

Drift Diffusion Simulation of an Organic Memristor

by

Cem Bonfil, B. Eng.

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Department of Electronics

Carleton University

Ottawa, Ontario, Canada

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Abstract

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The acknowledgements and the people to thank go here, don't forget to include your project advisor...

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Abbreviations

BTE	Boltzmann Transport Equations
CFL	Courant-Friedrichs-Lowy
ClO_4^-	Perchlorate
DD	Drift Diffusion
FD	Finite Difference
Li^+	Lithium
PEDOT	Poly(3,4-ethylenedioxythiophene)
PSS	Poly(styrenesulfonate)
SG	Scharfatter-Gummel

Physical Constants

Boltzmann Constant $k = 8.6173324 \cdot 10^{-5}$ eV/K

Elementary Charge $q = 1.6021765 \cdot 10^{-19}$ C

Vacuum Permittivity $\epsilon_0 = 8.8541878 \cdot 10^{-12}$ F/m

Symbols

D	Diffusivity	m^2/s
E	Electric Field	V/m
h	Unit Distance	m
I	Current	A
J	Current Density	A/m^2
L_D	Debye Length	m
l_f	Mean Free Path	m
M	Memristance	Ω
n	Electron Density	m^{-3}
N_A	Acceptor Density	m^{-3}
N_D	Donor Density	m^{-3}
n_i	Intrinsic Carrier Density	m^{-3}
T	Temperature	K
t	Time	s
t_{dr}	Dielectric Relaxation Time	s
U	Generation Recombination Rate	$m^{-3}s^{-1}$
V	Potential	V
V_{th}	Thermal Voltage	V
Δ	Unit Distance	m
ϵ_r	Relative Permittivity	unitless
μ	Mobility	$m^2/(Vs)$
φ	Flux Linkage	Wb
ρ	Charge Density	C/m^3
v	Drift Speed	m/s

For/Dedicated to/To my...

Chapter 1

Introduction

1.1 Thesis Objectives

The purpose of this thesis was to create a numerical simulation which captures the physics behind the operation of a memristor. This simulation can be used for researching the physics behind the actual device through further modeling or as a tool for designing memristors for a specific purpose.

A simple memristor model was created using only the essential components and physical effects. A numerical solver for drift diffusion and poisson equations were developed and tested. A memristor simulation was created by modifying the drift diffusion solver to accommodate all the essential physical effects. Finally the simulation results were compared with experimental data from a memristor fabricated at Carleton University.

1.2 Thesis Overview

Initially, discovery of memristor and challenges in memristor research is introduced in the background chapter. It emphasizes the need for better physical modeling for memristor and lack of simulation tools required for further analysis and research.

In chapter 2 , Boltzmann Transport Equations (BTE) are introduced. This introduction is followed by explanation of transport mechanisms captured through BTE. Additionally drift diffusion equations (simplified form of BTE) which will be used for the simulation of

the memristor are discussed. Finally analytic solutions to drift diffusion equations, such as charged particles moving over an infinite conductor and PN junction, are generated and plotted.

A numerical solution to drift diffusion equations is formed in chapter 3 to calculate the movement of all the charged particles in a memristor. First finite difference method, which is the basis for all the simulations in this thesis, is introduced. Then it is applied to drift diffusion equations. Additionally, a Poisson solver to be used with drift diffusion equations is developed in order to calculate the electric field generated by charged particles and metal contacts. Also, boundary conditions necessary for the solution of both drift diffusion and Poisson solver are discussed. All the equations and boundary conditions combined generates a set of equations to be solved for the memristor simulation. Various schemes for solving these differential equations as well as the numerical and physical limitations are discussed in detail.

In chapter 4, the numerical solver developed in chapter 3 is tested against analytic solutions as well as a commercially available simulator called COMSOL Multiphysics. A mechanism to limit the maximum density of any particle, which is essential for memristor simulation, is developed and tested.

After the stability and accuracy of the simulation scheme was tested in chapter 4, a memristor model is introduced in chapter 5. The difficulties in the simulation due to physical and numerical restrictions were discussed. A possible 1-D approximation for a 2-D memristor simulation was proposed and simulated. After demonstrating that the simulations produced reasonable results, the validity of the approximations made for 1-D and 2-D simulations are investigated.

A full 2-D simulation is discussed in chapter 6. A memristor with various PEDOT thicknesses were simulated. A memristor with various PEDOT:PSS thicknesses were simulated and compared to each other. The simulation with thinnest PEDOT is compared to 1-D simulations made in the previous chapter. Finally memristor simulations were compared to experimental data.

The conclusion chapter summarizes the findings of the thesis, discusses advantages and disadvantages of the proposed simulation methods and provides suggestions for improvements on the model and opportunities further research.

1.3 Background

The term memristor was first used by Leon Chua in 1971 in his paper called "Memristor The Missing Circuit Element" [1]. He theorized that there is a fourth passive circuit element yet to be discovered in addition to resistor, capacitor and inductor. He said that we already know and use five out of six possible combinations that can be made out of four fundamental circuit variables, current I , voltage V , charge q and flux linkage φ . Chua claimed that we were missing a circuit element which produces a relationship between flux linkage (time integral of the potential) and charge. He introduced a new variable named memristance which has units of resistance and it is a function of charge. The relationship between the current and the potential of a memristor is calculated by replacing the resistance by memristance in ohms law:

$$v(t) = M(q(t))i(t) \quad (1.1)$$

Theoretically memristor retains its resistance in the absence of any power source. When a potential is applied the resistance can be influenced by the direction and the magnitude of the current. If the current flows in one direction resistance increases and if it flows in the other direction resistance decreases. This produces an I-V response which looks like a pinched hysteresis curve. This response is the main characteristic of a memristor.

This new element remained mostly a theory and did not get much academic attention until a group of researchers in Hewlett Packard developed a fully functioning memristor. They successfully fabricated a nano scale memristor using TiO_2 (titanium dioxide). After the discovery in HP labs there was an increase of interest in different types of memristors due to their potential applications for data storage and addition of learning capabilities into passive circuits.

Recently it has been suggested that organic based memristors could be fabricated (ref). This thesis will be concerned with such devices. They are usually constructed on a larger scale than the ones fabricated in HP labs. The memristor studied in this thesis is in millimeter rather than nano meter scale and uses a conductor made out of a polymer called PEDOT:PSS. It is composed of two polymer chains, PEDOT and PSS attached together and conducts electricity via hole transport. Unfortunately the conduction mechanism is not perfectly understood and needs further research due to the complexity of the material(ref).

Unlike a semiconductors like silicon, the structure of a polymer is quite irregular. Polymers have individual molecules with different chain lengths and a variable amount of defects. Additionally, they can be amorphous or partially crystalline and further differences occur through aging. The conduction and electronic properties depend the orientation of polymer chains which can change in x,y and z directions. These irregularities in the structure makes these conducting polymers resemble amorphous inorganic semiconductors. Following the concept of charge transport in amorphous inorganic semiconductors, the conduction mechanism of conducting polymers is commonly explained by variable range hopping. This mechanism was first introduced by Mott in 1968. He proposed a model for charge transport in systems that are randomly disordered. In variable range hopping charge transport occurs via jumps between available sites. Every charge carrier has a probability of jumping between two sites depending on its energy and the distance to the next available site. Temperature has a big impact on conductivity since it changes the structure of the molecules and increases the energy of charge carriers.

Apart from temperature there are other ways to change the conductivity of PEDOT. It is possible to affect conductivity by either doping or counter doping. Depending on the method used, doping can be reversible or permanent. When reversible doping is employed, resulting device behaves like a memristor since its resistance is now dependent on charge. All these effects make physical modeling, experimentation and simulation very challenging.

There are few approximate analytic solutions for inorganic memristors similar to the one produced in HP labs. These solutions are mostly based on parameter fitting and some basic physics. Studies on organic memristors are more sparse than studies on inorganic ones and a standard method for simulating organic memristors is not developed. The physics behind the conduction mechanism and the changes in conductivity due to doping requires further research and development of a computer model can help in various ways. First of all it is very difficult to get experimental data on the movement of ions and holes inside PEDOT due its disordered structure. The thickness of PEDOT:PSS (usually in μm scale) complicates the tracing of the ion in all dimensions. Theories that explain the movement of charged particles and their interactions with each other are difficult to formulate since it is hard to obtain required experimental data. A simulation can be a useful tool in testing various theories without having to set up and perform complicated experiments. Also once a solid understanding of the conduction mechanism has been achieved, simulations can be very useful to test different device structures and optimize them before fabrication.

Chapter 2

Theory

Memristor studied in this thesis has a strip of PEDOT:PSS as a conductor. A drop of an electrolytic solution which has lithium and perchlorate ions is placed on top of this conducting strip. When the conductor has an applied potential, lithium ions inside the electrolyte solution migrate into PEDOT:PSS and modify its conductivity. Hole transport inside PEDOT:PSS as well as lithium and perchlorate movement is modeled using basic drift diffusion equations which are derived in the first part of this chapter. The second half of the chapter shows analytic solutions to drift diffusion equations which will be used to test the numerical methods derived in the following chapter.

2.1 Carrier Transport Equations

Drift diffusion equations, which are based on BTE, need to be solved in order to model the complex behaviour of the memristor. Drift-diffusion equations are derived by simplifying BTE equation via approximations. These simplifications dictate the limits of the drift-diffusion model and serve as guidelines for where this model can be used, therefore they need to be well understood.

Derivation of Boltzmann transport equation starts by stating that any charged particles can be defined its position in space \mathbf{r} and momentum \mathbf{k} in time t using a probability distribution function $f(\mathbf{k}, \mathbf{r}, t)$. This results in the most general form of Boltzmann transport equation.

$$\frac{d}{dt}f(k, r, t) = 0 \quad (2.1)$$

This general form of BTE needs to be expanded and relevant physical equations need to be placed in to get an appropriate equation describing a specific problem or a device. Many different device simulators use some sort of approximation to BTE. In a semiconductor simulations they are commonly used for the movement and the density distribution of charge carriers such as holes (p) and electrons (n).

After this brief introduction to BTE, rather than going through the mathematical derivation of the drift diffusion model, the approximations that are made along the process of derivation can be discussed in order to get a better insight on the model. As a particle travels in a solid state device it collides with other particles as well as the atoms in the device. For drift-diffusion equations individual lattice scattering events or collisions are averaged and the particles have an average constant velocity under the effects of an electric field. This means that all the particles respond instantaneously to the changes in the electric field. The movement of the particles due to electric field is called the drift current. The relationship between drift velocity and the electric field is given by the following equation:

$$v = \mu E \quad (2.2)$$

μ is called mobility constant and it determines the speed at which the particles are going to move when subject to an electric field. Drift current density can be derived based on drift velocity.

$$J_E = qn\mu E = qnv \quad (2.3)$$

Where q is the elementary charge and n is the electron density. In addition to the previous assumptions, it is assumed that the lattice is perfectly uniform, has a uniform temperature distribution and all the particles are close to the temperature of the lattice.

Based on this assumption it is possible say that all the particles that move due to thermal effects has the same thermal velocity (v_{th}) and mean free path (l_f). These quantities can be combined into one single coefficient called diffusion constant.

$$D = v_{th} l_f \quad (2.4)$$

Drift and diffusion coefficients are related to each other via Einstein relationship:

$$D = \frac{\mu k T}{q} \quad (2.5)$$

Where k is the Boltzmann constant and T is the lattice temperature. This results in a second term which contributes to carrier movement and it is called the diffusion current density.

$$J_D = qD \frac{dn}{dx} \quad (2.6)$$

Unlike the drift current density, which is directly related to the carrier density, diffusion current density is related to the carrier density's first order derivative in space. Combining these two terms results in the following the current density equation for electrons in one dimension.

$$\vec{J}_n^x = q\mu_n n \vec{E}_x + qD_n \frac{dn}{dx} \quad (2.7)$$

This equation can be easily extended to higher dimensions by simply using the appropriate terms.

$$\vec{J}_n^y = q\mu_n n \vec{E}_x + qD_n \frac{dn}{dy} \quad (2.8)$$

Current density equations can be used for both positively and negatively charged particles by changing the sign of the diffusion current density.

$$\vec{J}_p^x = q\mu_p p \vec{E}_x - qD_p \frac{dp}{dx} \quad (2.9)$$

Anisotropic drift and diffusion coefficients can be handled with ease by using different coefficients for different directions. Also Mobility and diffusivity can be a function of any variable such as position or temperature. This is a useful property for a memristor simulation since hole mobility depends on lithium density in the PEDOT:PSS at any given position.

For the memristor simulation the movement of lithium and perchlorate ions inside the electrolyte is modeled as if they were moving in a solid state device. So all the derivations that were made for positively and negatively charged particles include holes and electrons as well as lithium and perchlorate ions. Viscosity of the liquid and all possible deformations due to movement of ions are simply ignored. This approximation was made based on the assumption that the amount of ions in the electrolyte are very large compared what PEDOT:PSS can absorb. Additionally the solution is very dilute. So the distribution of ions inside the electrolyte remain mostly unchanged and the exchange of ions do not disturb the shape or the physical characteristics of the solution on top of PEDOT:PSS.

Current density equations by themselves are not enough to solve this time dependent problem. It is necessary to account for the movement of charge over time which is captured in the continuity equation. It is basically a statement of conservation of particle density over time. The change in the amount of carriers over time in a particular area must be equal to the difference in current density over the same area. Additionally the amount of charge can change due to generation-recombination of charged particles.

$$\frac{\partial n}{\partial t} = \frac{1}{q} \nabla \cdot \vec{J}_n + U_n \quad (2.10)$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \nabla \cdot \vec{J}_p + U_p \quad (2.11)$$

U_n and U_p are net generation recombination rates. These terms were not included in the modeling of the memristor.

Electric field can be generated in two different ways. One is through the distribution of net charge over the area and the other one is an externally applied potential. It is possible calculate the potential distribution over an area by using Poisson's equation. Once the potential is known the electric field can be obtained by just calculating the negative gradient of the electric potential.

$$\nabla \cdot (\varepsilon \nabla V) = -\rho = -q(p - n + N_D^+ - N_A^-) \quad (2.12)$$

$$\vec{E} = -\nabla V \quad (2.13)$$

Electric field can be split into one, two or three components depending on the dimensions of the problem. In a 2-D case they are \vec{E}_x and \vec{E}_y .

$$\vec{E}_x = -\frac{\partial V}{\partial x} \quad (2.14)$$

$$\vec{E}_y = -\frac{\partial V}{\partial y} \quad (2.15)$$

Once the electric field and current density is known, the amount of current in a particular place in the device can be easily calculated by using the following integral.

$$I = \int_s \vec{J}_{tot} \cdot ds = \int_s (J_n + J_p + \varepsilon \frac{\partial E}{\partial t}) ds \quad (2.16)$$

Through the electric field and net charge distribution, Poisson's equation and drift-diffusion equations are coupled and non linear. The strength of the non linear coupling depends on the size of the device and charge density which determines the total amount of charge over an area. In a strongly coupled system of differential equations, small changes in either the charge density or electric field can easily cause instabilities in the

simulation. This is further discussed in the next chapter while developing a numerical scheme to solve the system of equations described in this chapter.

The main equations for the drift-diffusion model that are used for memristor simulation can be compactly written as:

$$\nabla \cdot (\varepsilon \nabla V) = -q(p - n + N_D^+ - N_A^-) \quad (2.17)$$

$$\vec{J}_p = q\mu_p p \vec{E} - qD_p \nabla p \quad (2.18)$$

$$\vec{J}_{N_A^-} = q\mu_{N_A^-} N_A^- \vec{E} + qD_{N_A^-} \nabla N_A^- \quad (2.19)$$

$$\vec{J}_{N_D^+} = q\mu_{N_D^+} N_D^+ \vec{E} - qD_{N_D^+} \nabla N_D^+ \quad (2.20)$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \nabla \cdot \vec{J}_p \quad (2.21)$$

$$\frac{\partial N_A^-}{\partial t} = \frac{1}{q} \nabla \cdot \vec{J}_{N_A^-} \quad (2.22)$$

$$\frac{\partial N_D^+}{\partial t} = -\frac{1}{q} \nabla \cdot \vec{J}_{N_D^+} \quad (2.23)$$

This system of equations consist of 4 different charge carriers. There are 3 mobile species lithium (N_D^+) and perchlorate (N_A^-) and holes (p) and one fixed charge, electrons (n). The particles are coupled to each other through Poisson's equation since they all carry electric charge.

Unfortunately even after many approximations and simplifications to BTE, drift diffusion equations have analytical solutions for only few isolated cases. Analytical solutions developed in the rest of this chapter will be used in testing of the numerical method developed for simulating a memristor.

2.2 Analytic Solutions

Three different analytic solutions to drift diffusion equations will be developed in this section. It starts with a simple steady state problem with uniform electric field. Second example, which is more complex than the first one, is a transient solution for a charge distribution moving under uniform electric field. Finally PN junction problem incorporates drift diffusion equation with Poisson's equation therefore provides a steady state solution for electron/hole density distributions, potential and electric field.

2.2.1 Steady State Solution Over a Finite Domain

The problem that will be solved in this section consists of a finite amount of charge and a uniform electric field pushing this charge against a wall ($J=0$). It is assumed that the charge density is low enough not to affect the uniform electric field, therefore Poisson's equation is not needed. To simplify the problem even further, transient solution is ignored. Also it is important to note that the initial distribution of the charge density does not matter in this problem since everything will be redistributed in steady state. The only relevant information is the total amount of charge subject to the electric field. At steady state, drift and diffusion currents are in equilibrium and net current density is zero. Following equation shows hole density at equilibrium:

$$J_p(x) = q\mu_p pE - qD_p \frac{dp}{dx} = 0 \quad (2.24)$$

Total current density will only be zero when the drift current density generated by the electric field is completely balanced by the diffusion current density.

$$q\mu_p pE = qD_p \frac{dp}{dx} \quad (2.25)$$

$$\frac{\mu_p E}{D_p} p = \frac{dp}{dx} \quad (2.26)$$

This is a simple differential equation that can be solved by assuming that hole density has the following form:

$$p(x) = Ce^{ax} \quad (2.27)$$

C and **a** are arbitrary constants. Equation (2.27) can be placed into (2.26).

$$\frac{\mu_p E}{D_p} Ce^{ax} = aCe^{ax} \quad (2.28)$$

$$a = \frac{\mu_p E}{D_p} \quad (2.29)$$

A general form for the solution is generated by placing **a** back to equation (2.27).

$$p(x) = Ce^{\frac{\mu_p E}{D_p} x} \quad (2.30)$$

It is possible to solve for **C** by observing that the total number of charges at steady state must be equal to the initial number of charges. So the integral of the initial hole density distribution must be equal to the integral of charge density at steady state.

$$\int_0^L Ce^{\frac{\mu_p E}{D_p} x} dx = \int_0^L p(t=0, x) dx$$

$$C = \frac{\int_0^L p(t=0, x) dx}{\int_0^L e^{\frac{\mu_p E}{D_p} x} dx}$$

$$C = \frac{\int_0^L p(t=0, x) dx}{\frac{D_p}{\mu_p E} [e^{\frac{\mu_p E}{D_p} L} - 1]} \quad (2.31)$$

So the full solution takes the following form:

$$p(x) = \frac{\int_0^L p(t=0, x) dx}{\frac{D_p}{\mu_p E} [e^{\frac{\mu_p E}{D_p} L} - 1]} e^{\frac{\mu_p E}{D_p} x} \quad (2.32)$$

The solution shows that increasing electric field will concentrate the charge density at the edge of the area. Physically this behavior is reasonable, since the force that is pushing the particles against a wall is getting greater and it is making the charges accumulate even more. Following plot demonstrates the effect of increasing electric field on hole distribution.

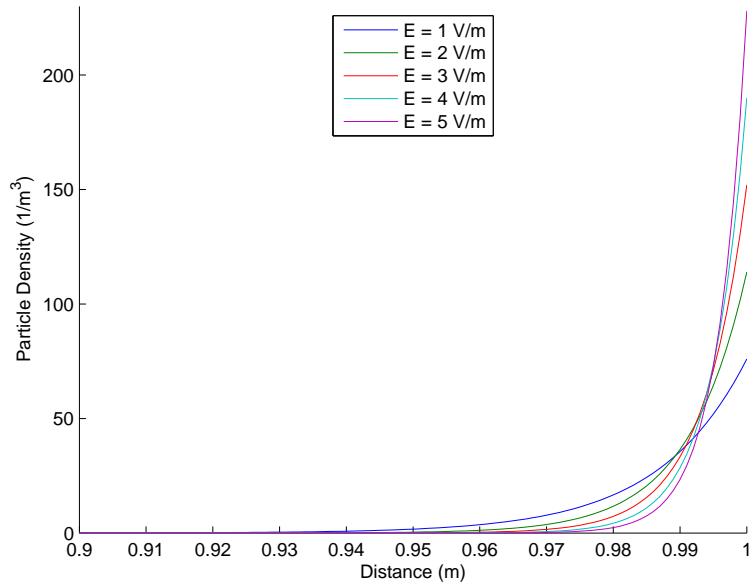


FIGURE 2.1: Increased accumulation of particles due to increased electric field

2.2.2 Transient Solution Over an Infinite Domain

The problem that will be solved in this section consists of an initial particle density distribution subject to a uniform electric field over an infinitely long conductor. The charge distribution will drift and diffuse over time. This requires a transient solution and the continuity equation (2.10) needs to be solved. Again, charged particles do not affect the electric field therefore solution of Poisson's equation is not necessary.

