Potential-Dependent Conductivity of Conducting Polymers Yields Opportunities for Molecule-Based Devices: A Microelectrochemical Push–Pull Amplifier Based on Two Different Conducting Polymer Transistors

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Conducting polymers represent an interesting class of materials[1] which have been proposed for use in applications such as wire, sensors,[2,3] drug-delivery systems,[4] batteries,[5,6] electrochromic displays,[7] light-emitting diodes,[8–10] solid state[11–14] and microelectrochemical transistors,[15–19] transistors[20] and capacitors[21] based on Langmuir–Blodgett films of conducting polymers,[22] high-efficiency solar cells,[23] and electromagnetic interference shielding.[24] In this communication we demonstrate that a pair of conducting polymer-based microelectrochemical transistors[15–19] can function as a push–pull amplifier.[25] Importantly, the overall function of the device stems from the different electrical characteristics of the two different polymers used as the device-active materials. The amplifier derives its inherent freedom from "crossover distortion" from the interesting finite window of high conductivity displayed by conducting polymers.[18]

It has previously been shown by work in this laboratory that a pair of closely spaced, individually addressable microelectrodes connected by a material such as polyaniline or polythiophene can function as a transistor (Figure 1).[15–19] Polymers such as polythiophene, polypyrrole, polyaniline, and polyacetylene, while insulating in their neutral form, become highly conducting upon partial oxidation. The polymers become insulating again when further oxidized, yielding the unusual I_D–V_G characteristic illustrated in Figure 1 for a polythiophene-based transistor.[18] The source-to-drain conductivity of the device is controlled by application of the appropriate gate potential, V_G. The unusual aspect of the I_D–V_G characteristic is that the device switches from off, to on, to off as V_G is increased, and therefore such microelectrochemical transistors can be operated in *either* the off-to-on or on-to-off mode. This capability is not shared by conducting polymer-based field-effect transistors or more conventional transistors such as MOSFETs, where I_D reaches a maximum and plateaus as V_G is increased rather than returning to zero, yielding only off-to-on switching.[26] Switching frequency of microelectrochemical transistors is limited by motion of electrolyte counterions in to and out of the polymer film. Such movement is required to compensate charge centers in the polymer as they are created and neutralized as V_G changes. The highest frequency operation with power gain demonstrated thus far is only about 10^4 Hz.[27] Thus, the switching frequency of microelectrochemical transistors is less than for solid-state semiconductor devices, but the interesting electrical properties of the polymer may yield devices having novel characteristics. A push–pull amplifier, involving two different conducting polymers (Figure 2), demonstrates a new way to utilize the materials properties of conducting polymers which give rise to the unusual switching characteristics of polymer-based microelectrochemical transistors.

The basic microelectrochemical transistor illustrated in Figure 1 consists of a film of polymer deposited onto two platinum or gold microelectrodes (1.5 μm apart, 1.5 μm wide, and 100 μm long, shown in cross section in Figure 1) which serve as the source and drain of the transistor. The oxidation state of the polymer is controlled by application of gate vltage, V_G, with respect to a reference electrode in the electrolyte solution. Gate current, I_G, corresponds to withdrawal from or injection into the polymer of electrons (oxidation or reduction) which controls the polymer conductivity. A drain potential, V_D, is applied across the polymer film and drain current, I_D, flows when the polymer is in its conducting state. Transistor action occurs because a small change in V_G gives rise to a large change in I_D. In Figure 1 the I_D–V_G characteristic for a polythiophene-based transistor is shown. The finite potential window of high I_D and the hysteresis in the scan are both typical of conducting polymer-based devices.[18,19] The high value of I_D corresponds to the partially oxidized, conducting state of polythiophene.

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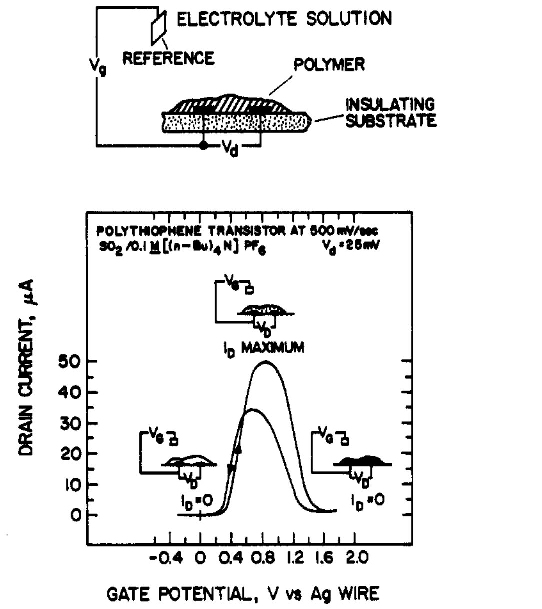

Figure 1. Top: cross-sectional view of a microelectrochemical transistor. The electrodes are functionalized with a film of polymer by electropolymerization of the appropriate monomer. Bottom: I_D–V_G characteristic of a polythiophene transistor. The neutral (no shading) and highly oxidized (dark shading) states of the polymer film are insulating. High conductivity occurs in the partially oxidized state (medium shading). See refs 18 and 19.

