Dynamic Response Characteristics of a Novel Electrolyte Transistor

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Abstract: Novel organic transistors utilizing acid/alkaline chemistry have been investigated for their unique device chemistry and customizability. The research presented here shows a multiphysics model for a polymer-electrolyte transistor (PET) simulated in COMSOL Multiphysics. Dynamic transient response and current-voltage characteristics are determined from multiple simulations of an alkaline-acid-alkaline PET in common collector configuration, showing transistor activity in the ionic currents of the device. This shows that increases to the emitter voltage, while holding all other parameters constant, leads to increased ionic currents in the base-collector channel. Similar results are found for varying the base voltage while holding all other parameters constant. These results show that through modification of the electrolyte composition of the device, customized transistor responses are obtained, which leads to custom logic built in to the device chemistry.

Keywords: Polymer-electrolyte transistor, acid/base chemistry, diffusion, electrokinetic flow.

1. Introduction

Novel organic transistors have good potential for development of unique logic devices that don't rely on conventional electronic designs. Compared to the electrons and holes in their semiconductor counterparts, organic transistors utilize charge carriers such as electrolytes to conduct a signal. These charge carriers can come from a variety of sources, such as acid/alkaline chemistry, which adds a new domain of customizability in transistor design.

Previous researchers have attempted to incorporate organic components in semiconductor devices by using a polymer as either the gating material of a transistor, or as the semiconductor medium [1]-[4]. While these devices show transistor activity, they can require voltages on the order of 50-100 V to operate [2]-[3]. Additionally, fabrication of these devices requires techniques that are friendly towards organic materials, which can limit additional processing of the device, due to the multitude of unfriendly solvents and high temperatures used in traditional semiconductor device fabrication.

Development of a simple organic electrolyte diode and transistor has been previously shown utilizing acid/alkaline chemistry [5]. The design has acid and alkaline source chambers separated by a polymer gel. The gel allows diffusion of the electrolytes between the source chambers, but not convection. As described in previous work, the electrolyte transistors have either an acid-alkaline-acid (SLS) or an alkaline-acid-alkaline (LSL) configuration, which both have unique device characteristics. According to the literature, the SLS electrolyte transistor is a stable, amplifying device, while the LSL transistor exhibits nonlinear output current characteristics [6]. The research performed thus far on the electrolyte transistor has been experimental measurements of steady state current values, which can take hundreds of seconds to reach [5]-[7]. So far the question of rapid transient response has not been fully explored, which is an important issue when developing novel transistors used in digital logic.

The LSL transistor appears to have interesting nonlinear characteristics that have the potential to lead to more rapid switching times. This paper focuses on examining the dynamic response of the LSL polymer-electrolyte transistor (PET), utilizing the finite element solver COMSOL Multiphysics. To reduce confusion, the word "base" will refer to the middle acidic region of the PET that operates as the *base* of a transistor, while the word "alkaline" will be used to reference an electrolyte of the composition B^+ and OH^- (a *chemical base*).

2. Model Definition

The LSL polymer-electrolyte transistor has a physical design similar to a basic PNP bipolar junction transistor. In the PET, three separate source regions of ions are connected by a polymer gel. This gel acts as a medium through which the ions are allowed to diffuse, but there is no direct convective path between the three source regions [5]-[6].

Figure 1 depicts the basic function of the PET, showing the device biased such that $V_E>V_B>V_C$. The ionic species present are the alkaline BOH and the acidic HA, where B^+ is a cation and A^- is an anion. In solution, HA and BOH dissociate into their respective ions. The H^+ and OH^- ions recombine with a very high reaction rate, producing non-conducting H_2O. Depending on the specific chemistry of the cation and anion, they can remain as ions in solution and conduct charge. For the specific case of strong acids and bases the cation and anion do not recombine with any of the electrolytes in solution, and thus act as good charge carriers [5]-[6].

With the voltage potentials as depicted in Figure 1, the EB region is forward biased and the BC region is reverse biased. In a forward-biased junction, the anion and cation flow into the middle region, and allow for ionic current to flow from E to B. A reverse-biased junction is one where the H^+ and OH^- ions flow into the junction and recombine, leaving very few ions to conduct a signal [5]. With the cation flow from the emitter, though, there will be a cation concentration in the BC junction that will contribute to the total ionic current.

3. Governing Equations

Ionic diffusion in the PET is described by Fick's second law of diffusion for each ionic species. This combined with the flow of ions under an electric field produces the electrokinetic flow equation, where the first term governs diffusive flux, and the second term governs ionic flux under an electric field:

$$\nabla\cdot(-D\nabla c - z\mu_m Fc\nabla V) = R \qquad (1)$$

Where D is the diffusion coefficient (m^2/s), c is the concentration of the given ionic species (mol/m^3), z is the charge number (unitless), μ_m is the ionic mobility ($s\cdot mol/kg$), F is Faraday's constant (C/mol), V is the electric potential (V), and R is the reaction, or source, term ($mol/m^3\cdot s$).

