

Electrochemical Control of the Conductivity in an Organic Memristor: A Time-Resolved X-ray Fluorescence Study of Ionic Drift as a Function of the Applied Voltage

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ABSTRACT Grazing-incidence X-ray fluorescence measurements were applied for a time-resolved study of an organic memristor conductivity variation mechanism. A comparison of these results with electrical measurements has allowed us to conclude that the variation of the fluorescence intensity of Rb ions is directly connected to the ionic charge transferred between the conducting polymer and the solid electrolyte, which made up the device. In addition, the conductivity of the memristor was shown to be a function of the transferred ionic charge.

KEYWORDS: organic memristor • X-ray fluorescence • conducting polymer • solid electrolyte • polyaniline

INTRODUCTION

The significant variation of the conductivity of conducting polymers upon transition between reduced and oxidized states can be effectively used for practical applications (1). The most studied device, based on this principle, is the electrochemical field effect transistor, known for more than 20 years (2). A considerable step forward was made when solid electrolytes were used as a medium for redox reactions (3).

Recently, a polymer-based device exhibiting both signal transduction and a memory effect was proposed (4); it can be considered as an organic memristor because it demonstrates properties similar to those theoretically predicted for the hypothetical electronic element (memristor) about 40 years ago (5).

At the heart of the device is the conducting channel, a thin polyaniline (PANI) layer, deposited onto an insulating support with two electrodes. A narrow stripe of solid electrolyte [lithium salt doped poly(ethylene oxide) (PEO)] is formed in the central part of the channel and is used as a medium for the redox reactions. The area of PANI under PEO is the active zone. A thin silver wire is inserted into the solid electrolyte to provide the reference potential; such a wire is connected to one of the electrodes on the solid support, kept at ground potential level.

Conductivity variations and memory properties of the organic memristor take place because of the redox reactions occurring in the active zone, where PANI is reversibly transferring from the reduced insulating state into the oxidized conducting one. According to (6), such a transformation must involve the drift of metal ions between the solid electrolyte medium and the PANI layer. This process has been investigated preliminarily by time-resolved micro-Raman spectroscopy (7). However, this study provided only indirect evidence of such an ionic drift.

The aim of this work was to detect the motion of metal ions between the active PANI layer and the electrolyte in order to confirm microscopically and directly the mechanisms underlying the conductivity variations in the memristor in real time, i.e., while it was functioning. Grazing-incidence X-ray fluorescence (8) was used to detect directly the presence of the metal ions. The measurements were performed using synchrotron radiation X-rays of the Beamline ID10B at ESRF (Grenoble, France).

The Li⁺ ions normally used to dope PEO were not adequate for such measurements because their fluorescent energy cannot be detected at atmospheric conditions. Thus, the heavier Rb ions were used. Because their mobility in the solid phase is much lower than that of Li, measurements were carried out using the gel phase of the electrolyte. Earlier preliminary data showed the feasibility of this approach (9).

EXPERIMENTAL METHODS

Poly(ethylene oxide) (PEO; MW 8 000 000 Da), polyaniline (PANI; MW 100 000 Da) and RbCl used in the work were purchased from Sigma. Water was purified with a Milli-Q system (resistance of more than 18.2 MΩ cm).

Monolayers were compressed on a Langmuir trough (KSV 5000) to a target pressure of 10 mN/m and transferred onto the

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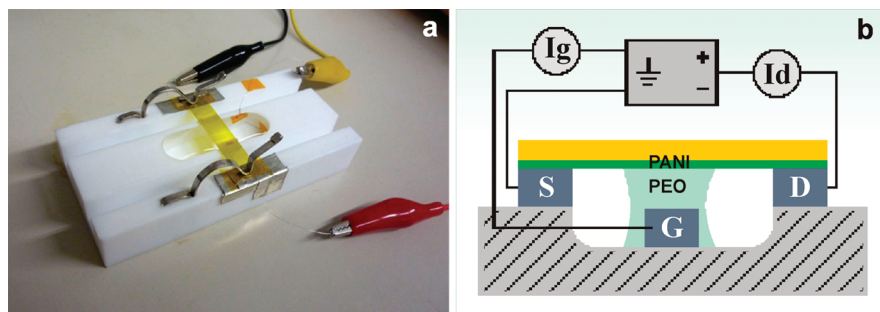