The first step of the solution process is the insertion of (2.7) into (2.10).

$$\frac{\partial n}{\partial t} = \frac{1}{q} \nabla \cdot (\vec{J}_n) \quad (2.33)$$

$$\frac{\partial n}{\partial t} = \frac{1}{q} \nabla \cdot (q\mu_n n \vec{E} + qD_n \frac{dn}{dx}) \quad (2.34)$$

For 1-D above equation can be simplified to:

$$\frac{\partial n}{\partial t} = \mu_n E \frac{dn}{dx} + D_n \frac{d^2 n}{dx^2} \quad (2.35)$$

Using separation of variables it is possible to assume that the solution can be separated into a time and space dependent functions.

$$n(t, x) = n(t)n(x) = n_t n_x \quad (2.36)$$

Placing equation (2.36) into (2.35) and dividing by $n(t,x)$,

$$\frac{1}{n_t} \frac{dn_t}{dt} = \mu_n E \frac{1}{n_x} \frac{dn_x}{dx} + D \frac{1}{n_x} \frac{d^2 n_x}{dx^2} \quad (2.37)$$

Assuming both sides of the equation are equal to a constant $-k$, time dependent part of the problem becomes a simple first order differential equation.

$$\frac{1}{n_t} \frac{dn_t}{dt} = -k$$

$$\frac{dn_t}{dt} = -kn_t$$

Based on the above differential equation n_t can take the following form:

$$n_t = C_1 e^{-kt} \quad (2.38)$$

Now for n_x assuming a solution of the form below,

$$n_x = C_2 e^{-j\omega x} \quad (2.39)$$

Placing (2.39) into (2.37)

$$\omega^2 D C_2 e^{-j\omega x} - j\omega \mu_n E C_2 e^{-j\omega x} + k C_2 e^{-j\omega x} = 0 \quad (2.40)$$

Simplifying equation (2.40) and solving for k gives,

$$k = \omega^2 D + j\omega \mu_n E \quad (2.41)$$

Combining equation (2.38), (2.39) and (2.41) to get the initial form of the solution.
($C = C_1 C_2$)

$$n = n_t n_x = C e^{(-\omega^2 D + j\omega \mu_n E)t} e^{-j\omega x} \quad (2.42)$$

The application of the superposition principle leads to:

$$n = n_t n_x = \int_{-\infty}^{\infty} C(\omega) e^{(-\omega^2 D + j\omega \mu_n E)t} e^{-j\omega x} d\omega \quad (2.43)$$

The distribution of n_x is known at $t=0$.

$$n(x, t=0) = \int_{-\infty}^{\infty} C(\omega) e^{-j\omega x} d\omega \quad (2.44)$$

$C(\omega)$ is just the inverse fourier transform of $n(x, 0)$.

$$C(\omega) = \int_{-\infty}^{\infty} n(x, 0) e^{-j\omega x} dx \quad (2.45)$$

The final form of the solution is generated by placing equation (2.45) into (2.43):

$$n = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} n(z, 0) e^{j\omega z} dz e^{(\omega^2 D - j\omega \mu_n E)t} e^{-j\omega x} d\omega \quad (2.46)$$

Rearranging equation (2.46),

$$n = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} n(z, 0) e^{(\omega^2 D - j\omega \mu_n E)t} e^{-j\omega x} e^{j\omega z} dz d\omega \quad (2.47)$$

Using a gaussian initial distribution results into:

$$n(x, 0) = e^{-(\frac{x-x_0}{\sigma})^2} \quad (2.48)$$

$$n(x, t) = \frac{1}{\sqrt{4D_n \sigma^2 t + 1}} e^{-\frac{(t\mu_n E - x + x_0)^2}{4D_n t + \sigma^2}} \quad (2.49)$$

If the initial distribution is a rectangular then the solution takes the following form:

$$n(x, 0) = \prod(w(x)) \quad (2.50)$$

$$n(x, t) = \frac{1}{2} \operatorname{erf}\left(\frac{w + 2t\mu_n E - 2x}{4\sqrt{D_n t}}\right) - \frac{1}{2} \operatorname{erf}\left(\frac{-w + 2t\mu_n E - 2x}{4\sqrt{D_n t}}\right) \quad (2.51)$$

Following plots show the evolution of two particle densities with different initial distributions described above.

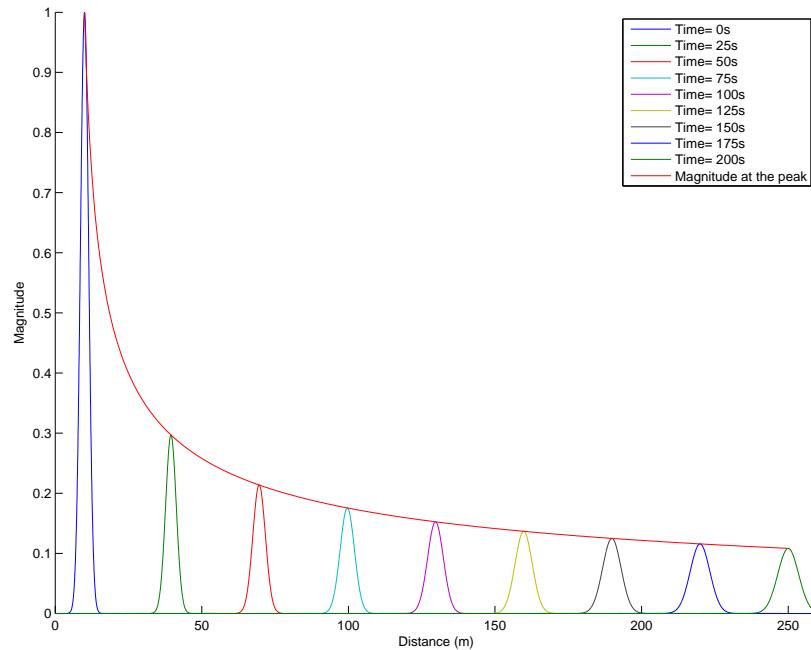


FIGURE 2.2: A gaussian particle density distribution drifting and diffusion over time

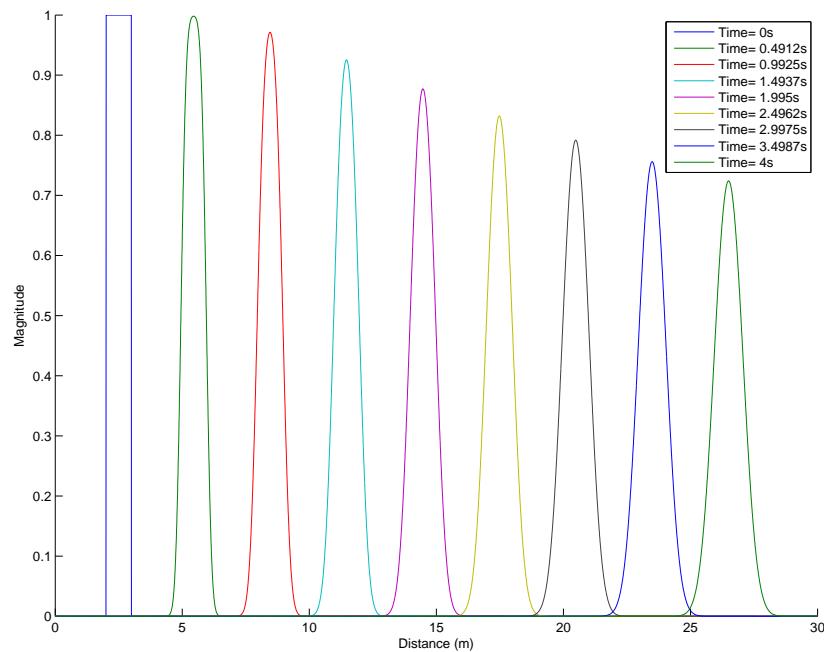


FIGURE 2.3: A gaussian particle density distribution drifting and diffusion over time

2.2.3 PN Junction

Previous analytical solutions involved the solution of Poisson's equation and continuity equation which were not coupled. An example where these equations are tightly coupled will be examined in this section. There are usually no direct analytical solution for coupled equations but it is possible to get a closed form solution by making use of certain approximations. One simple example of this situation is an abrupt p-n junction. An abrupt p-n junction is created when two materials of opposite doping, p type and n type, are brought together. A p type material has an excess number of acceptors N_A and an n type material has an excess number of donors N_D . The junction is defined at the interface where $N_A = N_D$.

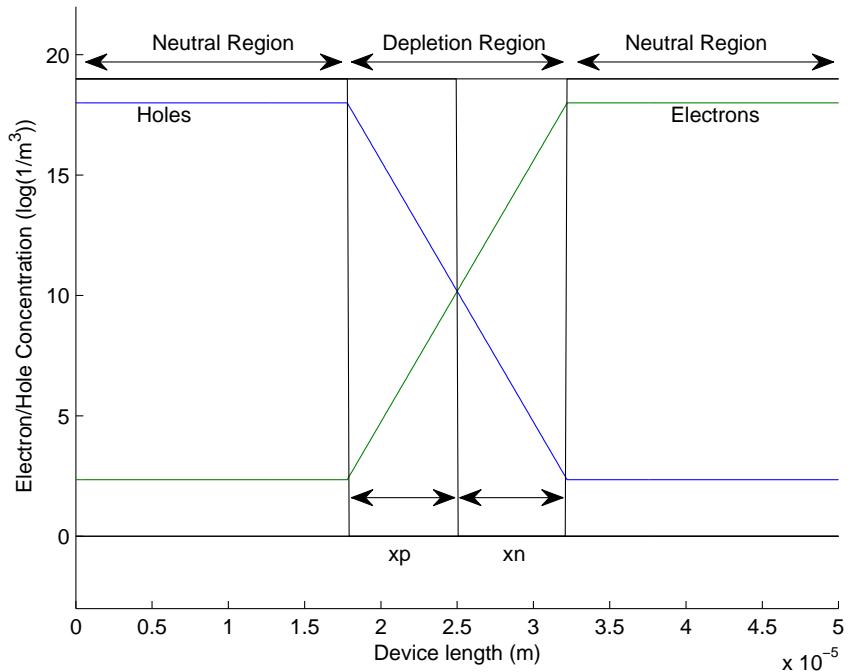


FIGURE 2.4: PN junction electron/hole density

In this example an analytical solution for an abrupt p-n junction will be derived. To get a solution for this problem depletion region approximation will be used. This approximation starts by assuming that the charges are fully depleted around the junction. All the electric field is confined in the depletion region and regions far away from the junction are neutral. Based on this the net charge density over the entire region is:

$$\frac{d\vec{E}}{dx} = \frac{\rho}{\varepsilon} = \frac{q}{\varepsilon}(-N_A + N_D) \quad (2.52)$$

$$\rho = \begin{cases} 0 & \text{for } x < -x_p \\ -qN_A & \text{for } -x_p \leq x \leq 0 \\ qN_D & \text{for } 0 \leq x \leq x_n \\ 0 & \text{for } x > x_n \end{cases} \quad (2.53)$$

The electric field over the entire region can be calculated by integrating ρ .

$$E = \begin{cases} \int \frac{-qN_A}{\varepsilon} dx + C_1 & \text{for } -x_p \leq x \leq 0 \\ \int \frac{qN_D}{\varepsilon} dx + C_2 & \text{for } 0 \leq x \leq x_n \end{cases} \quad (2.54)$$

It is possible to solve for C_1 and C_2 since electric field must go to zero at x_p and x_n .

$$E(x = -x_p) = 0 \Rightarrow C_1 = \frac{-qN_A}{\varepsilon}x_p \quad (2.55)$$

$$E(x = x_n) = 0 \Rightarrow C_2 = \frac{qN_D}{\varepsilon}x_n \quad (2.56)$$

Then $E(x)$ becomes:

$$E(x) = \begin{cases} \frac{-qN_A}{\varepsilon}(x + x_p) & \text{for } -x_p \leq x \leq 0 \\ \frac{qN_D}{\varepsilon}(x - x_n) & \text{for } 0 \leq x \leq x_n \end{cases} \quad (2.57)$$

Additionally, the electric field must be continuous across the interface therefore the electric field in the p-type side and the n-type side must equal each other at the interface or when $x = 0$.

$$\frac{-qN_A}{\varepsilon}(x_p) = \frac{qN_D}{\varepsilon}(-x_n) \quad (2.58)$$

$$N_A x_p = N_D x_n \quad (2.59)$$

This equation makes physical sense since it states that the total charge on one side of the junction must be the same as the total charge on the other. In other words, the net charge on each side keeps the electric field confined to the depletion region.

To find the voltage as a function of distance, equation 2.13 can be integrated.

$$V(x) = \begin{cases} \int -E(x)dx = \int \frac{qN_A}{\varepsilon}(x + x_p)dx = \frac{qN_A}{\varepsilon}(\frac{x}{2} + x_p) + C_3 & \text{for } -x_p \leq x \leq 0 \\ \int -E(x)dx = \int \frac{qN_D}{\varepsilon}(x - x_n)dx = \frac{qN_D}{\varepsilon}(-\frac{x}{2} + x_n) + C_4 & \text{for } 0 \leq x \leq x_n \end{cases} \quad (2.60)$$

The potential at one side of the junction can be set to zero. Defining the voltage on the p type side as zero, such that at $x = x_p$, $V=0$. This gives the constant C_3 as:

$$C_3 = \frac{qN_A}{2\varepsilon}x_p^2 \quad (2.61)$$

$$V(x) = \frac{qN_A}{2\varepsilon}(x + x_p)^2 \quad \text{for } -x_p \leq x \leq 0 \quad (2.62)$$

C_4 can be found by using the fact that the potential on the n-type side and p-type side are equal at the interface, such that:

$$V_p(x = 0) = \frac{qN_A}{2\varepsilon}x_p^2 = V_n(x = 0) = \frac{qN_A}{2\varepsilon}(x_n - \frac{x}{2})x + C_4 \quad (2.63)$$

$$C_4 = \frac{qN_A}{2\varepsilon}x_p^2 \quad (2.64)$$

Now an overall expression for $V(x)$ can be obtained.

$$V(x) = \begin{cases} \frac{qN_A}{\varepsilon}(x + x_p)^2 & \text{for } -x_p \leq x \leq 0 \\ \frac{qN_D}{\varepsilon}(-\frac{x}{2} + x_n)x & \text{for } 0 \leq x \leq x_n \end{cases} \quad (2.65)$$

The maximum voltage across the junction is at $x = x_n$, which is:

$$V_{bi} = \frac{q}{2\varepsilon}(N_D x_n^2 + N_A x_p^2) \quad (2.66)$$

Using (2.59) in the above equation and rearranging allows x_p and x_n to be determined.

They are:

$$x_n = \sqrt{\frac{2\varepsilon V_{bi}}{q} \frac{N_A}{N_D(N_D + N_A)}} \quad (2.67)$$

$$x_p = \sqrt{\frac{2\varepsilon V_{bi}}{q} \frac{N_D}{N_A(N_D + N_A)}} \quad (2.68)$$

The value of the built in potential can also be calculated using fermi levels of p and n doped materials.

$$E_{FN} - E_i = kT \ln\left(\frac{N_D}{n_i}\right) \quad (2.69)$$

$$E_i - E_{FP} = kT \ln\left(\frac{N_A}{n_i}\right) \quad (2.70)$$

E_{FN} and E_{FP} are fermi energy levels of electrons and holes respectively. The difference between the fermi levels divided by the single electron charge gives us the built in potential of the pn junction.

$$E_{FN} - E_{FP} = qV_{bi} = kT \ln\left(\frac{N_D}{n_i}\right) + kT \ln\left(\frac{N_A}{n_i}\right) = kT \ln\left(\frac{N_A N_D}{n_i^2}\right) \quad (2.71)$$

$$V_{bi} = \frac{kT}{q} \ln\left(\frac{N_A N_D}{n_i^2}\right) \quad (2.72)$$

The calculation of the built in potential completes all the necessary equations for the analytical solution of the pn junction without any external bias. Following graphs shows the plots of approximate solutions for net charge, electric field and the junction potential.

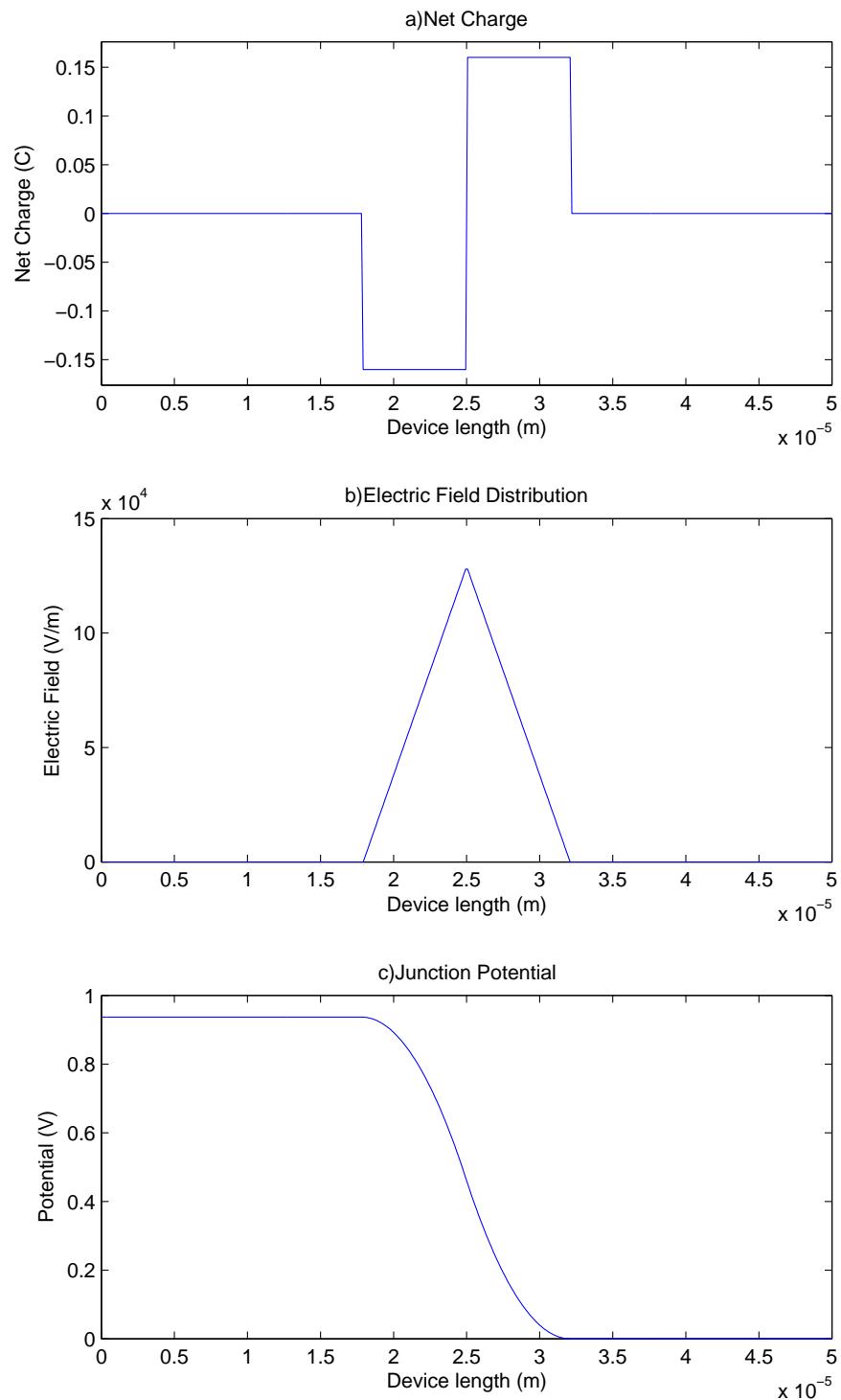


FIGURE 2.5: Approximate Solution of a PN Junction

Chapter 3

Numerical Solution of Drift-Diffusion Equation

As discussed in the introduction, physical memristor simulations are almost non existent. Memristor simulation developed in this thesis requires certain properties ,such as limitation of particle density or combination of 1-D and 2-D simulations, which may not be available in most commercial simulators. It is also possible that other unusual properties that are not studied in this thesis will be needed for further research. In this chapter a method for solving drift diffusion equations as well as Poisson's equation will be developed based on finite difference. This fully functioning simulator will have needed flexibility for current and future research opportunities.

