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Characterization of a "Solid-State" Polyaniline-Based Transistor: Water Vapor Dependent Characteristics of a Device Employing a Poly(vinyl alcohol)/Phosphoric Acid Solid-State Electrolyte

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Abstract: A "solid-state" polyaniline-based microelectrochemical transistor is described. The transistor can be fabricated by the chemical modification of a microfabricated ~3 mm × 3 mm chip consisting of an array of eight, individually addressable Pt microelectrodes, each ~50 μm long × ~2 μm wide × ~0.1 μm high and separated from each other by ~1.2 μm. Chemical modification of the chip consists of (1) placing a small spot of Ag epoxy adjacent to the microelectrode array to serve as a quasi-reference electrode, (2) anodic polymerization of aniline to coat and interconnect six of the eight microelectrodes with redox-active polyaniline, and (3) overcoating the entire chip with a thin film of poly(vinyl alcohol)/H_3PO_4, which serves as a solid-state electrolyte. The transistor function can be demonstrated by letting every other polyaniline-coated microelectrode serve as the source and the other three electrodes serve as the drain. With variation of the gate potential, V_G (the source–reference potential), the drain current, I_D (current between source and drain), at a fixed drain potential, V_D (source–drain potential), can be modulated. Depending on the atmosphere and V_G, the resistance (at small V_D) between source and drain can be varied from ~10^2 to 10^8 Ω at 298 K, approximately the same range found for a polyaniline-based device operated in aqueous 1.0 M H_3PO_4. The solid-state device shows negligible I_D (highest resistance) in an H_2O-free atmosphere at any V_G accessible, −0.5 to +1.0 V vs Ag. In an H_2O-saturated atmosphere (Ar, air, O_2) the device shows a maximum I_D (minimum resistance ~4×10^2 Ω) at V_G = +0.15 V vs Ag. For V_G more negative than ~−0.2 or more positive than ~+0.6 V vs Ag, I_D is negligible (resistance $\geq 10^8$ Ω) under any conditions. In an H_2O-saturated atmosphere the switching speed of the device is such that >80% turn on and turn off can be achieved in <50 ms at 298 K. At fixed V_G = +0.15 V vs Ag and V_D = 50 mV, the solid-state polyaniline-based device turns on ($I_D > 0$) and off ($I_D \approx 0$) reversibly as the atmosphere is varied from H_2O saturated ($I_D > 0$) to H_2O free ($I_D \approx 0$).

This paper describes the solid-state microelectrochemistry of polyaniline-coated microelectrodes and the characteristics of a transistor based on the potential-dependent conductivity of the polyaniline where the solid-state electrolyte is poly(vinyl alcohol)/H_3PO_4.[1] We recently communicated[2] an example of a solid-state microelectrochemical transistor based on the potential-dependent conductivity of poly(3-methylthiophene) and the use of poly(ethylene oxide)·$LiCF_3SO_3$ at ~393 K as the solid-state electrolyte. The new device reported here is significant because it can be operated at 298 K and because the characteristic of the device is chemically dependent in a manner that allows demonstration of reversible response to H_2O vapor.

Recent studies show that electrochemistry of molecular materials can be effected without the use of liquid electrolyte solutions.[3] It is also well appreciated that solid-state ionic conductors are useful in battery and fuel-cell applications.[4] "Solid-state" photoelectrochemical devices have also been reported that involve the use of solid-state ionic conductors.[5] The work reported here, and earlier by us,[2] and other electrochemical studies of molecular materials[3] in the solid state exploit the use of polymeric solid-state ion conductors.[6] One of the useful features of closely spaced microelectrodes is that relatively poor ionic conducting materials can be used to replace liquid electrolyte solutions in microelectrochemical devices.

Scheme I (not drawn to scale) illustrates a cross-sectional view of the solid-state microelectrochemical device that has been prepared and characterized based on the reversible oxidation of polyaniline in an H_2O-containing atmosphere. The source–drain separation in the device is ~1 μm, and like the solid-state poly(3-methylthiophene)-based transistor,[2] all of the ancillary components (reference electrode, counterelectrode, and electrolyte) are confined to the ~3-mm chip. Procedures similar to those previously described[7] have been employed to modify adjacent, micron-spaced microelectrodes with polyaniline, a well-known[8] redox polymer with significant conductivity depending on its state of charge.[7] The poly(vinyl alcohol)/H_3PO_4 material has recently been advanced in connection with an electrochemical device for sensing H_2.[1] Interestingly, our essential finding is that the solid-state device represented by Scheme I operates with about the same characteristics as a polyaniline-based device employing aqueous acid as the electrolyte. However, the most important discovery is that the device shows an H_2O-dependent set of characteristics that allow demonstration of a reversible response to variation in the gas above the device.

Experimental Section

Fabrication Procedures. The solid-state microelectrochemical transistor in Scheme I is fabricated by mounting and insulating the chip (~3 mm × ~3 mm) bearing eight individually addressable Pt microelectrodes (~2 μm wide, ~50 μm long, and ~0.1 μm thick) that are separated from each other by ~1.2 μm. The fabrication and mounting of such chips has been described previously.[9] Polyaniline is grown across six

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(1) Polak, A. J.; Petty-Weeks, S.; Beuhler, A. J. *Sens. Actuators* **1986**, *9*, 1.

