Capacitive Ionic Current Measurement in a Polymer-Electrolyte Transistor

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Abstract—**Organic transistors that use dissolved ions to conduct current are able to reproduce the current-voltage characteristics of semiconductor transistors. The polymer-electrolyte transistor (PET) consists of a three-source acid/base reaction system, where a polymer gel separates the three source electrolytes and allows for transistor activity in the movement of the ions through the gel. The ability to directly measure the ionic current in the polymer of a PET reaction system without interfering with the reaction is a difficult task. Understanding the interfacial properties of an electrode-polymer junction will allow for a non-invasive method of directly measuring the ionic currents of the PET. The complex dielectric properties of a polymer system are considered, as well as the effect of the polymer-electrode interface.**

I. INTRODUCTION

Electrical current and voltage measurement in semiconductor devices has been extensively researched throughout the evolution of modern electronics. Semiconductor transistors and diodes use electrons and holes to conduct charge, which can be detected simply by measuring the potential or current at any given node, as compared to a known reference point. As transistors are morphed into the organic domain, particularly in situations where the charge carriers are no longer electric, measurement of the signals of interest must take a different approach. The polymer-electrolyte transistor (PET) is one such organic device, which uses acid/alkaline chemistry mediated in a polymer gel to create transistor activity [1]-[3]. In this case, the dissolved chemical species become the charge carriers for the signal of interest, which is transmitted along an ionic current through the device. For a PET using a monovalent strong acid/alkali reaction, a total of four charge carriers are dissolved in solution, two from the acid and two from the alkali. This complex ionic system creates interfacing problems when attempting to measure the signal of interest, as the particular total flux of ions through the polymer is difficult to directly measure.

One possible scheme to measure the ionic current would be to use redox chemistry at an electrode placed in the polymer. Though this method would allow for a direct quantitative measurement of the ionic current, it would result in the consumption of charge carriers in solution. The problem of electrode degradation would also remain an issue for a redox measurement system. Another potential solution is the use of electrode systems that do not affect the ions in solution. Although these are a good basis for measurement of electrical signals traveling in an electrolyte solution, in the case of the PET the signal of interest is the ionic current rather than the electrical current. This paper focuses on the use of capacitive charge transfer for noninvasive real-time measurement of total ionic current in the PET using metal electrodes with a dielectric polymer coating.

II. PET DESCRIPTION

A. Function

The PET can be considered the electrolytic analog of the bipolar junction transistor (BJT), where instead of n and p doped regions it has acid (S) and alkali (L) regions. Figure 1 shows the functional schematic of an LSL PET biased in common-collector configuration, showing the direction of ionic flux for each of the species. The emitter (E) and collector (C) regions are “doped” with monovalent alkaline solution BOH, which dissociates fully into B^+ and OH^-. Similarly, the base (B) region of Figure 1 is “doped” with the monovalent acidic solution HA, which dissociates fully into H^+ and A^-. The model depicted assumes the use of strong acids at a low concentration where the B^+ and A^- do not recombine in solution, but remain as mobile charge carriers.

With the given voltage configuration in Figure 1, the emitter-base junction is forward biased while the base-collector junction is reverse biased. A forward biased junction means that the non-recombinative charge carriers B^+ from the emitter and A^- from the base flow freely into the junction and conduct an ionic current. With the common-collector voltage

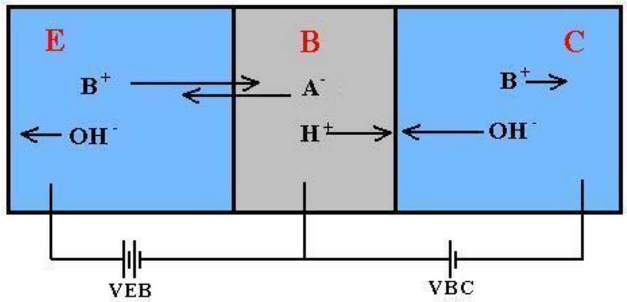

Figure 1. Functional schematic of the ion movement in a PET with a common-collector voltage bias.

bias, the B^+ ions will eventually flow to the collector region of the device while the A^- ions from the base will be swept into the emitter region. The base-collector junction in Figure 1 is reverse-biased, meaning the H^+ and OH^- ions recombine to form electrically neutral H_2O. With the PET biased in this configuration, the direction of positive ionic current flows from emitter to collector. This device has been shown through simulation and measurement to have transistor characteristics exhibited in the total ionic current flowing through the base-collector channel [1]-[3].