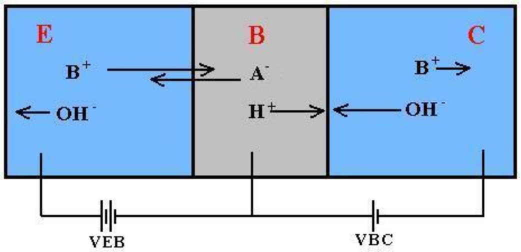

Figure 1. A basic PET schematic showing electrolyte migration through the emitter "E", base "B", and collector "C" under the effect of a voltage potential.

When initially determining the system of equations to govern this system, the equation for current flow due to electrons in a semiconductor material was investigated. In a semiconductor device, flux of charge carriers due to diffusion and drift is shown below:

$$J = qD_n\nabla n + q\mu nE \qquad (2)$$

Where J is the current density of electrons (A/m^2), q is the elementary charge (C), n the number density of electrons ($1/m^3$), E the electric field (V/m), and all other units the same as equation (1) [8].

To set up the voltage potentials in the system, the conductive media DC application is used. The governing equation for this system, shown below, is simply Ohm's law in differential equation form:

$$-\nabla\cdot d(\sigma\nabla V) = dQ_j \qquad (3)$$

Where d is the thickness (m), σ is the conductivity (S/m), V is the voltage (V), and Q_j is the charge density per time ($C/m^3\cdot s$).

4. Modeling Approach

The model created in COMSOL Multiphysics consists of three source regions of electrolytes, separated by a polymer, shown in Figure 2. As modeled in 2D, the device is 4.5 mm long in the x-direction, by 2.3 mm wide in the y-direction. The top portion of Figure 2 is the actual model built in COMSOL, including the mesh. There is a denser mesh in the regions where H^+ and OH^- recombine, due to the very high value of the reaction coefficient associated with their recombination. This high constant in the source term leads to large oscillations in H^+ and OH^- concentrations when the mesh is not fine enough, which produces singularities when modeling. Thus the mesh is more refined in areas where recombination occurs, to improve model accuracy.

In the bottom half of Figure 2, the different regions are color coded to more clearly show the different regions of the device. The emitter and collector are both colored green to depict the source of the alkaline electrolyte, BOH. Shown in blue, the base region is the source of the acidic electrolyte, HA. The polymer gel plug is shown in orange, with enlarged areas in the three source regions due to expected gel swelling [5]. The electrodes that set up the voltage potentials are shown in silver, with one for each source region. All concentration and voltage sources are defined along the external boundary of the individual region, while bulk properties such as diffusion coefficients are defined along the subdomain.

Modeling parameters were chosen such that the acidic solution had the properties of HCl, and the alkaline solution KOH [9]. These values were picked due to their previous use [5]-[6]. The properties of the modeled gel were determined from comparing diffusivity and mobility measured for various electrolytes in polymer gels [10]. Concentrations and bias voltage ranges were chosen for values expected to be used during testing of a fabricated PET.

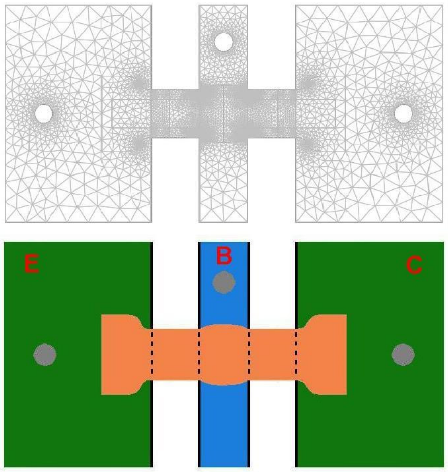

Figure 2. PET model showing the mesh in COMSOL (top) and the different regions colored for clarity (bottom).

Multiple simulations were run for: i) varied salt electrolyte concentration added to the base, ii) different values of alkaline concentration (i.e. “doping”) in the emitter, iii) varied levels of the voltage V_E, and iv) varied levels of the voltage V_B. Simulations for (i) were performed for steady state values of ionic current using transient simulations run until a constant steady-state behavior was observed. For (ii)-(iv), transient responses for 2 s, with samples taken every 0.5 ms, were modeled to observe the times required to switch the device on, which will be important when using the PET for logic applications. Simulation times were on the order of 30 minutes to 6 hours, depending on voltage potentials and source concentrations.

