much less than the amount of charge passed between the two microelectrodes. The notion of amplification in this sense can be appreciated by considering the two-terminal device to be in a flowing stream of solvent/electrolyte with an electrochemical potential where the device is off, $I_D = 0$, but into which is introduced repetitive injections of a redox reagent such that the device can be turned on, $I_D>0$. The amplification of the repetitive signal can then be measured by determining the charge passed in the drain circuit vs. the charge passed in effecting turn on of the device. In this sense, amplification of $IrCl_6^{2-}$ injected into a flowing stream has been demonstrated using a poly(3-methylthiophene)-based device: the charge passed in the drain circuit was >10^4 times the charge needed to turn on the device (Thackeray, 1986 and Thackeray et al., 1985). The amplification factor depends on many factors including the signal frequency (controlled by flow rate of the flowing stream), the kinetics for turn on/turn off, and the nature of the redox material comprising the device.

Catalysis of the sort illustrated with Pt can be extended to systems which involve the use of immobilized enzymes as the catalyst. The use of enzymes could bring about response to specific biological redox agents (Carr and Bowers, 1980).

Catalysis can obviously be useful, too, in improving the speed (response time) of a sensor device, by improving the rate of redox reaction of the active device surface with the chemical to be detected. The fastest response possible, of course, depends on the diffusion of the chemical to be detected. The electrically driven turn on/turn off (on the timescale of 50 ms) establishes that the poly(3-methylthiophene)-based device can be fast, but slow response to chemical signals may be found due to poor kinetics. There is one other significant point to be made concerning catalysis: a catalyst can provide a way to bring about amplification of a chemical signal. The amplification provided by an enzyme can enhance the sensitivity beyond that associated with the amplification by the two-terminal device described above. For example, an enzyme that can be activated by a chemical signal can serve as an amplifier of that signal in the sense that, once activated, the enzyme can catalytically produce a species that can be detected. There are several possible ways to exploit enzyme catalysts in connection with improving speed, sensitivity, and specificity of microelectrochemical devices.
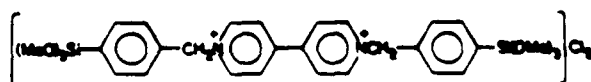
WO_3-Connected Microelectrodes: Use of an Electroactive Inorganic Material with an Intrinsic pH-Dependence. Catalysis of the equilibration of the O_2/H_2O and H_2O/H_2 redox couples with redox polymers is clearly a way to prepare a composite material system that has an O_2- or H_2-dependent conductivity (at fixed pH) or pH-dependent conductivity at fixed O_2 or H_2 concentration. However, there are redox active materials that have an intrinsic pH dependence. Such materials include electroactive metal oxides. WO_3 is known to be such a redox active material and has been widely studied in connection with electrochromic display devices (Dautremont-Smith, 1982). Scheme IV illustrates a WO_3-based microelectrochemical device that shows a pH-dependent I_D-V_G characteristic.

Scheme IV. A WO$_3$-based transistor that turns on (I$_D$>0) when V$_G$ is moved from V$_G^1$ where WO$_3$ is oxidized and insulating to V$_G^2$ where WO$_3$ is reduced and conducting. The WO$_3$-based device can also be turned on and off by varying the pH at fixed V$_G$. Cf. Figure 3 for the I$_D$-V$_G$ charactistic of a WO$_3$-based transistor at different pH's. (Natan, 1986 and Natan, et. al., 1986b).

Unlike the poly(3-methylthiophene)-based device which has the same I_D-V_G characteristic over a wide pH range, the WO_3-based device shows a pH dependence such that the device turns on at more negative values of V_G at higher pH's, Figure 3. Thus, the WO_3-based device shows a variation in I_D upon variation in pH at a fixed V_G (Natan, 1986 and Natan et al., 1986b).
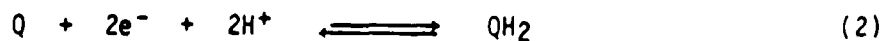
At fixed pH the WO_3-based device of Scheme IV is like the poly(3-methylthiophene)-based device of Scheme III, except that a negative potential excursion turns on the WO_3-based device. Thus, in a two-terminal mode at fixed pH the WO_3-based device can be turned on by reducing agents and turned off by oxidizing agents. From the I_D-V_G characteristic at pH ≈ 7 the WO_3-based device begins to turn on at V_G ≈ 0.0V vs. SCE and turns on to the maximum extent by V_G ≈ -1.2V vs SCE. Thus, a variety of biological reducing agents can turn on the WO_3-based device. Interestingly, at pH ≈ 7 the I_D-V_G curve shows its sharpest change in the vicinity of -0.6 V vs. SCE, close to the formal potential of the co-factor $NAD^+/NADH$ (Burton and Wilson, 1953 and Rodkey, 1955). This potential is also close to that of the well-known viologen mediator system (Kuwana and Heineman, 1976 and Heineman, 1978) for equilibrating electrode surfaces with various redox enzymes. The WO_3 has the additional intrinsic virtue that it is an oxide. Aside from being extremely rugged, oxides are known to be easily modified with redox molecules having $-Si(OR)_3$ functionality (Murray, 1984) as for the viologen derivative II (Dominey et. al., 1983). Modification of WO_3-based transistors with II may yield rapid equilibration of the WO_3 with a variety of enzymes of significance in connection with biological sensors.

II

The WO_3-based transistor, Scheme IV and Figure 3, exemplifies the behavior of a microelectrochemical device based on a material with an intrinsic pH dependence. There are many other oxides that are electroactive and pH-dependent such as iridium oxide (Katsube, et al., 1982) or nickel oxide (Barnard, et al., 1981). These active materials, like WO_3, are rugged and may comprise the basis for pH sensors that function over a wide pH range. Each material is expected to give a device with a unique I_D-V_G characteristic, since the electrochemical behavior of each differs. For example, nickel oxide-based transistors are pH-responsive like WO_3 but turn on at positive, not negative, potentials (Natan, et. al., 1986a). Metal oxide-based devices are quite analogous to the chemically sensitive field effect transistors (ChemFET) that respond to pH (Janata and Huber, 1985). Whether devices based on the electroactive oxides are superior in practical terms is not clear, but it is clear that the electroactive oxides do provide an entry to a wide variety of new microelectrochemical devices.