FIGURE 1. Experimental setup (a) and scheme of electrical connections (b) for X-ray fluorescence measurements. The thickness of the PANI layer is about 110 nm, the length of the active zone is 1.5 cm, the width of the active zone is 1.0 cm, and the depth of the well (gel electrolyte thickness) is 1.0 cm.

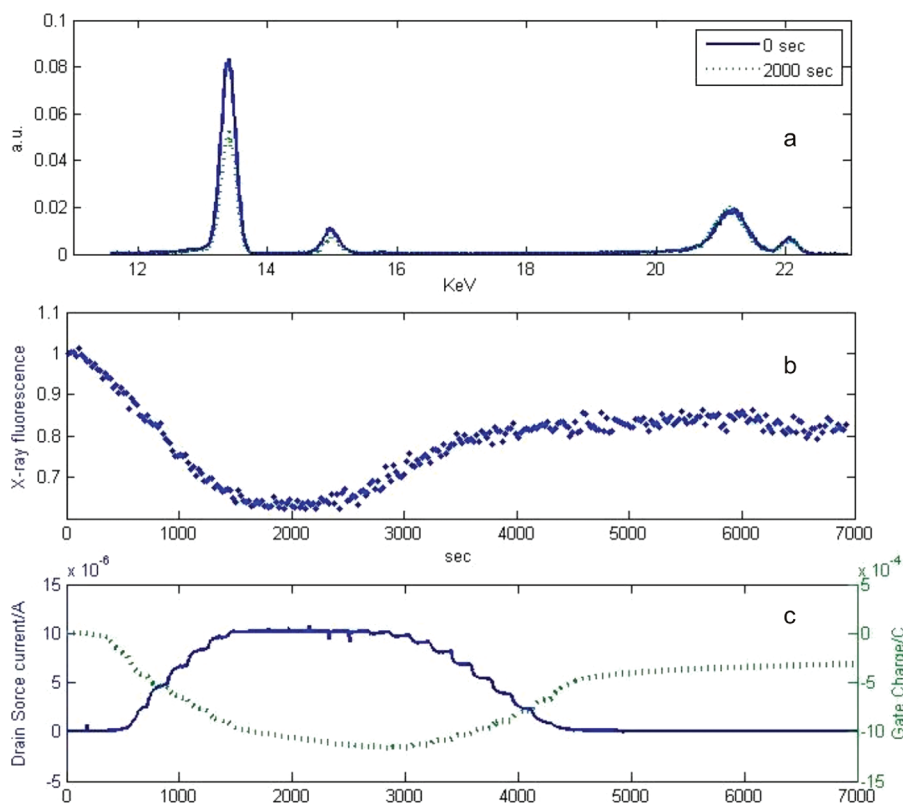


FIGURE 2. Fluorescence spectrum of the sample, acquired during the device functioning (a); temporal behavior of the normalized Rb fluorescence (b); drain current and transferred ionic charge (c) of the structure shown in Figure 1.

surface of a polyimide Kapton film (thickness $12.5 \mu\text{m}$). Thin PANI films (48 monolayers) were deposited by a modified Langmuir–Schaefer technique (10).

A special experimental setup was constructed for these measurements (Figure 1a). A Kapton film with a deposited PANI layer was placed on a Teflon support with two electrodes and a well in the central part. The well then was filled with a gel of PEO ($c = 5 \text{ mg/mL}$) in a 0.1 M of RbCl/water solution. The Kapton film was placed on a Teflon support in such a way that the PANI layer was in contact with the PEO electrolyte. A silver wire was fixed on the bottom of the well and used as the reference electrode. An electrical connection scheme of the realized structure is shown in Figure 1b for a better understanding.