(2) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 8.

(3) (a) Skotheim, T. A.; Inganas, O. *J. Electrochem. Soc.* **1985**, *132*, 2116. (b) Skotheim, T. A. *Synthetic Metals* **1986**, *14*, 31. (c) Reed, R. A.; Geng, L.; Murray, R. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *208*, 185. (d) Jernigan, J. C.; Chidsey, C. E. D.; Murray, R. W. *J. Am. Chem. Soc.* **1985**, *107*, 2824. (e) Tsumura, A.; Koezuka, H.; Tsunoda, S.; Ando, T. *Chem. Lett.*, **1986**, 863. (f) Aizawa, M.; Yamada, T.; Shinohara, H.; Akagi, K.; Shirakawa, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1315. (g) Calvert, J. M.; Manuccia, T. J.; Nowak, R. J. *J. Electrochem. Soc.* **1986**, *133*, 951. (h) Honda, K.; Kuwano, A. *J. Electrochem. Soc.* **1986**, *133*, 853. (i) Sammells, A. F.; Pujare, N. U. *J. Electrochem. Soc.* **1986**, *133*, 1270.

(4) (a) Hong, H. Y.-P. *Adv. Chem. Ser.* **1977**, *No. 163*, 179. (b) Wiener, S. A. *Adv. Chem. Ser.* **1977**, *No. 163*, 205. (c) Obayashi, H.; Kudo, T. *Adv. Chem. Ser.* **1977**, *No. 163*, 316.

(5) (a) Skotheim, T. A.; Lundstrom, I. *J. Electrochem. Soc.* **1982**, *129*, 894. (b) Sammells, A. F.; Ang, P. G. P. *J. Electrochem. Soc.* **1984**, *131*, 617. (c) Sammells, A. F.; Schmidt, S. K. *J. Electrochem. Soc.* **1985**, *132*, 520.

(6) (a) Armand, M. *Solid State Ionics* **1983**, *9/10*, 745. (b) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854 and references cited therein.

(7) (a) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441. (b) Lofton, E. P.; Thackeray, J. W.; Wrighton, M. S. *J. Phys. Chem.* **1986**, *90*, 6080.

(8) (a) Mohilner, D. M.; Adams, R. N.; Argersinger, W. J., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 3618. (b) Langer, J. *Solid State Commun.* **1978**, *26*, 839. (c) Yu, L. T.; Borredon, M. S.; Jozefowicz, M.; Belorgey, G.; Buvet, R. *J. Polym. Sci., Part C* **1967**, *16*, 2931. (d) Jozefowicz, M.; Yu, L. T.; Belorgey, G.; Buvet, R. *J. Polym. Sci., Part C* **1967**, *16*, 2943. (e) Jozefowicz, M.; Yu, L. T.; Perichon, J.; Buvet, R. *J. Polymn. Sci., Part C* **1969**, *22*, 1187.

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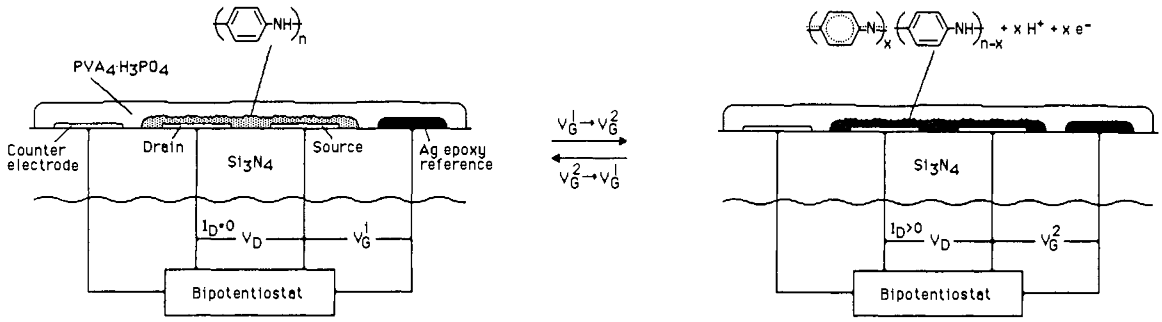
Scheme I. Solid-State Polyaniline-Based Transistor



adjacent microelectrodes by cycling the potential of the microelectrodes between 0.0 and 0.9 V vs. SCE in aqueous 0.45 M aniline solution containing 0.5 M $NaHSO_4$ and 0.6 M H_2SO_4.[7] During the anodic polymerization process, the two remaining Pt microelectrodes are held at −0.5 V vs. SCE to deter polyaniline growth. Deposition of polyaniline is continued until a sufficient amount of the dark green polyaniline interconnects the six microelectrodes as revealed by optical microscopy. The thickness of polyaniline is typically 5–10 μm.[7] Electrochemical characterization of the polyaniline-coated electrodes shows coverage corresponding to withdrawal of $\sim 10^{-7}$ C/cm^2 in a linear sweep from −0.3 to +0.6 vs SCE at 100 mV/s in 1.0 M H_3PO_4 solution. As described previously,[2] the solid-state device uses the two naked Pt microelectrodes as the counterelectrode and a small spot of Ag epoxy on the chip as a quasi-reference. One drop of an aqueous solution containing 0.15 mM poly(vinyl alcohol) (PVA, MW = 1.33×10^5) and 0.11 M phosphoric acid (H_3PO_4) is applied to cover the polyaniline and the electrodes. The solid-state device is completed by evaporation of the H_2O at 35 °C for 24 h. The resulting transparent film (~100 μm in thickness) containing one H_3PO_4 per four PVA repeating units, $(PVA)_4 \cdot H_3PO_4$, is adherent and durable.

