

Faradaic effects in all-organic transistors

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Electrochemical (Faradaic) effects play an important role in the unusual field-effect phenomenon observed in an all-organic transistor-type device that use films of doped electronic polymers, such as polyaniline (emeraldine-HCl) and poly-3,4-ethylenedioxythiophene polystyrene sulfonate, as the channel and gate. Small leakage currents through the dielectric are sufficient to affect reversible redox reactions in the polymer film in the active region of the device, i.e., where the channel and gate regions overlap. In the case of polyaniline, these redox reactions are accompanied by color changes corresponding to the different oxidation states of polyaniline that can be visually observed and also spectroscopically monitored. © 2008 American Institute of Physics.

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I. INTRODUCTION

There have been several reports describing an unusual phenomenon in transistors using highly doped and electrically conducting poly-3,4-ethylenedioxythiophene polystyrene sulfonate (PEDOT-PSS) as the channel in which the current passing through the channel is significantly affected upon exposure to an electric field.¹⁻⁶ Unlike classical field-effect transistors (FETs) in which the channel is semiconducting, the conductivity of PEDOT-PSS is in the metallic regime ($\sigma > 1$ S/cm) and what makes the phenomenon unusual is that the electric field applied across the dielectric is not expected to penetrate beyond the Debye screening length for metals.¹ For devices in which both the channel and the gate are made of PEDOT-PSS, both capacitive and Faradaic mechanisms have been proposed, e.g., the “beaches and islands” model, wherein the applied field influences only the semiconducting regions (capacitive)³ and electrochemical dedoping caused by ion migration in the presence of moisture (Faradaic).² In a recent study of a device using a metallic gate, the phenomenon was attributed to an unusual type of field effect (capacitive) in which ion diffusion coupled with the free carrier motion on the polymer backbone is responsible for the change in the channel current. It was proposed that conductance is modulated when only 2% of hole carriers are compensated by mobile ions, which is not expected to cause significant electrochemical changes in the polymer backbone. In the present study, we have used doped polyaniline as both channel and gate materials to further probe this phenomenon. Unlike the transparent and essentially colorless PEDOT-PSS, polyaniline displays a range of colors depending on the polymer oxidation state and any electrochemical redox reaction taking place in the channel or the gate should be visible to the naked eye. Importantly, since the dark green conducting oxidation state of polyaniline, which is emeraldine, straddles the two insulating states, which are leucoemeraldine (colorless) and pernigraniline (violet), it should be

possible to probe electrochemical effects by monitoring the channel conductance under both positive and negative applied gate biases. Under our experimental conditions, not only do we visually observe color changes in the channel and gate as a function of channel conductance but we also find that the channel conductance decreases for both positive and negative applied gate biases and the color changes at negative V_G are exactly reversed to what are observed at positive V_G . Importantly, the color changes are apparent only in the region where the channel and gate cross, which is different from what has been previously reported for a PEDOT-PSS channel using an Al gate.¹ However, our results are consistent with the dedoping observed in devices having PEDOT-PSS as both channel and gate.²

Parent polyaniline and its ring-substituted derivatives have been previously evaluated as the channel material in hybrid field effect transistor (FET) devices, which consist of a “global” gate made of a commercial silicon wafer and a thin layer of silicon oxide as the dielectric.⁷⁻¹⁶ In most of these systems, polyaniline was used either in its undoped emeraldine base form or in its lightly doped, semiconducting form (doped with HCl). In some instances, these hybrid devices have been used as a chemical sensor.¹⁷ To the best of our knowledge, there has not been any report on the use of doped polyaniline as a channel material in an all-organic, FET-type configuration, although there is one report describing classical FET behavior in what appears to be doped, metallic polyaniline in a hybrid Si backgated configuration.¹⁵

It must be pointed out that the “polyanilines” used in all of the above mentioned studies differ from each another. Polyaniline can exist in different oxidation states and one can have different doping levels for each oxidation state.⁴ Two of these oxidation states can be doped to the metallic regime. In addition, even minor variations in the synthetic conditions can lead to polyanilines with very different properties.^{18,19} In some instances, the relative humidity of the atmosphere plays a crucial role.¹⁸ The present work refers to polyaniline synthesized by using our previously described *in situ* adsorption polymerization method by which strongly adherent, op-

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tically transparent, substrate-supported films of highly doped emeraldine-HCl can be obtained from insulating substrates.^{20,21} It was this specific form of polyaniline that was used in the present study.

