Non-equilibrium electrical behaviour of polymeric electrochemical junctions

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Abstract
Current oscillations were observed at constant applied voltage in electrochemical heterostructures, composed of conducting polymer, solid electrolyte and a charge accumulating system (graphite electrode or capacitor). These oscillations were attributed to the periodic modulation of the conductivity in the active zone of conducting polymer (polyaniline) due to ionic flow in the solid electrolyte (polyethylene oxide with $LiClO_4$).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Starting from their discovery, conducting polymers have been studied by numerous research groups due to their interesting properties and perspectives in their utilization for electronic and optoelectronic devices [1]. In this framework, the application of an electrochemical approach to element fabrication is a very attractive and innovative pathway, since it differs from conventional solid-state electronic methods and can make links between microelectronic devices and biological systems [2]. Electrochemical working principles have already been applied successfully to the realization of light emitting diodes [3], rectifying devices [4] and logic elements [2]. Recently, a polymeric nonlinear element was realized, which can be the basis for the fabrication of an adaptive network [5]. More specifically, the element increases its conductivity in time when biased positively and decreases it when biased negatively, with two different time constants. Such behaviour allows the establishment of preferential signal pathways according to the previous experience and external training of the network, in which

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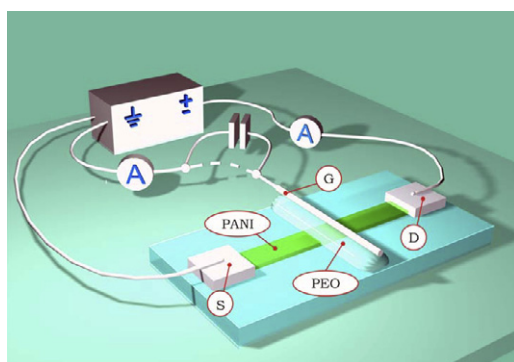
Figure 1. Scheme and connections of the nonlinear polymeric electrochemical device. With a graphite gate electrode, the capacitor is absent.

such elements are the programmable nodes [6]. Model circuits mimicking adaptive behaviour of simple biological systems have been realized [7].

In this paper, we present a study of the effect of internally generated variation of the gate potential on the electrical behaviour of the device [5]. We have found self-sustaining non-equilibrium current oscillations connected to the highly nonlinear behaviour of the structure that was fabricated. We give a qualitative explanation of the phenomenon and connect it to the well-known Belousov–Zhavatinski reaction [8], whose importance, especially for biological systems, has been elucidated by Prigogine [9].

2. The electrochemically controlled device

The scheme of the element is shown in figure 1. Two metal (Cr) electrodes, called, in analogy to field-effect transistors (FETs), the source (S) and the drain (D), are connected to an active layer of polyaniline (PANI). A narrow stripe of the solid electrolyte, 0.1 M $LiClO_4$ in polyethylene oxide (PEO), is then deposited onto the PANI layer between the S and D electrodes and a third electrode (gate (G)) is contacted to it. In the measurement configuration, both S and G electrodes were connected to the ground potential level.

The variation in conductivity in this structure was attributed to the oxidation and reduction of the portion of the PANI layer directly underneath the electrolyte (active zone) according to the polarity of the potential applied to the D electrode [5]. Li^+ ions from the solid electrolyte are involved in these reactions according to the following scheme:

$$PANI^+:Cl^- + Li^+ + e^- \Leftrightarrow PANI + LiCl.$$
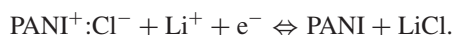
Strong displacement of Li^+ in the structure according to the polarity of the D potential has been demonstrated by microRaman spectroscopy [10].

The typical temporal behaviour of the variation in drain current in the configuration shown in figure 1 at fixed characteristic potentials revealed a monotonic increase or decrease in the conductivity for applied positive and negative voltages at the drain electrode, respectively [5].