Electrochemical Experimentation with Solid-State Polyaniline Transistors. Electrochemical experimentation was carried out with use of a Pine Instruments Model RDE-4 bipotentiostat. Voltammetric traces were recorded on a Kipp and Zonen Model BD 91 XYY′ recorder with an optional time base function. A PAR Model 175 universal programmer was used for the generation of the step signals that were fed into the RDE-4. Examinations by optical microscopy were done with use of a long working distance Bausch and Lomb Microzoom microscope equipped with a coaxial illuminator. A Nicolet Model 40984B digital oscilloscope with Model 4570 digitizer and Model F-43 disk-drive plug-ins was used for recording V_G, I_G, and I_D in the high-frequency characterization experiments. The sinusoidal waveform for V_G variation was obtained by using the internal oscillator output of a PAR Model 5204 lock-in amplifier.

When rapid change of the gaseous atmosphere was needed, microelectrochemical transistors constructed into a single flow cell package with ~0.3-mL internal volume were used. The flow cells were made from Hewlett-Packard crimp-top HPLC autosampler vials. The bottom half of the vials was sawed off. The top half of the vial was sealed around the header enclosing the chip with use of ordinary epoxy. After the H_2O was driven out of $(PVA)_4 \cdot H_3PO_4$ at 35 °C, the mouth of the vial was crimp-sealed with the aluminum cap and septum. The saturated atmospheres (Ar, air, and O_2) were generated by purging through a gas washing tower filled with distilled H_2O and delivered through the septum of the device via syringe needles. Ambient air was pulled through the flow cell by connecting the outlet to house vacuum. The "percent H_2O saturation" conditions were generated by dividing a stream of dry Ar gas into two streams with an H_2O-filled gas washing tower connected in series with only one of the streams. The flow rates from the two streams were controlled and blended in a Matheson Model 7351H proportioner, and the outlet was fed into the flow cell. The total flow rate of the combined streams was kept constant. Approximately 1 h was allowed between changes of the flow rates to produce steady-state H_2O saturation levels.

Results and Discussion

a. Cyclic Voltammetry of Polyaniline-Coated Microelectrodes in $(PVA)_4 \cdot H_3PO_4$ Electrolyte.

Figure 1 shows a comparison, for a typical device, of the cyclic voltammetry as a function of sweep rate for a polyaniline-modified microelectrode array in aqueous 1.0 M H_3PO_4 and in solid $(PVA)_4 \cdot H_3PO_4$ under Ar saturated with H_2O. In both instances the reference electrode is the small spot of the Ag epoxy on the chip, and the data are for the same polyaniline-coated microelectrodes. The counterelectrode in each case is the pair of "naked" microelectrodes. While it is evident that the cyclic voltammograms have a slightly different shape, the essential features in the liquid and solid electrolyte are the same. In each case the six polyaniline-derivatized microelectrodes show the same cyclic voltammogram in a given medium, and the areas of the cyclic voltammograms are approximately the same in liquid and solid electrolyte. The two microelectrodes held at −0.5 V vs SCE during the derivatization procedure do not show cyclic voltammograms that would be expected to accompany polyaniline redox processes. Accordingly, we conclude that the eight-microelectrode arrays can be derivatized in the manner desired, with six microelectrodes, 1–6, derivatized with polyaniline and the remaining two microelectrodes, 7 and 8, free of polymer to serve as the counterelectrode (Chart I, not drawn to scale).

An important aspect of the cyclic voltammetry data is that the cyclic voltammogram found at 100 mV/s for the surface-bound polyaniline has the same shape and area for any one of the six microelectrodes, and each of the cyclic voltammograms for the