The system realized for these measurements, shown in Figure 1a, corresponds well to the organic memristor (the scheme is shown in Figure 1b). One of the lateral electrodes and the reference electrode were connected to the ground potential level, while the voltage was applied to the other lateral electrode. Two currents were recorded: one in the drain circuit, representing the total current through the device, and the other

between the reference electrode and ground level, representing the ionic flow between the PANI layer and electrolyte. Applied potential and drain current measurements were performed by a 236 source measure unit (Keithley), while the current in the reference electrode circuit was measured by a 6514 system electrometer (Keithley). Both units were connected to the computer and controlled using *MATLAB* software. Measurements of the cyclic voltage–current characteristics were performed in the following way: the applied voltage was increased from 0 to +1.2 V with a step of 0.1 V. The applied voltage range was chosen in order to avoid irreversible overoxidation processes, occurring at voltages higher than 1.5 V. Each applied voltage was maintained for 1 min before the next step to reach equilibrium. After the maximum positive value was reached, the voltage was decreased with the same algorithm until -1.2 V . It was then brought to 0 V with the same step and equilibrating time.

X-ray fluorescence measurements at a grazing-incidence beam were performed on Beamline ID10B of the European Synchrotron Radiation Facilities (Grenoble, France). The energy

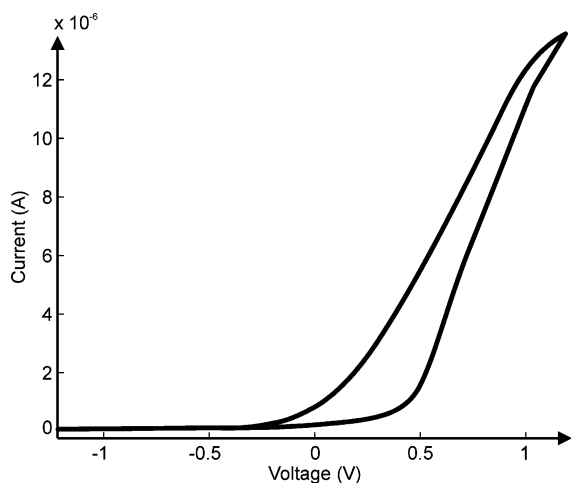


FIGURE 3. Cyclic voltage–current characteristic of the structure shown in Figure 1.

of the incident X-ray radiation was 22.08 keV. Excitation was performed by X-ray illumination of the sample parallel to its surface. Fluorescence was recorded with a Röntec Xflash detector placed 10 mm above the sample. Initially, the detector was calibrated using known spectrum lines of Cu, Au, and Cs. The presence of the Rb ions was detected as the integral intensity of fluorescence at two characteristic energies (13.39 and 14.96 keV) and normalized to the elastic scattering intensity in order to get rid of any dependency of the geometrical factor related to the experimental configuration. Fluorescence measurements were performed simultaneously with the electrical ones, allowing a direct comparison of the conductivity variation and ion motion.

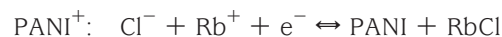
RESULTS AND DISCUSSION

Results of the measurements are presented in Figure 2. Figure 2a shows the fluorescence spectrum of the sample, indicating the variation of the characteristic fluorescence intensities during the device functioning, while the peaks corresponding to the elastic scattering remain at the same intensity. Figure 2b shows the kinetics of the variation of the normalized fluorescence intensity, corresponding to the presence of Rb ions. Figure 2c shows the contemporary variation of the drain current through the structure and integral of the gate current (transferred ionic charge). The presentation of the second curve as an integral of the gate current allows one to make a direct parallel to the hypothetical memristor properties. In fact, according to the suggestions by Chua (5), the value of the resistance must be a function of the transferred charge. Figure 2c demonstrates that in our case the conductivity of the layer (drain current) is directly related to the transferred ionic charge (integral of

the gate current), perfectly corresponding to the suggested memristor property.