3.1 Finite Difference Method

There are many different methods that can be used to solve drift diffusion equations such as finite elements, finite difference or meshless methods. Finite difference was chosen as an appropriate method for this thesis due to its simplicity which allows straightforward implementation of unusual physical properties. Finite difference uses an approximation for the derivative of a function based on the mathematical definition of the derivative.

$$\frac{df}{dx} = \lim_{h \rightarrow 0} \frac{f(x + h) - f(x)}{h} \quad (3.1)$$

It is possible to obtain a numerical approximation for the first derivative by dropping the limit and assuming that h is small enough to get a value for the derivative reasonably close to the actual value. As h gets smaller the approximation becomes more and more accurate. The difference between the calculated value and the real value is called the truncation error and it is captured using $O(h^n)$ notation. n signifies the order of h which determines how fast the approximation is approaching the real solution as h decreases.

$$\frac{df}{dx} = \frac{f(x+h) - f(x)}{h} + O(h) \quad (3.2)$$

It is possible to uniformly discretize the entire region over which a function is defined in order to calculate its derivative. The first step is the division of the region over which the function is defined into $n-1$ segments. This creates n number of points. Then the length of each segment is defined using the following relationship:

$$h = \frac{L}{n} \quad (3.3)$$

A function is defined at the edge of every segment. All the points can be labeled consecutively, $x_0, x_1, x_2 \dots x_{n-1}$ where $x_i = ih$. The function is discretely defined on $f_i = f(x_i)$ where $i=0,1,2..n-1$. It is possible to use equation 3.2 to discretely calculate the first derivative of the function with respect to x .

$$\frac{df(x_i)}{dx} = \frac{f(x_{i+1}) - f(x_i)}{h} + O(h) \quad (3.4)$$

Above equation is called forward difference because the derivative for point x_i was calculated using the point that is coming right after it, x_{i+1} .

$$f'_i = \frac{f_{i+1} - f_i}{h} + O(h) \quad (3.5)$$

Forward difference is not the only way to calculate a discrete derivative. Here are a few other ways calculate the same derivative by making use of different points.

$$f'_i = \frac{f_i - f_{i-1}}{h} + O(h) \quad (3.6)$$

$$f'_{i+\frac{1}{2}} = \frac{f_{i+1} - f_i}{h} + O(h^2) \quad (3.7)$$

Equation 3.6 is called backward difference and equation 3.7 is called central difference. One important aspect to note here is that in the central difference formula the derivative falls exactly in the middle of two points. It also gives more accurate results using the same number of points as forward and backward difference.

Using finite difference formulas it is possible to construct higher derivatives. A formula for a second order derivative at point x_i using central difference can be calculated using first order derivative on $x_{i-\frac{1}{2}}$, x_i and $x_{i+\frac{1}{2}}$

$$f'_{i+\frac{1}{2}} = \frac{f_{i+1} - f_i}{h} \quad (3.8)$$

$$f'_{i-\frac{1}{2}} = \frac{f_i - f_{i-1}}{h} \quad (3.9)$$

$$f'_i = \frac{f_{i+\frac{1}{2}} - f_{i-\frac{1}{2}}}{h} \quad (3.10)$$

Second order derivative is constructed by taking the second derivative of the last function. Then equations 3.8 and 3.9 is placed into 3.10.

$$f''_i = \frac{f'_{i+\frac{1}{2}} - f'_{i-\frac{1}{2}}}{h}$$

$$f''_i = \frac{\frac{f_{i+1}-f_i}{h} - \frac{f_i-f_{i-1}}{h}}{h}$$

$$f_i'' = \frac{f_{i+1} - f_i - f_i + f_{i-1}}{h^2}$$

Second order derivative takes the following form:

$$f_i'' = \frac{f_{i+1} - 2f_i + f_{i-1}}{h^2} + O(h^2) \quad (3.11)$$

Overall these finite difference equations are enough to solve drift diffusion equations. Even though all the derivations were done in 1-D it is trivial to extend them to higher dimensions. This method can be used to solve Poisson's equation and drift diffusion equations.

3.2 Poisson Solver

Poisson's equation needs to be solved before drift diffusion equations in order find the potential distribution as well as the electric field inside the device. In order to solve for electric field and potential Poisson's equation is simplified through assumptions and then finite difference is used to solve this simplified equation. The first step of simplification is assuming that the permittivity is isotropic.

$$\nabla \cdot (\varepsilon \nabla V) = -\rho \quad (3.12)$$

$$\nabla \cdot (\varepsilon \nabla V) = \varepsilon \nabla^2 V \quad (3.13)$$

Dividing both sides by permittivity and expanding the left hand side,,

$$\nabla^2 V = -\frac{\rho}{\varepsilon} \quad (3.14)$$

$$\nabla^2 V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} \quad (3.15)$$

After discretizing electric potential over a 2-D uniform grid and using the second order central finite difference formula (3.11) laplacian of the electric potential can be calculated using:

$$\nabla^2 V_{i,j} = \frac{V_{i+1,j} - 2V_{i,j} + V_{i-1,j}}{\Delta x^2} + \frac{V_{i,j+1} - 2V_{i,j} + V_{i,j-1}}{\Delta y^2} \quad (3.16)$$

Since the grid is uniform the distance between two nodes in x and y directions are equal therefore only one variable is need for distance between two points.

$$\Delta = \Delta x = \Delta y \quad (3.17)$$

Net charge density and the permittivity is also discretized over the same uniform mesh. Discretized form of Poisson's equation is generated by combining equations 3.14 ,3.16 and 3.17.

$$\nabla^2 V_{i,j} = \frac{V_{i-1,j} + V_{i,j-1} - 4V_{i,j} + V_{i+1,j} + V_{i,j+1}}{\Delta^2} = -\frac{\rho_{i,j}}{\varepsilon_{i,j}} \quad (3.18)$$

This equation can be rearranged into the form below:

$$\varepsilon_{i,j}(V_{i-1,j} + V_{i,j-1} - 4V_{i,j} + V_{i+1,j} + V_{i,j+1}) = -\Delta^2 \rho_{i,j} \quad (3.19)$$

Equation 3.19 is valid for almost all the nodes in the system except two cases, boundary nodes and interface nodes. There are two different types of boundary conditions. The first one is Dirichlet boundary condition which forces a particular value for the potential at the boundary.

$$V_{i,j} = V_b \quad (3.20)$$

Where V_b is the value of the potential at the boundary. The other possible boundary condition is called Neumann boundary condition which states that the derivative of the potential at the boundary is zero. This gives the following equation:

$$\frac{\partial V}{\partial x} = \frac{V_{i+1,j} - V_{i,j}}{\Delta} = 0 \quad (3.21)$$

So for a boundary over y axis:

$$V_{i+1,j} = V_{i,j} \quad (3.22)$$

Neumann boundary condition over x axis is obtained using the same procedure.

$$V_{i,j+1} = V_{i,j} \quad (3.23)$$

Combining the equations above (3.19, 3.20, 3.21 and 3.22) it is possible to turn Poisson's equation, which is a second order differential equation, into a linear equation.

$$D_2 \vec{V} = -\Delta^2 \vec{\rho} - \vec{V}_b \quad (3.24)$$

One can easily get the potential distribution by simply solving the matrix equation obtained by using finite difference. Due to the nature of the problem resulting matrix is quite sparse and using a sparse LU decomposition dramatically increases the computational efficiency.

$$\vec{V} = D_2^{-1}(-\Delta^2 \vec{\rho}_{i,j} - \vec{V}_b) \quad (3.25)$$

After solving for the potential distribution it is straightforward to calculate the electric field distribution discretely using the relationship between electric field and electric potential (2.13) and central difference equation (3.7).

$$E_{i,j}^x = -\frac{V_{i+1,j} - V_{i-1,j}}{2\Delta} \quad (3.26)$$

$$E_{i,j}^x = -\frac{V_{i,j+1} - V_{i,j-1}}{2\Delta} \quad (3.27)$$

3.3 Current Density Equations

Both drift and diffusion currents can be calculated over the entire grid. Drift current does not involve any differentials but it is a function of electric field and the diffusion current can be calculated using first order central difference. The current density is calculated in such a way that it falls between two points which simplifies the application of the boundary conditions.

$$J_{i+\frac{1}{2},j,k}^x = q\mu_n n_{i+\frac{1}{2},j,k} E_{i+\frac{1}{2},j,k}^x + D_n \frac{n_{i+1,j,k} - n_{i,j,k}}{\Delta} \quad (3.28)$$

The electric field was calculated exactly on the nodes and linear interpolation was used in order to get a value between the nodes. Same argument is also valid for particle densities p and n . They were defined on the nodes but they were linearly interpolated to be used in current density equations.

$$\begin{aligned} n_{i+\frac{1}{2},j,k} &= \frac{n_{i+1,j,k} + n_{i,j,k}}{2} \\ E_{i+\frac{1}{2},j,k}^x &= \frac{E_{i+1,j,k}^y + E_{i,j,k}^y}{2} \end{aligned}$$

Current density in y direction is calculated following the same method:

$$\begin{aligned} J_{i,j+\frac{1}{2},k}^y &= q\mu_n n_{i,j+\frac{1}{2},k} E_{i,j+\frac{1}{2},k}^y + D_n \frac{n_{i,j+1,k} - n_{i,j,k}}{\Delta} \quad (3.29) \\ n_{i,j+\frac{1}{2},k} &= \frac{n_{i,j+1,k} + n_{i,j,k}}{2} \\ E_{i,j+\frac{1}{2},k}^y &= \frac{E_{i,j+1,k}^y + E_{i,j,k}^y}{2} \end{aligned}$$

3.3.1 Boundary Conditions

For a drift diffusion problem there are few different possibilities for boundary conditions. The first one is when the particles cannot go past through a certain boundary, no flow boundary condition. This can be achieved by using Dirichlet boundary condition and

setting the flow at the boundary to zero.

$$J = 0 \quad (3.30)$$

For memristor simulation this boundary condition is used to conditionally limit the lithium density. The implementation of the limiting process is discussed in detail and tested thoroughly in section 4 of chapter 4. Dirichlet boundary condition is also used for metal contacts. It is assumed that metal contacts have infinite amount of positive and negative charge and the boundary is always charge neutral. For example for holes, electrons, positive and negative doping it is assumed that at the boundary positive charge concentration will be equal to the negative charge concentration.

$$N_D + p = N_A + n \quad (3.31)$$

For a semiconductor holes and electrons have to obey mass action law.

$$np = n_i^2 \quad (3.32)$$

n_i is the concentration of the semiconductor at equilibrium before getting doped. Solving (3.32) and (3.31) together results in the equation below:

$$n = \frac{1}{2}(N_D - N_A + \sqrt{(N_D - N_A)^2 + 4n_i^2}) \quad (3.33)$$

Once electron concentration is obtained it is possible to calculate the hole concentration using mass action law.

$$p = \frac{n_i^2}{n} \quad (3.34)$$

During simulation, the application of this boundary condition differs from the no flow boundary which was applied implicitly. All the boundaries are simulated using a no flow

condition but their values are set to the appropriate value at the end of every time step. Lack of charge is compensated and excess charge is taken off by the metal contact. The difference between the boundary value of the charge density and its actual value is used to calculate the derivative of the current density with respect to time. Current in and out of the device is calculated by integrating the derivative of the current density over time.

$$\frac{dn}{dt} = \frac{n_{cr} - n_{ct}}{\Delta t} \quad (3.35)$$

n_{cr} is the excess carrier density and n_{ct} is the equilibrium carrier density at the contact. Using these boundary conditions for holes and electrons and the following two equations it is possible to calculate incoming and outgoing currents.

$$Q = An \quad (3.36)$$

$$I = \frac{dQ}{dt} \quad (3.37)$$

Equation 3.36 is an approximate relationship between charge and charge density where Q is total charge, A is the area holding that charge. Equation 3.37 is simply the general definition of current. By combining these two equations it is possible to derive a formula for calculating current at any metal contact.

$$I = A \frac{dn}{dt} \quad (3.38)$$

3.3.2 Continuity Equation

Continuity equation is needed to calculate a transient solution for drift diffusion equations. The equation is simple to discretize using finite difference method. There are two terms that need to be discretized, a first order derivative in time and a first order derivative in space. First the divergence term in equation (2.10) needs to be evaluated.

$$\nabla \cdot J = \frac{\partial J}{\partial x} + \frac{\partial J}{\partial y} = \frac{dJ_x}{dx} + \frac{dJ_y}{dy} \quad (3.39)$$

It is possible to replace the derivative with central finite difference terms.

$$\frac{dJ_x}{dx} = \frac{J_{i+\frac{1}{2},j,k}^x - J_{i-\frac{1}{2},j,k}^x}{h} \quad (3.40)$$

$$\frac{dJ_y}{dy} = \frac{J_{i,j+\frac{1}{2},k}^y - J_{i,j-\frac{1}{2},k}^y}{h} \quad (3.41)$$

$$\nabla \cdot J_{i,j,k} = \frac{J_{i+\frac{1}{2},j,k}^x - J_{i-\frac{1}{2},j,k}^x}{h} + \frac{J_{i,j+\frac{1}{2},k}^y - J_{i,j-\frac{1}{2},k}^y}{h} \quad (3.42)$$

This is the general form of the divergence of the current density. Placing current density formulas in equation 3.42 and collecting all the terms in a matrix gives rise to the following equation:

$$\nabla \cdot J_k = B \quad (3.43)$$

The time derivative can also be replaced by a forward or backward finite difference terms respectively.

$$\frac{\partial \vec{n}_k}{\partial t} = \frac{\vec{n}_{k+1} - \vec{n}_k}{\Delta t} \quad (3.44)$$

$$\frac{\partial \vec{n}_k}{\partial t} = \frac{\vec{n}_k - \vec{n}_{k-1}}{\Delta t} \quad (3.45)$$

It is possible to find a numerical transient solution for the drift-diffusion problem by combining finite difference form of the time derivative ((3.44) or (3.45)) and the divergence of the current density equations (3.43).

Forward difference approximation can be used to get an explicit solution for continuity equation.

$$\frac{\vec{n}_{k+1} - \vec{n}_k}{\Delta t} = B$$

$$\vec{n}_{k+1} = \vec{n}_k + \Delta t B \quad (3.46)$$

Both forward and backward difference formulas work sequentially in order to generate a transient solution. Solution from the previous time step is needed to calculate the next time step. Forward difference gives an explicit solution which has few advantages. This solution can be implemented, without forming any matrices by directly calculating the divergence of the current density for each node and then marching through time using equation 3.46. Additionally, unlike backward difference, there are no equations to be solved for every time step. These two properties ease the computational load of the problem and speed up the solution process. Unfortunately this scheme has very strict stability conditions which has to be met in order to get produce solution.

Backward difference can be used instead of forward difference to get an implicit solution.

$$\frac{\vec{n}_k - \vec{n}_{k-1}}{\Delta t} = \frac{1}{q}(qB)$$

$$\vec{n}_k - \Delta t B = \vec{n}_{k-1}$$

Since all the equations in B matrix are linear n can be taken and out of the parenthesis ($B = Cn$).

$$\vec{n}_k - \Delta t C \vec{n}_{k-1} = \vec{n}_{k-1}$$

$$\vec{n}_k = (I - \Delta t C)^{-1} \vec{n}_{k-1} \quad (3.47)$$

This solution needs a matrix inversion every time step but it is unconditionally stable if not used together with Poisson's equation. The decision to use implicit or explicit solution is not very simple and it will be discussed in detail the next section.

3.4 Stability and Computational Efficiency

Before discussing numerical limitations of solving drift diffusion equation via finite difference it is important to look into physical limitations of the problem. These limitations persist no matter what kind of numerical scheme is employed to solve drift diffusion equations.

3.4.1 Physical Limitations

Debye length is the length over which mobile charge carriers screen out an external electric field. It determines how steeply charges will accumulate over a certain distance when subject to an electric field.

$$L_D = \sqrt{\frac{\varepsilon V_{th}}{qn}} \quad (3.48)$$

Debye length limits how coarse the grid can be since the distribution of charge density needs to be accurately captured. As it can bee seen from the formula above the higher the charge density is the steeper the charge will accumulate. This can become a major problem for device sizes in millimetre range and high charge concentrations since the mesh density needs to be extremely high.

The amount if time it takes for charge fluctuations to disappear is called Dielectric relaxation time. It limits the maximum time step of a simulation since the fluctuations that are not properly resolved over time will make the simulation unstable.

$$t_{dr} = \frac{\varepsilon}{qn\mu} \quad (3.49)$$

Dielectric relaxation time is only important when electric potential is highly affected by redistribution of charge over time. Otherwise it has minimal impact on the stability of the problem.

3.4.2 Numerical Limitations

There are also numerical limits which can affect convergence and stability of a solution when using an explicit scheme. These are called Courant-Friedrichs-Lowy (CFL) conditions. CFL conditions for pure diffusion and pure drift are shown in the following equations.

$$\frac{\Delta^2}{2D_n} > \Delta t \quad (3.50)$$

Above condition is for pure diffusion and it restricts the maximum time step. Following condition is for drift dominated systems:

$$\frac{2\Delta}{\mu E} > \Delta t \quad (3.51)$$

This is the second numerical restriction on the simulation. The condition for drift depends on the electric field therefore it needs to be satisfied as the electric field changes over time during simulation.

Both physical and numerical constraints have to be evaluated and mesh density and time step need to be selected in order to satisfy all these conditions discussed above. Particularly mesh density have a very strong effect on the accuracy, stability and computational efficiency of the simulation. Increasing mesh density increases the computational time needed to calculate every time step since there are more points. Additionally because of the CFL condition for diffusion time step is related to the square of the mesh size. This means that maximum allowed step size decreases much quicker than the mesh density. Also, increasing charge density can decrease the maximum mesh size to a very small value. This can be fixed by using a non uniform mesh which can dramatically decrease the amount points needed for the simulation. Unfortunately this is usually not very straightforward to implement in a finite difference scheme. Also small mesh size requires small time steps. This cannot be avoided through non uniform meshing. Numerical and physical constraints for memristor simulation are further discussed in chapter 5.

3.4.3 Explicit vs. Implicit Solution

Overall explicit and implicit solutions have their advantages and disadvantages. Choosing one over the other requires careful analysis of the problem. Implicit solution by itself is unconditionally stable therefore it can support very large time steps without any stability issues. However with increased time step, the accuracy of the transient solution decreases but the steady state solution does not get affected. So for steady state solutions it is better to use an implicit method which can reach steady state very quickly. This advantage disappears when particle densities are high enough to affect the electric field and Poisson's equation needs to be solved for every time step. In this scenario the maximum step size is determined by dielectric relaxation time which can be around the same order as CFL conditions or even smaller. Now since the time step is going to be around the same order for both implicit and explicit methods it is reasonable to use the explicit one because it is computationally less expensive.

Usually implicit solution is preferable when there is no coupling between Poisson's equation and drift diffusion equations and the transient response is not very important. Explicit solution have an edge over the implicit solution due to its lower computational resource requirement when the equations are coupled and the time steps for both schemes are restricted to fairly small values. For memristor simulation, drift diffusion equations are strongly coupled with Poisson's equation. For this reason all memristor simulations in this thesis use explicit time stepping.

3.5 Simulation Procedure

Different equations and schemes that are used to solve drift diffusion and Poisson's equation was shown over the past few sections. Using all this information it is possible create a general approach to solve a drift diffusion problem.

The geometry and physical properties of the problem as well as all initial and boundary conditions need to be defined at the beginning of the solution process. Initialization sets up the first time step of the problem at $t = 0$. Once this first step is done it is possible generate required vectors and matrices and solve the problem for the next time steps, $t = t_i$.

The solution process starts by solving Poisson's equation using the charge distribution at current time step. Once it is solved, the electric field distribution is calculated and used in drift diffusion equations to calculate current density distribution. Next explicit time stepping is used to determine carrier density in the next time step. Finally once the carrier distribution for the next step is calculated it is possible check for a stopping criterion. If this criterion is not met then the whole process will start all over again with a small difference. If the charge concentration is so small that the equations are decoupled then it is possible to skip solving Poisson's equation for the rest of the simulation which speeds up the solution process.

There are two different criteria that can be used to decide whether to finalize the simulation process or not. The simulation can stop if it reaches a certain time point. This is quite simple since the current time can be checked and if it is equal or greater than the required simulation time then the simulation can be stopped. It is also possible to simulate until the simulation reaches steady state. This can be determined by comparing the current carrier distributions with distribution at the previous time step. If the difference is very small then the time derivatives of the carrier densities are very close to zero and the simulation has reached steady state therefore the simulation process can be stopped. The flowchart in figure 3.1 summarizes the solution procedure.