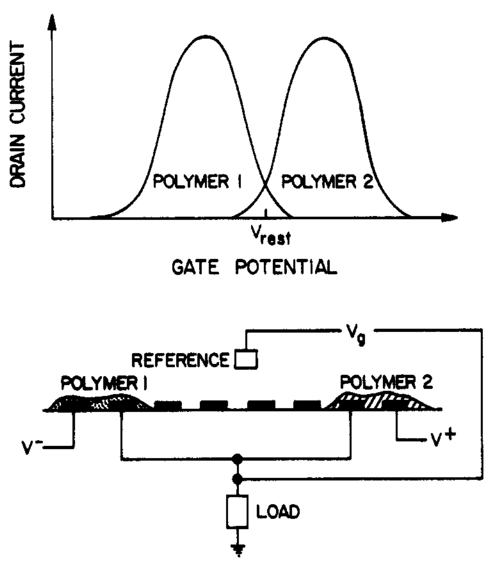

Figure 2. Microelectrochemical push–pull amplifier based on two conducting polymers having I_D–V_G characteristics overlapping as shown. As gate potential, V_G, is moved positive of V_{rest}, polymer 2 becomes conducting. Negative of V_{rest}, polymer 1 becomes conducting.

Microelectrochemical transistors like that represented in Figure 1 can function as amplifiers at low frequency.[27,28] Insertion of a load into the drain circuit allows the device to function as a basic one-transistor amplifier. Such one-transistor amplifiers can provide output current in only one direction even though a load such as a speaker can and should be driven with current in both directions. The purpose of a push–pull amplifier is to provide an output which can both source *and* sink current, i.e., drive a load positive and negative of zero.[25] The push–pull amplifier,

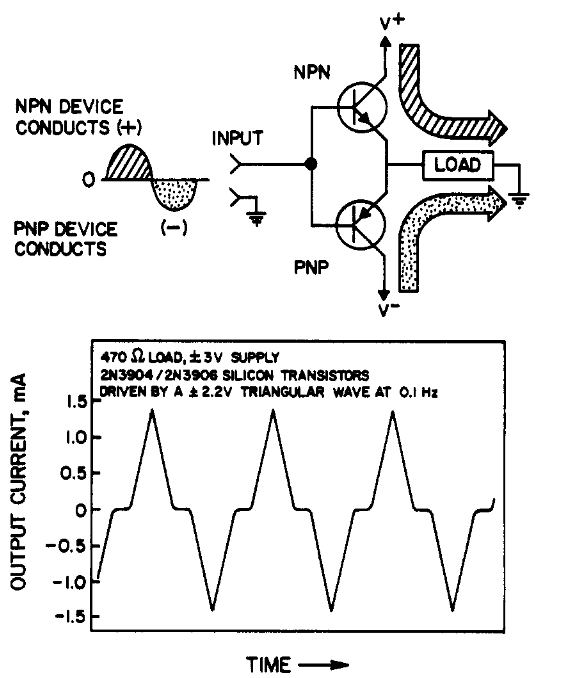

Figure 3. Schematic and output waveform of a silicon bipolar push–pull amplifier. The distortion as the output crosses zero is due to the 0.6-V p–n junction barrier potential in the silicon devices.

shown in Figure 3 in its most basic form, sees wide use as the output stage in, for example, audio amplifiers and operational amplifiers. One transistor handles the positive side of operation and the other the negative side. The NPN transistor conducts in response to a positive input voltage, causing current from the positive supply, V^+, to flow, and the PNP transistor conducts in response to a negative input, causing V^- current to flow. In this way the load can be driven both positive and negative of ground. The response of a push–pull amplifier based on silicon bipolar transistors is shown in Figure 3. Notice that the amplifier output shows a dead zone as it crosses zero, commonly referred to as "crossover distortion". The crossover distortion is due to silicon's 0.6 V p–n junction barrier potential which must be exceeded before a bipolar device begins to turn on. The result is a dead zone between +0.6 and −0.6 V in input voltage where neither transistor conducts, giving rise to the plateau in the output as it crosses zero. In most applications this crossover distortion is undesirable and is typically overcome by additional circuitry which holds both transistors slightly above their turn-on threshold.[25]

Figure 2 shows a push–pull amplifier implemented with microelectrochemical instead of solid state transistors. The unusual I_D–V_G characteristic of conducting polymers allows conducting polymer-based microelectrochemical transistors to be operated on *either side* of the peak in the I_D–V_G characteristic. As a result, a positive or negative dI_D/dV_G can be selected for a given application by the range of V_G over which the transistor is operated. Further, a number of conducting polymers with different potential windows of high conductivity are available.[15–19] The significance of these two materials properties is that we can determine the manner in which two transistors complement each other electrically in a commonly-gated pair by the conducting polymers we choose. Currently known conducting polymers can accommodate requirements ranging from transistor pairs with windows of