Quinone-Viologen Connected Microelectrodes: Use of an Electroactive Molecular Material With An Intrinsic pH Dependence. WO_3 is an example of an electroactive inorganic material with an intrinsic pH dependence that can be exploited in microelectrochemical devices. Molecular materials can also be found that exhibit an intrinsic pH dependence that can be exploited in microelectrochemical devices. Polyaniline-based transistors show a pH-dependent characteristic (Paul et al., 1985), but there is only a relatively narrow pH range over which polyanilire is durable. In principle, any molecule with a pH-dependent redox potential can be the basis for a polymeric material with a pH dependence. For example, quinones, Q, undergo reversible $2e^-/2H^+$ reduction to the dihydroxy form, QH_2, equation (2).

$$Q + 2e^- + 2H^+ \rightleftharpoons QH_2 \tag{2}$$

For pH's below the pK_a of QH_2 the formal potential, $E°'$, of the Q/QH_2 redox couple is expected to vary 59 mV/pH unit. If a polymer of Q (or any other molecule having a pH-dependent $E°'$) were used in a microelectrochemical transistor, the significance of the pH dependence would be that the polymer-based transistor would have a pH-dependent I_D-V_G curve.

Polymers based on conventional redox reagents differ in some important practical ways from the so-called conducting polymers like poly(3-methylthiophene), polyaniline, and polypyrrole. The differences stem from the fact that the conventional redox polymers, such as polyvinylferrocene (Merz and Bard, 1978) or the viologen polymer from hydrolysis of II (Dominey et al., 1983), can be regarded as merely an assembly of highly concentrated (~2-3 M) redox centers that do not strongly interact. In the conventional redox polymers the charge carriers are well-localizeu. Reduction of the viologen polymer from II results in formation of localized viologen radicals, and likewise oxidation of polyvinylferrocene results in formation of localized ferrocenium (radical) centers. The conducting polymers differ in the sense that oxidation of poly(3-methylthiophene), for example, gives rise to a material where the radical is delocalized over several monomer units. While the conductivity of the conducting polymers is limited by chain-to-chain charge transfer, every charge transfer process in the conventional polymer is a kind of self-exchange redox event between an oxidized unit and a reduced unit of the polymer. A major practical consequence of the conjugation of monomer units in the conducting polymer compared to the lack of electronic interaction in the conventional redox polymer is a large difference in the maximum conductivity: the conducting polymers can have better than five orders of magnitude higher conductivity than the conventional redox polymers.

Conventional redox polymers are only "conductors" by virtue of the high concentration of redox subunits in the polymer and reasonably large rate

constants for the self-exchange electron transfer process, k_{se}. The "conductivity" of conventional redox polymers is related to the value of k_{se} and the concentrations of oxidized, [ox], and reduced, [red], sites by equation (3). A conventional redox polymer thus shows maximum conductivity when

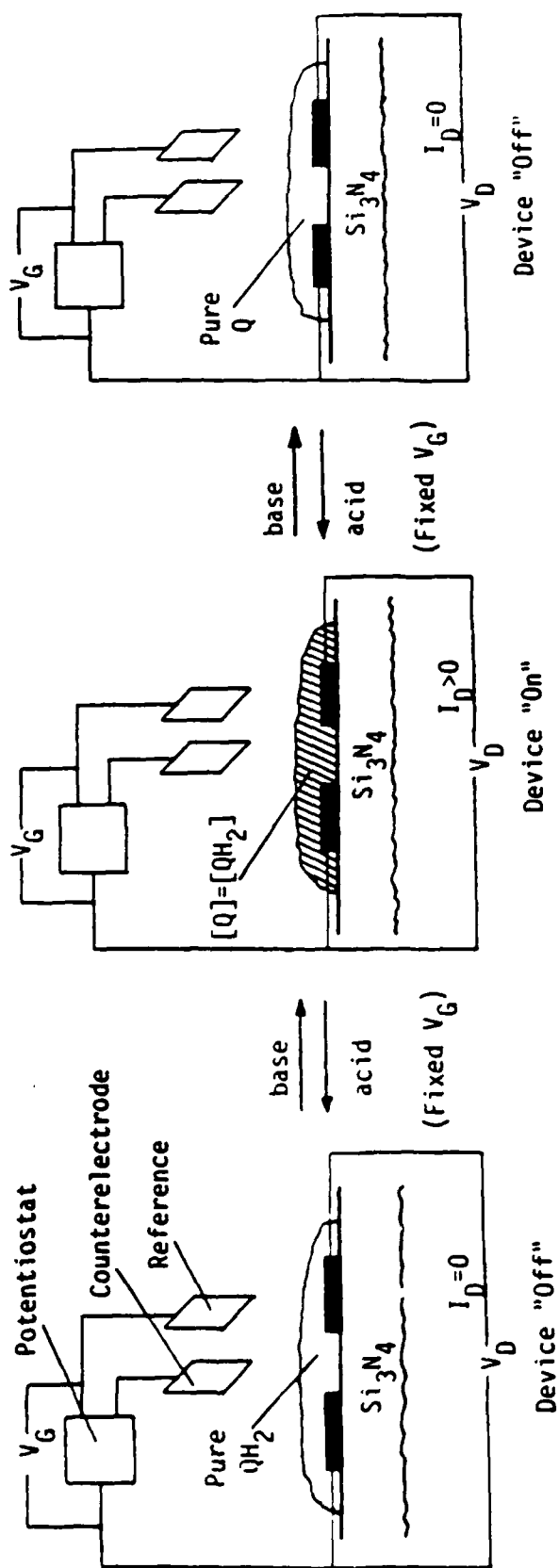$$\text{"Conductivity"} \propto k_{se}[ox][red] \qquad (3)$$

[ox] = [red], which occurs whenever the polymer is at its formal potential, $E^{\circ\prime}$. In a transistor based on a conventional redox polymer the I_D-V_G (at fixed V_D) plot will thus show a maximum at $V_G = E^{\circ\prime}$. Moreover, equation (3) also predicts that I_D will only be significant over a narrow range of V_G (for small V_D), since the [ox]/[red] ratio depends sharply on potential. The sharp I_D peak at $V_G = E^{\circ\prime}$ for a transistor based on conventional redox polymers is an electrical characteristic that is very different from that for solid state transistors which show a region of V_G where $I_D = 0$ (off) and a region of V_G where $I_D > 0$. In principle, all redox polymers could show a peak in the I_D-V_G plot, but the so-called conducting polymers show a large region of V_G where $I_D > 0$. In fact, the poly(3-methylthiophene)-based devices behave in a manner similar to solid state devices. The polyaniline-based devices show a broad peak in the I_D-V_G plot, but in general the conventional redox polymers will give rise to devices having the smallest "on" region. In order to exploit the narrow region of conductivity of the conventional redox polymers small values of V_D must be used; values of V_D <100mV are typically appropriate, because there is a significant amount of both oxidized and reduced centers for $V_G = E^{\circ\prime} \pm 100mV$.