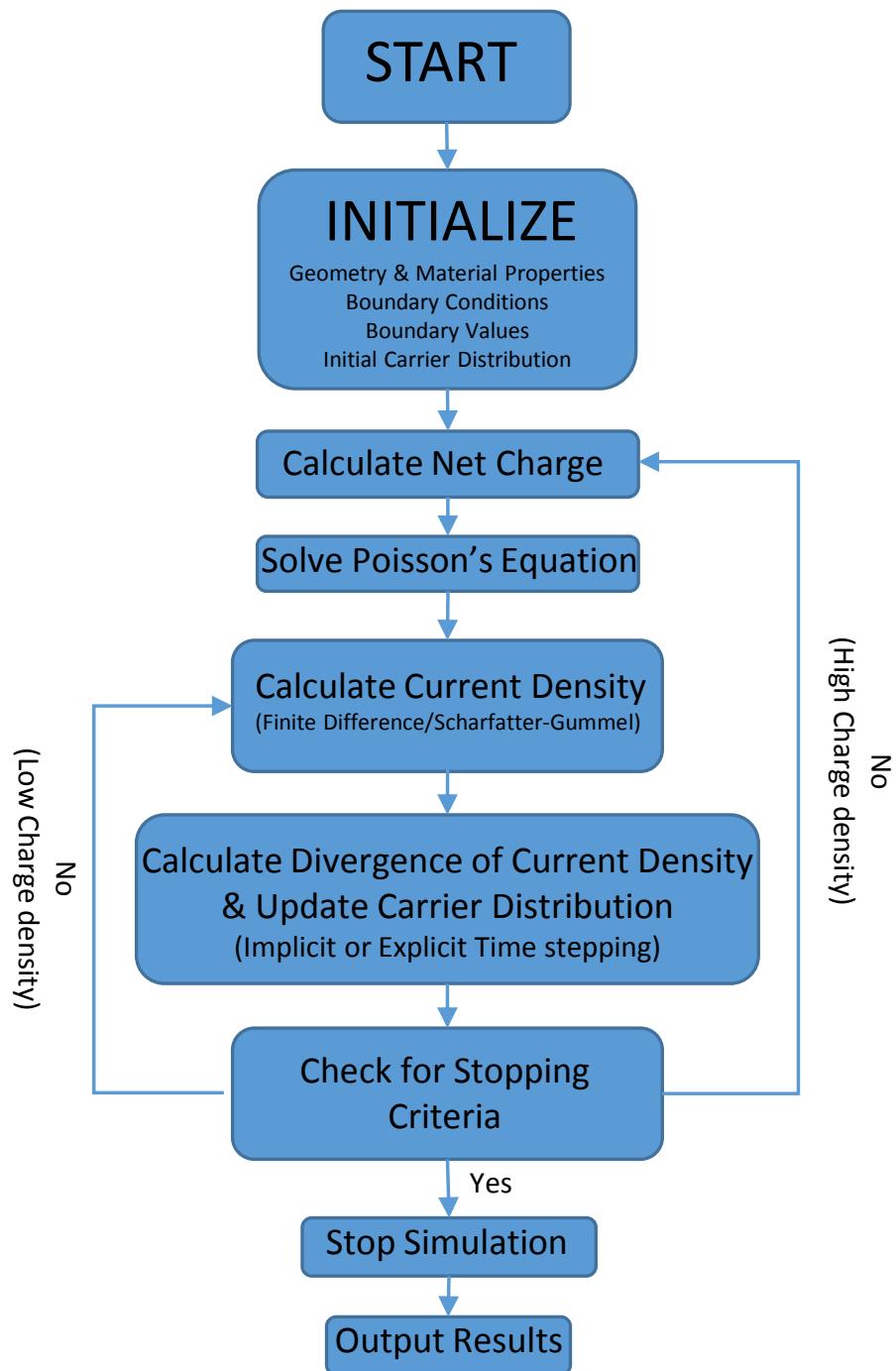


FIGURE 3.1: Finite Difference Drift-Diffusion Scheme Flowchart

Chapter 4

Testing Drift Diffusion Solver

Past chapter went through the details of how to solve drift-diffusion and Poisson's equation using finite difference method. In this chapter steady state and transient analysis for drift diffusion equations using finite differnce is compared to analytical solutions as well as a commercially available simulator called 'COMSOL Multiphysics' which uses finite element method instead of finite difference. Following test cases were made to ensure that the key parts of the finite difference scheme runs properly and does not produce unexpected results.

4.1 Solution for Closed Boundary

In this section the accuracy of the finite difference solution in steady state will be tested. In order to do this simple 1-D problem with a finite number of negatively charged particles over a certain distance subject to constant electric field is used. This is the same problem that was solved analytically in section 3.3.1. It is also assumed that the charge density is very low and does not affect the electric field. Both ends of the simulation domain have no flow boundary conditions for charged particles. The solution process requires an initial distribution for charge density over the area. For this problem the density of the negative particles was initialized to be uniform over the entire region.

Since the differential equations are uncoupled solving Poisson's equation only once is sufficient to determine the electric field over the course of the entire simulation. Figures

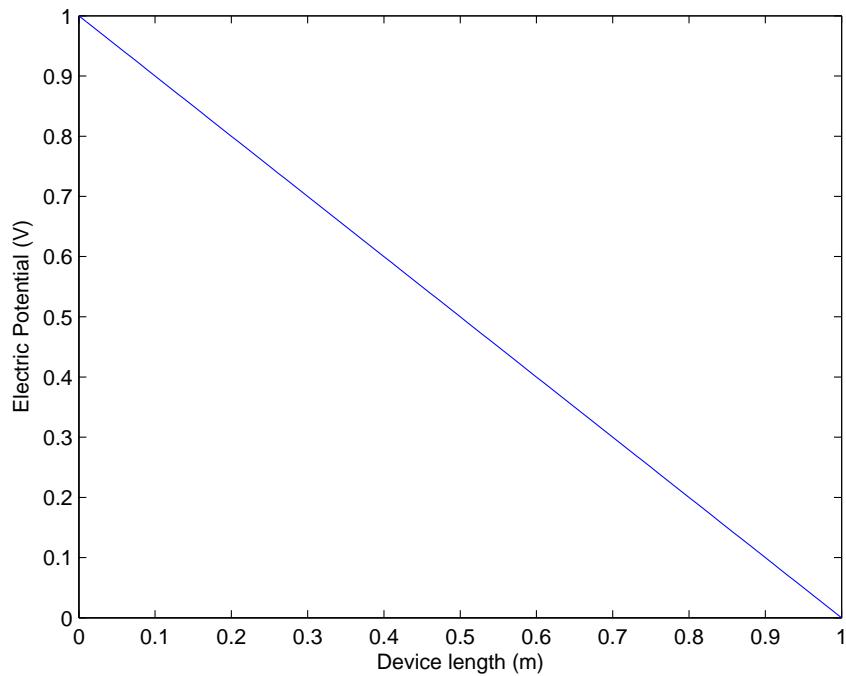


FIGURE 4.1: Potential Distribution

[4.2](#) and [4.1](#) show the potential and the electric field distribution over the entire simulation area calculated from Poisson's equation using finite difference.

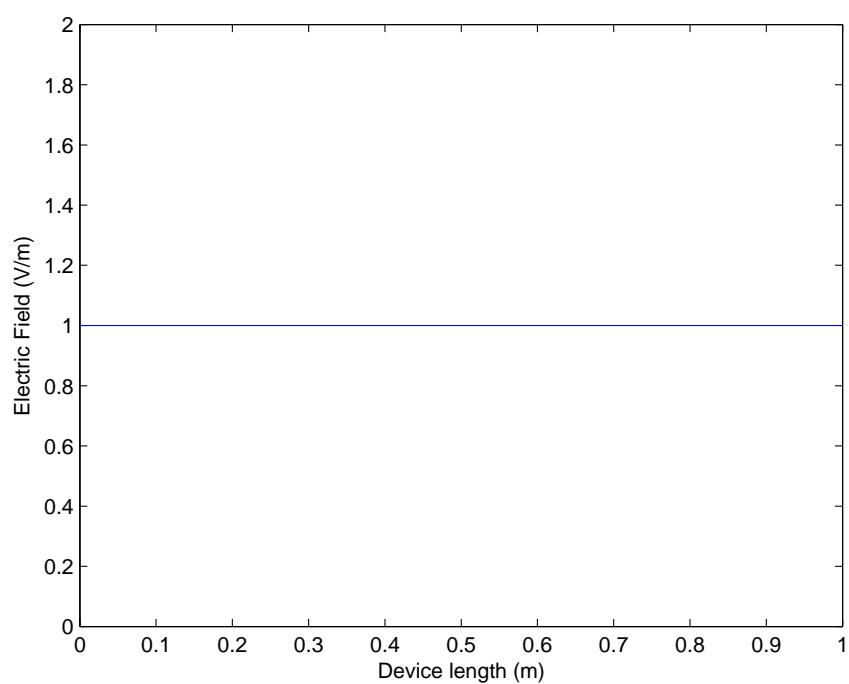


FIGURE 4.2: Electric Field Distribution

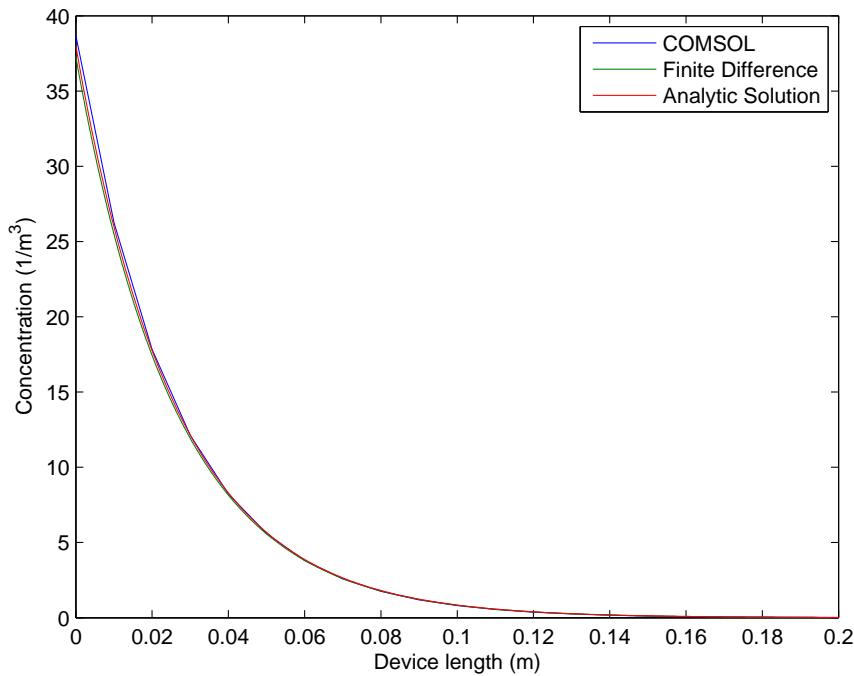


FIGURE 4.3: Steady State Negative Charge Density

Figure 4.3 has two simulation results as well as the exact solution of this problem. The green line represents the result given by the finite difference method at steady state. It can be seen from the graph that the steady state solution generated by both COMSOL and finite difference matched the analytical solution.

While deriving an analytical solution for this problem it was assumed that at steady state the drift current density must be equal to the diffusion current density. In figure 4.4 we see drift and diffusion current densities in log scale. Overall both currents match quite tightly.

Even though the simulation results are good for this example high electric fields due to either applied potential or high charge densities can introduce inaccuracies. If the electric field is very high then the accumulation of the charge can get very steep. The exponential accumulation requires higher mesh densities for accurate calculation.

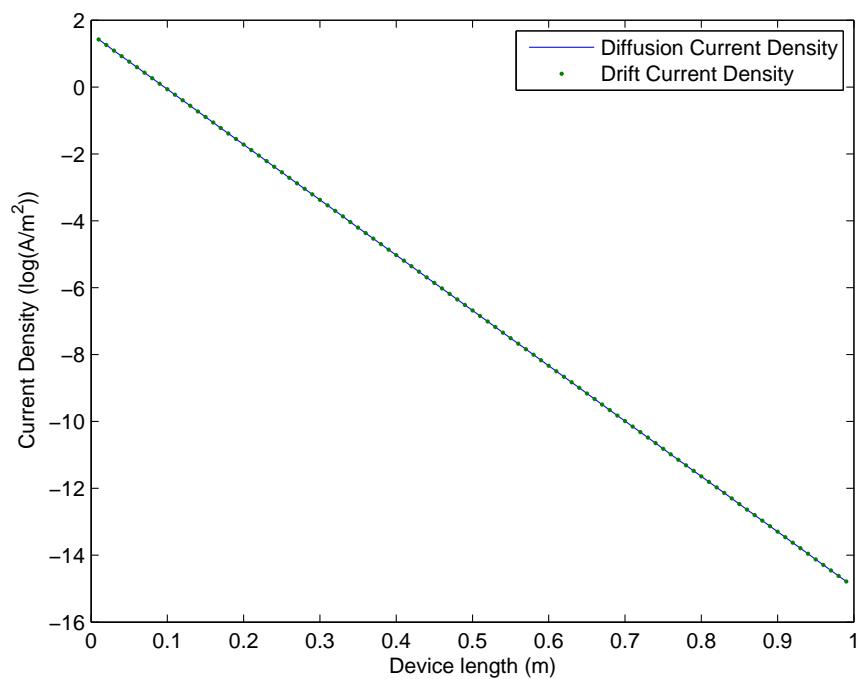


FIGURE 4.4: Finite Difference Drift and Diffusion Current Densities

4.2 Solutions for Open Boundary

Another crucial aspect of drift-diffusion simulation is its transient response. Like the previous test case, the analytic solution can be used to test the accuracy of the transient response. Two different analytic solutions for a similar drift diffusion problems which involved infinite boundaries and a uniform electric field were generated in section 3.3.2. The only difference between two cases are their initial carrier distributions. One has a rectangular and the other one has a gaussian initial carrier distribution. Finite difference scheme does not allow simulation over an infinitely long conductor. For this test case, simulation will only be carried until the carrier distribution gets close to a wall.

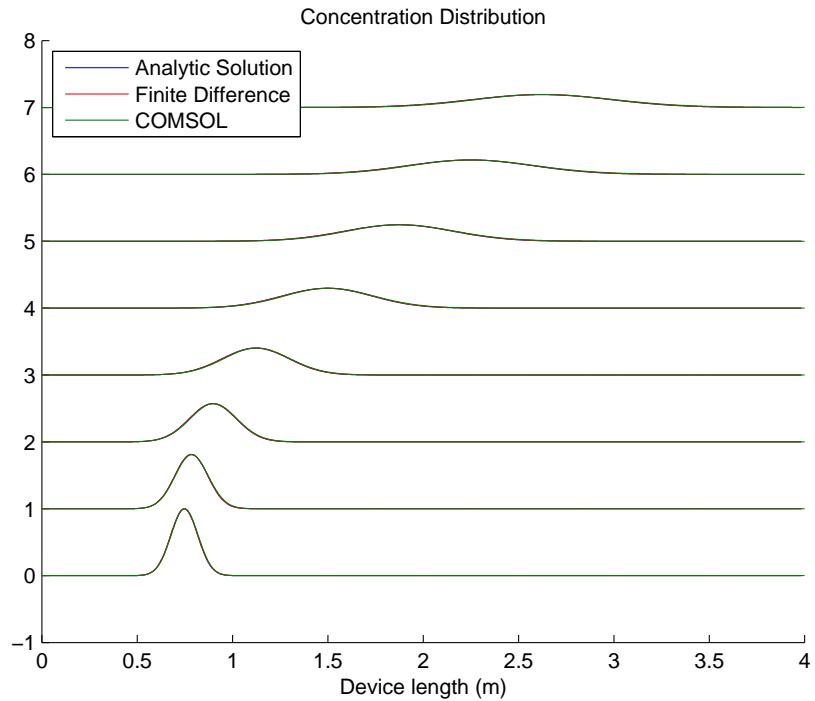


FIGURE 4.5: Gaussian Carrier Distribution Evolving Over time

Figure 4.5 has the transient response from COMSOL, finite difference and analytical solution. Snapshots of the carrier distributions were taken for each method at different time steps and they were superposed on top of each other. Increasing levels on y axis represent a carrier distributions at a different time starting from the bottom and moving forward in time towards the top. Figure 4.5 has a gaussian initial carrier distribution. It can be seen from that the transient solution generated by both COMSOL and finite difference are quite close to the analytical solution.

4.3 PN Junction

In previous test cases, Poisson's equation was not coupled with drift diffusion equations. In this example both drift diffusion and Poisson's equation will be tested to investigate how well they work when they are coupled together. A simple pn junction is quite adequate for this task since it has analytical solutions (under certain assumptions) for electric potential, electric field and carrier distribution.

For the simulation, initial hole and electron distributions were determined using mass action law and they were assumed to be constant at the boundaries. Keeping carrier density constant creates a mechanism in which the charge can move in and out of the simulation domain. If the charge density at any time step is higher than the fixed density then the difference will move out of the system. If there is a lack of charge at the boundary then carriers will move in to fill in the gap. Following figure (4.6) shows the final result of bringing p and n type materials together.

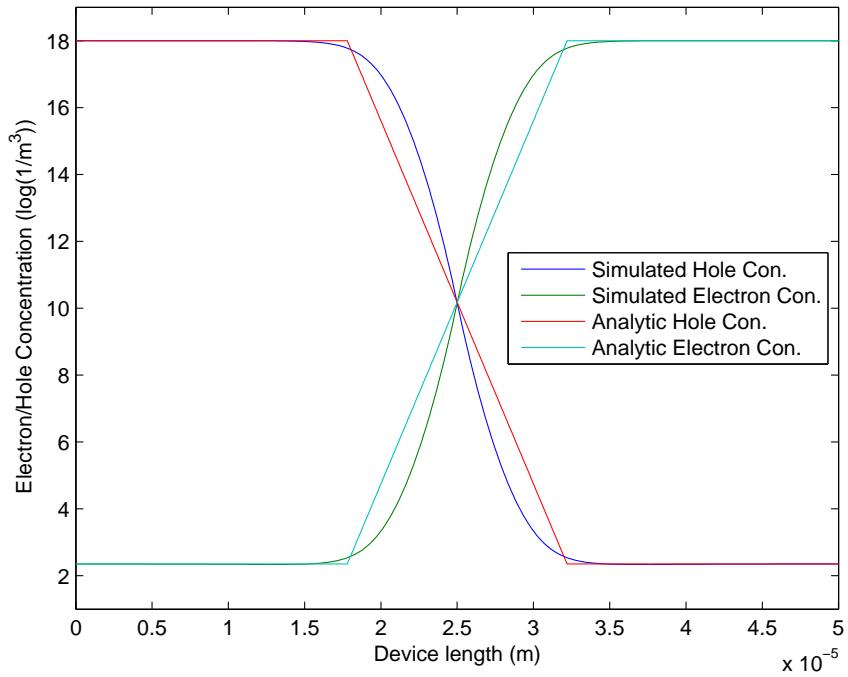


FIGURE 4.6: Electron/hole Concentration of a PN Junction

There is a little mismatch between simulated and analytic charge densities. Analytic

solution have sharp edges and simulated solution does not. This is due to all the assumptions made in order to find an analytic solution. This mismatch can also be seen for electric field, electric potential and net charge .

Figure 4.7 shows the potential distribution for simulated and analytic solutions. Close match in electric potential distribution shows that coupled equations can generate accurate solutions.

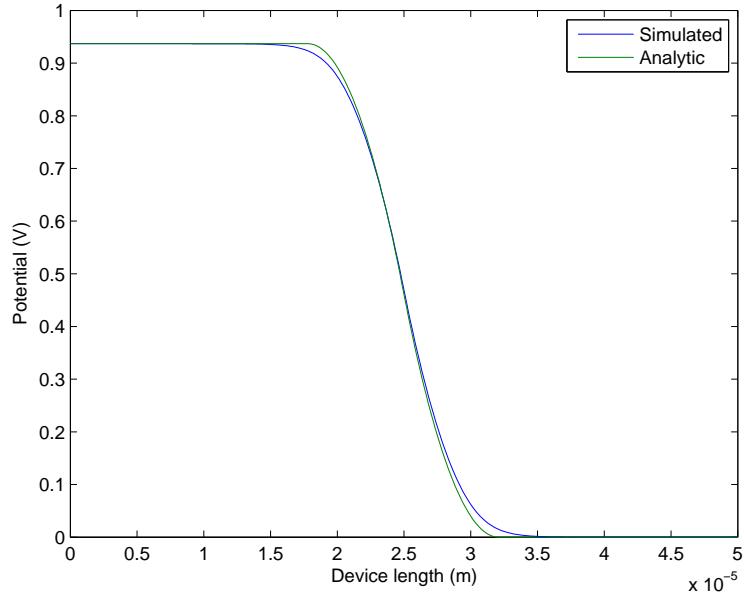


FIGURE 4.7: Potential Distribution of a PN Junction

Calculation of the electric field involves one basic derivative. Since simulated potential is matching the analytic solution quite nicely the electric field should follow a similar pattern. Figure 4.8 shows that this is indeed the case, simulated electric field matches the calculated electric field.

Figure 4.9 shows the total charge distribution at steady state. Simulated net charge density follows the analytic one except the abrupt changes at two ends.

This example showed that simulation of a system of coupled equations, drift diffusion and Poisson's equation, using finite difference can produce accurate results. This accuracy depends on the strength of the coupling. High charge densities will produce strongly coupled systems. This effect shows the importance of CFL conditions as well as physical limitations of the simulation.