II. EXPERIMENTAL

A. Materials and instruments

Aniline (99%), ammonium peroxydisulfate (99%), toluene, methylethyl ketone, and concentrated hydrochloric acid were purchased from Sigma-Aldrich (Milwaukee, WI). Materials used as the dielectric include UV-curable polyacrylate-based resin Norland 65 from Norland Products (New Brunswick, NJ), 40 μm thick weighing paper from Fisherbrand, ~ 70 μm thick sheets of standard office paper from TOPS Business Forms (St. Charles, IL),²² and 12 μm thick MylarTM purchased from DuPont (Wilmington, DE). Polystyrene micron spacers were purchased from Polysciences (Warrington, PA). Baytron-P (PEDOT-PSS) was purchased from Bayer Corp. (Pittsburgh, PA). A Keithley model 2400 voltage source, a Keithley model 4200 semiconductor characterization system (SCS), and a Keithley model 197A multimeter interfaced with LABVIEW 5 software were used to record the electrical measurements. UV/visible spectra were obtained by using a model 50 CARY Bio spectrophotometer (Varian Instruments). Nashua XF-20 polyethylene terephthalate (PET) (“overhead transparency”) sheets were purchased from Nashua Corp. (Plymouth, MA). Optically transparent gate electrodes were made from indium tin oxide (ITO) conducting coatings on PET, which were purchased from IS Films (Baekert, CA).

The line patterning method used to prepare patterns on the PET film has been previously described.³ A thin coating of emeraldine-HCl was obtained on the patterned PET film by using the following procedure.

B. Coating of polyaniline film on PET

Aniline (20 ml) was dissolved in aqueous 1M HCl (300 ml) in a 1 l beaker equipped with a magnetic stir bar. Separately, 11.5 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was also dissolved in aqueous 1M HCl (200 ml). Both solutions were cooled to approximately -4 $^\circ\text{C}$ by using an ice/salt bath. The PET sheet containing the pattern was then immersed into the aniline/HCl solution. After 20 min, the PET sheet was removed from the solution and the ammonium peroxydisulfate solution was added all at once. The PET sheet was then immersed into the reaction mixture, ensuring that it was freely suspended from the top without touching the bottom of the beaker or disturbing the magnetic stir bar. After 1.5 h, the PET sheet containing the ~ 100 nm thick (profilometry) *in situ* deposited film of emeraldine-HCl (deposited on both sides of the sheet) was removed and repeatedly washed in aqueous 1M HCl to remove any adhering unreacted monomer and any loosely adhering polyaniline powder. Following air drying (10 min), the toner lines were removed by bath sonication in toluene (1–2 min) and methylethyl ketone (40–60 s), as previously described elsewhere for PEDOT-PSS.²

