

Origin of current oscillations in a polymeric electrochemically controlled element

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(Received 4 January 2008; accepted 6 March 2008; published online 12 May 2008)

We present a model for describing electrical properties of an electrochemically controlled heterojunction between a conducting polymer (polyaniline) and a solid electrolyte (lithium salt doped polyethylene oxide). In particular, the difference in the kinetics of the conductivity variation for different polarities of the bias voltage and appearance of current oscillations at constant applied voltage are considered. The results of our simulation are in good agreement with published experimental data. © 2008 American Institute of Physics. [DOI: 10.1063/1.2921267]

INTRODUCTION

Rhythmic processes in steady-state environmental conditions attract high interest as they are considered a very important feature of living systems.¹ Therefore, cyclic chemical reactions, such as the Belousov–Zhabotinsky (BZ) reaction,² are widely studied. However, most of these reactions describe cyclic variation of the reactant's relative concentration resulting in the alternation of optical and/or viscoelastic properties of the reaction medium. Instead, in living organisms rhythmic behavior should concern electrochemical properties as, for example, it occurs in the well-studied nervous system of the pond snail (*Limnea Stagnalis*), where one neuron generates a durable sequence of potential pulses as a response to the single activation.³ In this context, recently reported results^{4,5} on the cyclic variation of the electrical conductivity in a constantly biased electrochemically controlled polymeric device, containing an element acting as a charge reservoir, seem to indicate a possible material system which shares some of the features of biological components.

Electrochemical processes have been used for the realization of polymer-based molecular electronic devices, in which conductivity is strongly dependent on the redox state of the material.⁶ For polyaniline (PANI), for example, the difference of the conductivity between the reduced insulating and the oxidized conducting states can be as high as 8 orders of magnitude.⁶ Several devices, such as diodes,⁷ light-emitting diodes,⁸ and logic elements,⁹ were fabricated using electrochemical control principles.

This approach was also used for the construction of an electrochemically controlled nonlinear polymeric heterojunction which could be a key element for the fabrication of a self-assembled network with adaptive properties.¹⁰ The central component of the device was an ultrathin active PANI channel with two attached electrodes called source and drain, respectively. The source electrode was maintained at the ground potential level, while the bias voltage was applied to the drain electrode. A narrow stripe of solid electrolyte [polyethylene oxide (PEO) doped with lithium perchlorate] was deposited in the central part of the channel. The PANI area

directly under the PEO strip was considered as the active area of the element because all electrochemical reactions occurred in this zone. A third electrode (silver wire) was attached over the PEO stripe and also connected to the ground potential. This electrode was used as the reference electrode and it was called as “gate electrode” in analogy to the field effect transistor. The potential of the active zone with respect to the reference electrode and, therefore, its reduced or oxidized state were dependent on the sign and value of the applied drain voltage. This, together with the strong dependence of the conductivity on the redox state of the polymer, is responsible for the strongly nonlinear behavior of the device. A detailed description and experimental characterization of the device can be found in Ref. 10.

When biased at constant drain voltage, the device has exhibited the expected variation of the conductivity due to the reduction or oxidation in the PANI in the active zone. However, the kinetics of the conductivity variation for positive and negative applied voltages were significantly different. Transfer of the element into the insulating form for the negative drain voltage was much faster with respect to the transition into the highly conducting oxidized form for the positive voltage. The explanation of this observed difference is not so obvious considering that both transformations are due to the redox processes and are connected to the Li⁺ ion diffusion to and from the PANI layer.^{11,12}

The other surprising behavior of the element was observed when a capacitor was introduced between the reference electrode and the ground potential level, or when the reference electrode was realized with a material capable of charge storage, such as graphite.⁵ In both cases, current flow in the electrolyte could result in charge accumulation and, therefore, in the variation of the reference electrode potential. As a result, oscillations in both gate and drain currents were observed at the fixed drain voltage in such systems.