We can expect that if, in a such device, the reference potential is not fixed at the ground level anymore, the active area conductivity may be modulated, leading to the appearance of the current oscillations. Of course, this cannot be done using some external generator, because the system will be not closed. Thus, the electrochemical device must be modified with some element attached to the gate electrode, capable of accumulating charge and, therefore, of varying the reference potential. In the simplest case, it can be an external capacitor.

3. Materials and methods

Emeraldine base polyaniline was purchased from Sigma (M_n of about 10 000). First, the fraction soluble in chloroform was extracted from the powder. With such a treatment, the concentration of point-like defects in the deposited films was decreased and the film conductivity was somewhat increased. The rest of the polyaniline powder was dissolved in 1-methyl-2-pyrrolidone (NMP) and carefully filtered. The real concentration of the solution was determined and then NMP was added to achieve the final concentration of 0.2 mg ml^{-1}.

The active layer was a PANI Langmuir–Blodgett (LB) film deposited with a KSV 5000 LB trough, using a modified Langmuir–Schaefer (horizontal dipping) technique [11]. Pure water, prepared with a Milli-Q system, was used as the subphase (with a resistivity of 18.2 MΩ cm).

Mono-component monolayers of polyaniline were compressed up to the target surface pressure of 10 mN m^{-1} at a rate of 1 cm min^{-1}; the barriers were stopped and the deposition of multilayers was carried out as described elsewhere [11] using separation of the trough surface into independent sections. The total trough width was equal to 10 cm, separated into 24 independent sections; the total amount of polyaniline solution spread on the water surface was 250 μl.

A total of 48 molecular layers (for a thickness of about 48 nm) were deposited. The resulting films were doped in 1 M HCl for 2 min. In approximately 1–2 h, doping was repeated to obtain higher and more stable values of conductivity.

PEO (average molecular weight 8000 000) and LiCl were purchased from Sigma. A solution of PEO was prepared in 0.1 M LiCl and 0.1 M HCl at a concentration of 30 mg ml^{-1}. Such a concentration of salt was found to be the best for the actual element performance [5].

The scheme of the fabricated electrochemical element is presented in figure 1. The PANI layer was deposited onto a glass substrate with two Cr electrodes, marked S (source) and D (drain) in the scheme. The source was kept at the ground potential. A narrow stripe of PEO was deposited by solution casting over the PANI layer. Its thickness was 5–10 μm. Ag wire (gate electrode (G)) was placed onto this stripe. External capacitors of 0.1–5 μF were connected between the gate electrode and the ground level. In the other configuration, a freshly cleaved stripe of the highly oriented pyrolytic graphite was used as the gate electrode. This was attached to the cast PEO stripe instead of silver wire. No external capacitor was used in such a configuration.

Two current values were measured, namely the drain current I_D (the total current through the active layer) and the gate current I_G (the current passing through the electrolyte). Application of the constant drain voltages and I_D measurements were performed with a 236 Source measure unit (Keithley), while I_G measurements were performed with a 6514 System electrometer (Keithley).