5. Results & Discussion

Multiple simulations were run to obtain each set of data shown in this work. Typical plots of concentration values are shown in Figure 3, where the concentration is represented for a species on the vertical axis, with the color scale showing its counterpart. As is seen for H^+ and OH^-, there is no overlap between the warmer colors and a positive vertical height, implying that recombination is occurring at the interface between alkaline and acidic zones.

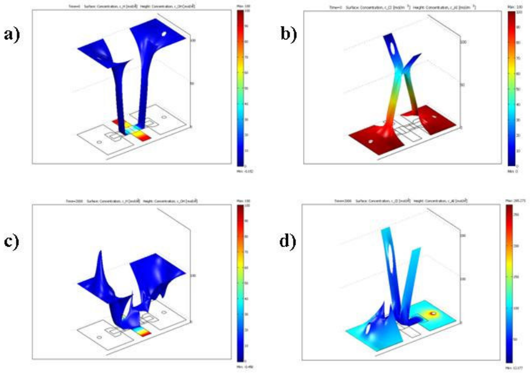

Figure 3. On top, results for initial value of steady state diffusion for (a) concentration H^+ color scale and OH^- height scale, (b) concentration B^+ color scale and A^- height scale. On bottom, results for steady-state value of electrokinetic flow for (c) concentration H^+ color scale and OH^- height scale, (d) concentration B^+ color scale and A^- height scale.

Convergence time to reach steady state depended on both the applied voltage, as well as the concentrations of the alkaline and acidic sources, but was on the order of tens to hundreds of seconds. Although this may seem like a long time, previous research has shown that the time to reach steady state is proportional to the square of the depth of the diffusion region [7]. This implies that shrinking the device by about one order of magnitude will result in times to reach steady state of a few seconds or less.

5.1 Varied Electrolyte in the Base Region

Injection of charge carriers into the base region of the PET results in a noticeable change in the steady state ionic currents. This was accomplished by adding additional salt electrolyte concentration to the base region, and observing its effect on the total ionic current change from initial to steady state. Voltage values in the device were held constant at $V_E = 3.5$ V, $V_B = 2.0$ V, and $V_C = 0$ V.

From Figure 4, the ionic currents through the BC region of the device grow more positive with the increase of additional salt, while the ionic currents in the EB region become more negative. This makes sense, given the voltage bias of the device, since the anion would flow towards the more positive emitter region and the cation would flow towards the more negative collector region. Depending on specific device chemistry, this property of the PET to add additional charge carriers to specific regions can be exploited to modify logic and switching points of the device, and is relatively simple to accomplish.

5.2 Emitter Region "Doping"

In BJTs, the emitter is typically doped more heavily with charge carriers than the collector, to allow for a very small diffusion region through the base [11]. This increases the speed of the device, since diffusion of charge carriers through the base is a speed-limiting factor.

The concentration of the alkaline source in the emitter of the PET was varied from 0.1 M to 0.4 M, and the transient ionic current response of the device was plotted for the BC and the EB channel. From Figures 5 and 6, the ionic currents show an inverse relationship to the increased emitter doping. For increasing doping values, the BC channel ionic current becomes more negative, while the EB channel ionic current grows more positive.

From Figures 5 and 6, specific device characteristics can be modified. To obtain a maximum positive ionic current through both the EB and BC channel, an emitter doping between 0.2 M and 0.3 M would be ideal. Choosing a concentration in that range would produce a current profile most similar to a conventional BJT in the active mode. Because of the variable nature in the PET ionic currents for different emitter doping values, a large degree of customizability is available without loss in function.

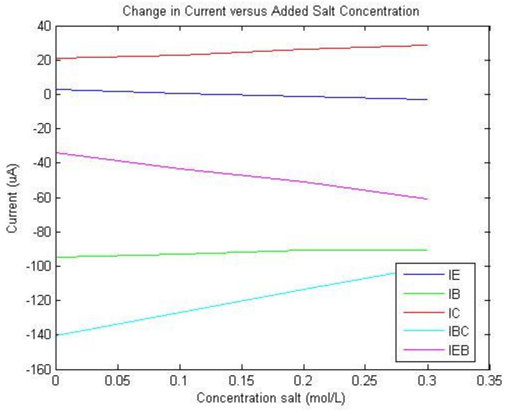

Figure 4. Steady-state current plot for the different regions of the device versus an increase in the concentration of salt electrolyte added to the base region of the PET.