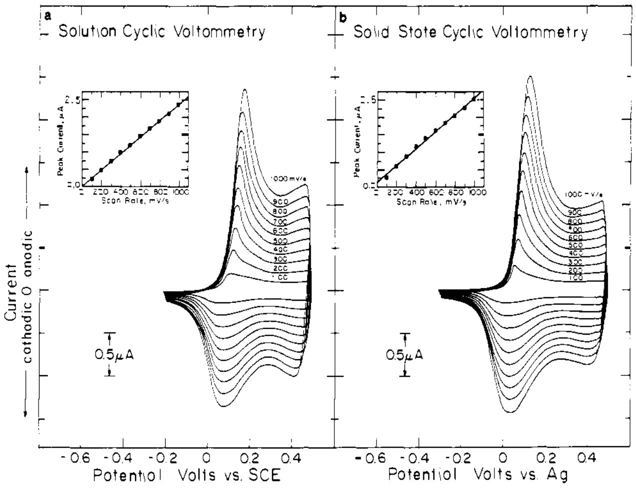
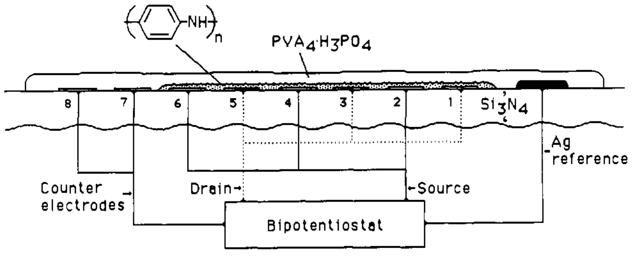


Figure 1. Comparison of the 298 K scan rate dependence of the cyclic voltammograms for six polyaniline-coated microelectrodes with (a) aqueous 1.0 M H_3PO_4 electrolyte under Ar and (b) $(PVA)_4 \cdot H_3PO_4$ electrolyte under Ar saturated with H_2O. The insets show plots of anodic peak current vs. sweep rate.

Chart I. Arrangement of Polyaniline-Modified Microelectrode Array



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(9) (a) Kittlesen, G. P.; White, H. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 7373. (b) Kittlesen, G. P.; Wrighton, M. S. *J. Mol. Electron.* **1986**, *2*, 23.

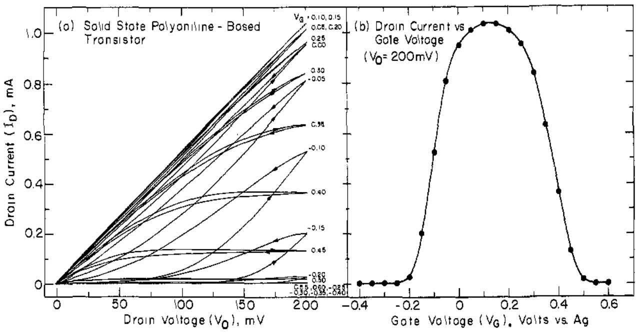

Figure 2. (a) I_D vs V_D (0–200 mV, 10 mV/s) at fixed V_G and (b) steady-state data for I_D vs. V_G at fixed V_D (200 mV) for the solid-state polyaniline-based device shown in Scheme I. The data are for a device exposed to ambient air at 298 K.

individual microelectrodes has the same shape and area as that found when all six microelectrodes are driven as one electrode. The conclusion from these observations is that all of the polyaniline is accessible by addressing any one of the six polyaniline-coated electrodes, consistent with the optical microscopic observation that the polyaniline connects the six microelectrodes as shown in Chart I. If the microelectrodes were not connected by polyaniline, the area of the cyclic voltammogram where all six electrodes are driven as one would be the sum of areas of the cyclic voltammograms for the electrodes driven individually. The finding that all of the polyaniline is accessible by addressing only one microelectrode is essential to being able to demonstrate a rapid-response transistor device, which depends on having the source and drain microelectrodes connected with the active material.

Data in Figure 1 show that for the solid and fluid electrolyte the peak current (anodic or cathodic) is directly proportional to the sweep rate for sweep rates up to 1 V/s. This linear relationship is that expected for electrode-confined redox reagents where the oxidation/reduction process is not limited by any diffusion process.[10] The fact that the solution- and solid-state data are essentially the same is consistent with the conclusion that the $(PVA)_4{\cdot}H_3PO_4$ is a rather good ionic conductor. In terms of device implications the cyclic voltammetry data show that turn on/turn off should occur in less than 1 s, the time to move the polyaniline from reduced (insulating) to oxidized (conducting) and back to the reduced state. The final issue in connection with the cyclic voltammetry concerns the moisture dependence of the cyclic voltammetry in the case of the solid-state electrolyte. Data shown in Figure 1 are for an H_2O-saturated Ar atmosphere. If the atmosphere is H_2O free (<50 ppm H_2O) by using pure Ar (or O_2), the cyclic voltammetry is qualitatively different: The cyclic voltammogram is at least a factor of 10 smaller in area, and the anodic current peak moves to a slightly more positive value. Generally, purging the device with dry Ar ultimately results in the inability to see any electrochemical response. Presumably, the effect stems from a lack of ionic conductivity in the dehydrated $(PVA)_4{\cdot}H_3PO_4$. Changing the atmosphere back to H_2O-saturated Ar regenerates the original cyclic voltammograms within 2 min. The effect on the cyclic voltammetry of polyaniline in the solid-state electrolyte from varying the atmosphere from Ar/H_2O to Ar is essentially reversible and can be correlated with the characteristics of the solid-state transistor (vide infra).