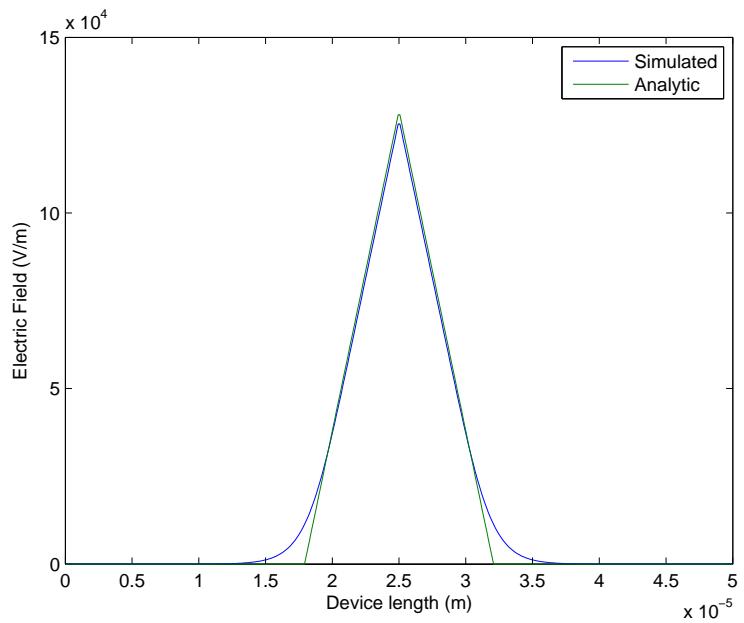


FIGURE 4.8: Electric Field Distribution of a PN Junction

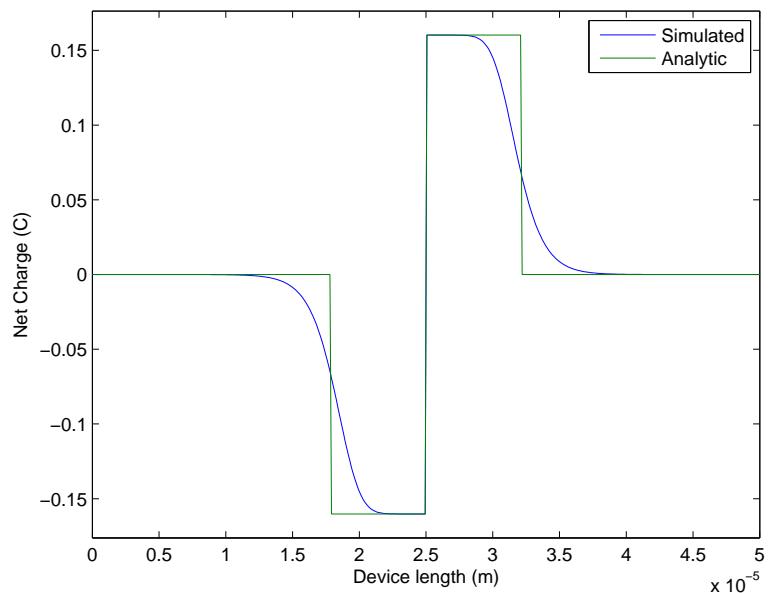


FIGURE 4.9: Total Charge Distribution of a PN Junction

4.4 Region Specific Particle Density Limit

The last property of the drift diffusion simulation scheme to be tested concerns the movement of lithium ions. As lithium ions move into the PEDOT:PSS they bond with PSS polymers and replace holes. PEDOT:PSS can only absorb lithium as long as there are available PSS polymers to bond with therefore PEDOT:PSS has limited capacity to accept lithium ions. This behavior can be captured during simulation by using a Dirichlet boundary condition ($J=0$) to stop the particle flow into a node if the density will go over a set limit. This can be achieved in two different ways.

A soft limit can be set by making particle mobility a function of its density. This function can be defined in such a way that it switches from high to a low value when the particle density approaches its limit. This implementation is straightforward and can be used in commercial simulators but it has a drawback. Once the particle density is reached the mobility and diffusivity of the lithium particles are stuck at very low values. If there is an outflux of particles from that particular node then the density is stuck at the limit until the mobility function goes back to a value which allows particle flow. This can introduce a considerable lag in the response of lithium current density.

An alternative approach is precalculating the particle density of a density limited node at the next time step, setting any influx to zero if the density is going to go over the limit and finally recalculating the particle densities at the next time step using the updated current densities. This mechanism sets a hard limit on the density since there is a sudden break instead of a gradual slowdown in the current flow. This density limiting mechanism is more responsive than the previous one but it requires the calculation of the next time step twice for the species that has a limit. Also large currents caused by either a big time step or high electric field can force the algorithm to cut the current flow into a node before the density reaches its limit.

To avoid adding any lag into the system latter method was chosen for memristor simulations in this thesis. This method was implemented in finite difference drift diffusion solver and it is tested in this chapter. Also a soft limit was implemented in COMSOL for comparison since it did not support the hard limit method.

In order to test density limiting method implemented for memristor simulation a simple example was set up. Two positively charged particles were initialized like the figure below (4.10). One set of particles has a concentration limit of $2 \times 10^{10} m^{-3}$ on the right half of the simulation area and no limit on the left half. The other set has no restrictions.

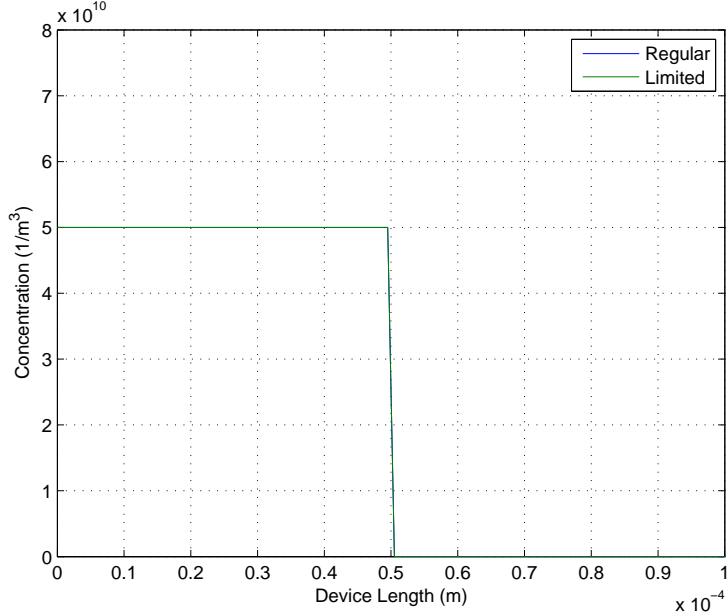


FIGURE 4.10: Initial Particle Density

This transient simulation was done using a potential train. The potential is applied at the left side of the device and the right side is always grounded. For the first half of the simulation applied potential was positive and for the second half it was negative. Figure 4.10 shows how two simulations differ when the particles are pushed towards the right wall due to the electric field created by the positive potential. Particles with no limit on the right side move freely and accumulate on the right side. The limit for the other particles is effectively stopping them from going in and accumulating freely. Once the limit is reached at a certain node the density cannot increase any further and that node turns into a no flow wall.

When the potential is switched all the particles accumulate freely to the left side of the simulation domain since there are no restrictions on this side (figure 4.12).

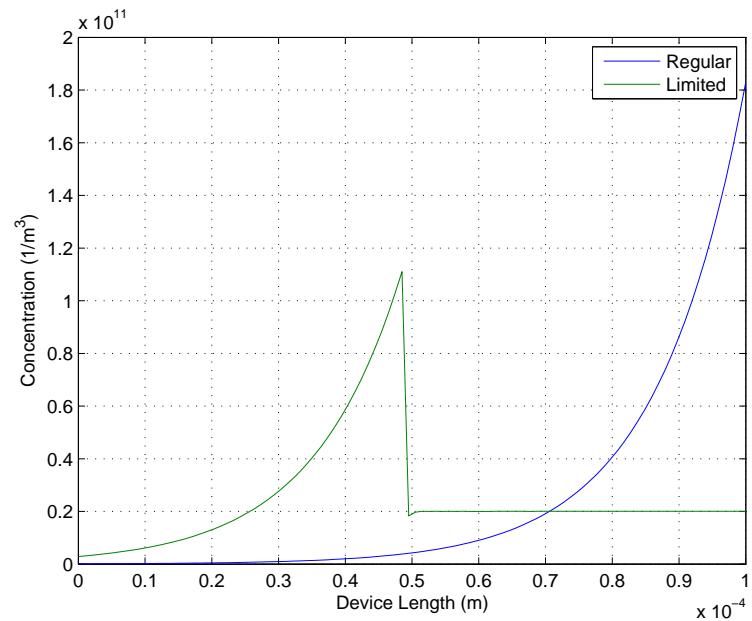


FIGURE 4.11: Limited Concentration Accumulation on the Right Side

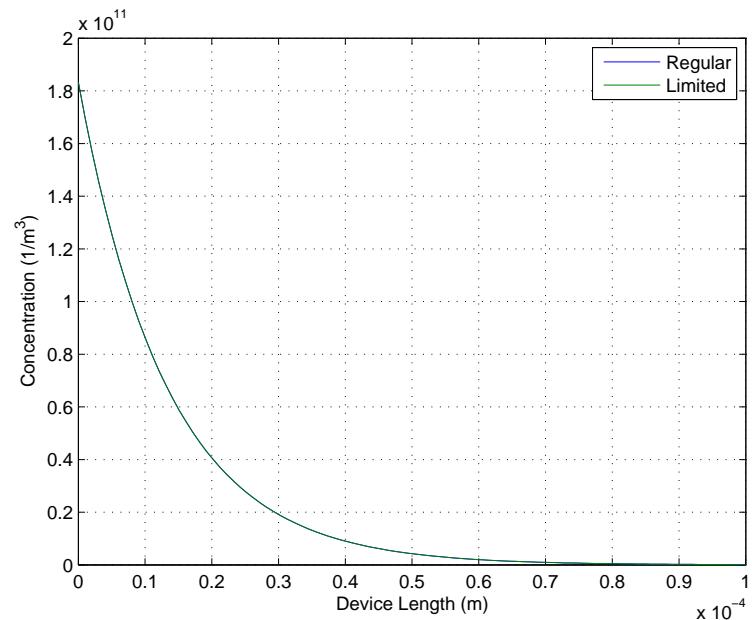


FIGURE 4.12: Limited Concentration Accumulation on the Left Side

This last figure (4.13) shows the transient response over time of a single node on the right side. The potential is positive for the first 1.5 seconds and it is switched to negative for the last 1.5 seconds. The node without limit keeps accepting charge until steady state has been reached but the node with a limit on stops accepting charged particles once the limit is reached. After the potential is switched density limited node has no problem releasing the particles.

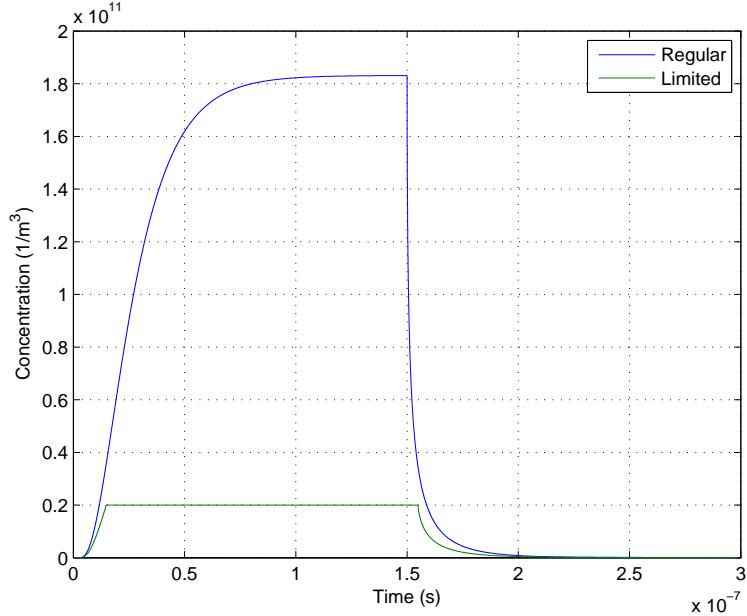


FIGURE 4.13: Accumulation at the right wall over time

Additional to the test that was run for finite difference, COMSOL was used to test the soft limiting mechanism. COMSOL does not have a built in option that allows limiting particle density. One possible solution to this is making particle mobility and diffusivity a function particle density. It is possible to use a sigmoid function which switches from 1 to 0 very quickly when particle density is close to its limit. Here is the equation of the sigmoid function used to limit the particle flow:

$$\mu = \frac{\mu_0}{1 + e^{\sigma(n - n')}} \quad (4.1)$$

μ_0 is the original mobility of the charge carrier. σ controls the sharpness of the switch and n' determines the density at which the switch will be.

Another problem with COMSOL was the definition of mobility and diffusion coefficients over different areas. If these constants are defined as one single value per area COMSOL simulates without any errors but if they are defined as a function of concentration it causes convergence issues. This can be overcome by using two more sigmoid functions to distinguish between two areas with different mobilities and diffusion constants. Left sigmoid in figure 4.14 was multiplied by the mobility/diffusivity of the left side of the area and the right sigmoid was multiplied by the mobility/diffusivity of the right side of the area. Both functions were summed to obtain a function which describes the characteristics of the entire area.

$$\mu = \frac{\mu_l}{1 + e^{\sigma_x(x-x')}} + \frac{\mu_r}{1 + e^{-\sigma_x(x-x')}} \quad (4.2)$$

In this problem μ_r is the same as equation 4.1 since the region on the right side has a particle density limit. A sharp switch between right and left side mobility using the function above would be ideal for this simulation but unfortunately it causes convergence issues in COMSOL therefore there is a gradual change between two mobilities.

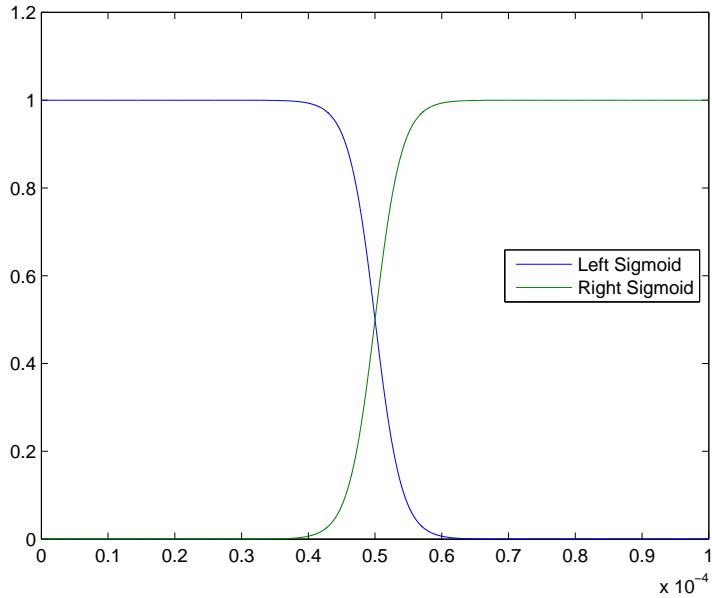


FIGURE 4.14: Mobility change from left to right side

The initial carrier distribution for COMSOL was set to be exactly the same as finite difference simulation. Figures 4.15 and 4.16 show results for both COMSOL and finite

difference simulations at steady state before the potential switch. The plot on the left side gives insight on how COMSOL simulation behaves for limited and limitless accumulation on the right wall. Due to the gradual change of mobility and diffusion constants between two areas we end up with concentration on the right side higher than the limit which is 2×10^{10} . Additionally, the particle density goes over its limit near the right wall. In figure 4.16 the difference between COMSOL and finite difference becomes more visible. In FD simulation the accumulation goes much higher due to higher electric field and unlike COMSOL it does not penetrate the right half of the simulation domain.

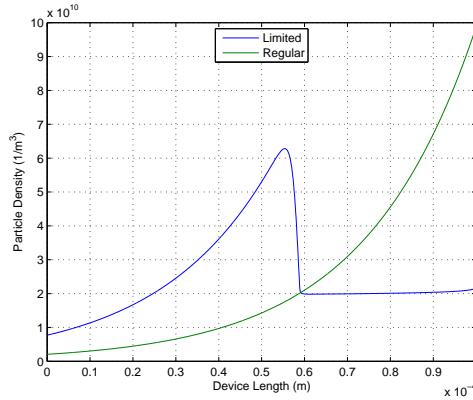


FIGURE 4.15: COMSOL Simulation for Particle Density Limit

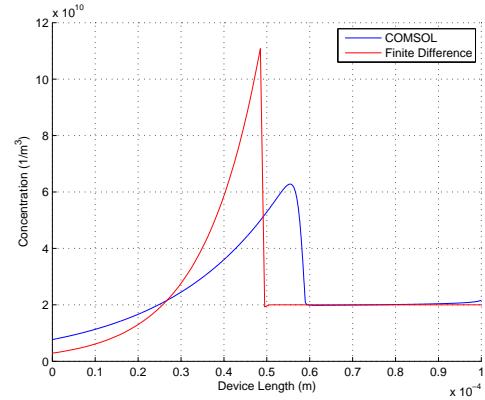


FIGURE 4.16: COMSOL and Finite Difference Simulation

In figure 4.17 it is possible to see the accumulation of charge near the middle after the potential is switched. This is due to mobility being a function of distance and concentration. As the ions move from left to right they go from a low mobility region to a high mobility region and they slowly accumulate around the area where the change in mobility occurs. Figure comparing both COMSOL and finite difference shows that the accumulation does not happen in the case of finite difference due to the way concentration limiting mechanism was implemented.

With the decrease of ion concentration on the limited region the difference between low and high mobility regions diminish. Once the concentration on the limited side is low enough the whole system behaves as if there was no limit and ion mobility becomes equal for all regions and the ions freely accumulate on the left wall (figure 4.19). Aside from the difference in electric field strength both simulations behave the same way as they approach steady state. Figure 4.20 shows concentration densities at steady state.

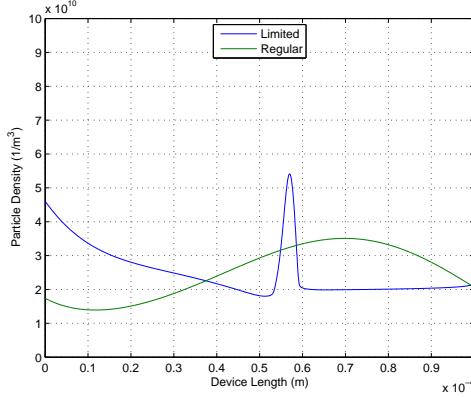


FIGURE 4.17: COMSOL Simulation for Particle Density Limit

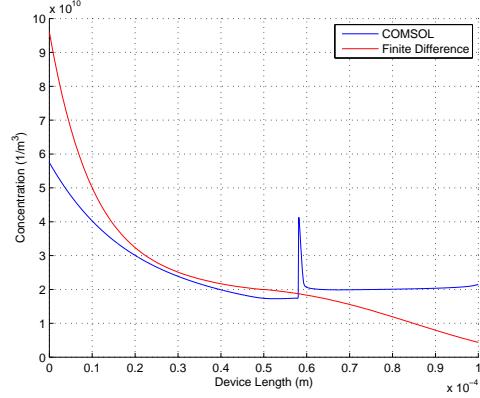


FIGURE 4.18: COMSOL and Finite Difference Simulation

COMSOL simulation has a lower electric field since it has convergence issues with high electric fields.

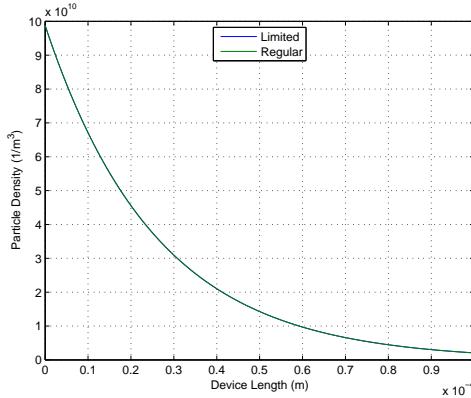


FIGURE 4.19: COMSOL Simulation for Particle Density Limit

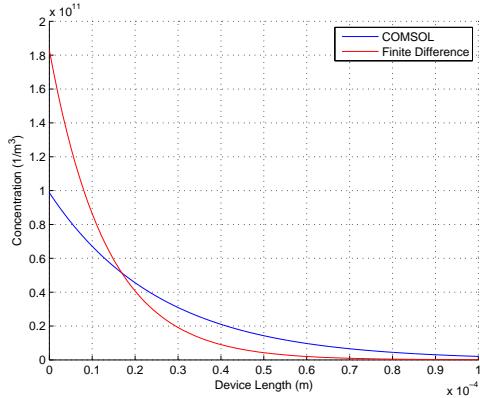


FIGURE 4.20: COMSOL and Finite Difference Simulation

This comparison can be finalized by looking the particle density transient response of the rightmost node. For the first half of the simulation everything is the same as the finite difference case except COMSOL goes a little bit over the limit. When the potential is switched, node without the limit has no noticeable difference in behaviour. The node with concentration limit has a lag when it comes to releasing the particles. This is due to the sigmoid function used to achieve a limiting behaviour. Once the limit is reached mobility and diffusivity are stuck at a very low value until the particle density starts to go lower than the limit.