The fact that conventional redox polymers can be used to produce transistors where I_D maximizes at $V_G = E^{\circ\prime}$ means that specific sensors can be made. A two-terminal microelectrochemical device will only turn on when the electrochemical potential of the contacting medium brings the polymer to a

potential where [red] ≈ [ox]. Further, a transistor device configured as in
Scheme III can be a useful sensor whenever the polymer has an $E°'$ that
depends on the chemical environment. A pH-dependent $E°'$ means, for example,
that at fixed V_G and V_D, I_D will depend on pH. The device will only turn on in
a narrow pH range, Scheme V. The WO_3-based device of Scheme IV, in contrast,
is one where there is a range of pH's where the device is off and a range of
pH's where the device is on. Likewise, the two-terminal, pH responsive
poly(3-methylthiophene)/Pt-based device of Scheme II is off or on depending on
pH. With the pH-dependent conventional redox polymer there is the prospect of
devices that can be truly tailored with a turn on only in a certain pH range.

The specificity possible with conventional redox polymer based devices
represents a genuine advantage. However, the low conductivity of conventional
redox polymers means that the magnitude of I_D will be very modest in comparison
to I_D values for devices based on conducting polymers or oxides. Further, the
charge transport properties of conventional redox polymers make the devices
slower in response time. The diffusion coefficient for charge transport in
polyvinylferrocene is only $\sim 10^{-10}$ cm^2/s (Daum and Murray, 1981) resulting in a
switching time of the order of several seconds for a transistor configured as in
Scheme III (~ 1 μm source-drain separation) whereas the poly(3-methylthiophene)-
based device (with the same dimension) switches in <50 ms. Despite the
relatively low values of I_D and the relatively slow response, devices based on
conventional redox polymers offer a rational path to very specific devices. It
is now clear that conventional redox polymers can be formed that can be made
responsive to a wide variety of interesting reagents (gases such as N_2, CO,
CO_2 or ions such as Li^+, Na^+, Ca^{2+}) which are themselves not electroactive.
The viability of this claim stems from the fact that the "binding" of such
species to electroactive centers can influence $E°'$ just as pH variation affects

Potentiostat

Counterelectrode

Reference

V_G

Pure
QH_2

Si_3N_4

$I_D=0$

V_D

Device "Off"

(Fixed V_G)

base

acid

V_G

$[Q]=[QH_2]$

Si_3N_4

$I_D>0$

V_D

Device "On"

(Fixed V_G)

base

acid

V_G

Pure
Q

Si_3N_4

$I_D=0$

V_D

Device "Off"

Scheme V.   Q-based device operated at a fixed V_G and V_D that responds to pH.
Since $E^{\circ\prime}(Q/QH_2)$ moves more negative with increasing pH, the device
is expected to turn on to maximum extent at a pH where $V_G = E^{\circ\prime}$, as
outlined in the text.

the $E^{\circ\prime}$ of Q. Moreover, low values of I_D and slow response can be overcome by making devices having a smaller source-drain separation. For the geometry given in Scheme III, the switching time, t, is given approximately by equation (4) where x is the source-drain separation and D_{ct} is the diffusion coefficient

$$t \approx \frac{x^2}{D_{ct}} \qquad (4)$$

for charge transport in the polymer. The maximum value of I_D is given approximately by equation (5) where n is the number of electrons transferred, F

$$I_D(max) \approx \frac{nD_{ct}FAC}{x} \qquad (5)$$

is the Faraday, A is the area of the drain electrode, and C is the concentration of redox centers in the polymer. With electron beam writing it should be possible to prepare devices with crucial dimensions (source-drain separation) of the order of a few hundred Angstroms. Such dimensions will lead to substantially improved microelectrochemical devices generally and will open the use of redox polymers that exhibit only modest conductivity.

Unfortunately, pure Q-based polymers appear to have such poor charge transport properties (Miller et. al., 1984) that preparing devices with ~1 μm source-drain separation is impractical, even at the research laboratory stage. However, results for a device based on the pH-sensitive polymer derived from I have been obtained. Figure 4 shows the values of I_D (at V_G = -0.7 V vs. SCE) at several pH's, establishing that the device is responsive to pH (Smith et. al., 1986b). For the polymer derived from I, however, the pH dependence is not straightforward as would be the case in a pure Q-based polymer. In fact, the $[(BV-Q-BV)^{6+}]_n$ polymer does not transport charge to a significant extent via

Q/QH_2 self-exchange events as would be necessary to give a straighforward pH-dependence. The composition (one Q, two BV^{2+}) and structure (hydrolysis of $-Si(OMe)_3$ on BV^{2+}) of the polymer and the relatively small value of k_{se} prevents the Q centers from carrying charge via Q/QH_2 self-exchange. At all pH's where the polymer is durable (pH <9) the $BV^{2+/+}$ redox couple transports charge. Whenever the pH is such that $E^{\circ\prime}(Q/QH_2)$ (at pH = 7, -0.35 V vs. SCE) is close to the pH-independent $E^{\circ\prime}(BV^{2+/+})$ (-0.45 V vs SCE) the cross redox process represented by equation (6) can contribute to the charge transport process. At

$$2BV^+ + 2H^+ + Q \rightleftharpoons QH_2 + 2BV^{2+} \qquad (6)$$

low pH, the $BV^{2+/+}$ system only carries the charge with the Q/QH_2 system behaving passively as a concentration diluent. At low pH (pH < 5) the reduction process given by equation (6) is effectively irreversible, since QH_2 does not have the (thermodynamic) reducing power to return charge to the BV^{2+} centers. As Figure 4 illustrates the $[(BV-Q-BV)^{6+}]_n$-based device does show a pH-dependent value of I_D. Devices based on $[(BV^{2+})]_n$, from II, do not show a pH-dependence, consistent with the above arguments (Smith et. al., 1986b). Further, the ~30% decline in the maximum value of I_D upon lowering the pH from 8 to 5 is consistent with the dilution of charge carrying species, considering that $1/3$ of the redox subunits, Q/QH_2, are effectively removed by lowering the pH from 8 to 5. It is tempting to conclude that the "dilution effect" accounts entirely for the pH dependence of the $[(BV-Q-BV)^{6+}]_n$-based device. However, this cannot be verified, in part, because the rate constant for the cross reaction according to equation (6) is not known.