b. Characterization of a Solid-State Polyaniline-Based Transistor. The device illustrated in Scheme I can be fabricated by regarding microelectrodes 1, 3, and 5 of the chemically derivatized chip shown in Chart I as the drain and microelectrodes 2, 4, and 6 as the source. A bipotentiostat can then be used to control the source potential relative to the quasi-reference to the desired value, V_G, and the drain potential relative to the source, V_D. When the current in the drain circuit, I_D, is monitored upon variation in V_D at fixed V_G or upon variation in V_G at fixed V_D, the device characteristics illustrated in Figure 2 are found. The data are for a device operated in ambient laboratory air containing H_2O vapor. As previously found for aqueous acid electrolyte,[7] the solid-state device turns on (I_D >0) upon moving V_G from negative values to positive values corresponding to the oxidation of the polyaniline, but at sufficiently positive values of V_G the device turns off. The general shape of the V_D vs V_G curve for liquid[7] and solid electrolyte is the same: There is a restricted range of V_G where the device is on. The partially oxidized polyaniline shows maximum conductivity, whereas fully reduced (V_G more negative than ~−0.3 V vs Ag) and fully oxidized polyaniline (V_G more positive than ~+0.6 V vs Ag) are effectively insulating. The resistance of polyaniline between source and drain is measured by the slope at $V_D = 0$ of a plot of I_D vs V_D for ΔV_D of ±50 around $V_D = 0$. The measured resistance can be varied by at least 5 orders of magnitude depending on V_G, with a broad minimum of $\sim 10^2\ \Omega$, for V_G between 0.1 and 0.3 V vs Ag. The resistance of polyaniline vs V_G is merely another way of representing the I_D vs V_G characteristic shown in Figure 2. The data are quite similar to those obtained in 0.1 M H_2SO_4.[7a]

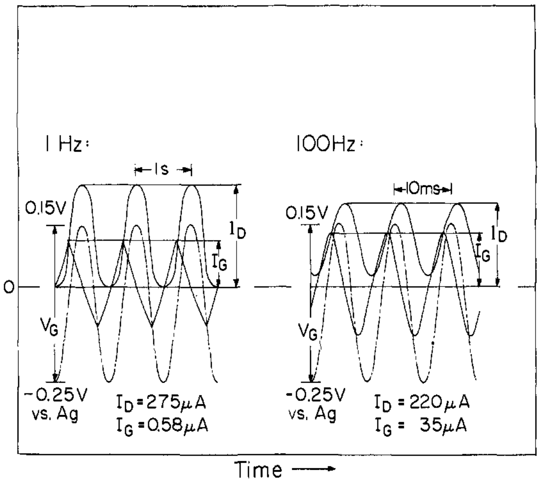

Figure 3. Comparison of I_D, I_G, and V_G vs. time at 1 and 100 Hz for a solid-state polyaniline-based transistor operated at 298 K under H_2O-saturated Ar. The change in V_G is from −0.25 to 0.15 V vs. Ag and V_D = 100 mV. The smaller value of I_D reflects incomplete turn on as the frequency is increased from 1 to 100 Hz. At the higher frequency, the value of amplification drops to ~1.6 or approximately the break-even point in power gain vs. frequency. Cf. Table I for data summarizing these and intervening frequencies.

The solid-state microelectrochemical transistor based on the $(PVA)_4{\cdot}H_3PO_4$/polyaniline system is remarkably durable and reproducible. Indeed, the solid-state device seems to be more durable than the liquid electrolyte case, especially at more positive values of V_G. The liquid electrolyte case usually gives irreversible degradation at positive potentials where there is still a significant value of I_D. Too positive a potential also degrades the polyaniline in the $(PVA)_4{\cdot}H_3PO_4$, but the solid-state case does show essentially complete turn off at positive values of V_G that do not cause degradation. Turn on/turn off cycles are found upon step variations in V_G at fixed values of V_D. Every on/off cycle is essentially identical, and the turn on is somewhat sluggish compared to the turn off. The appearance of the turn on/turn off cycles is not substantially different from that found for solution characterization.[7] For step variation in V_G between −0.3 (off) and +0.4 (on) V vs Ag, the turn on/turn off times are ~50 ms. A more quantitative measure of turn on/turn off has been carried out by applying a sinusoidal variation in V_G at frequencies from 1 to 100 Hz. The data are illustrated in Figure 3 for the 1- and 100-Hz cases, and Table I summarizes all of the findings for the device. As can been seen, the maximum extent of turn on, as reflected in the magnitude of I_D, is less at 100 Hz than at 1 Hz, but the turn on remains >80% of the maximum steady-state I_D even at 100 Hz. Figure 3 also illustrates that I_D does not go to zero at 100 Hz, but turn off to <20% of the maximum I_D is still possible. Earlier results[7b] for polyaniline-based transistors operated in 0.5

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(10) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980. (b) Hubbard, A. T.; Anson, F. C. *Electroanal. Chem.* **1970**, *4*, 129.

Table I. Frequency Dependence of Power Gain for Polyaniline-Based Solid-State Transistor[a]

f,[b] Hz	max I_D,[c] μA	max I_G,[d] μA	amplification[e]
1	275	0.58	120
3	250	1.65	38
10	245	5.00	12
30	233	13.3	4.4
100	220	35.0	1.6

[a] Data for 1 and 100 Hz are shown in Figure 3. [b] Frequency of sinusoidal variation in gate potential, V_G, from −0.25 to +0.15 V vs Ag. [c] Maximum drain current observed at a fixed drain potential, V_D = 0.1 V. [d] Maximum gate current, I_G, associated with oxidation/reduction of polyaniline. [e] Ratio of average power available in the drain circuit to the average power used in the switching. Cf. ref 7b.