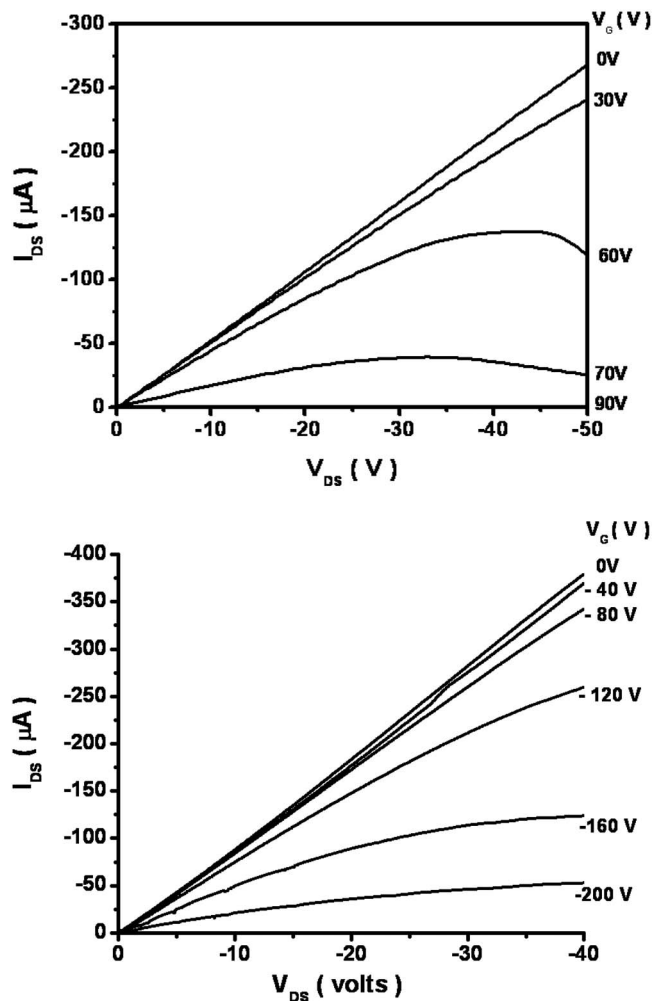


FIG. 1. (a) Output characteristics of a type-1 polyaniline device at different applied gate biases V_G (0, 30, 60, 70, and 90 V). (b) Output characteristics of a type-1 polyaniline device at different applied gate biases V_G (0, -40 , -80 , -120 , -160 , and -200 V).

C. Device fabrication

Two types of devices were fabricated by using 80–100 nm thick films of emeraldine-HCl (or PEDOT-PSS) as both the channel and the gate. The detailed description of the device design and fabrication is reported elsewhere.³ Type-1 devices had a narrow channel area (0.5×5 mm^2) and a 6–22 μm thick dielectric layer of polyacrylate (Norland 65) optical adhesive.² Type-2 devices had a wider channel area (2.5×2.5 mm^2) and a 70 μm thick “dielectric” layer composed of a strip of standard office paper. Type-2 devices were used in experiments requiring independent UV/visible measurements on the channel and gate active area of the device. In selected experiments, a commercial conductive coating of ITO on PET was used as the gate.

III. RESULTS AND DISCUSSION

Figure 1 describes the output curves of a typical type-1 polyaniline device. The channel current (I_{DS}) is highly linear at low applied positive gate voltages (V_G) with no saturation observed even at high drain-source bias (V_{DS}), which is consistent with a highly conducting polyaniline channel (σ

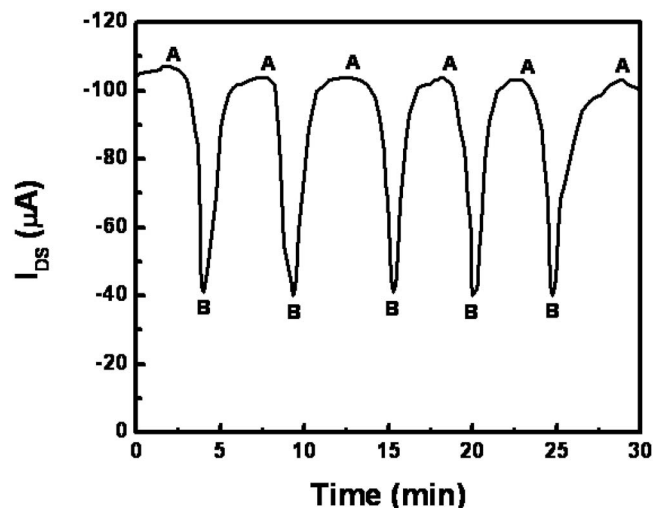


FIG. 2. (Color online) I_{DS} vs time plot for type-1 polyaniline device as a function of continuous application of gate bias at constant source bias. A gate voltage $V_G=+40$ V is applied at points indicated as A, and $V_G=-40$ V is applied at points indicated as B. The V_{DS} was held constant at -5 V.