The $[(BV-Q-BV^{6+}]_n$ polymer is clearly not ideal as a device material in configurations considered to this point. However, the pH-dependent behavior of single electrodes modified with $[(BV-Q-BV^{6+}]_n$ suggests that useful pH-sensitive

devices can be made. The intriguing property of electrodes modified with $[(BV-Q-BV)^{6+}]_n$ is that at pH < 5 reduction of the polymer occurs by $4e^-/2H^+$, $1e^-$ into each of the BV^{2+} centers and $2e^-$ and $2H^+$ into the Q center, but only the $2e^-$ added to the BV^{2+} can be electrochemically withdrawn. In contrast, at higher pH's $4e^-$ can be added and withdrawn. The "rectification" at low pH's is due to the fact that the Q centers do not equilibrate directly with the electrode and the reduction of the Q centers occurs only via equation (6). The point is that complete reduction of $[(BV-Q-BV)^{6+}]_n$ can occur at low pH's, but the charge used to reduce Q to QH_2 is "trapped", because at low pH's the QH_2 is incapable (thermodynamically) of delivering the charge back to the BV^{2+} center; the only path to deliver the charge from QH_2 back to the electrode is thus blocked. In principle, the rectification exhibited by an electrode modified with $[(BV-Q-BV)^{6+}]_n$ can be exploited in pH sensors based on the charge recoverable from the $4e^-/2H^+$ reduced polymer: at low pH's $2ne^-$ can be recovered whereas at high pH $4ne^-$ can be recovered. Considering that the rectification is observed with electrodes modified with only ~2 x 10^{-10} mol/cm^2 of I (Smith et. al., 1986a), there is the prospect of making devices with an ultrasmall source-drain separation. The ultimate goal is a pair of microelectrodes connected by an array of single molecules! Since rectification can be observed on a single electrode at a coverage not too different than that expected for a monolayer coverage, there appears to be no fundamental limitation to preparing such a device. Rather, the significant problem that emerges is one of microfabrication.

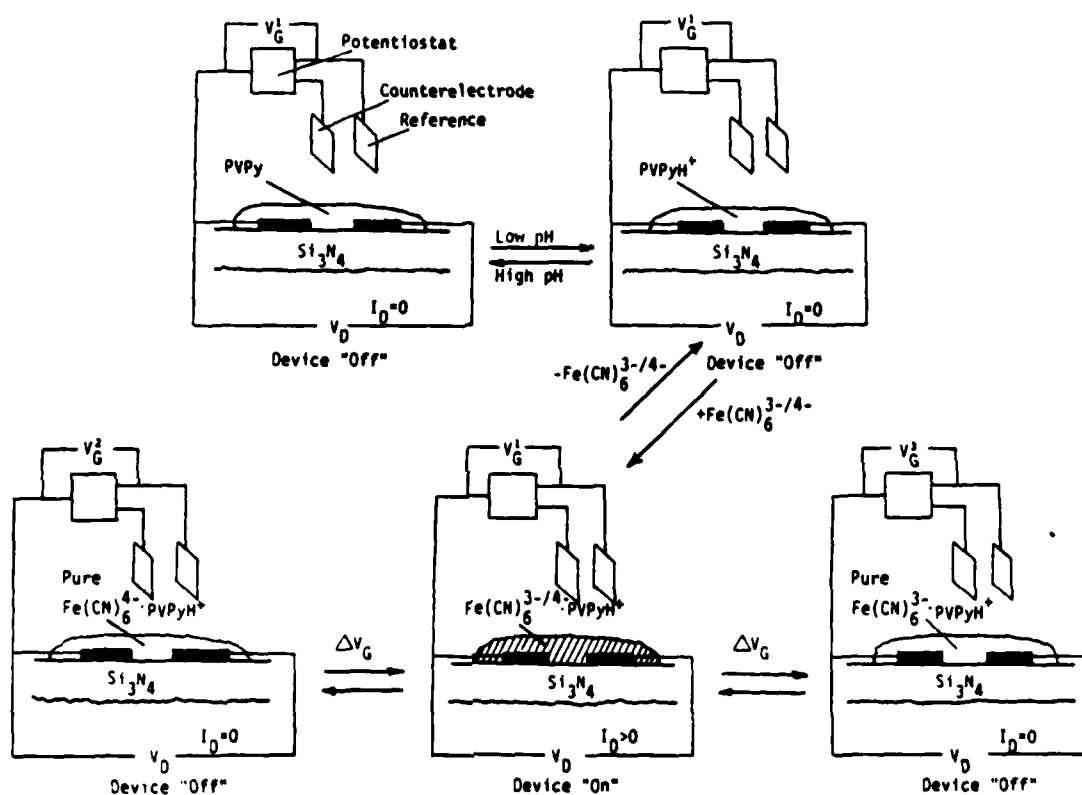Poly(4-vinylpyridine)-Connected Microelectrodes: Two-Stimuli Response Transistors.
In the foregoing sections three different types of pH-dependent devices have been described. Poly(4-vinylpyridine)-connected microelectrodes provide yet another kind of pH-responsive system: a device where turn on (at fixed V_G and fixed V_D)

depends on the presence of two chemicals where neither reagent alone is effective. While the applications for such a device are not obvious, there is considerable interest in sensor arrays where different device formations can be useful in providing a "signature" for a given environment. Multi-stimuli response electronic devices are of interest in a variety of contexts. Two-stimuli, poly(4-vinylpyridine)-based transistors are based on the reversible protonation of the pyridine nitrogen, equation (7),that yields a cationic polymer capable of reversibly (electrostatically) binding electroactive anions such as $Fe(CN)_6^{4-}$, equation (8). The electrostatic binding of electroactive

$$PVPy \ + \ H^+ \ \xleftarrow{\hspace{1cm}}\xrightarrow{\hspace{1cm}} \ PVPyH^+ \qquad\qquad (7)$$

$$PVPyH^+ \ + \ nFe(CN)_6^{4-} \ \xleftarrow{\hspace{1cm}}\xrightarrow{\hspace{1cm}} \ [PVPyH^+\cdot nFe(CN)_6^{4-}] \qquad (8)$$

species to charged polymers was first studied with the system represented by equations (7) and (8) (Oyama and Anson, 1980), but such systems are now relatively common. Interestingly, the protonated poly(4-vinylpyridine) polymer can very effectively concentrate the electroactive anion from very dilute solutions.