The simulations above showed that is possible to impose a density limit over any area using a simple no flow boundary condition in finite difference. For COMSOL some

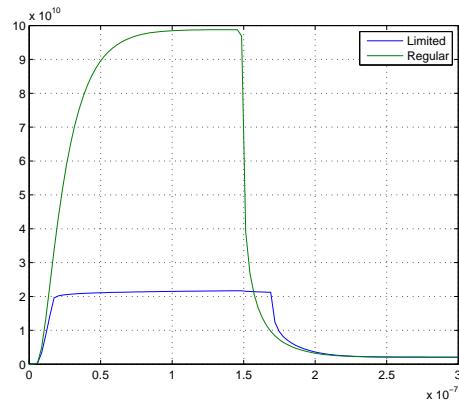


FIGURE 4.21: Density on the right wall over time using COMSOL

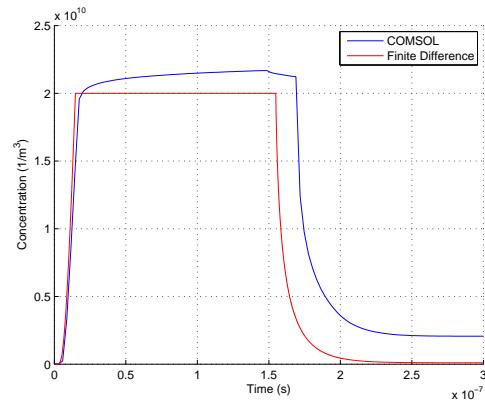


FIGURE 4.22: Density on the right wall over time, COMSOL vs. Finite Difference

workarounds had to be implemented in order to simulate the same behavior which caused convergence issues.

Chapter 5

Memristor Simulation

A numerical method for a memristor simulation was developed and tested in previous chapters based on drift-diffusion equations and finite difference. This chapter introduces the memristor's structure and physical parameters used for the simulation. It continues with a preliminary problem analysis to determine required mesh density and maximum possible time step. This preliminary analysis is followed by 1-D simulations of a memristor under various conditions.

5.1 Memristor Structure

Following figure (5.1) shows the structure of a simple memristor which will be taken as a basis for all the memristor simulations presented in this thesis. It consists of 2 metal contacts, a polymer conductor (PEDOT:PSS) and an electrolyte solution which has lithium and perchlorate ions (perchlorate/lithium density $\approx 6.02 \cdot 10^{23} m^{-3}$). The memristor is about 1 cm long and 1 mm wide. The thickness of the conductive layer is around 1 μm . During experimentation electrolyte solution is deposited on PEDOT via a syringe so its thickness can vary drastically but as long as the amount of ions in the electrolyte solution is enough to saturate PEDOT this does not make a significant difference in the operation of the memristor. For simulation it was assumed that there were always more than enough ions to saturate the PEDOT so the electrolyte was modeled as an infinite source/sink of ions. The top boundary of the electrolyte was

assumed to be charge neutral at all times which provides a mechanism for moving ions in and out of the system. This way the movement of ions near the surface of the PEDOT can still be captured without having to simulate the ion movement for the entire electrolyte solution which is variable in size.

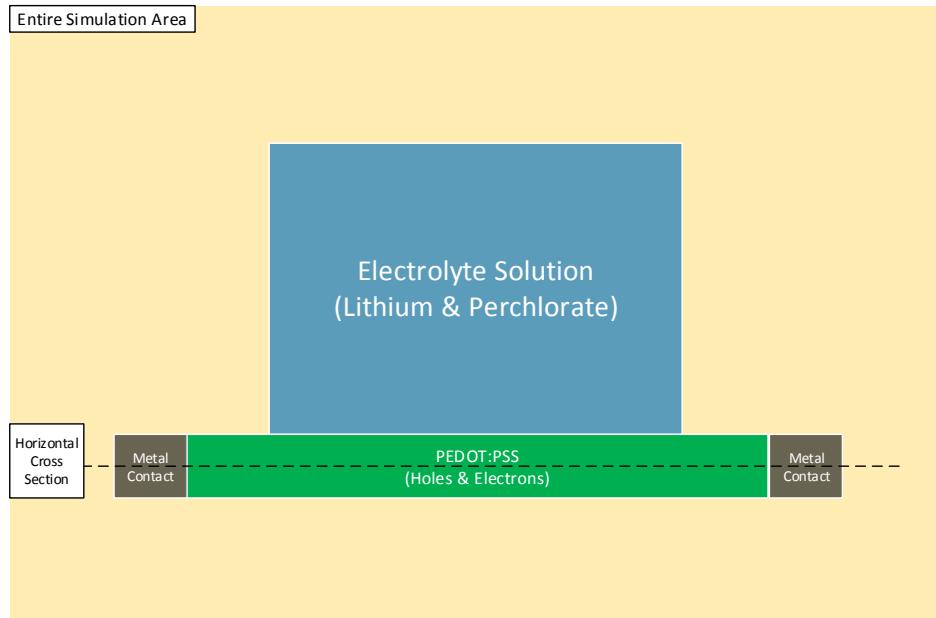


FIGURE 5.1: The structure of the memristor used for simulation (not to scale)

The initial conditions for all the charge carriers are the same. All charges are balanced and uniformly distributed but the carrier density in the electrolyte solution is higher than the carrier density in PEDOT. Perchlorate ions are not allowed to move outside the electrolyte solution so a no flow boundary condition is used around the electrolyte. Lithium ions are free to move between PEDOT and the electrolyte solution but their maximum concentration is limited inside the PEDOT. The mobility of lithium ions has further restrictions inside PEDOT. Lithium has higher mobility in PEDOT right under the electrolyte solution, wet PEDOT, than the region without any contact with electrolyte, dry PEDOT. In fact due to this difference very little amount of lithium reaches the metal contacts. This decrease in mobility was modeled by making the mobility of lithium a function of position in PEDOT:PSS. The mobility of lithium ions were assumed to be 100 times slower than the mobility of holes in the wet PEDOT and it is zero in the dry PEDOT($\mu_{hole} \approx 10^{-3} m^2/Vs$).

PEDOT:PSS is a regular conductor with fixed negative charge and mobile holes. Holes can move in and out of the PEDOT through the metal contacts which hold the charge neutrality of the initial condition throughout the simulation. The interface between PEDOT and electrolyte only allows the exchange of lithium ions. During simulation, the movement of lithium ions changes the conductivity of the PEDOT by increasing or decreasing the amount of available holes through coulomb forces. In the actual device lithium ions also change the conductivity via various physical effects like changing the mobility of holes through modifying their hopping distance. Even though the mobility of the holes can simply be made a function of lithium density, the shape of the function is not known. The physical details of these additional affects are beyond the scope of this thesis.

5.2 Simulation Requirements

It is important to analyze computational requirements of a simulation in order to assess the feasibility of the computation scheme. In this case, it is possible to determine spatial and temporal requirements using the equations 3.48 and 3.51 which describe physical and numerical limitations of the simulation. Following graph 5.2 shows the requirements for a memristor of the scale discussed above and a typical semiconductor device size around $1 \mu\text{m}$. The mesh density has to be high enough in order to capture the exponential charge accumulation for charge shielding so the minimum step size was set to be 5 times smaller than the Debye length. Plots 5.2.a and 5.2.c show the amount of points required to simulate a semiconductor and a memristor based on minimum step size. It is important to note that these values are for 1-D simulation and they can be converted to 2-D and 3-D by squaring or cubing y axis values respectively. Plots 5.2.b and 5.2.d were created using CFL conditions for drift and diffusion and dielectric relaxation time. A typical simulation time was estimated using mobility and electric field. Based on the estimated simulation time the number of time steps were calculated using the minimum time step obtained from CFL conditions and dielectric relaxation time.

It can be seen from graphs 5.2.a and 5.2.c that memristor simulations require much higher mesh densities compared to a typical semiconductor simulation such as $1 \mu\text{m}$ long PN diode. This is due to the larger size and higher charge density of the memristor. Graph 5.2.a 5.2.b show that a memristor with 10^{26} m^{-3} charge density of the electrolyte would require close to 10^9 points and 10^{14} time steps to simulate in 1-D. These requirements make the simulation of the memristor extremely challenging. In order to investigate and find possible solutions for this issue, first a memristor with low charge density ($\approx 10^{15}$) was simulated in order to ensure that the simulation functions as designed. Then memristors with different charge densities were simulated and compared with each other to assess whether the behavior at low charge densities will be comparable to behavior at high charge densities.

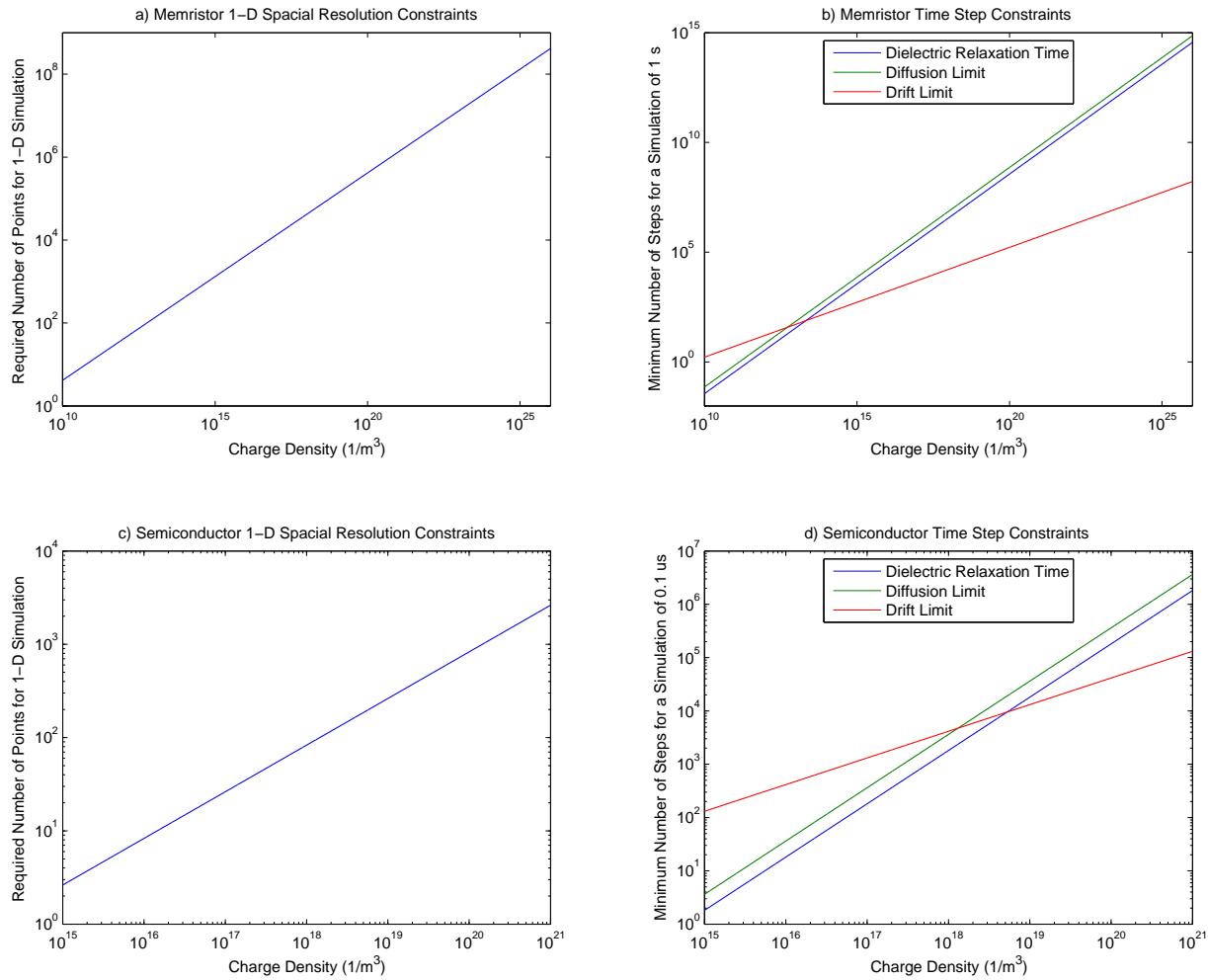


FIGURE 5.2: Spatial and temporal requirements for simulation

5.3 1-D Memristor Approximation

The horizontal cross section from figure 5.1 has the most crucial elements of the memristor but its simulation in 1-D is not straight forward. This cross section through the PEDOT does not include the vertical movement of lithium. Without this effect, PEDOT is just a regular conductor with a uniform current density. In order to overcome this problem a generation/recombination term for lithium ions, calculated at every time step, was added to capture the vertical movement in addition to regular drift diffusion equations which represents the horizontal movement. This generation/recombination term can be symbolized as a current source with a resistor connected to all the nodes (figure 5.3). Perchlorate ions were not included in the simulation since they do not move into the PEDOT.

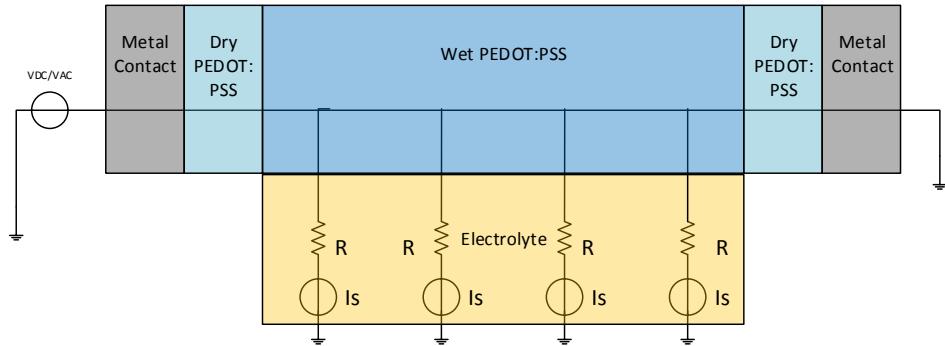


FIGURE 5.3: 1.5-D Memristor Structure

The lithium source has two different terms, one for drift and another one for diffusion. It was assumed that the concentration of lithium was always constant in the electrolyte. This way the vertical diffusion current density can be calculated using the difference between the lithium density in PEDOT and electrolyte. For the diffusion term an electric field had to be estimated between the PEDOT and the electrolyte. First the potential of the electrolyte was assumed to be half of the net applied potential. Then an electric field was calculated using the electrolyte and the instantaneous potential of the PEDOT at different positions.

Since the main characteristic of memristor is the change in resistivity over time it is important to develop a standard approach for measuring the resistivity. Initially, simulations in this chapter and the following one, were run until steady state without the movement of lithium/perchlorate ions. Ions in the electrolyte start to move after the steady state has been reached. The movement of ions create another transient which involves changes in resistivity. The current density (at steady state) obtained from the initial simulation was used as a normalizing factor in order to determine the changes in resistivity after the ion movement has started.

5.4 1-D Memristor Simulations

Following simulations were made based on the memristor approximations discussed above. First two simulations are repeated in the next chapter using a 2-D drift diffusion and Poisson solver which captures a broader range of physical effects. Both approaches can be compared in order to understand their advantages and disadvantages under different circumstances.

5.4.1 1-D Memristor Simulation Using a Pulse Train

For the following simulation a potential pulse train, slow enough to let the memristor reach steady state, was applied at the left contact. Following plot 5.4 shows the resistivity measured using both contacts separately. As expected the resistance of the device more than doubled as the lithium ions move in. Additionally, it can be seen from the graph 5.4 that the resistivity measurements from left and right contacts are not always the same over the duration of the simulation. This is normal since it is due to PEDOT layer losing holes on one side and gaining holes on the other which produces a difference in measured resistivity between contacts. The scale of the difference depends on the rate of change in resistivity on one side. When holes are not fast enough to track the change in resistivity, the current on each side take different values.

The resistivity in figure 5.4 shows a sudden drop when the potential is switched from 1 to 0 and vice versa. This sudden drop occurs because of the accumulation of lithium ions and holes near the negative contact which opposes the electric field generated due to the applied potential (see figure 5.5). When the potential changes suddenly, previously opposing electric field now helps the movement of holes and lithium towards the other end of the device. This additional electric field momentarily reduces the resistivity of the device.

Figure 5.6 demonstrates the replacement of holes by lithium ions over time which directly effects resistivity seen in figure 5.7. As lithium ions get pulled in from the electrolyte toward the contact they accumulate inside PEDOT and push holes out via coulomb

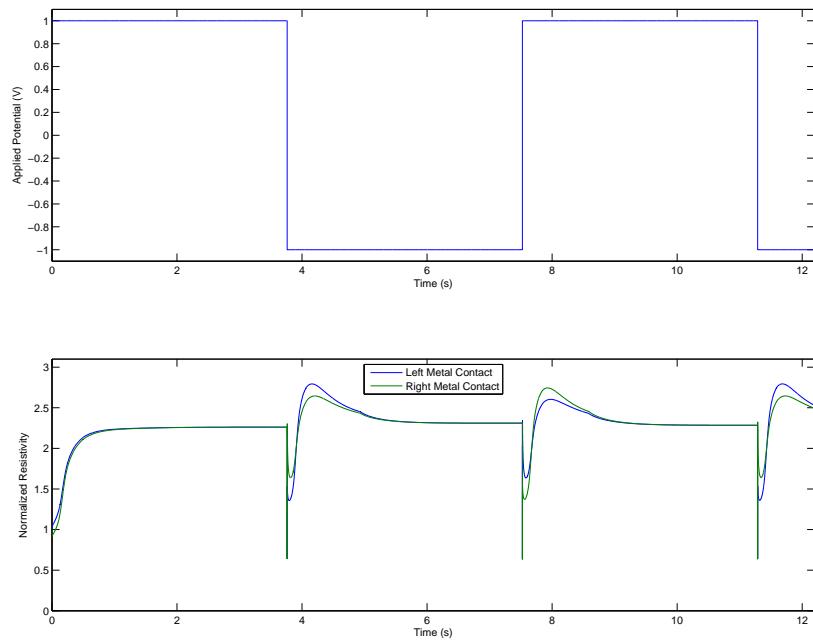


FIGURE 5.4: Change in resistivity over time due to applied potential

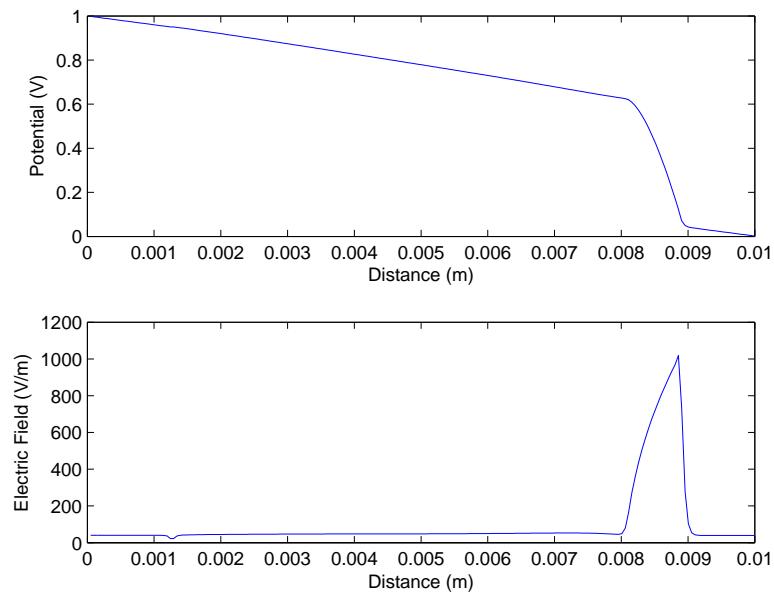


FIGURE 5.5: Potential and electric field at steady state

forces. Decreased hole concentration in the PEDOT increases the resistivity of the material. This change in resistivity over time is illustrated in figure 5.4.