$\sim 1-5$ S/cm). With increasing positive gate bias, drain-source current decreases and tends to saturate at high V_{DS} , which is consistent with a p channel. The applied electric field strength through the gate across the dielectric is $\sim 10^7$ V/m. The on/off ratio obtained falls within the range of 10–1500, which depends on the thickness of the dielectric (6–22 μm), with the transistor being initially in the “on” state for $V_G=0$ V. The depletion of the drain current upon application of a positive gate bias is similar to results obtained in analogous devices made of highly conducting PEDOT-PSS channels ($\sigma \sim 30$ S/cm).³

Surprisingly, for both type-1 and type-2 polyaniline devices, I_{DS} decreases upon application of a *negative* V_G [Fig. 1(b)], suggesting a change from p type to n type. Since we know that emeraldine-HCl is p doped with no immediate chemical rationale for n doping under ambient conditions, it is clear that this apparent ambipolar behavior points to a mechanism other than a classical field effect. As we will show below, Faradaic (electrochemical) effects play an important role in pinching off the channel current, i.e., polyaniline redox reactions take place in the region where the channel and gate overlap. It is to be noted that considerable hysteresis is observed in the I_{DS} - V_{DS} curves at different gate biases upon repeated measurements, as reported in earlier publications.²³

To further investigate this phenomenon and draw parallels between polyaniline and PEDOT-PSS devices, the current versus time characteristics of the polyaniline devices were studied. The drain-source current was continuously monitored with time as a function of gate bias at a fixed drain-source bias (Fig. 2). Initially, at $V_G=0$ V, a stable I_{DS} of 103 μA was reached. When a $V_G=+40$ V was applied (field strength of $\sim 4 \times 10^6$ V/m), the I_{DS} began to rapidly decrease. When the I_{DS} reached 40 μA over a period of ~ 90 s, a $V_G=-40$ V was applied. The I_{DS} increased and reached the original value of ~ 103 μA over a similar time

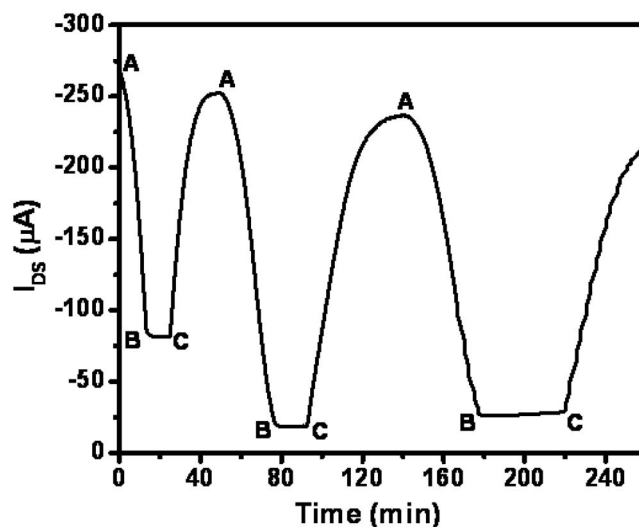


FIG. 3. (Color online) I_{DS} vs time plot for type-1 polyaniline device. A gate voltage $V_G=+48$ V is applied between points A and B and a $V_G=-48$ V is applied between points C and A. Between points B and C, no gate bias was applied. The V_{DS} was held constant at -5 V.

period. This cycle was repeated many times. This response is qualitatively similar to that of PEDOT-PSS devices.³

There are, however, differences in the decay and recovery of drain-source current upon exposure to a continuous gate bias between channels made of polyaniline and PEDOT-PSS.^{3,24} For example, in the case of PEDOT-PSS, after applying a positive V_G when the gate is turned off, the I_{DS} begins to rise and recovers to $>90\%$ of its original value, whereas in the case of polyaniline, the I_{DS} stays at a low value (Fig. 3). A negative gate bias is then necessary to bring the I_{DS} back to its original value in the case of polyaniline. We believe that this could have potential in a prototype memory storage device in which the positive and negative voltage biases could be used to read and erase information.²⁵

The long response times observed suggest that phenomena other than those normally associated with a classical field effect are involved. We believe that the experimental results are qualitatively similar to what is observed in conventional electrochemical FETs, which, typically, are also characterized by long response times driven by a slow ionic movement.^{2,26–30} For example, the gate bias was kept constant at $V_G=+40$ V for an extended period of time (not shown) until the I_{SD} fell to very low values (nanoamperes or picoamperes). At this point, when the channel and gate sections were physically separated and visually examined, the channel appeared to be light yellow green in color rather than the expected bright-green color of emeraldine-HCl. This suggests that polyaniline was no longer in the highly conducting (half-oxidized) emeraldine oxidation state but closer to the less conducting (reduced) leucoemeraldine oxidation state (Fig. 4). Importantly, the corresponding gate area above the channel was considerably darker in color (dark blue), suggesting that polyaniline was in the less conducting (oxidized) pernigraniline oxidation state. Importantly, when a *negative gate bias* was applied and constantly maintained until the current falls to zero, the color changes in the channel and gate were exactly reversed, as were their UV/visible