M H_2SO_4 show switching to be superior than illustrated in Figure 3 for the solid-state system. Data at frequencies exceeding 300 Hz show essentially the same degree of turn on as at 1 Hz in the solution devices previously reported.[7b] A significant difference, aside from the use of the solid-state electrolyte, in the device reported here is that more polyaniline has been used in the active region of the device. In any case, switching in the solid-state case is expected to be somewhat slower than for the solution case, at equivalent polyaniline coverage, owing to lower ionic conductivity for the solid electrolyte.

The data in Figure 3 include that needed to show that the solid-state polyaniline transistor shows power gain in the sense that is normally applied to solid-state transistors.[11] Power gain can be claimed when the average power available in the drain circuit exceeds the average power (in the gate circuit) associated with turning the device on and off. Thus, the amplification in Table I is the ratio of the average power in the drain circuit to that in the gate circuit. Since the energy required for switching is fixed for a given device, the average power in the switching process will increase linearly with switching rate. Thus, the amplification is frequency dependent and will fall as the frequency is raised. Data in Table I show that amplification exceeds 1 up to at least 100 Hz. Power gain at higher frequency can be achieved if smaller amounts of redox polymer are involved, and operation with power gain to at least 300 Hz has been demonstrated. The point is that the maximum frequency where power gain can be established depends on the volume of polymer to be oxidized and reduced in the switching process: Larger volume means more energy is required to switch. Lowering the amount of polymer to be switched to achieve equal maximum I_D requires a new microfabrication design. The maximum frequency where power gain can be realized ultimately hinges on intrinsic properties of the redox polymer/electrolyte system and the geometry of the microelectrode array.[7b] For the solid-state system the intriguing finding is that rather high-frequency operation can be achieved for an electrochemical device. The 10-ms switching time is similar to the best electrochromic display systems[12] and not very much slower than liquid crystals.[13] Solid-state semiconductor-based transistors can be switched at $>10^9$ Hz,[11] but the switching does not involve the movement of ions. Fast switching of the microelectrochemical device will depend on achieving qualitatively smaller dimensions than the approximately 1 μm used to date.[7b]

c. Moisture Dependence of the Solid-State Transistor. The characteristics of the polyaniline transistor employing $(PVA)_4 \cdot H_3PO_4$ electrolyte described in the foregoing section are for an atmosphere above the device that has a significant H_2O content. Oxidation/reduction of the polyaniline on the microelectrodes is generally unobservable when the atmosphere is H_2O-free Ar (or O_2), showing that the ionic conductivity of the $(PVA)_4 \cdot H_3PO_4$ declines dramatically in the absence of H_2O vapor. This result leads to the conclusion that the operation of the solid-state polyaniline transistor requires H_2O vapor in the atmosphere above the device. Indeed, if the device in Scheme I is operated in H_2O-saturated Ar, the characteristics shown in Figure 2 are found, but if the atmosphere is changed to H_2O-free Ar, the I_D–I_G curve changes such that the region of any turn on becomes more narrow and the maximum I_D falls. Within ~30 min at 298 K the transistor does not show turn on (I_D < 20 nA) after changing from H_2O-saturated to H_2O-free Ar. These results alone establish that the transistor could be potentially useful as a moisture monitor, because the power gain of the device diminishes to zero as the atmosphere is varied from H_2O saturated to H_2O free.

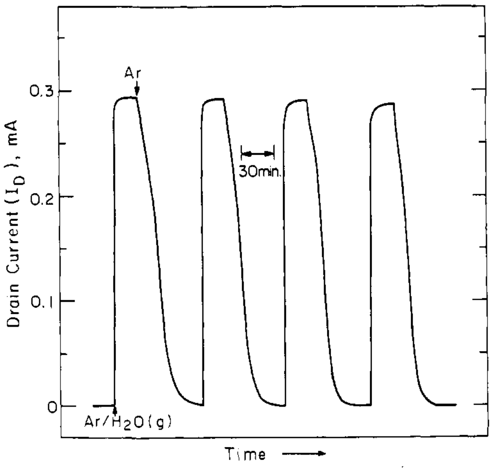

Figure 4. Response of solid-state polyaniline-based transistor in Scheme I to variations in the atmosphere from pure Ar to H_2O-saturated Ar at 298 K, V_D = 50 mV and V_G = 0.15 V vs. Ag.