4. Results and discussion

The temporal characteristics of the drain and gate currents for an applied voltage of 1 V in the circuit with silver wire and an external capacitor of 1 μF are shown in figures 2(a) and (b), respectively. As is clear from the figure, the amplitude of the oscillations in drain current is more than two orders of magnitude higher than that of the gate. The gate current can be negative or positive, oscillating near its zero value, while the drain current oscillates near the average positive current value. A very important feature is the presence of a phase shift between the drain and gate current oscillations. This shift corresponds to about 100 s delay in the drain current oscillations with respect to those of the gate. This time is comparable with the characteristic time of the variations in conductivity recorded in the simpler structures without a capacitor [5]. Taking into consideration the mobility of Li$^+$ ions in PEO and this
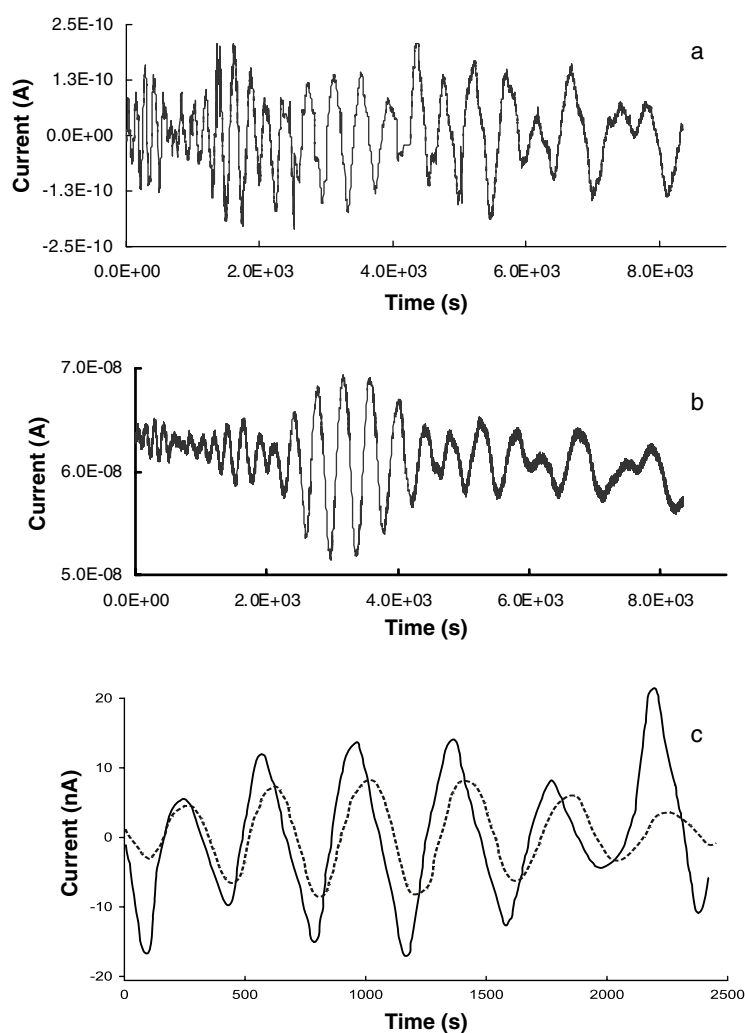
Figure 2. Temporal behaviour of the gate (a) and drain (b) currents measured in the circuit shown in figure 1 at a constant drain voltage of 1.0 V and an attached capacitor of 1.0 μF. Parts of both characteristics are shown in (c) for comparison (value of gate current (solid line) is multiplied by 100; value of the drain current (dashed line) is shifted by -0.5 nA).

characteristic time, we obtain a characteristic diffusion length of about 10 μm, which is of the order of magnitude of the PEO thickness between the G electrode and the PANI active layer.

Current oscillations in electrochemical systems have already been observed in liquid media and were associated with several effects, such as streaming phenomena [12] (with or without stirring of the solution), the inhomogeneous adsorption of ions onto the electrode surface [13] and the formation/destruction of passivating layers on the electrode surface [14]. In our case, the system is a solid one and all listed mechanisms cannot be responsible for the observed oscillations. As the only difference between this structure and those previously reported [5] is the presence of the capacitor, the reason for such behaviour of the current must be connected to the possibility of the charge accumulation and, therefore, variation in the reference potential.
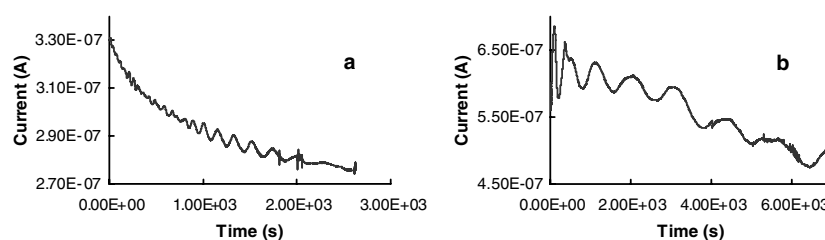
Figure 3. Temporal behaviour of the drain current measured in the circuit shown in figure 1 with a graphite gate electrode (without capacitor) at drain voltages of $+5.0$ V (a) and -5.0 V (b).