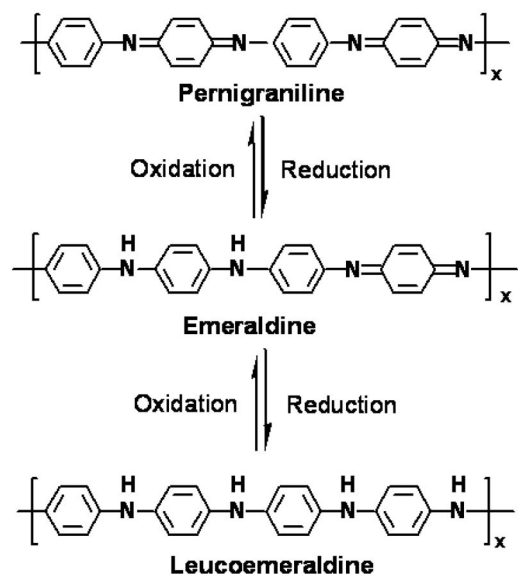


FIG. 4. The different oxidation states of polyaniline shown in the “base” form (insulating form).

spectra. Qualitatively similar results are observed when ITO (coated on PET) was used as the gate.

In order to investigate this phenomenon in greater detail, the experiment was conducted by using type-2 devices with a much wider active device area ($2.5 \times 2.5 \text{ mm}^2$) and a dielectric material that did not adhere to the polymer. Paper was chosen as a test dielectric material³¹ for two main reasons: (i) after the experiment, the channel and gate sections could be separated and independently analyzed and (ii) the relatively uniform thickness of paper ($\sim 70 \text{ }\mu\text{m}$) improves experimental reproducibility, e.g., as mentioned earlier, the thickness of the UV-curable polyacrylate resin widely varies during device fabrication. It is to be noted that in spite of the large dielectric thickness in the case of paper (and polyacrylate resin), the field strength applied is in the same order of magnitude in both cases, e.g., a $V_G=98 \text{ V}$ translates to a field strength of $1.4 \times 10^6 \text{ V/m}$ for a thickness of $70 \text{ }\mu\text{m}$. The significantly larger amount of redox-active material present in the active region of type-2 devices, however, requires longer response times for changes in the I_{DS} to be observed, although the overall effect is qualitatively similar to those observed in type-1 devices (Fig. 5 versus Fig. 2). In the last cycle (Fig. 5), the negative gate bias was kept on (points labeled “C”) until the current reached a very low value (points labeled “D”). Initially, the source current rises (as expected), but after reaching a peak value of $215 \text{ }\mu\text{A}$, it begins to fall until it reaches a very low value (point D). At this point, the channel and gate sections were separated and their UV/visible spectra were measured in the active region (Fig. 5, inset). The colors were exactly reversed compared to our previous results when a positive V_G was applied. At point D, the absorption at 864 nm characteristic of the highly conducting emeraldine oxidation state (curve I) is shifted to 770 nm in the channel, indicating that polyaniline was closer to the insulating (oxidized) pernigraniline oxidation state in the protonated state (curve II). At the gate, the absorption at 864 nm is significantly reduced (curve III), indicating that poly-