Once bound into the polymer the $Fe(CN)_6^{3-/4-}$ redox system represents a mechanism for propagating charge through the polymer. Thus, when the $Fe(CN)_6^{3-/4-}$ system is bound into the protonated polymer there is a degree of conductivity of the sort associated with conventional redox polymers. Accordingly, a two-stimuli response transistor can be fabricated as in Scheme VI (Bélanger and Wrighton, 1986). The device only turns on ($I_D > 0$) when the pH is in a certain range, below the pK_a of poly(4-vinylpyridine), and when the $Fe(CN)_6^{3-/4-}$ concentration is sufficient to be bound in the charged polymer at a level that gives significant conductivity. Figure 5 illustrates the I_D-V_G characteristic for the two-stimuli response device in an acidic solution of

Scheme VI. Configuration and behavior of a device based on the protonation of poly(4-vinylpyridine), PVPy, and the subsequent electrostatic binding of $Fe(CN)_6^{3-/4-}$. Cf. Figure 5 for the I_D-V_G characteristic of the transistor (Bélanger and Wrighton, 1986).

$Fe(CN)_6^{3-/4-}$ showing the sharp region of V_G where $I_D > 0$ expected for a conventional redox polymer. Note also the small maximum value of I_D that is a consequence of the small value of D_{ct} for $Fe(CN)_6^{3-/4-}$ when bound in the protonated poly(4-vinylpyridine). An appreciation for the low value of D_{ct} in the polymer can be gained by comparing I_D to the value of the maximum steady state current that will flow between two adjacent Au microelectrodes (that are not modified with polymer) immersed in a solution of only 1m$\underline{M}$ $Fe(CN)_6^{3-}$/1m$\underline{M}$ $Fe(CN)_6^{4-}$. In such a case the steady state current is associated with the reduction of $Fe(CN)_6^{3-}$ at one microelectrode and oxidation of $Fe(CN)_6^{4-}$ at the other. The mass transport limited current is ~10 nA versus the ~1.5 nA I_D value for the polymer-confined system in Figure 5. The value of the diffusion coefficient for the $Fe(CN)_6^{3-/4-}$ system is 6.5 x 10^{-6} cm^2/s, more than three orders of magnitude larger than D_{ct} for $Fe(CN)_6^{3-/4-}$ in the protonated poly(4-vinylpyridine) (Oyama and Anson, 1980). The fact that the current for the solution and polymer-confined systems are similar, then, stems from the high concentration of redox centers in the polymer (~1 $\underline{M}$) compared to the 1m$\underline{M}$ solutions.

As shown in Figure 5 the [PVPyH$^+$·$Fe(CN)_6^{3-/4-}$]-based transistor responds as expected for a system based on a conventional redox polymer. The key is that I_D(peak) occurs at $V_G = E^{\circ\prime}$ for the electrostatically bound $Fe(CN)_6^{3-/4-}$. Note that the absolute value of I_D is well below that associated with the WO_3-based transistor, Figure 3, or the poly(3-methylthiophene)-based device, Figure 2. The data in Figure 5 establish that microelectrochemical transistors can have a narrow turn-on region that may be useful in an array of microelectrochemical sensors. For the example shown there is the additional principle established that transistors can be designed to turn on only when two chemicals are present. In sensor applications specificity may be achieved by exploiting both the narrow region of turn-on associated with the use of conventional redox polymers and the multi-stimuli response.

Conclusions

Modification of pairs of closely spaced microelectrodes with electroactive materials has been demonstrated to give rise to a variety of chemically responsive microelectrochemical devices. In this article we have introduced the principles associated with the operation of devices which are analogous to solid state transistors where the active material is one whose resistance changes as a function of its state of charge. In solid state transistors, such as a M/SiO$_2$/Si field effect transistor (MOSFET) (Sze, 1981) the function of the device depends on movement of capacitative charge in the gate circuit to effect a change in the carrier distribution of the Si between source and drain and just below the oxide of the gate. In the microelectrochemical devices the function depends on actual oxidation/reduction of the active material connecting the source and drain. Thus, faradaic charge must be moved in the gate circuit to effect turn on/turn - off. This leads to intrinsically slower response for the microelectrochemical devices compared to solid state transistors, because faradaic processes require the movement of ions.

Microelectrochemical transistors function in the same way that the solid state devices do, including the function of power amplification (Lofton et. al., 1986). Operational frequencies of solid state transistors exceed 10^9 Hz (Sze, 1981) whereas the microelectrochemical devices have only been demonstrated up to 10^3 Hz (Lofton et. al., 1986), in the best of circumstances. At the other extreme, even 1 Hz operation is not possible with the [PVPyH$^+$·Fe(CN)$_6$$^{3-/4-}$]-based devices (Bélanger and Wrighton, 1986), because the charge transport properties of conventional redox polymers are so poor. Considering that the microelectrochemical devices are presently much slower than their solid state analogues there is no realistic expection that microelectrochemical transistors will displace conventional solid state devices. However, the microelectrochemical devices do function in chemical environments,