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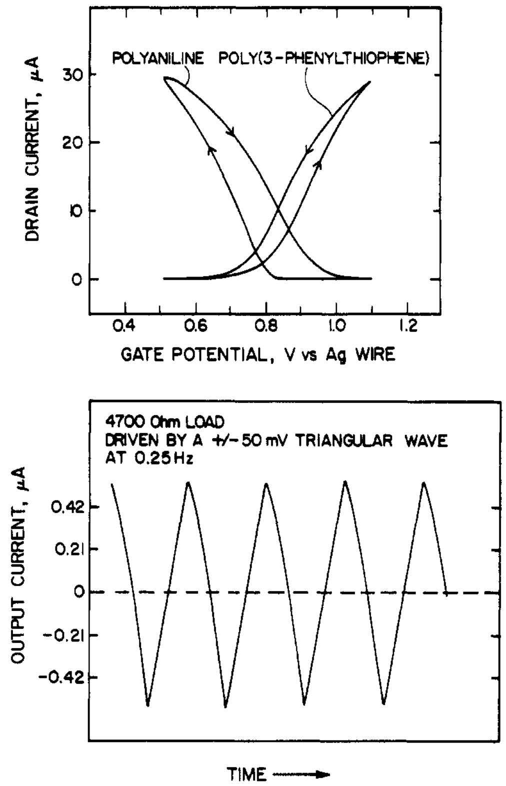

Figure 4. Top: I_D–V_G characteristics of polyaniline (V_D = 50 mV) and poly[3-phenylthiophene] (V_D = 35 mV) in the window of push–pull operation. The transistors were fabricated on a single microelectrode array and characterized in 0.1 M $LiClO_4$/0.4 M F_3CCO_2H/CH_3CN. Bottom: output waveform for a polyaniline/poly(3-phenylthiophene) push–pull amplifier illustrating its clean zero-crossing. An array of eight platinum microelectrodes was functionalized by electropolymerization of aniline and of 3-phenylthiophene to obtain the two transistors which were used in the circuit shown in Figure 2 (polymer 1 = polyaniline, polymer 2 = poly(3-phenylthiophene), V^+ = 150 mV, V^- = 25 mV, V_{rest} set for zero output current at zero input voltage, operated in 0.1 M $LiClO_4$/0.4 M F_3CCO_2H/CH_3CN).

conductivity overlapping completely to windows separated by a significant gap. By choosing two conducting polymer transistors with I_D–V_G's overlapping as shown in Figure 2, we obtain transistors with the responses appropriate for a push–pull amplifier.

Polyaniline and poly(3-phenylthiophene) represent a pair of materials suitable for demonstration of a push–pull amplifier. Transistors of these materials were fabricated on a single microelectrode array and the overlap of their I_D–V_G characteristics is shown in Figure 4. From the potential at which the I_D–V_G characteristics cross, V_{rest} in Figure 2, moving negative drives polymer 1 (polyaniline) into conduction and polymer 2 (poly[3-phenylthiophene]) negative of turn-on where it is insulating. Moving positive of V_{rest} results in conduction by polymer 2 and insulation by polymer 1. This system responds to an input signal, added to V_{rest}, in the same manner as the conventional push–pull amplifier in Figure 3 but with an important difference: there is no crossover distortion since the overlap of the I_D–V_G characteristics of the two transistors is chosen such that at V_{rest} both transistors are in partial conduction, and no dead zone intervenes where the transition between conduction by one transistor to conduction by the other occurs. Figure 4 includes the response of the polyaniline/poly(3-phenylthiophene) push–pull amplifier, driven by a triangular wave, demonstrating clean zero-crossing of the output. Interestingly, despite the unusual hysteresis in the I_D–V_G curves for the transistor, the push–pull amplifier shows high fidelity amplification. Note, however, that ΔV_G is only 100 mV and hysteresis in polymer response declines as ΔV_G is reduced. The poly(3-phenylthiophene) transistor, operating on the side of its I_D–V_G negative of peak drain current, drives the load during positive excursions of the output while negative output current corresponds to conduction by the polyaniline transistor, operating on the side of its I_D–V_G positive of peak drain current.

In conclusion, we have prepared and characterized a microassembly of materials which achieves the function of a push–pull amplifier where conducting polymers are the device-active elements. The unusual I_D–V_G characteristic of conducting polymer-based microelectrochemical transistors is a result of the finite window of high conductivity displayed by the active material. From this unique aspect of conducting polymer behavior is derived a microelectrochemical push–pull amplifier inherently free from crossover distortion.

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