B. *Device Specification*

The ionic currents in the PET are affected by a concentration-driven diffusion and a voltage-driven drift. Figure 2 shows the functional layout of the PET, where green regions show the microfluidic channels and wells that hold the electrolyte, blue regions show the Cr/Au wires, and the orange region shows the polymer placement. Voltage potentials are set up by the electrodes in Figure 2 labeled V_E, V_B, and V_C, which are located in the emitter, base, and collector electrolyte source wells, respectively. The wires labeled V_{EB} and V_{BC} will be used to measure the ionic currents in the polymer, using the measurement scheme described in section III.

The fabricated PET has an isotropic channel etch of approximately 260 μm depth, with Cr/Au wires of 700 nm thickness and 100 μm width patterned into the channels and wells as shown in Figure 3. In the electrolyte source wells, these wires directly contact the electrolyte solution. In the polymer channel region, however, the wires directly contact the polymer gel. This creates a dielectric layer over the electrode that is nonuniform over the length of the electrode. The polymer to be used is polyvinyl alcohol (PVA) with a glutaraldehyde crosslinker [2].

III. CAPACITIVE ELECTRODE MEASUREMENT

The four charge carrier system of the PET presents a unique challenge in measuring and analyzing the signal of interest carried by the ionic current. With the polymer-Au contact area on the recording electrodes, a nonuniform layer of dielectric forms on the surface of the metal. Since a porous polymer will be used, the volume of polymer covering the surface will have an irregular thickness and there will likely be regions on the electrode surface where ions can directly contact the metal through pores. Since the system is designed such that no redox chemistry will occur, electrolytes adjacent to the electrode will simply induce charge rearrangement at the surface of the electrode directly rather than through a capacitive effect [4]. Overall there will be an average dielectric thickness for the polymer coating the electrode. This thickness will be determined by measuring the dielectric relaxation of the polymer for various concentrations of electrolytes, and determining an appropriate value.

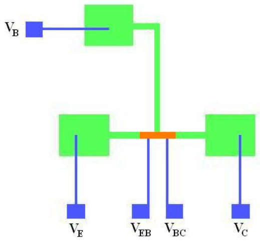

Figure 2. Schematic of fabricated PET showing the layout of the different components. Blue are the Cr/Au electrodes, green are the electrolyte source channesl and wells,and orange is the polymer gel.

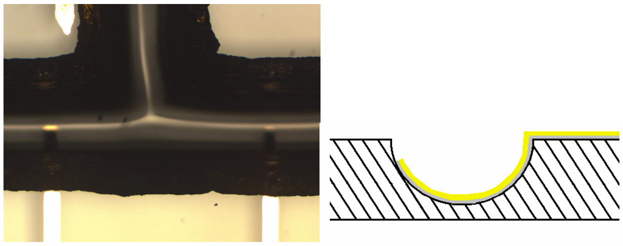

Figure 3. Microscope picture of the channel junction of the fabricated PET showing the recording wires V_{EB} and V_{BC} (left), and a schematic depicting the isotropic channel etch with the wires deposited in the channel (right).