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Figure Captions

Figure 1. Typical "chip" consisting of an array of eight Au microelectrodes.
The top photograph shows the entire chip, ~3 mm x ~3 mm. The large,
numbered squares are the contact pads. The bottom photograph shows
an enlargement of the microelectrode array; the active area is ~50 μm
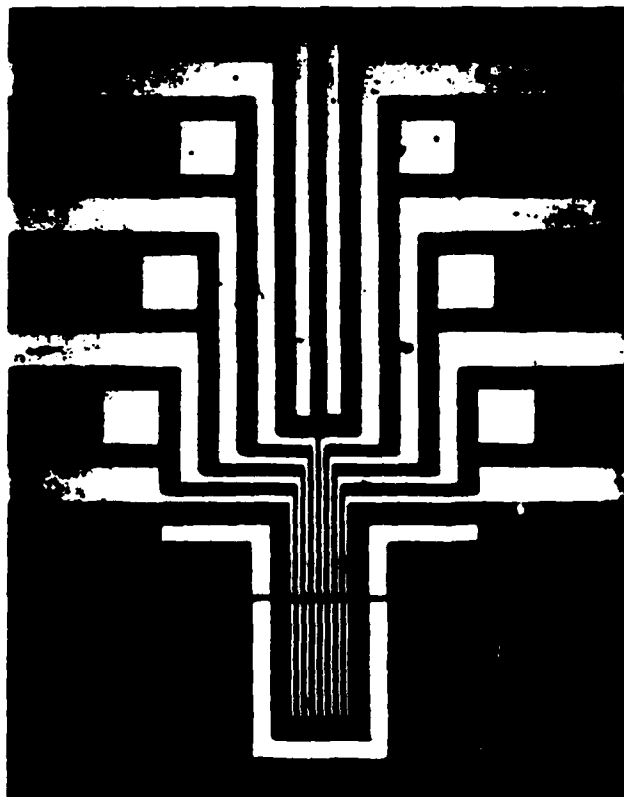x 50 μm. Cf. Scheme I for a cross-sectional view of the eight
microelectrodes.
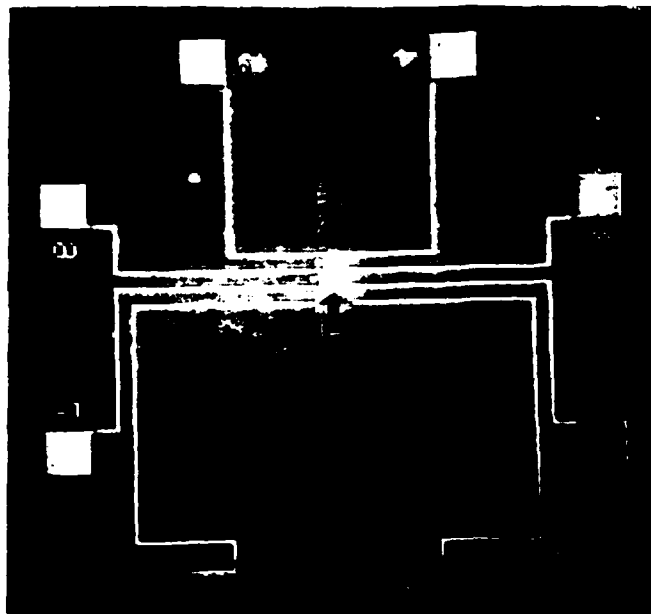
Figure 2. Response of the device illustrated in Scheme II to O_2 and H_2 at 298K.
In the absence of the Pt catalyst the device is unresponsive to O_2 or
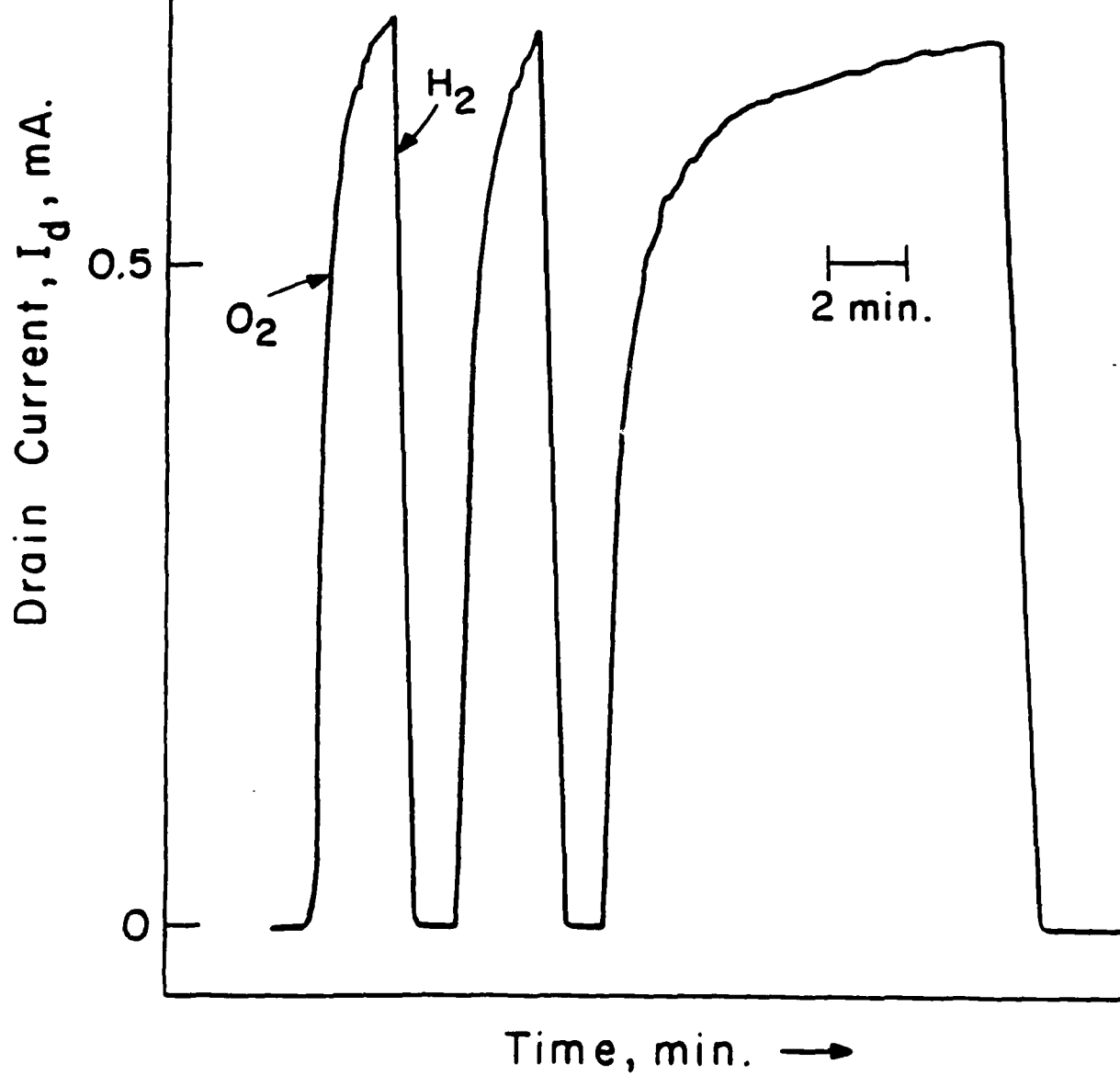H_2 (Thackeray, Wrighton, 1986).