It is possible to realize elements with similar behaviour while avoiding using any standard electronic elements, such as the capacitor in our case. For this, it is necessary to substitute the silver wire of the gate electrode with some material capable of accumulating charge. The ability of graphite to accumulate ions due to their percolation into the lattice is well known and is used, for instance, for the construction of batteries [15]. Thus, we substituted the silver electrode with a narrow graphite stripe as the gate electrode. In this case no external capacitor was connected to the element. Typical time dependence curves of the drain current are shown in figures 3(a) and (b) for drain voltages of $+5.0$ and -5.0 V, respectively. Drain current oscillations were observed even at lower voltages, but turned out to be more pronounced when about 5 V was applied to the structure.

It is necessary to consider two interconnected processes for a qualitative explanation of the observed oscillations. The first process is connected to the motion of ions in the electrolyte, guided by the actual potential difference between the gate electrode and the under-electrolyte zone of the PANI layer, resulting in charging of the capacitor. The second process is connected to the variation of the conductivity distribution along the PANI layer covered by the electrolyte, according to the actual potential at each point in the direction from S electrode to D electrode with respect to the reference potential at the gate electrode.

Thus, a qualitative explanation of the observed oscillations can be the following. Let us suppose that we have applied a negative potential (figure 4); similar considerations apply to the case of a positive potential. Application of the drain voltage causes a potential difference between the active PANI layer and the gate electrode. At the beginning, the whole active area of the PANI has a negative potential with respect to the reference potential. Thus, transformation of this area into insulating reduced form starts. In parallel, charging of the capacitor takes place (figure 4(a)). At a certain moment, the whole active area will be transferred into insulating form (figure 4(b)). Thus, practically all the applied drain voltage will be distributed in this area—zones closer to the source electrode will be practically at zero potential. However, the gate potential is not zero anymore, as it varied due to the ionic gate current and is negative with respect to ground. Therefore, zones of the active area close to the source begin to be at an oxidizing potential with respect to the reference potential on the gate electrode. As a consequence, these zones start to be transferred to the conducting form (figure 4(c)). After transferring into the highly conducting state, these zones will be excluded from those where most of the applied voltage is distributed. Thus, new zones, also close to the source, will be at an oxidizing potential with respect to the reference electrode, which will result in their successive transformation into the conducting form (figure 4(d)). This process will be continued until the residual reduced insulating zones of the active area close to the drain electrode will have a resistance comparable to the total resistance of the whole conducting area. Thus, the situation will be rather close to that in the figure 4(a) and the process will
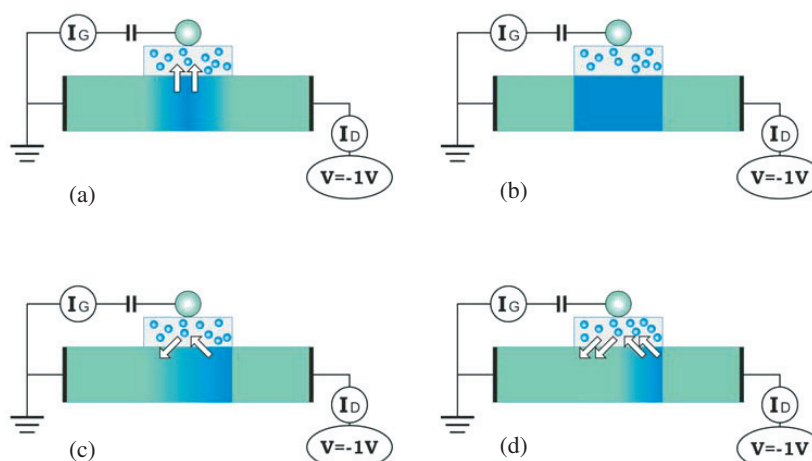
Figure 4. Variation in conductivity of the PANI active area during device functioning (arrows indicate the opposite direction of Li^+ flow). (a) After application of the negative gate potential, the active area begins to transfer into the insulating state simultaneously with capacitor charging. (b) The active layer is insulating, the capacitor is charged and the applied voltage is distributed mainly along the active area. (c) Zones of active area at the oxidizing potential begin to transfer into the conducting state, redistributing the potential profile. (d) Propagation of the conducting zones towards the drain until the resistance of the insulating zones is comparable with the total resistance of all conducting zones.