With the PET as described above, the electrolytes in solution will have the ability to move through the porous polymer over the electrode with a thin layer separation distance caused by the adhered polymer. This thin layer will allow for capacitive measurement of the voltage induced ionic currents in the PET in accordance with Coulombic forces between the ionic species and the electrode. This can be seen by considering the volume of polymer-electrolyte directly above the electrode. Since the channel is an isotropic etch of approximately 260 μm depth, the volume above the electrode is a hemi-cylinder of radius 260 μm and width 100 μm. A total ionic charge due to the ions in solution above the electrode will exist that will have a net charge given by:

$$Q_{ion}(t) = \frac{1}{2}\pi r^2 wN \sum_{i=1}^{4} z_i q_i c_i(t) \qquad (1)$$

$Q_{ion}(t)$ is the total charge at time t, r is the radius of the cylinder, w is the width of the cylinder, N is Avogadro's constant, z_i is the charge number of species i, q_i is the charge of species i, and $c_i(t)$ is the concentration of species i in the volume directly above the electrode at time t. Through electrostatic forces, the charge $Q_{ion}(t)$ above the electrode will induce a charge rearrangement on the electrode surface, assisted by the dielectric layer of the polymer. For any change in $Q_{ion}(t)$, there will be a proportional readjustment of charge on the electrode as well. The charge on the electrode is the signal of interest for the ionic current in the PET. From this, the PET will be able to measure a voltage that is directly proportional to the ionic current in the BC channel, which is given by:

$$I_{BC} = \frac{dQ_{ion}(t)}{dt} \tag{2}$$

From (2) the PET acts as a differentiator with respect to the total charge above the electrode, which is a function of concentration for the dissolved electrolytes.

One of the major factors in determining the measurement response of the electrode/polymer system is the dielectric relaxation of the polymer gel. This is a complex valued function of the form:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) \tag{3}$$

The first term on the right side describes the real part of the permittivity of the system, while the second term refers to the loss factor [5]-[6]. This equation describes in general the ability of a dielectric material to store energy. As an electric field is applied to a polymer chain, polar groups on the chain will rotate in the field to attempt to reorient themselves in the direction of the field. This reorientation stores energy in the bonds of the polymer chain, as the polar groups of the chain rotate towards the field direction [6].

In addition to being a function of frequency, the dielectric relaxation is also affected by temperature and the chemical composition of the polymer [5]-[13]. The typical approach to account for these effects is to create groups of curves for a dielectric material over a range of temperatures at a set concentration value. The Havriliak-Negami equation gives a method of determining the important parameters in the dielectric relaxation process:

$$\frac{\varepsilon^*(\omega) - \varepsilon_{\text{inf}}}{\varepsilon_s - \varepsilon_{\text{inf}}} = \frac{1}{[1 + (j\omega\tau_0)^{\alpha}]^{\beta}} \tag{4}$$

$\varepsilon^*(\omega)$ is the same as in (1), ε_{inf} is the high frequency dielectric relaxation, ε_s is the low frequency dielectric relaxation, τ_0 is the relaxation time, α and β can take any value from 0 to 1, inclusive, and are material dependent [9], [14]-[16]. Determination of the parameters in (4) for the PVA-glutaraldehyde used in the PET will be essential to properly characterize the response of the system at different frequencies. This is necessary for proper ionic current detection, as any transients in the ionic current will have a response time dependent on the dielectric properties of the polymer. Groups of these curves will be created for a variety of operation temperatures of the PET to further improve accuracy of ionic current measurement.

IV. DISCUSSION

One of the major factors in capacitive charge is the dielectric relaxation of the material storing the charge. A large permittivity value for an electrode coating allows for a higher capacitive charge to be generated from a thinner film. This effect is due to the orientation of dipoles within an electric field. In the case of the PVA-glutaraldehyde film coating the Cr/Au electrode, the film layer is nonuniform due to the porosity of the material. The individual polymer chains also affect one another due to interference at close range inhibiting rotation under the influence of an electric field. These parameters can be controlled by maintaining a constant concentration of polymer and regulating the temperature of the system.

By Coulomb forces, ionic charges in the near vicinity of a sensing electrode will either attract or repel the electrons on the surface of that electrode. If the sensing electrode is connected to a measurement device with very high input impedance, relatively small changes in charge at the end of the electrode should translate into a measurable signal. By utilizing the capacitive effects of a polymer coating on the surface of the electrode, detection of ionic currents in a polymer will be achieved in a non-invasive manner for the PET system.

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