Figure 3. Electrical characteristics of a WO_3-based transistor, Scheme IV, as a
function of pH at 298K (Natan et al., 1986).

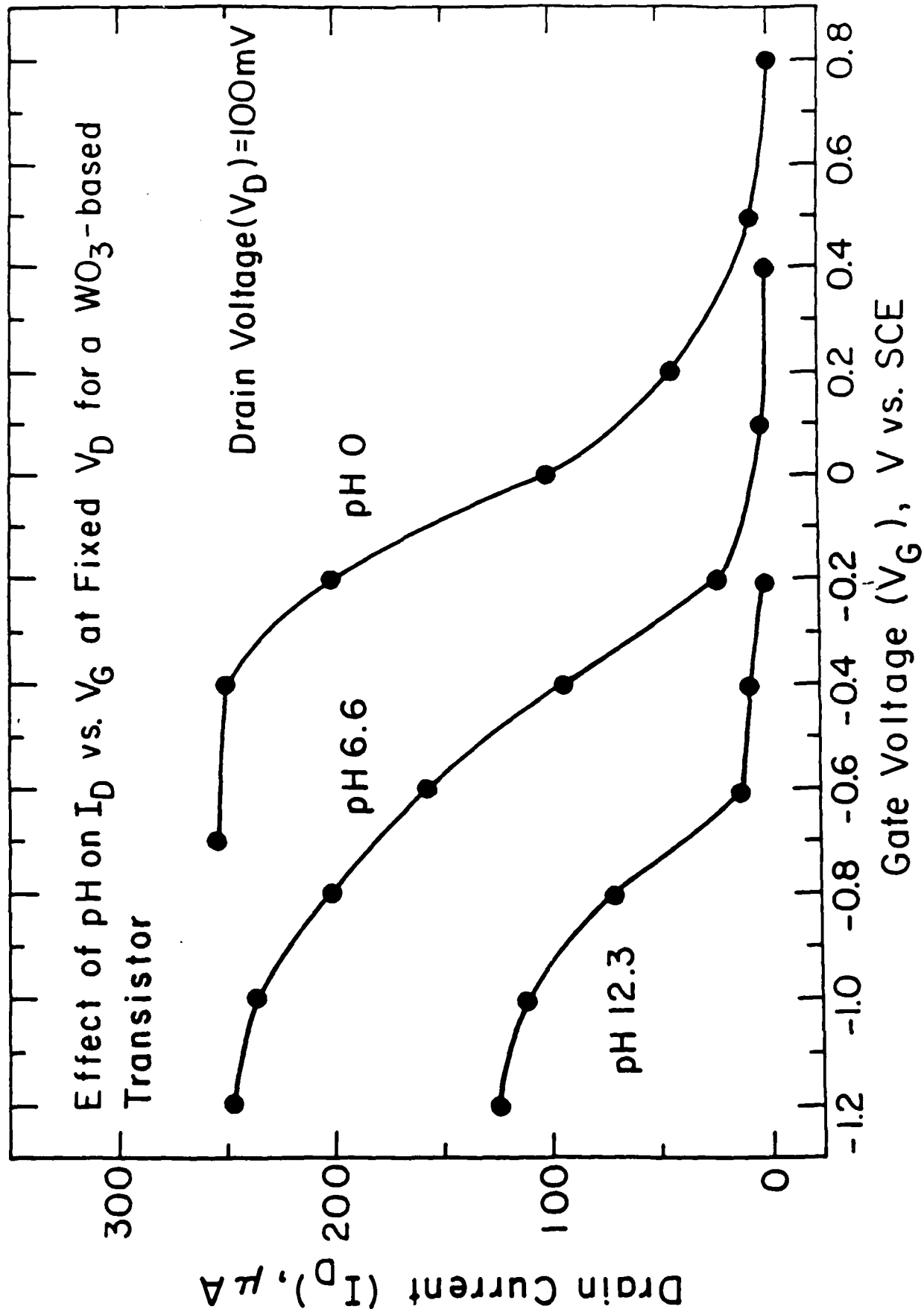Figure 4. Change in I_D with variation in pH for a transistor based on the
polymer derived from I, $[(BV-Q-BV)^{6+}]_n$, at 298K (Smith et al., 1986b).