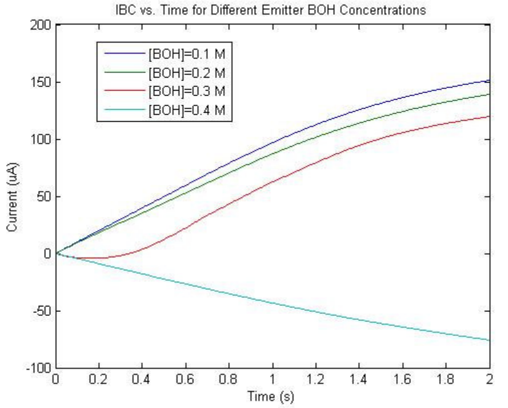

Figure 5. Plot of current in the BC channel versus time for different concentration doping of the alkaline source at the emitter.

5.3 V_{EC} Modulation

With the PET voltage biased in common collector mode, such that $V_E > V_B > V_C = 0$ V, an increase in V_{EC} above 0 V should result in an increase in ionic current through the device, while a decrease in V_{EC} below 0 V should lead to decreased ionic currents. This is observed in Figure 7, where more negative values of V_E show a decrease in the ionic current through the device. Although there is a residual amount of leakage current, the device exhibits transistor-like behavior, where increasing V_E causes a greater flux of ions through the device.

5.4 V_{BC} Modulation

Similar to modulating V_{EC}, modulating V_{BC} should increase the ionic currents in the device for values of $V_{BC} > 0$, while values of $V_{BC} < 0$ should decrease the ionic currents to a small value. This is seen from the results in Figure 8, where values of $V_{BC} < 0$ show a very small current even at a time point of 2 s, whereas for $V_{BC} > 0$, a large increase in ionic current is seen for increasing values of V_{BC}.

From Figures 7 and 8, the PET shows good potential for use as an organic transistor. The ability to regulate the amount of current through the device in a manner similar to a BJT allows for a starting point in studying the possible interconnects between multiple PETs to create a logic function.

6. Conclusions

This paper has shown the use of COMSOL Multiphysics to run finite element simulations on the complex chemical system of the polymer-electrolyte transistor. The PET is a good candidate for novel logic applications, due to its transistor-like characteristics. By carefully selecting the acid/base chemistry and the composition of the polymer, specific logic can be built in to the chemistry of the device, rather than the structure. This will lead to a new domain of organic transistor design, where the transistor no longer has to mimic its semiconductor counterpart, but will operate based on new methods of logic that work well in the chemical domain. Additionally, use of COMSOL Multiphysics will allow for rapid prototyping of specific device chemistry and composition, which will save time in the production and testing of new devices.

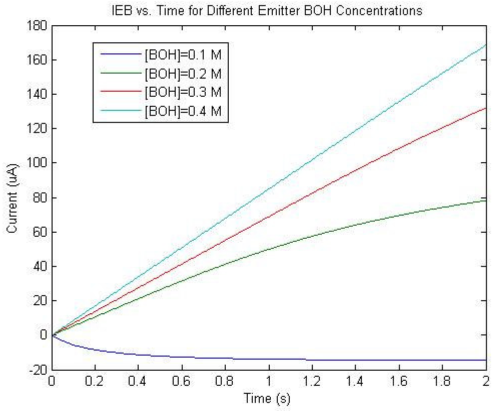

Figure 6. Plot of current in the EB channel versus time for different concentration doping of the alkaline source at the emitter.

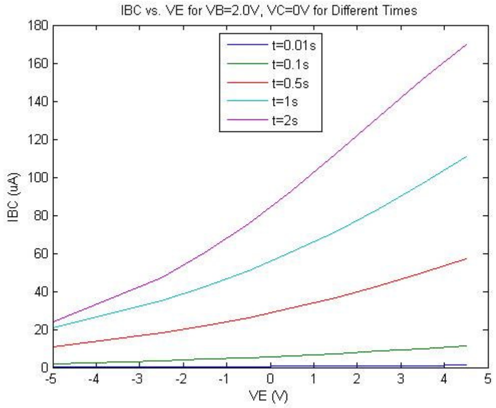

Figure 7. Plot of current through BC channel versus varying V_E over different values of time from 0.01 s to 2 s.

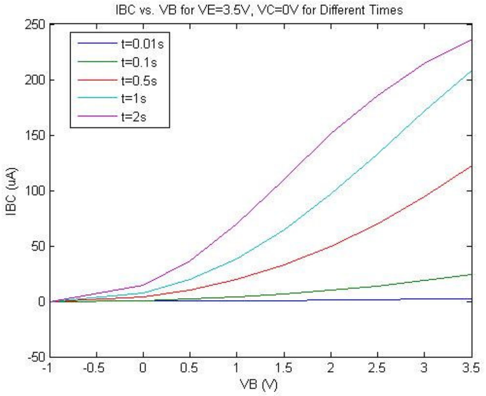

Figure 8. Plot of current through BC channel versus changing V_B for different values of time from 0.01 s to 2 s.

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