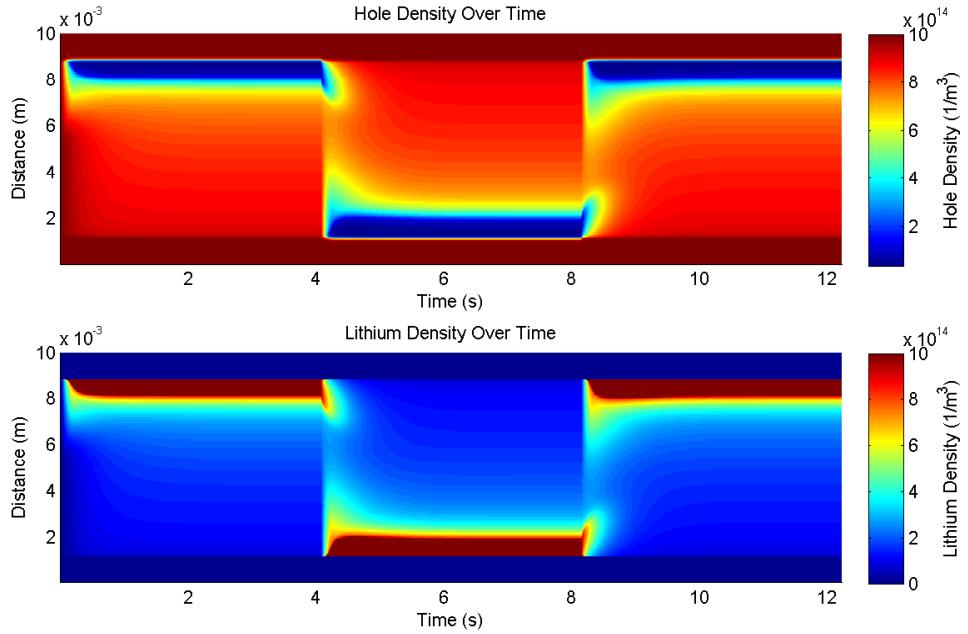


FIGURE 5.6: Lithium and hole density distribution over time

It is important to note that lithium ions are free to move in x and y direction. In figure 5.6 it can be seen that after the potential is switched as the lithium density moves from side to the other. Most of the lithium movement happens through the exchange of ions between PEDOT and the electrolyte since the distance between them is far less than the length of the PEDOT. So lithium ions, traveling from the positive to the negative contact, are pulled into the electrolyte before they reach the other side. Near the negative contact lithium ions are quickly pulled into the PEDOT and accumulate at the wet/dry interface. Figure 5.7 shows the changes in resistivity throughout PEDOT due to the accumulation of lithium. The resistivity is increased in regions where there is high lithium accumulation.

By examining the resistivity plot of PEDOT it is possible to conclude that it is composed of 3 distinct regions. 2 dry regions, where there is no contact with the electrolyte, have constant uniform resistance. Between these two resistances there is a variable non uniformly distributed resistance controlled by hole/lithium concentration and hole mobility.

So this model captures the main characteristic of the memristor which is a variable resistance where the resistance at any time depends on the past of the device. Following equation gives the total resistance/memristance for the memristor model developed for this thesis:

$$M(q(t))_{tot} = 2R_{dry} + R(Li, p, \mu_{hole}) \quad (5.1)$$

The minimum resistance of this device is just the total resistance of the PEDOT without the lithium ions. The maximum resistance depends on different factors such as applied potential and the distribution and concentration of lithium ions inside PEDOT.

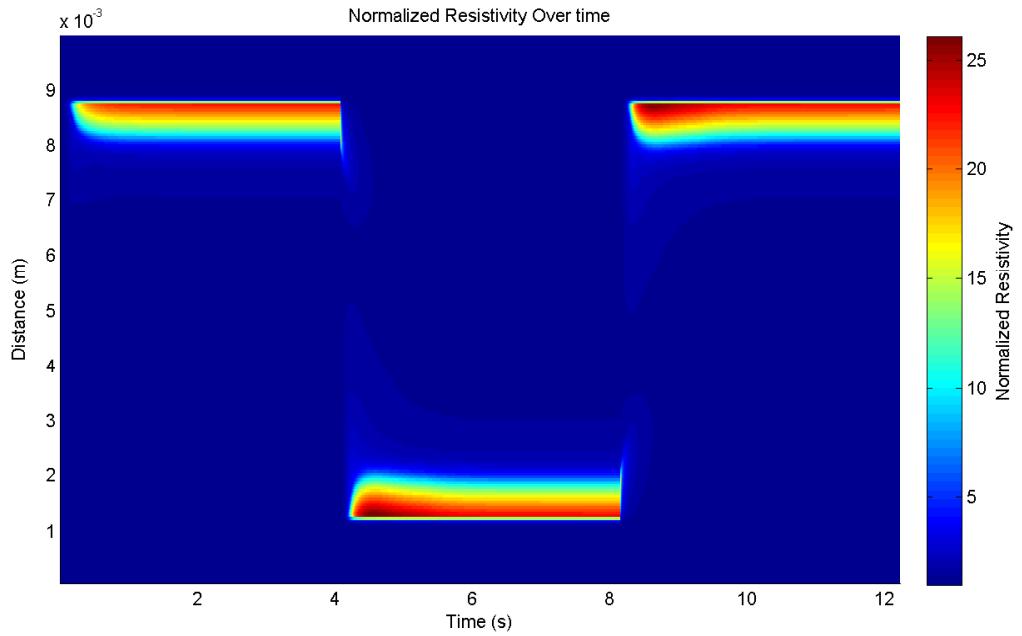


FIGURE 5.7: Normalized resistivity over time

5.4.2 1-D Memristor Simulation Using a Sinusoid

Memristor with a pulse train simulation shows the change in resistivity over time due to an applied potential but it does not clearly demonstrate memory effects. The memory effect of the memristor can be clearly demonstrated in an I-V curve using sinusoidal potential. Following four graphs (figure 5.8) were created using an AC potential with different frequencies at the contacts. All the plots show that current can have more than one value for the same potential at different times. This means that simulated memristor's past states affects its present output, therefore the device has memory. There is a pinch in the current for negative applied potential because it is measured from one contact which sees a higher resistance for a period of time during transient.

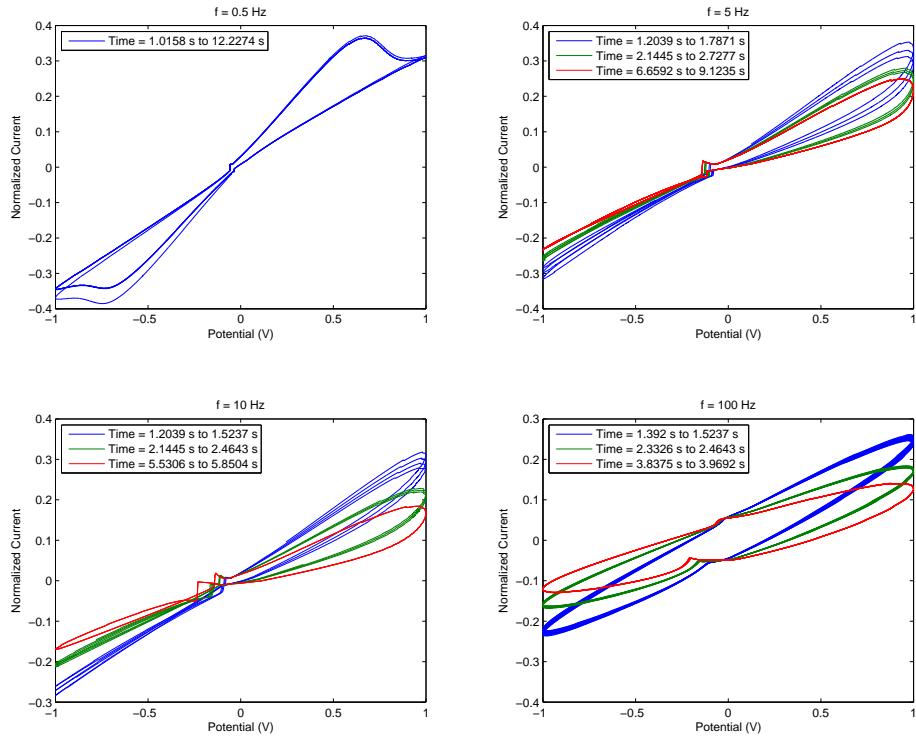


FIGURE 5.8: Normalized Current vs. applied potential at different frequencies

The sudden changes in current around 0 V can be attributed to the density limiting mechanism for lithium. Instead of a slowdown in the movement of lithium ions near maximum concentration, the current flow into that region is completely blocked. Even though this makes the lithium density more responsive to changes, sudden movement

block combined with large time steps can result in fast changes which can be directly seen as abrupt changes in the hole/lithium current density during transient simulations.

As AC potential pushes lithium ions from one side to the other, an equilibrium is reached over time. The change in resistivity starts to repeat itself and after a while it becomes periodic. Figure 5.9 shows the changes in memristor current over time for the right metal contact. At first, as lithium moves into the PEDOT there is a drop in current on average. Once enough lithium settles into the PEDOT, high resistivity region simply shifts from left to right but it stays fairly constant on average.

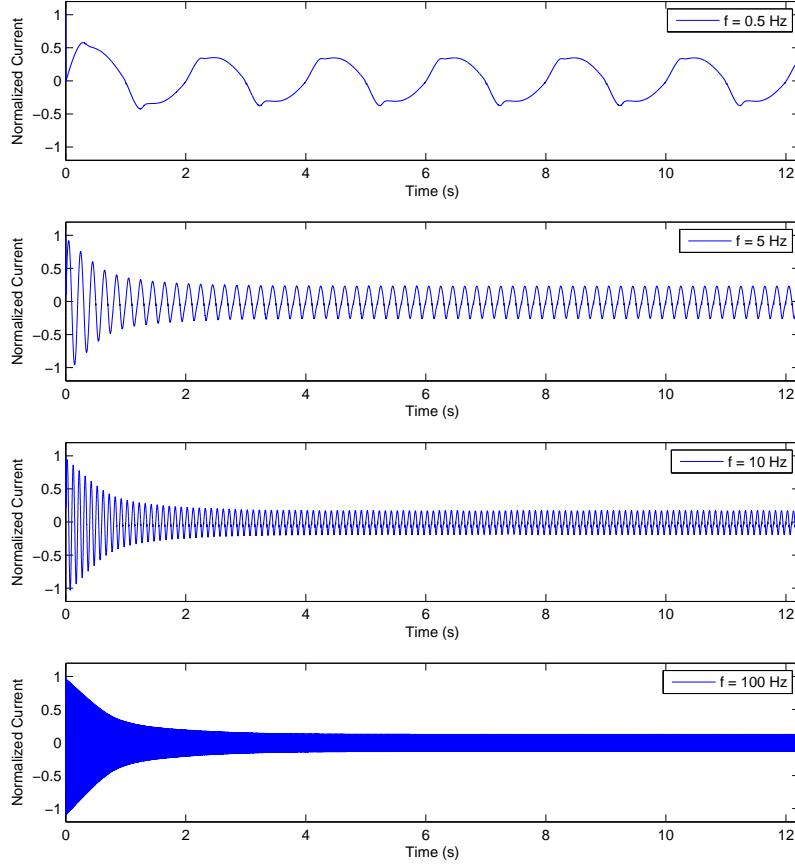


FIGURE 5.9: Normalized current over time

Figures 5.10, 5.11 and 5.12 show the changes in resistivity, hole and lithium density in PEDOT over time. A visual comparison of the plots show that changes in lithium density induces changes in hole density. As frequency increases diffusion becomes more dominant than drift. At 100 Hz drift due to applied potential is barely present.

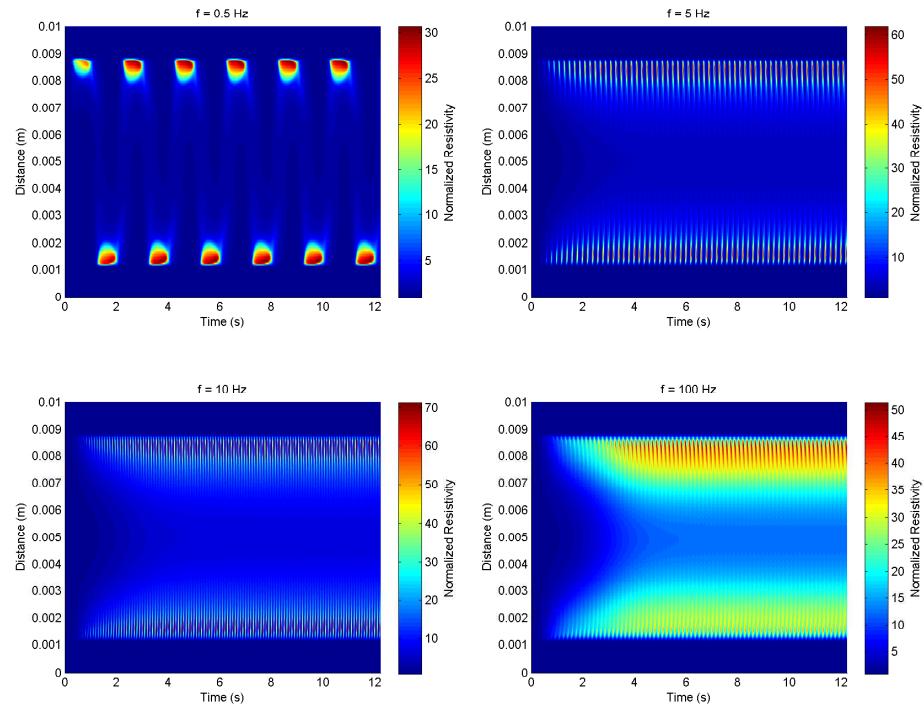


FIGURE 5.10: Normalized resistivity over time at different frequencies

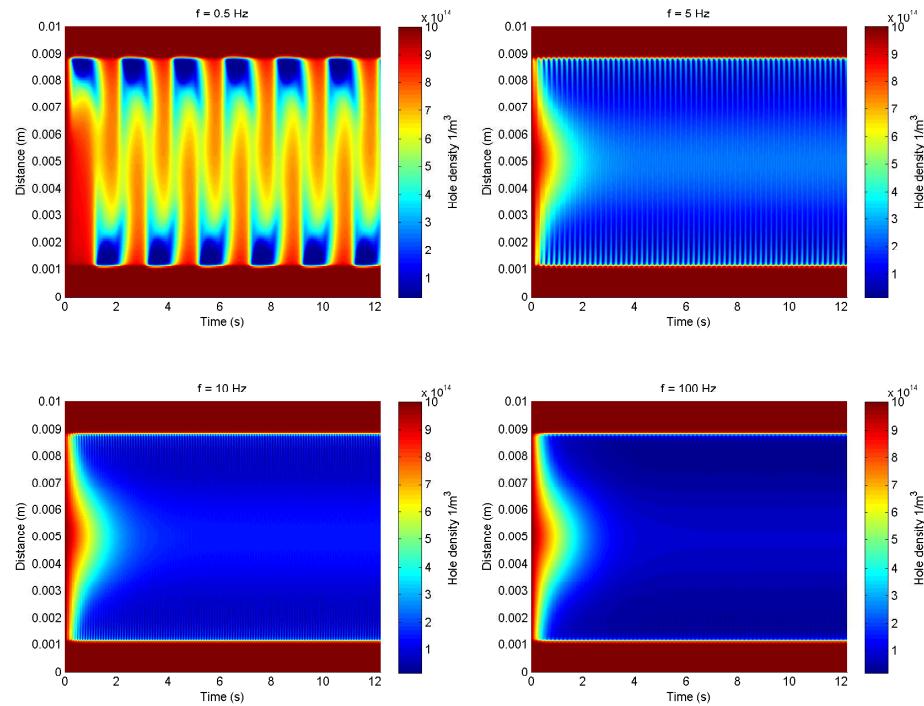


FIGURE 5.11: Hole density over time at different frequencies

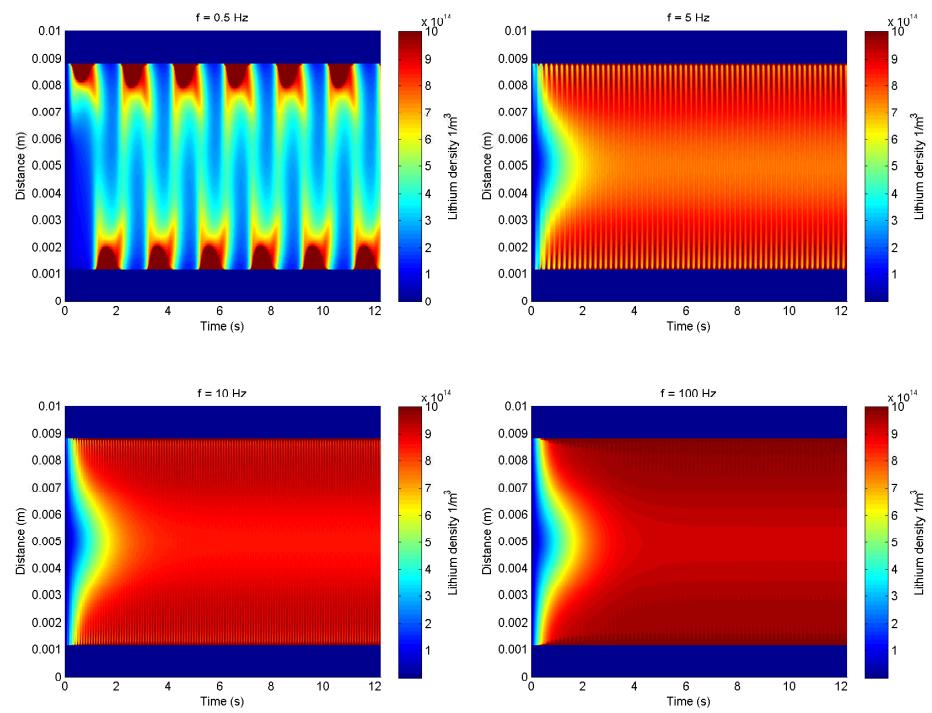


FIGURE 5.12: Lithium density over time at different frequencies

5.4.3 1-D Memristor Simulation With Increasing Charge Density

After establishing that the simulation behaves as expected it is important to investigate how charge density effects this model since the size of the device limits the maximum charge density that can be simulated. The actual device has a hole density in the range of $\approx 10^{22} \text{ m}^{-3}$ but the simulation is restricted to $\approx 10^{15} \text{ m}^{-3}$. In theory, if the densities used for simulation does have a limited affect on the behavior of the memristor then simulations in low densitiy can be used as a proxy for the actual device which operates in much higher carrier densities.

Following 3 graphs ([5.13](#), [5.14](#) and [5.15](#)) show hole and lithium densities at steady state as well as the current density over time at the right metal contact for various charge densities. The simulations were done on high mesh densities to allow stable simulation at high charge concentrations. 20 different simulations were made using densities ranging from $5 \times 10^{15} \text{ m}^{-3}$ to $1 \times 10^{17} \text{ m}^{-3}$ but only 5 of them were plotted for illustration purposes. All the values were normalized to the initial plot using respective hole/lithium density ratios. Following equations were used for the normalization procedure.

$$n_{norm} = \frac{n_i}{r} \quad (5.2)$$

$$J_{norm} = \frac{J_i}{r} \quad (5.3)$$

$$r = \frac{n_{initial}}{n_0} \quad (5.4)$$

n_i is the charge carrier density which could be either holes or lithium ions depending on the plot. J is the current density calculated from the right metal contact. r is the normalization constant which is calculated using initial carrier density ($n_{initial}$) of a simulation to be normalized and n_0 which is the carrier density of the initial plot ($5 \times 10^{15} \text{ m}^{-3}$). After the normalization of various variables, all the plots were placed in the same graph to visually illustrate how increasing charge density affects the simulation.

Plots for lithium ions (figure 5.14) and holes (figure 5.13) are nearly identical to each other in terms of the plot shapes. They both get sharper around the area where there is a substantial accumulation of lithium. This is not unexpected since the Debye length gets smaller with increasing carrier density concentration. So with increased density it is expected that the density accumulation at the wet/dry PEDOT interface will be more narrow. This effect is not as strong for lithium ions since there is a maximum concentration limit on them. Lithium and hole plots only show the difference carrier density makes at steady state. The effect of Debye length on device operation can be further explored by looking at the current density over time.

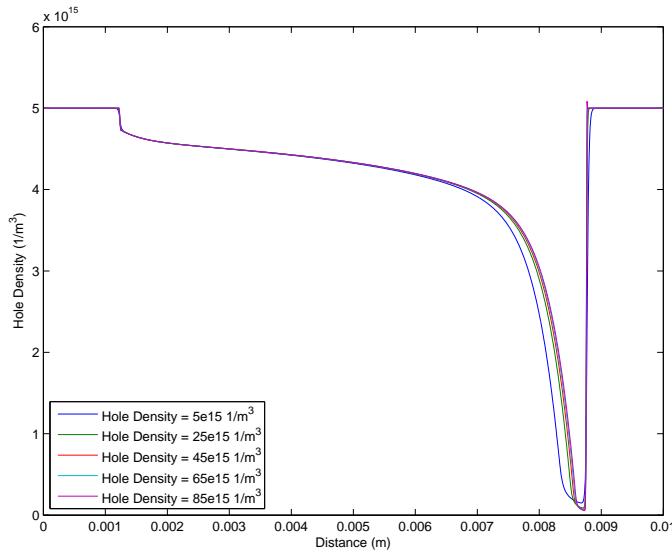


FIGURE 5.13

First few milliseconds of this simulation was run without the movement of lithium ions. At this stage normalized currents are identical to each other which means a simulation with low density can be scaled up to any density without introducing any error. The introduction of lithium ions slowly deviates the current plots from each other over time but the overall behavior of the memristor remains unchanged. The current density decreases over time and reaches a steady state value. After the first plot which has the lowest hole density, consecutive plots get closer and they are almost impossible to distinguish from each other at steady state.