restart. Summarizing, two parallel, but strongly correlated, processes take place during the structure function. First, redistribution of the potential along the length of the active PANI area takes place (most of the potential difference will be localized in the less conductive zone, close to the D electrode). Second, redistribution of the active layer conductivity will result in the fact that some under-electrolyte areas will be at an oxidizing potential with respect to the gate electrode, and a discharge of the capacitor will occur with back current flow to these zones (more conductive zones are close to the source electrode). This ionic current redistributes ions and consequently the conductivity profile along the active area, resulting in a new potential distribution. As we see from figure 2(b), gate current oscillations take place at around the zero value. Thus, in each time period there is a preferential direction of ionic flow. An increase and a decrease in the conductivity of the active area are connected to the direction of ionic flow in the electrolyte. However, some time is required for the effective conductivity variation due to the relatively low mobility of ions in the solid electrolyte. The observed time delay of the drain current oscillations with respect to that of the gate coincides well with that found for conductivity variation time kinetics in independent experiments [5]. In the case of the utilization of graphite as a gate electrode, attachment of the capacitor is not necessary for oscillating current behaviour, because the graphite electrode itself can accumulate ions, functioning as an ion pump, and therefore it mimics the presence of a capacitor.

It is also possible to connect the observed phenomenon to the Belousov–Zhabotinsky (BZ) reaction. The BZ reaction implies the simultaneous flow of several processes, including redox reactions as well as the production and inhibition of the catalyser [8]. In our case, we also have redox reactions in the active area of the PANI layer. Variation of the reference potential and redistribution of the potential profile in the active zone can play the same role as processes responsible for the production and inhibition of the catalyser. It is interesting to note that we

have observed non-equilibrium rhythmic response of the electrical characteristics, which is essential for linking cyclic BZ-like reactions to processes occurring in biological systems.

This seems to be a particularly interesting feature of our results, since practically all previous observations of BZ reaction were connected to the cyclic variations of optical and viscoelastic properties of the reaction medium, and here we report electrochemically controlled modulations of the electrical response: this makes the connection of our device to biological systems more cogent. In particular, a characteristic feature of any biological system is the necessity to provide cyclic behaviour even if the environmental conditions are fixed. Schrödinger wrote 'Living matter evades the decay to equilibrium' [16]. This is the reason why Prigogine had claimed the BZ reaction to be one of the most important discoveries of the 20th century, as it represents chemical reactions in non-equilibrium conditions similar to those in living organisms. If we consider a simple biological example, more specifically the pond snail (*Limnea Stagnalis*) nervous system, we can recognize one neuron, namely the N1M neuron, whose behaviour is different from all the others [17]. Being activated once, it produces a rather long sequence of potential pulses. These pulses then interfere with the nervous system's treated signals from sensory elements, providing learning and performing commands to executive organs. A very attractive feature of our results is the possibility of imitating such kinds of behaviour, on the basis of elementary cognitive processes in living systems, with a synthetic molecular structure.

5. Conclusions

Current oscillations were observed at a constant bias voltage in thin-film heterostructures constructed from a conducting polymer, a solid electrolyte and a charge accumulating element. We have attributed these current oscillations to periodic conductivity variation along the active PANI layer due to the continuous redistribution of the potential profile, resulting in successive reduction–oxidation reactions responsible for the insulator–conductor transitions.

Clearly, these results may have strong implications for several applications. The possibility of the external reversible control of electronic conductivity can be used in training processes for adaptive networks. Furthermore, the periodic spatial modulation of conductivity due to the ion flux, in a strong feedback situation, can be used not only to fabricate specific devices such as chemical or biological sensors in novel, unconventional ways, but also to model specific biological mechanisms involving ion transport and the space modulation of action potentials.

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