A qualitative interpretation of the observed results indicated the following interconnected processes: variation of the reference potential due to the charge accumulation, redox reactions occurring in the active zone due to the potential difference of the zone regions with respect to the reference

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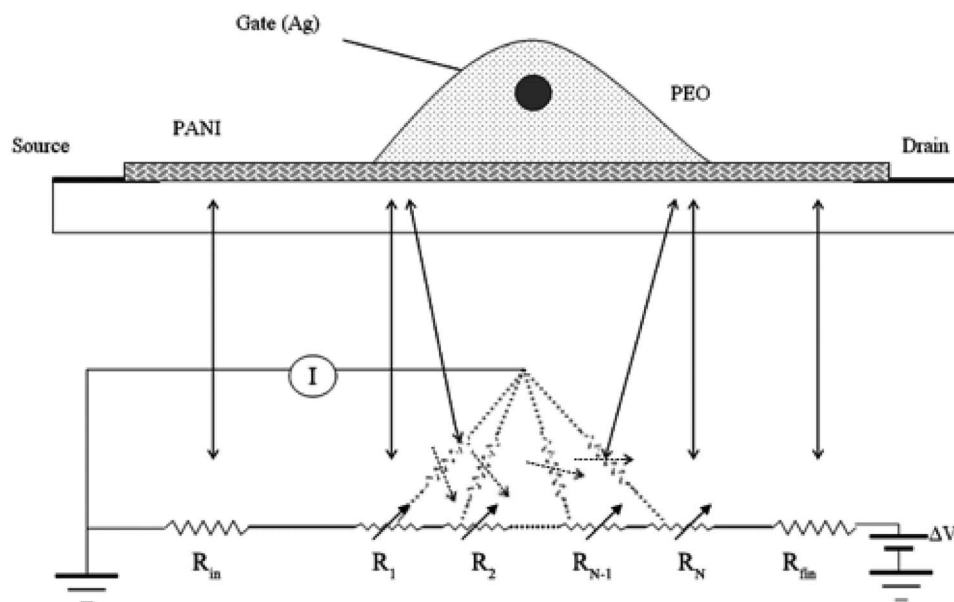


FIG. 1. Model-related electrical circuit. Variable resistors constitute active PANI and solid electrolyte layers.

potential, and redistribution of the potential profile along the active zone resulting from the relative rearrangement of conducting and insulating areas.

The aim of the present work was to develop a model, based on the consideration of all electrical phenomena occurring in the system, that can describe the electrochemical device behavior. In this work, we do not use the approach, usually applied for the BZ reaction description, that considers the system as a whole. Instead, the model is based on the separation of the active area into narrow zones, considering the variation of properties in them. In particular, the model must explain the two unexpected characteristics, namely, the difference in the conductivity variation kinetics for negative and positive drain voltage and the appearance of drain and gate currents oscillations at fixed bias drain voltage.

MODEL DESCRIPTION

The model was based on several assumptions. First of all, it was suggested that all processes occur in the active zone of PANI channel under the PEO stripe and variations of the PANI conductivity in the active zone are due to the redox reactions.⁶ Two zones of the channel, not covered by PEO, can be represented as passive resistors.

The scheme, illustrating the model, is shown in Fig. 1. The geometry of the electrochemical device suggests that all points of the active zone within a line perpendicular to the PANI channel should have the same electric potential. Thus, we assume that the only relevant coordinate is the distance from the drain (or source) electrode to this line. Therefore, the active zone was divided into narrow stripes and we have assumed that the potential within the stripe is constant. Thus, we assume that no gradients occur within each stripe and all processes simultaneously and homogeneously take place there. Each stripe has its own resistance (“drain resistance,” to distinguish from the “gate resistance” that will be considered below), the value of which can vary according to the stripe potential with respect to the reference potential level and to the time passed after reaching reduction or oxidation

potentials. The time dependence of the resistance variation of the stripe after reaching the reduction or oxidizing potentials with respect to the reference electrode potential was taken from the experimental data for the negative drain bias voltage¹⁰ when the material reduction simultaneously occurs for the whole active area.⁴ The resistors, corresponding to the channel active zone stripes, are connected in series. In addition, each stripe is connected to the gate (reference) electrode through a resistor, corresponding to the solid electrolyte (PEO). These resistors must have constant and variable contributions. The value of the constant contribution depends on the coordinate of the stripe due to the electrolyte geometrical length from the stripe to the gate electrode (smallest for the central one and largest for the stripes at the ends of the active area).