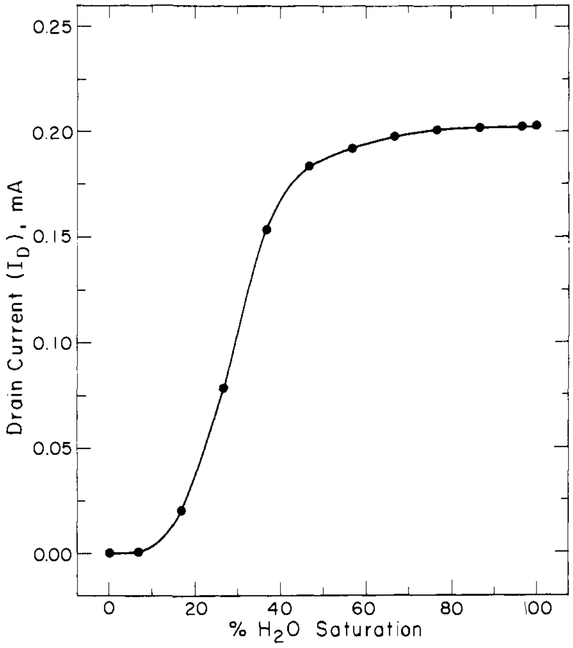

Figure 5. I_D of a polyaniline-based solid-state transistor (V_D = 50 mV) as a function of the atmosphere to which the device is exposed. Each data point represents the steady-state drain current that remains unchanged for >30 min after each change of the level of H_2O saturation.

Figures 4 and 5 show some "steady-state" data giving the dependence of I_D on H_2O content of the atmosphere over the polyaniline device. The experimental data are "steady state" in the sense that the values of V_G and V_D are fixed for the device. Clearly, rapid change in the H_2O content (Figure 4) or controlled H_2O-content variation (Figure 5) show that I_D depends on the H_2O content of the atmosphere. The same results are obtained if H_2O-saturated and H_2O-free O_2 are used instead of Ar. Data in Figure 4 show that the response to H_2O vapor is reversible, and such reversible response has been observed for a period of at least

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(11) Sze, S. M. *Physics of Semiconductor Devices*, 2nd ed.; Wiley: New York, 1981.

(12) (a) Hamada, H.; Yano, K.; Take, H.; Inami, Y.; Matsuura, M.; Wada, T. *Displays* **1983**, *4*, 221. (b) Chang, I. F. *Displays* **1981**, *2*, 275. (c) Bookbinder, D. C.; Wrighton, M. S. *J. Electrochem. Soc.* **1983**, *130*, 1080.

(13) Sugimura, A.; Takao, K. *Jpn. J. Appl. Phys., Part 1* **1985**, *24*, 905 and reference therein.

10 h without significant deterioration in properties of the solid-state polyaniline device.

The data in Figures 4 and 5 are somewhat difficult to interpret, because the inability to electrochemically switch the device under a H_2O-free atmosphere does not explain why the oxidized polyaniline would become resistive upon removing the H_2O. The resistance of oxidized polyaniline can be monitored as a function of the gas atmosphere by merely applying a small potential (~50 mV) between two polyaniline-connected microelectrodes. Indeed, if the polyaniline is oxidized to +0.15 V vs. Ag and the atmosphere is varied from H_2O-saturated to H_2O-free Ar while the resistance of the polyaniline is monitored, there is, in fact, essentially no change: The oxidized polyaniline remains a good conductor with and without H_2O in the contacting atmosphere. Similarly, if a polyaniline-coated microelectrode array (without a $(PVA)_4{\cdot}H_3PO_4$ coating) is withdrawn from an aqueous acidic solution in the oxidized state and then dried with a stream of H_2O-free Ar, there is only modest variation in the resistance measured between two of the microelectrodes. The conclusion is that neither oxidized (conducting) polyaniline coated with $(PVA)_4{\cdot}H_3PO_4$ nor oxidized (conducting) polyaniline without solid electrolyte can be rendered nonconducting by merely changing the H_2O content of the contacting atmosphere. Thus, either the conductivity of conducting polyaniline is not intrinsically H_2O dependent or merely purging with the H_2O-free gas stream at 298 K is inadequate to bring about the necessary changes in H_2O content in the polymer to diminish conductivity. The $(PVA)_4{\cdot}H_3PO_4$ can clearly be altered by purging with a H_2O-free gas stream at 298 K because the cyclic voltammetry waves of the polyaniline decline dramatically upon changing from an H_2O-saturated to H_2O-free atmosphere. These facts together do not account for the H_2O-content I_D dependence shown in Figures 4 and 5 for fixed V_G and V_D.