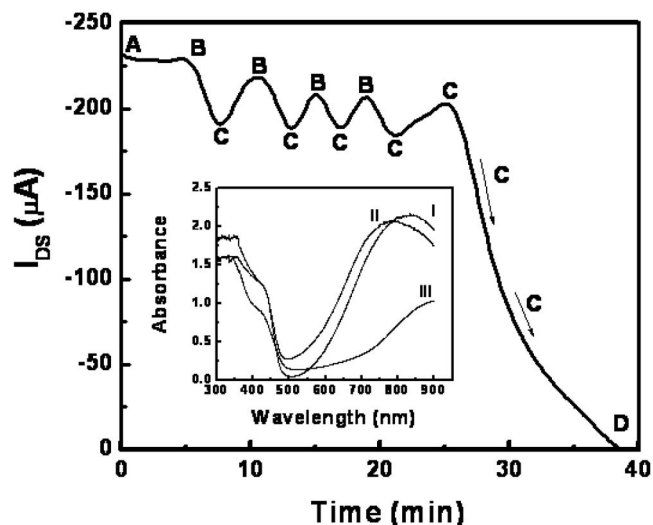


FIG. 5. I_{DS} vs time plot for type-2 polyaniline device. At point A, $V_G=0 \text{ V}$. $V_G=+98 \text{ V}$ is applied at points indicated as B, and $V_G=-98 \text{ V}$ is applied at points indicated as C. In the last cycle, a $V_G=-98 \text{ V}$ was continuously applied until the I_{DS} fell to a value less than 200 nA (point D). The channel and gate sections were then separated and the color changes in the active region of the device were spectroscopically monitored. Shown in the inset are the UV/visible spectra of the polyaniline film before the experiment (curve I) and at point D (channel: curve II; gate: curve III). The V_{DS} was held constant at 5 V .

aniline was no longer in the highly conducting emeraldine oxidation state but closer to the insulating (reduced) leucoemeraldine oxidation state.⁴

It would appear that when V_G is negative, the gate functions as the cathode of an electrochemical cell and the channel functions as the anode. Correspondingly, one observes the cathodic reduction of emeraldine to leucoemeraldine at the gate and anodic oxidation of emeraldine to pernigraniline at the channel. Reversing the polarity of the gate and channel electrodes results in their spectroscopic changes to also be reversed.

Clearly, these electrochemical reactions are driven by leakage currents across the dielectric, resulting in slow ionic diffusion associated with the redox behavior. A study of leakage current as a function of applied gate potentials (using an electrometer) shows that in the voltage range of $0\text{--}500 \text{ V}$, the leakage current for the Norland 65 resin increases at a rate of $\sim 1 \text{ nA/V}$, while for paper, it increases at a rate of $\sim 0.75 \text{ nA/V}$. While these leakage currents may be a small percentage of the I_{DS} , they are sufficiently large to induce electrochemical changes over the time period of the experiment. For example, at $V_G=98 \text{ V}$ for paper dielectric, the leakage current, while numerically small ($30\text{--}50 \text{ nA}$), is still sufficiently high to permit a significant amount of Coulombs of charge to be transferred across the dielectric over a period of 20 min . Rough calculations based on the approximate dimensions of the source-drain channel show that for leakage current of 20 nA over a period of 20 min , $\sim 63\%$ of electrons are available to either fully reduce or fully oxidize the polyaniline in the channel.³² Expectedly, when the paper dielectric was pre-exposed to high moisture levels, the electrochemical effects are significantly enhanced.

It is important to note that it is not necessary to electro-

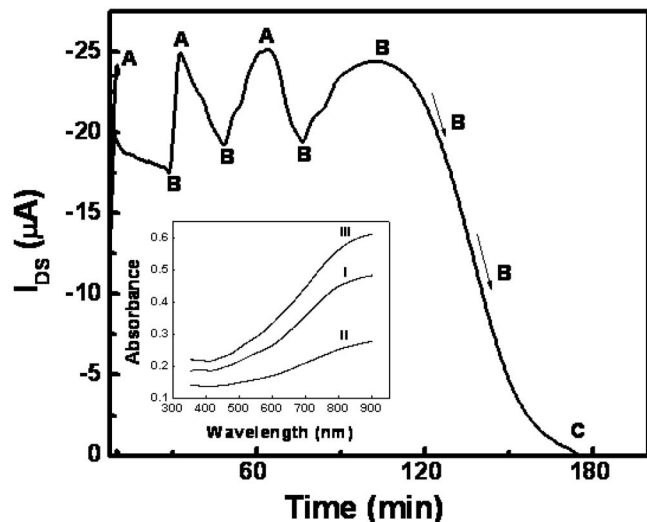


FIG. 6. (Color online) I_{DS} vs time plot for type-2 PEDOT-PSS device. $V_G = +51$ V is applied at points indicated as A, and $V_G = -51$ V is applied at points indicated as B. In the last cycle, a $V_G = -51$ V was continuously applied until the I_{DS} fell to a value less than -200 nA (point C) when the channel and gate sections were separated and changes in the active region of the device were spectroscopically monitored. Shown in the inset are the UV/visible spectra of the PEDOT-PSS film before the experiment (curve I) and at point C (channel: curve II; gate: curve III). The V_{DS} was held constant at -5 V.