The cyclic voltage–current characteristic of the same structure (the same measurements) is shown in Figure 3 for a better understanding.

Initially, the memristor is in its insulating state. It shows low conductivity (voltage range from 0 V until about +0.4 V) and the presence of the Rb ions in the layer (Figure 2b). An increase of the applied positive voltage results in the oxidation of the PANI layer and, consequently, in an increase of its conductivity (Figures 2c and 3). This transformation is accompanied by the displacement of Rb ions away from the PANI layer (Figure 2b). When the highest conducting state is reached, the normalized intensity of the Rb fluorescence comes to the minimum value. During the voltage scan from the maximum positive value to zero, we note the linear behavior of the voltage–current characteristic. PANI is in its oxidized conducting state, and no Rb ions enter the layer. After passing to the negative branch of the characteristic, we see that the conductivity of the device decreases together with an increase of the Rb fluorescence intensity. Ions enter the PANI active zone and transfer it into an insulating state. The transformation can be described by the following formula:



PANI in the oxidized conducting state can be reduced by the external electron, while the Rb ion neutralizes the acid anion (Cl^-) that was associated with the polymer chain in the oxidized state. The process is reversible, and the state of PANI is determined by the applied potential. Schematically, the process is shown in Figure 4. When the structure is biased negatively (left part), metal ions can penetrate the PANI layer, while for the positive bias (right part), they are displaced into the electrolyte.

An interesting feature of the characteristics shown in Figure 2 is the practically absolute coincidence of the Rb fluorescence spectrum and integral of the gate current (transferred ionic charge). The drain current (conductivity of the memristor) is directly related to the variation of these two parameters. Such behavior allows one to conclude that the conductivity variation is really connected to the metal ionic flux between the PANI layer and solid electrolyte. In addition, the results imply that the resistance of the realized device is a function of the transferred ionic charge, which

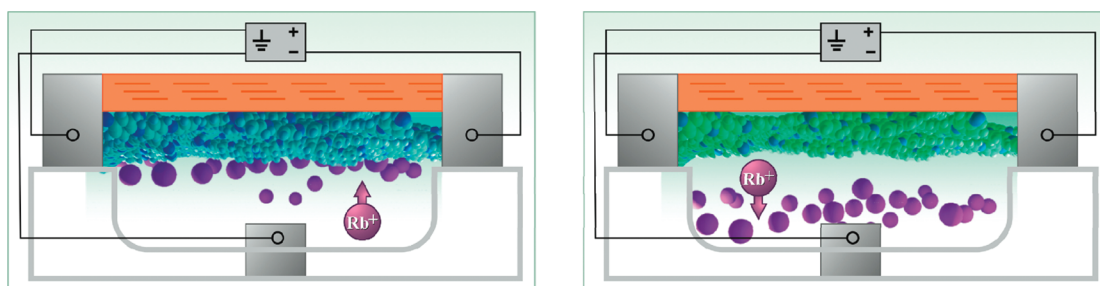


FIGURE 4. Scheme of the process occurring in the structure for negative (left) and positive (right) applied voltage.

corresponds directly to the suggestion by Chua on the hypothetical memristor properties.

CONCLUSIONS

Simultaneous measurements of the electrical characteristics and X-ray fluorescence have allowed us to demonstrate directly that on the microscopic level the mechanism of the electrochemically induced conductivity variation of the organic memristor involves the motion of the metal ions between the active layer of PANI and the solid electrolyte. The memristor conductivity value was found to be directly related to the number of Rb ions in the PANI active zone, measured by the X-ray fluorescence and ionic current in the structure. Even if the realized structure is different from that used in previous studies (gel instead of solid electrolyte, heavier ions), we can claim that the obtained results can be effectively used for the explanation of the properties of solid-state elements. In fact, the temporal characteristics of the reported structure are well comparable to those of previously reported devices (4). This can be due to the fact that the increase of the ion mobility due to the utilization of gel instead of solid electrolyte was compensated for by the decrease of mobility due to the use of a larger ion (Rb instead of Li).

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