The key to understanding the H_2O-content dependence of I_D for the three-terminal device at fixed V_G and V_D comes from an appreciation of the fact that a small, apparently very significant, leakage current occurs in the gate circuit under conditions where V_G and V_D are fixed. The small I_G that flows is such that there is a net cathodic process at the polyaniline-coated microelectrodes and a net anodic process at the counterelectrode. In H_2O-saturated atmospheres the leakage I_G is ~50 pA for a typical device at $V_G = +0.15$ V vs. Ag and $V_D = 50$ mV where $I_D = 0.3$ mA. Obviously, in comparison to the value of I_D, I_G is small. But in absolute terms 50 pA can be significant because of the small amounts (~10^{-11} mol of aniline monomer) of redox material involved in the devices. The leakage I_G actually increases to ~200 pA, but is very erratic, upon switching the atmosphere to an H_2O-free gas. As the system is purged, the ionic conductivity of the $(PVA)_4{\cdot}H_3PO_4$ apparently falls and the polyaniline is difficult to hold under potentiostatic control. The leakage I_G likely yields H_2 evolution at the Pt microelectrodes coated by polyaniline, leading to an increase in local pH. The loss of H_2O from the film precludes transport of H^+ to the surface, owing to the lowered H^+ conductivity of $(PVA)_4{\cdot}H_3PO_4$ upon dehydration. Polyaniline tends to become less conducting at higher pH's,[7a] and this may be enough to cause the H_2O-content response shown in Figure 4 and 5. Thus, the small but significant leakage I_G and loss of ionic conductivity in $(PVA)_4{\cdot}H_3PO_4$ lead to a solid-state polyaniline-based device that shows H_2O-dependent characteristics, which might be useful in monitoring the H_2O content of gases. If the leakage I_G current does correspond to H_2 evolution at the polyaniline-coated microelectrodes and O_2 evolution at the counterelectrode, the device can be expected to have long life because only H_2O need be sacrificed. While no tests longer than 24 h have been carried out, we observe only slight deterioration in properties of the solid-state device during such tests.

Conclusions

Our new work demonstrates an extension of our earlier report[2] on a polymer-based solid-state microelectrochemical transistor. In the case at hand, $(PVA)_4{\cdot}H_3PO_4$ is used as the solid-state electrolyte instead of poly(ethylene oxide)$\cdot LiCF_3SO_3$. We find that significant ionic conductivity for the $(PVA)_4{\cdot}H_3PO_4$ requires moisture in the surrounding atmosphere. Thus, we suggest that the conductivity is like that in so-called "ready hydrates".[14-16] It is worth noting that even the H^+ conductivity of β''-alumina requires high water content.[17] However, it should be emphasized that the hydrated $(PVA)_4{\cdot}H_3PO_4$ does not have the physical properties or appearance of a liquid at 298 K. Under a H_2O-containing atmosphere the polyaniline-based microelectrochemical transistor has electrical characteristics that are nearly the same as for a device operated in liquid (aqueous acid) electrolyte solution.[7] Perhaps surprisingly the switching speed for the solid-electrolyte device is nearly the same as for the liquid-electrolyte case. We suggest the exploration of hydrated $(PVA)_4{\cdot}H_3PO_4$ as an electrolyte for polyaniline-based batteries[18] and electrochromic displays.[19] The use of proton conduction in hydrogen sensors[1] and batteries[14] has been suggested previously. The chemistry of $(PVA)_4{\cdot}H_3PO_4$ necessary to understand the H^+ conductivity is not known. It is likely that phosphate esters form, but the structure, degree of esterification, and the role of H_2O in structure and H^+ conductivity have not been established. Work is under way in these laboratories to better characterize the $(PVA)_4{\cdot}H_3PO_4$ system.

An important finding in our work is the moisture sensitivity of the solid-state polyaniline transistor. The dehydration of $(PVA)_4{\cdot}H_3PO_4$ alone could be useful in designing an H_2O-responsive electrochemical device, but the "system" responds to H_2O content as a consequence of both the H_2O dependence of the ionic conductivity and the leakage current in the gate circuit that causes the device to turn off in the absence of H_2O in the atmosphere, owing to a reductive process at the polyaniline-coated microelectrodes. It is the *combination* of changes in H^+ ionic conductivity of $(PVA)_4{\cdot}H_3PO_4$ and the faradaic chemistry due to the leakage current that gives rise to the moisture dependence of the transistor at fixed V_G and V_D (Figures 4 and 5). The significant conductivity of oxidized polyaniline alone does not appear to be very sensitive to the H_2O content of the atmosphere on a time scale where the transistor responds rapidly. Thus, the H_2O sensitivity of the device is not intrinsic to the conducting polymer as suggested in a number of other situations where two terminal devices have been used to detect variations in a gaseous atmosphere.[20] Microsensors of all kinds, including ones that respond to moisture, are now the object of much attention.[21,22] In conclusion, the moisture sensitivity of the solid-state polyaniline transistor is a consequence of the integration of the properties of the conducting redox polymer, the solid-state ionic conducting polymer, and the way in which these materials are arranged on a microfabricated structure.

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(14) Childs, P. E.; Howe, A. T.; Shilton, M. G. *J. Power Sources* **1978**, *3*, 105.

(15) Shilton, M. G.; Howe, A. T. *Mater. Res. Bull.* **1977**, *12*, 701.

(16) Murphy, K. E.; Flanagan, T. B. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1188.

(17) Bates, J. B.; Frech, R.; Engstrom, H.; Wang, J. C.; Kaneda, T. *Solid State Ionics* **1980**, *1*, 15.

(18) Kitani, A.; Kaya, M.; Sasaki, K. *J. Electrochem. Soc.* **1986**, *133*, 1069.

(19) Kobayashi, T.; Yoneyama, H.; Tamura, H. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *161*, 419.

(20) Miasik, J. J.; Hooper, A.; Tofield, B. C. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1117.

(21) Sibbald, A. *J. Mol. Electron.* **1986**, *2*, 51.

(22) Janata, J., Huber, R. J., Eds. *Solid State Chemical Sensors*; Academic: New York, 1985.