chemically reduce or oxidize the entire channel area in order to observe changes in the I_{DS} . A thin, contiguous insulating strip of either leucoemeraldine or pernigraniline formed in the channel should be sufficient to interrupt the flow of current in the channel. It is also possible for the amorphous regions in the polymer to be more susceptible to electrochemical changes (more room for ion movement). Changing the oxidation state of these amorphous regions could induce bulk change in conductivity with much of the sample (the crystalline domains) still being present in the emeraldine oxidation state. We propose, therefore, that even in devices with shorter response times,²⁴ Faradaic effects driven by leakage currents ought not to be ignored. Devices constructed by using Mylar™ as the dielectric layer provide additional evidence consistent with leakage currents playing an important role.²² In these devices, we could not measure any significant leakage current even at very high V_G , and consequently, no gate effect is observed.

Qualitatively similar results were also obtained in devices that use PEDOT-PSS as the channel and the gate. Figure 6 shows that under similar experimental conditions, i.e., at negative V_G , changes in the I_{DS} are consistent with electrochemical oxidation in the PEDOT-PSS film. The corresponding reduction reaction at the gate is also spectrophotometrically observed. While these changes cannot be visually observed due to the high optical transparency of the PEDOT-PSS films, they can be spectroscopically monitored (Fig. 6, inset). It is important to note that unlike the recovery in the I_{SD} observed when negative V_G was used, no recovery is observed in this case (point C in Fig. 6). This is consistent with polymer degradation associated with oxidation in the case of PEDOT.³³

It could be reasoned that both capacitive field effect and

electrochemistry simultaneously occur but at different time scales and that redox-driven changes in I_{SD} are observed only over long time periods and/or under high leakage currents. Attempts to mechanistically account for a “field effect” in highly conducting systems include the beaches and islands model, wherein the applied electric field influences the lowly conducting amorphous regions that separate crystalline metallic domains.⁵ This model does not account for the lack of any observable field effect when the temperature is lowered by just 10 °C.¹ The model based on field-driven ion migration in inhomogeneous polymers using a metallic gate¹ argues against Faradaic effects by claiming that a 2% hole charge compensation by mobile ions is not sufficient to cause large electrochemical changes while still causing a 3 orders of magnitude change in the channel conductance. However, the large changes in the electronic absorption spectra observed as a function of applied V_G in our devices indicate a significant hole compensation that is driven by redox reactions coupled with ion migration. The absence of a field effect in devices using Mylar™ as the dielectric also provides additional evidence in favor of Faradaic effects playing an important role. The strong qualitative similarities among the phenomena observed in samples with diverse architectures, active layer (polyaniline, PEDOT), and gate composition (electronic polymer, ITO) also suggest that Faradaic effects driven by leakage currents could be important. These results do not, however, rule out any unique effects resulting from a combination of field effects and those driven by leakage currents, i.e., capacitive charge buildup coupled with processes triggered by Faradaic phenomena. There is, for example, no *a priori* reason to believe that highly inhomogeneous doped electronic polymers should behave similarly to well established classical semiconductors.

IV. CONCLUSIONS

While interpreting a field-effect phenomenon in devices made of films of highly conducting doped electronic polymers as channels, special attention should be paid to the role of parasitic Faradaic (redox) processes. Clearly, by using polyaniline as the channel and the gate, redox reactions driven by leakage currents across the dielectric can be visually observed and spectroscopically monitored. In many ways, the observed phenomenon appears to have features common to those observed in electrochemical FETs. The extent to which these effects are playing a role in devices made of PEDOT, polypyrrole, etc., is not certain, although we believe they could be very important in the analysis of the data. At least until additional experimental results become available, it might be important to reconsider the use of the term field-effect while describing this phenomenon.

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