The temporal variation of the drain resistance is connected to the reduction or oxidation processes within the stripe when it reaches an appropriate potential value with respect to the reference (gate) potential. This behavior is connected to the Li^+ ions diffusion from the PEO to PANI layers and vice versa.¹² The analytical representation of this dependence was obtained by fitting previously obtained experimental data with similar elements for constant negative bias (for the positive bias, the dependence was different and it will be discussed below). Resistance variation kinetics was assumed to be the same for increasing and decreasing voltages.

When the potential difference between the stripe and the gate electrode is below a certain level called reduction potential (0.1 V) (Ref. 13) and is still getting lower, the resistance will rise. Likewise, if the potential difference is above a value called oxidation potential (0.3 V) (Ref. 13) and is still rising, the resistance will diminish. To each stripe of the active zone we have associated a “timer,” a virtual device which keeps track of the history of the stripe. Upon passing the variation point (reduction or oxidation potential), the timer was set to time zero and resistance begins to vary ac-

cording to the law obtained from experimental data fitting (increasing when passing reduction potential and decreasing when passing oxidation potential).

Time counts and resistance values for each stripe of the active area were absolutely independent.

Gate resistance (resistance between the stripe and gate electrode) is due to the ionic current in the solid electrolyte. Moreover, it is mainly due to the Li^+ ions flow as ClO_4^- ions have much lower mobility. Gate resistance must also be variable. In fact, Li^+ ions must enter and exit PANI film participating in the redox reactions resulting in the PANI conductivity variations. Thus, during oxidation and reduction in the PANI active zone, ion concentration in the electrolyte will be changed, which will lead to the variation of its conductivity. In the model, we have assigned the variation of the gate current to be proportional to the variation of the drain conductivity. This suggestion was based on the fact that lithium ions must participate in the redox processes, according to the formula (1),¹¹



SIMULATION

Using the model described above, we have simulated the behavior of our device under two different conditions that have already been experimentally studied and have revealed unexpected results. Namely, a constant potential was applied to the drain electrode of the electrochemical device with and without a capacitor connected between the gate electrode and ground potential. The time counting in the simulations was a discrete one, usually with time units of 1 s, and simulations were usually performed for 5000–40 000 time units. When positive constant potential was applied, the model was initialized with all stripes of the active area in their most insulating state. When the potential to be applied was negative, all the drain active area resistances were in their most conductive state at the beginning of the simulation.

The simulations were based on two MATLAB scripts, called “environment script” and “active script” (the programs used for the simulations are presented as supplemental materials).¹⁴ For each time unit, the environment script performs readout and records of the resistance values for each stripe, calculations and records of the potential distribution along the entire active zone, as well as calculations and records of the drain current value and the linear component value of the gate current. After this, the active script is activated. The active script checks if there are regions, where the conditions stated above are met (beginning of reduction or oxidation), modifies the timer and resistance value for those regions, and calculates the nonlinear component value for the gate currents. Then, the environment script records the gate current value and updates the cycle count until it reaches the final value (predetermined number of time points). When the cycle is finished, it plots the “drain current versus time” and the “gate current versus time” curves. If the simulation was performed with the presence of a capacitor in the element, the “capacitor charge versus time” curve was also plotted.

The values used for the attribution to physical parameters in our model were taken from the experimental data

available from our previous works^{4,5,10} and from literature.^{6,7,11,13} Values of R_{max} and R_{min} were attributed in such a way that, when all stripes of the active zone were in their most conductive state, the total drain resistance was 0.5 M Ω . It was 1000 M Ω when all the stripes in the active zone were in the most insulating state. The resistance of the PANI film between source and active zone and the one between active zone and drain were attributed to 200 and 100 k Ω , respectively. The constant value of the gate resistance for each active region was 50 M Ω , and the proportionality coefficient between drain resistance variation and nonlinear gate current contribution was -6×10^{-13} A s/ Ω . Reduction and oxidation potential were set at 0.1 and 0.3 V,¹³ the time constant value that controls the exponential resistance variation was obtained from fitting of experimental dependences and was equal to 104 s.¹⁰

Other parameters used in the model, such as the total number of stripes, the drain potential, and the capacity value of the capacitor, were not directly connected to physical characteristics of our device. In the simulations, we have used potentials between -2 and $+20$ V and capacities ranging from 0.1 to 100 μF . The total number of stripes into which the active zone was divided was 100, a good compromise in our opinion between spatial resolution and computational weight (the environment script needs to invert a size $2 \times n$ (n =number of stripes) matrix in order to calculate the potential distribution).