Figure 5. Electrical characteristic of a $[PVPyH^+ \cdot Fe(CN)_6^{3-/4-}]$-based transistor
(Scheme VI) at pH = 1.8, at 298K. The coverage of $Fe(CN)_6^{3-/4-}$ for
this device was 1.5 x 10^{-7} mol/cm^2. I_D values shown are steady-state
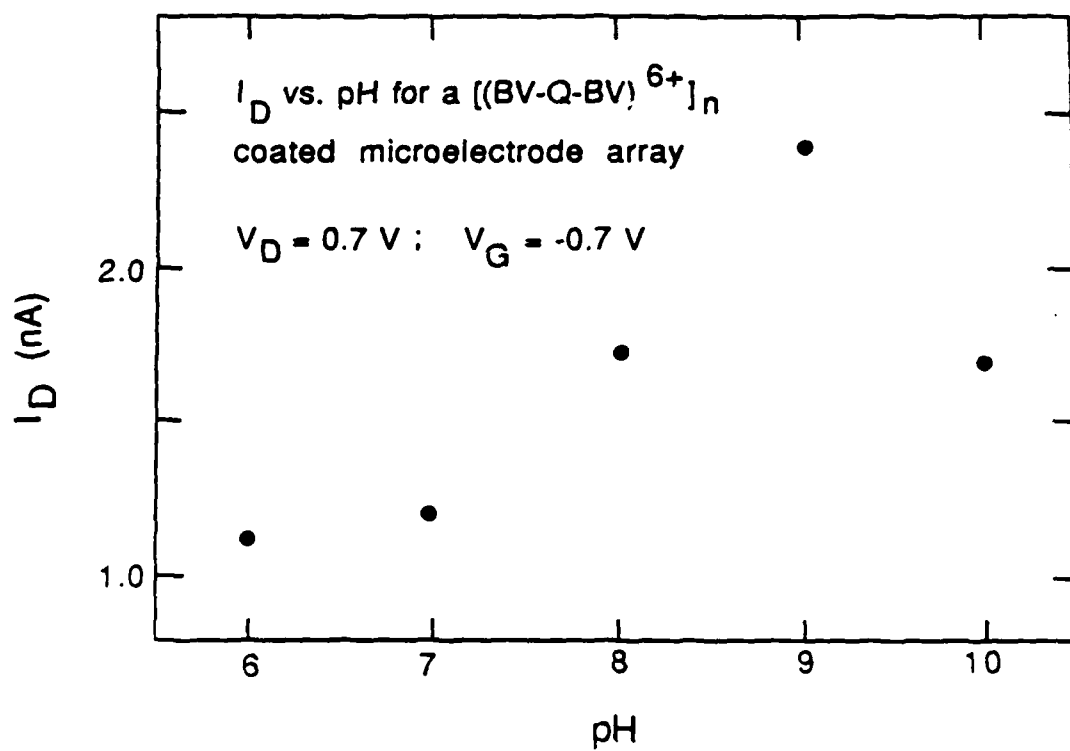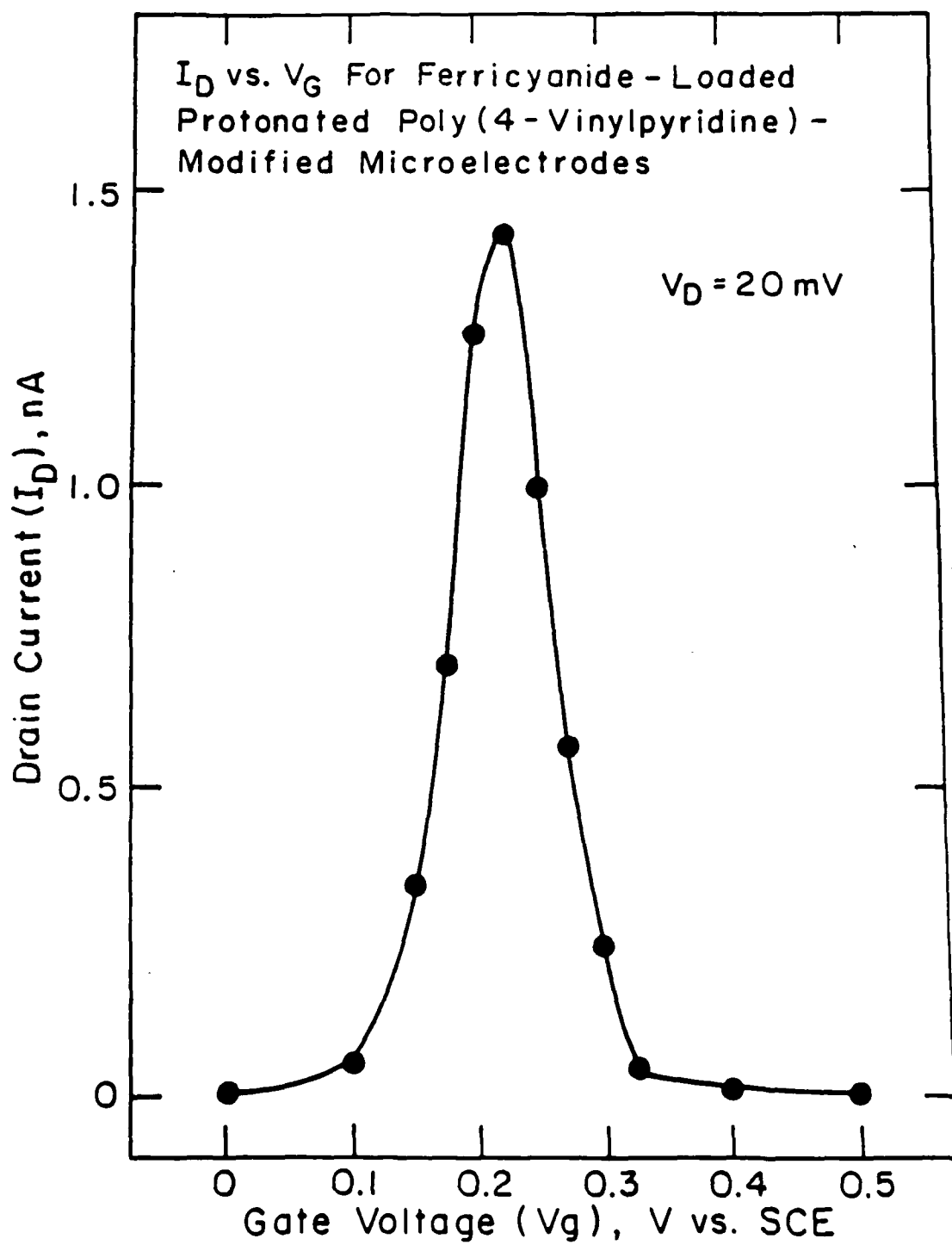values recorded at ~2-3 min after setting V_G.

Drain Current Response vs. Time for a [Poly-3-methylthiophene-Pt] Transistor upon alternate cycling of 1 atm. O_2/H_2 in 0.1 $\underline{M}$ $HClO_4/H_2O$, $V_D = 0.200$ V.

Effect of pH on I_D vs. V_G at Fixed V_D for a WO_3-based Transistor

Drain Voltage(V_D)=100mV

pH 0

pH 6.6

pH 12.3

Gate Voltage (V_G), V vs. SCE

Drain Current (I_D), μA

I_D vs. pH for a $[(BV-Q-BV)^{6+}]_n$ coated microelectrode array

$V_D = 0.7$ V ; $V_G = -0.7$ V

I_D (nA)

2.0

1.0

pH

6   7   8   9   10

I_D vs. V_G For Ferricyanide-Loaded Protonated Poly(4-Vinylpyridine)-Modified Microelectrodes

$V_D = 20\,mV$

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0-8