Time unit was equal to 1 s in all calculations except modeling of the element with a capacitor with values less than 1 μF , when shorter intervals were also used.

RESULTS AND DISCUSSION

Time asymmetry

As stated above, previously published experimental results show a significant difference in the device temporal conductivity variations for positively and negatively constantly biased drain electrode.¹⁰ Considering that the conductivity variation is connected to the Li^+ ions drift, the obtained result does not seem like an obvious one. Therefore, the first application of the suggested model was to simulate the drain current temporal behavior at fixed negative and positive applied drain voltages.

Time dependences of the drain current (both experimental and simulated) for drain voltage of $+0.6$ V are shown in Fig. 2. For the negative bias voltage, the absolute coincidence of calculated and experimental data was reached as these experimental data were taken for the analytical representation of the conductivity variation kinetics used in this model. Both experimental and calculated data have revealed a significant difference in the conductivity variation kinetics for different polarities. In the simulation for $V_{\text{drain}} = -0.1$ V, the current decreased to 50% of its starting value within 100 s and to 10% after about 500 s. For $V_{\text{drain}} = 0.6$ V, the current reached 50% of its maximum value in 1700 s and 90% in 2700 s.

The observed difference in the kinetics for positive and negative polarities is connected to the variation of the potential distribution within the active zone. When negative potential is applied, all stripes of the active area are at a potential,

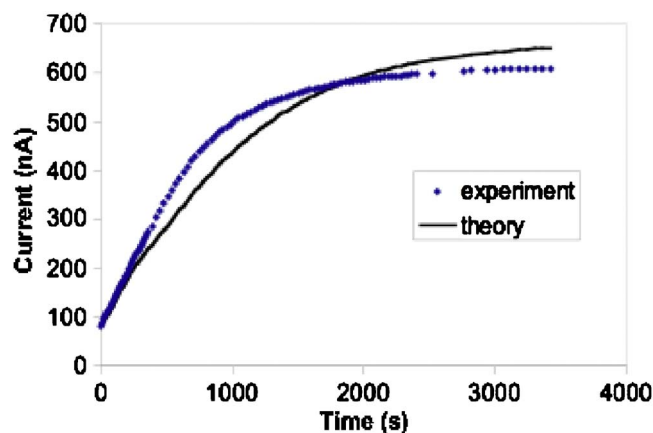


FIG. 2. (Color online) Kinetics of the drain current variation at +0.6 V drain voltage: experimental results (rhombs) and simulation data (solid line).

lower than the reduction one. Therefore, the transition of the PANI into the insulating form simultaneously takes place in all stripes. In the case of positive potential, the situation is quite different. As we have supposed, the PANI in the active zone is in its reduced insulating form. Thus, the applied positive drain potential will be mainly distributed in the active area (practically 0 V in the beginning of the area and practically +0.6 at the end closed to the drain electrode). Therefore, only the part of the active zone material is under the suitable potential for the beginning of the oxidation (more than +0.3 V). After the transfer of this part of the active zone into the oxidized conducting form, the potential profile along the active area will be redistributed and the main potential difference will be located in the areas that are still in the insulating form. Therefore, new stripes will be at the suitable potential. This process can be iterated until practically all stripes will be transferred into the conducting state.

Summarizing, the main difference in the conductivity variation for negative and positive fixed applied voltages is due to the fact that, for the negative polarity, PANI in the active zone is simultaneously transferred into the insulating state for the whole active area length, while for the positive polarity there is a gradual space displacement in the conducting area in the direction to the source electrode.

Oscillations

The reported experimental results have already demonstrated that the capability of the charge accumulation at the gate electrode, performed by the external capacitor or by using graphite as the gate electrode material, leads to the appearance of oscillations for both gate and drain currents at fixed applied voltage. These oscillations have different amplitudes and they are shifted for about a quarter of period with respect to each other. Figure 3 reports the results of the drain current simulation when the drain voltage was equal to 5 V and a 1 μF capacitor was introduced between the gate electrode and ground level.

The results presented features similar to the experimental data although these current oscillations are superimposed to an increasing drain current rather than to a decreasing one. Figure 4 demonstrates the mutual temporal behavior of the

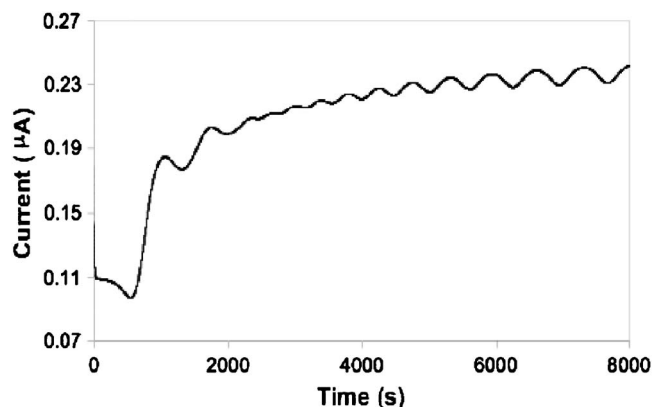


FIG. 3. Simulation results of the temporal behavior of drain current at drain voltage of +5.0 V and external capacitor of 5 μF .

drain and gate currents. Values of the gate current were multiplied by 10 and shifted for 0.21 for better representation.

As it is clear from the figure, the developed model explains the appearance of the current oscillations at fixed applied voltage for the described electrochemical device. Even if it does not provide complete coincidence of the experimental and simulation results, several important features, observed in the experiment, can be recognized in the calculated data. First, drain current oscillations reach their maximum about one quarter of period earlier with respect to that of the gate current. Second, oscillation period is not constant and it increases in time. Finally, the amplitude of the oscillations is also not constant.

In order to refine our model, we then proceeded to study the effects of the parameters values on the current oscillations. We varied each parameter over a wide range, often covering two orders of magnitude or more, while the other parameters were maintained at fixed value. We then analyzed relationships between the varied parameter values and a characteristics of the oscillations, such as the total oscillation duration, the amplitude or period of the last oscillation, or the final value of the drain current. It should be noted that characteristics were influenced by more than one parameter. However, their effect on the variation of the current curve shapes was found to be different. We also note that not all combinations of the parameters have resulted in the appear-

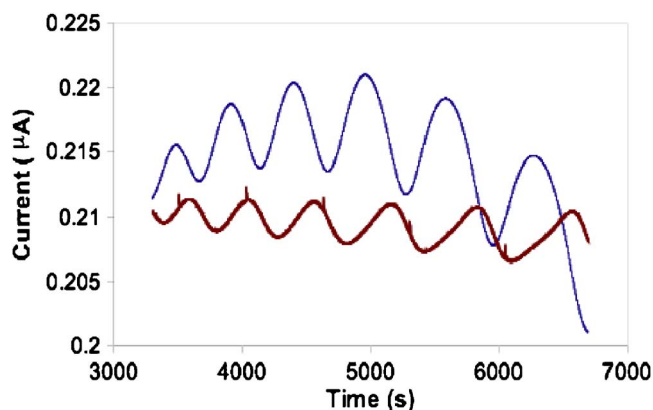


FIG. 4. (Color online) Comparative kinetics of the drain (solid line) and gate (dashed line) current oscillations. For scaling, the gate current values were multiplied by 10 and shifted for 0.21.

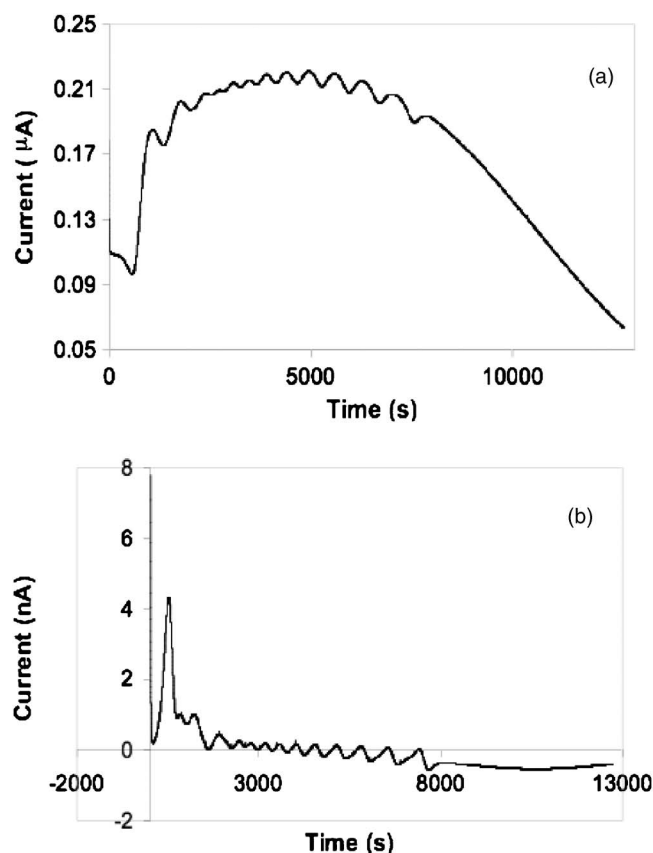


FIG. 5. Kinetics of the drain (a) and gate (b) current oscillations for the model considering the degradation in the PANI conductivity.

ance of the oscillations in the calculated dependences. This situation is in agreement with experimental data, when oscillations were observed only for some fabricated structures as well as for particular values of the applied drain voltage and the capacity of the external capacitor.

The only serious difference in the temporal behavior of the calculated current dependences with the experimental data is the continuous increase in the drain current. In order to overcome this discrepancy, the temporal degradation in the PANI conductivity was taken into consideration for further development of the model. In fact, stability of the conducting polymers is a key parameter limiting their wide application for device production.¹⁵ For this reason, a temporal increase in the PANI elements resistance was introduced into the model. The law of this conductivity variation was taken from the experimental measurements. All the other parameters of the model were not changed. The results of the calculation for the model with the temporal degradation of the PANI conducting properties are shown in Figs. 5(a) and 5(b) for drain and gate currents, respectively.

As it is clear from the figure, the value of the drain current is diminishing and in time resembles better the real experimentally observed situation.

CONCLUSIONS

The developed model describes the electrical characteristics of the polymeric electrochemical junction. In particular, it was developed in order to explain two unexpected

experimentally observed phenomena, namely, the difference in the temporal conductivity variation behaviors for different polarities of the applied drain voltage and the appearance of the current oscillations at constant bias voltage when the structure contained an element capable of charge storage. The model is based on the redox variations of the PANI layer conductivity in the active area. It also considers currents in the conducting polymer and solid electrolyte. Finally, it recalculates each time electric potential profile along the PANI layer and with respect to the reference potential.

In the case of the difference of the kinetics of the conductivity variation, the calculated results have provided a rather good quantitative correspondence to the observed experimental data. In the case of oscillation, we have obtained a qualitative agreement with the experimental data. However, we had to include a time deterioration in the electrical characteristics of PANI. This implies that more effort in the fabrication of devices with stable characteristics is necessary, if this type of heterojunction is to be used for more complex applications.

Finally, our success in parametrizing the device behavior allows the exploration of possible analogies with the already mentioned BZ reaction, including the possibility that our polymeric device shows spontaneous out of equilibrium characteristics, which are typical of biological systems. Further attempts will be performed for describing the observed oscillating phenomena in terms of BZ reaction, i.e., using Lotka–Volterra type equations for the modeling the behavior of the whole system. In particular, we shall try to demonstrate analogies between the physical parameters of the model presented in this paper and those which characterize the nonlinear equations which describe the BZ oscillations. We feel that this should add interest to the study of the behavior of simple polymeric mixtures of conductors and electrolytes.

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