The impact of increasing charge density can be numerically explored using normalized plots. Following formula was used to calculate a percentage difference between different

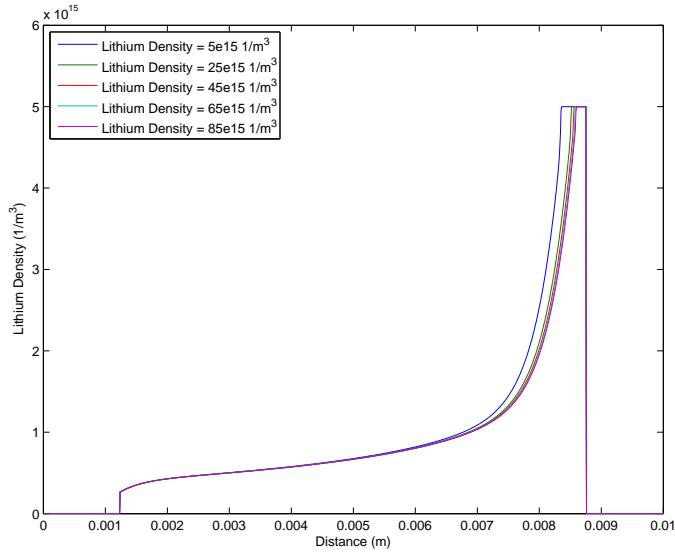


FIGURE 5.14

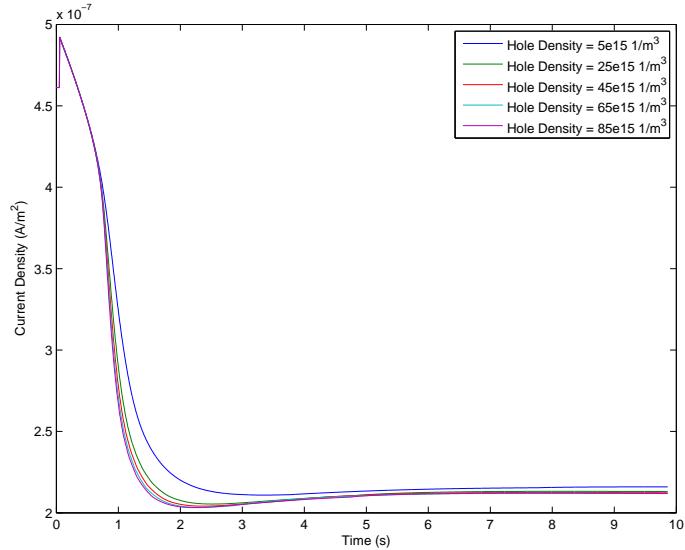


FIGURE 5.15

normalized carrier densities as well as normalized current densities.

$$P_i = \frac{1}{K} \sum_{k=1}^K |100 \frac{n_i(x_k)/r - n_0(x_k)}{n_0(x_k)}| \quad (5.5)$$

$$P_i = \frac{1}{T} \sum_{k=1}^T |100 \frac{J_i(t_k)/r - J_0(t_k)}{J_0(t)}| \quad (5.6)$$

K is for total number of points along x axis and T is the total number of time steps taken by the simulator. x_k and t_k are used to for a point in x axis and a point in time respectively. r is the normalization constant described in equation 5.4. Both equations start by taking a point in either space (lithium/hole density) or time (current density) for a simulation with a certain carrier density and normalize them. After that point is normalized its difference from the lowest carrier density simulation is calculated as a percentage. Finally all the differences are averaged and used as a measure of the difference between simulations with different charge densities. They can also be used as an approximate error during scaling.

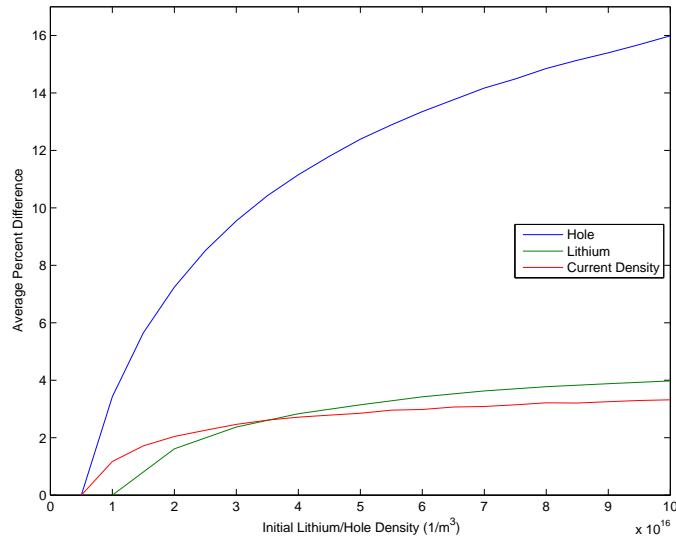


FIGURE 5.16

Figure 5.16 shows the difference hole/lithium density makes in the simulation. Carrier densities in the dry regions of the PEODT change very little between consecutive simulations since lithium ions do not reach there. For this reason only the densities at the wet PEDOT were used to measure the difference between plots.

In all 3 cases, there is an increase in average difference for increasing carrier density. Hole density shows the most difference between plots. Since holes are free to move inside the PEDOT they directly get effected by the change in debye length due to the increase in hole density. This is not the case for lithium ions because their movement is restricted by the limit on lithium density. In contrast, current density is not as sensitive to density changes as lithium and hole distributions.

An approximate error estimation can be made for current density if a low hole/lithium density is used for simulation and then scaled up to match the actual memristor. Figure 5.16 shows around 3.3 % difference for 2 orders of magnitude increase in hole density. Assuming the error scales linearly after that point a total of 6 orders of magnitude will result in 9.9 % error introduced in order to linearly scale from 10^{15} to 10^{21} . The actual error is likely to be less since the error progresses sub linearly. Following the same procedure 6 orders of magnitude difference produces a 12 % error for lithium distribution and 48 % error for hole distribution. The difference in hole distribution looks very large but the overall shape of the plot is still reserved, most change occurs around the wet/dry PEDOT interface where lithium accumulates. Based on these error margins and previous plots it can be concluded that the behavior of the memristor simulated using low charge density is very similar to the simulation at high carrier density.

Chapter 6

2-D Memristor Simulation

Even though 1-D simulation was able to capture the main characteristics of the memristor it is still lacking certain physical effects that can be captured in a 2-D simulation such as the movement of ions inside the electrolytic solution which cancels some applied electric field. This chapter shows the simulation of a memristor in 2-D and compares the results with 1-D simulations. It starts with the simulation of a memristor with different PEDOT:PSS layer thicknesses and shows the changes in particle distributions, electric field and current density. Transient simulations with a pulse train and a sinusoidal potentials are presented and compared to 1-D simulations. Finally current vs time and I-V curves for an actual memristor is used to show the accuracy of 2-D simulations in capturing the behavior of the actual device .

6.1 Effect of PEDOT:PSS Thickness

The physical dimensions of the memristor was presented in the previous chapter. Thickness of the PEDOT:PSS layer is very small compared to the other dimensions of the device such as the thickness of the electrolyte and length of the conductive material. This complicates the simulation of the PEDOT:PSS strip using a uniform mesh. Although non uniform meshing seems like an appropriate solution an examination of the

numerical limitations show that this is not the case. Decreasing the mesh size in one dimension severely reduces the maximum time step size for the entire simulation therefore non uniform meshing is not an appropriate solution for this problem.

An alternative solution to this meshing problem is using an infinitesimally thin PEDOT:PSS layer in a 2-D simulation. This method is used for the memristor simulations in this chapter. For PEDOT:PSS effects in 2-D are ignored since the layer thickness is 10000 times smaller than other dimensions such as the thickness of the electrolyte. For holes in the conductive layer only the horizontal component of the electric field is used and all the current densities are calculated in 1-D. Following plots compare two simulations with PEDOT:PSS thicknesses higher than the actual device and a 2-D simulation with 1-D PEDOT:PSS layer.

The memristor was simulated using a constant potential at the contacts. Left metal contact is kept at 1 V and the right metal contact is grounded. Resistivity measured at the right contact for different PEDOT:PSS thicknesses is shown in figure 6.1. Resistivity plots show as the thickness gets smaller the device responds faster. This is due to the decrease in the distance lithium ions have to travel inside PEDOT:PSS in order to change its resistivity. Another change in the behavior of the memristor is its resistivity at steady state. The increase in resistivity for different thicknesses at steady state can be attributed to the ion/hole interaction at the interface between PEDOT:PSS and electrolyte solution which is illustrated in the following figures 6.2, 6.3 and 6.4. **(not sure about this)**

Figure 6.2 shows hole distribution in PEDOT:PSS at steady state for different thicknesses. The electrolyte is on top of PEDOT:PSS but it is not visible in these plots since its hole concentration is zero at all times but they do affect the distribution of holes. As lithium ions move into the PEDOT:PSS they move towards the negative contact and pushes the holes out. This effect can be seen in figures 6.2 and 6.3. For all thicknesses there is a section of the hole density which is missing due to lithium ions.

The accumulation of holes at the surface of the PEDOT:PSS is due to perchlorate ions accumulating near the positive contact in the electrolyte (figure 6.4). As perchlorate ions accumulate to cancel the electric field they also attract holes towards the surface.

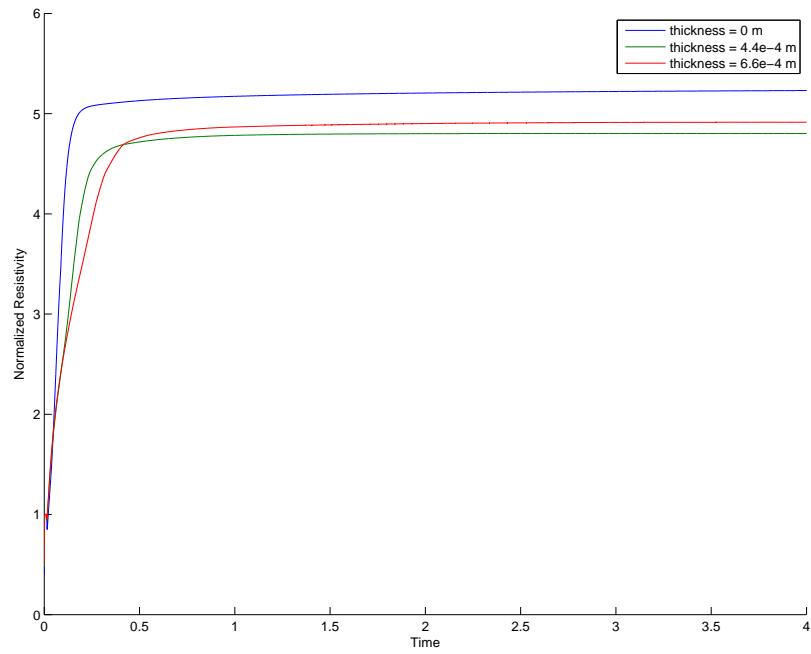


FIGURE 6.1

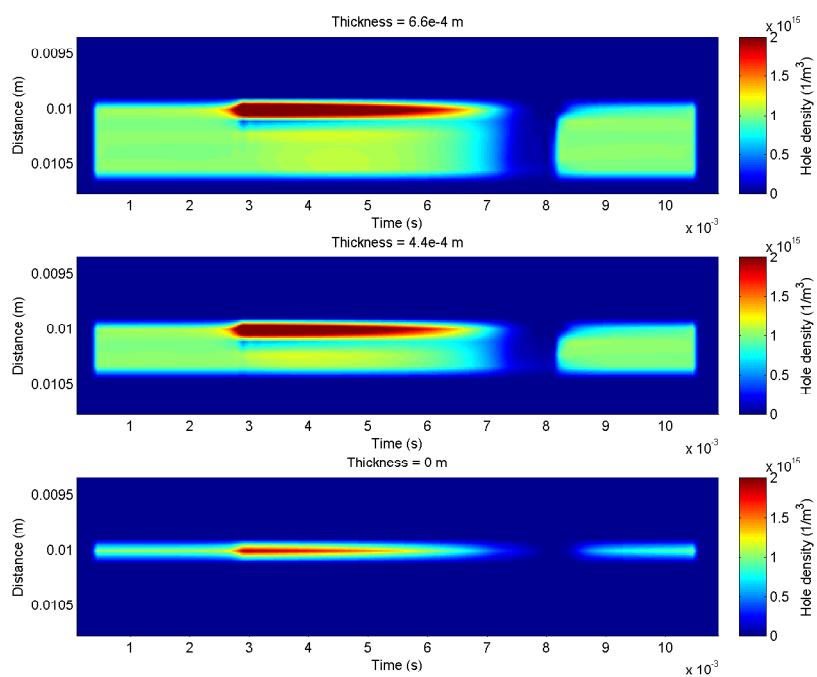


FIGURE 6.2

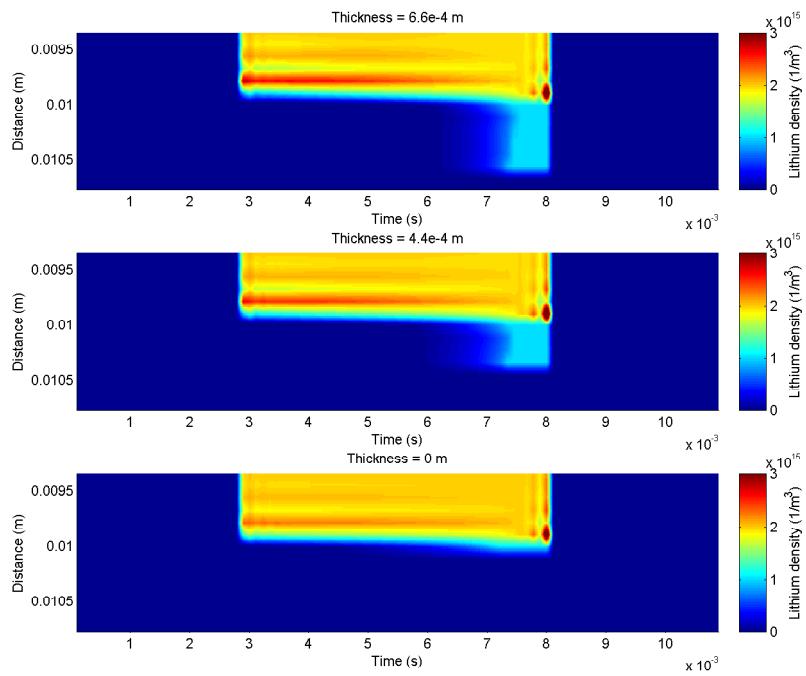


FIGURE 6.3

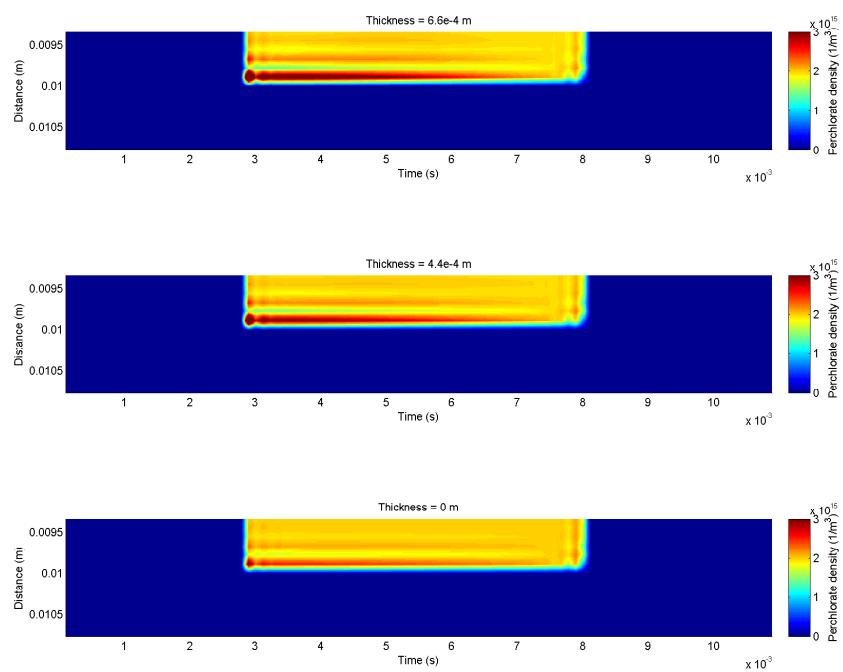


FIGURE 6.4

Figure 6.5 shows the hole charge density at the surface of the PEDOT:PSS and net charge density in the electrolyte near PEDOT:PSS. Again negative charges that accumulate on the left side of the electrolyte attract holes and positive charges on the right side push them out. This additional mechanism is the key difference between 1-D and 2-D simulations. In 1-D simulation, ion density inside the electrolyte and the changes in the electric field due to these charges were not present.

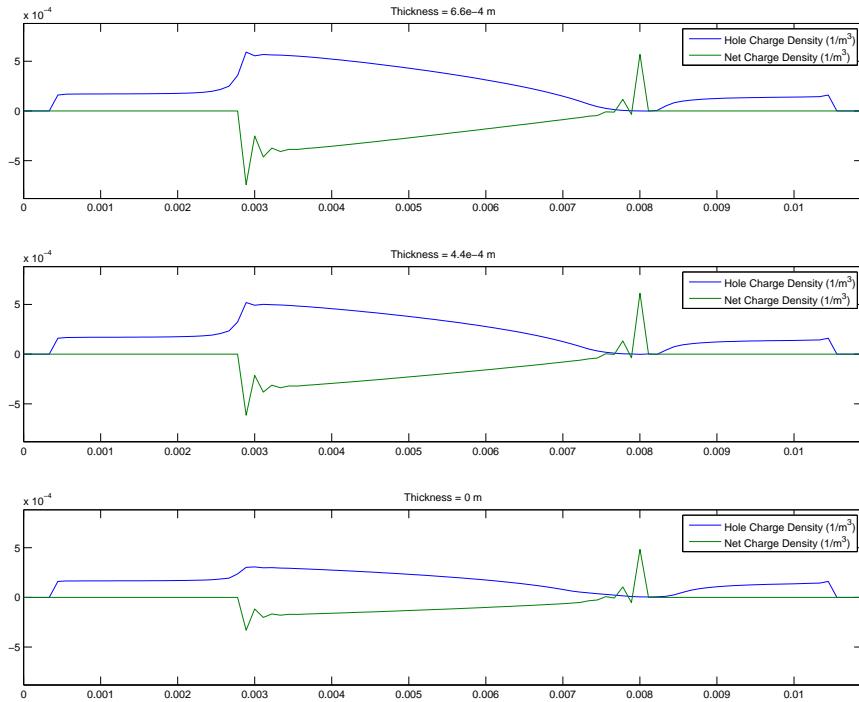


FIGURE 6.5

As shown in the previous chapter, electric field has the highest value where lithium ions accumulate. Figure 6.6 shows the change in the accumulation of the electric field as PEDOT:PSS gets thinner. For all thicknesses most of the potential drop occurs where lithium ions accumulate and it is concentrated at the surface of the PEDOT:PSS.

Above plots showed that changing the thickness of the PEDOT:PSS does not have a drastic effect in the operation of the memristor since most of the changes occur at the interface between electrolyte and PEDOT:PSS. 1-D approximation the polymer conductor contains all the necessary physics for the simulation of the memristor described in chapter 5.

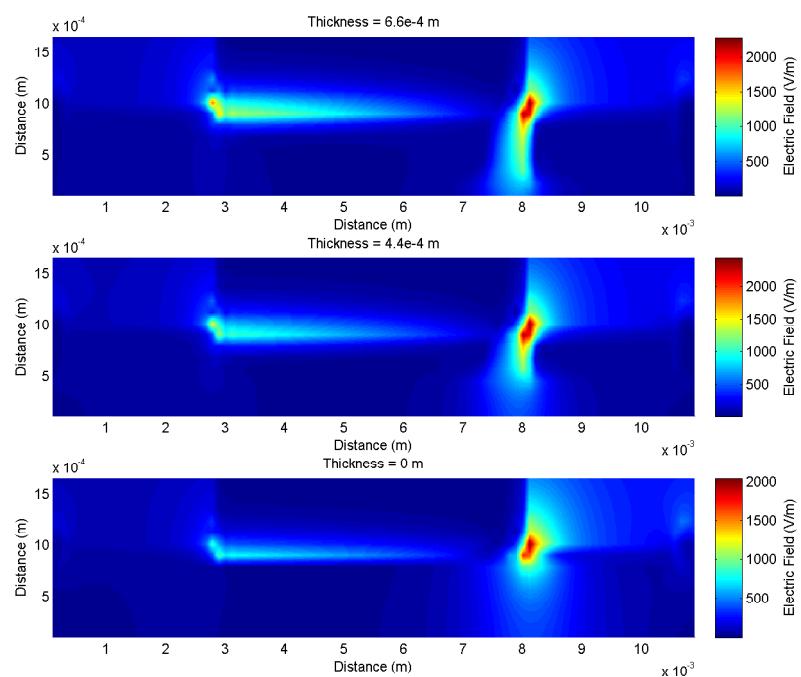


FIGURE 6.6

6.2 2-D Memristor Simulation Using a Pulse Train

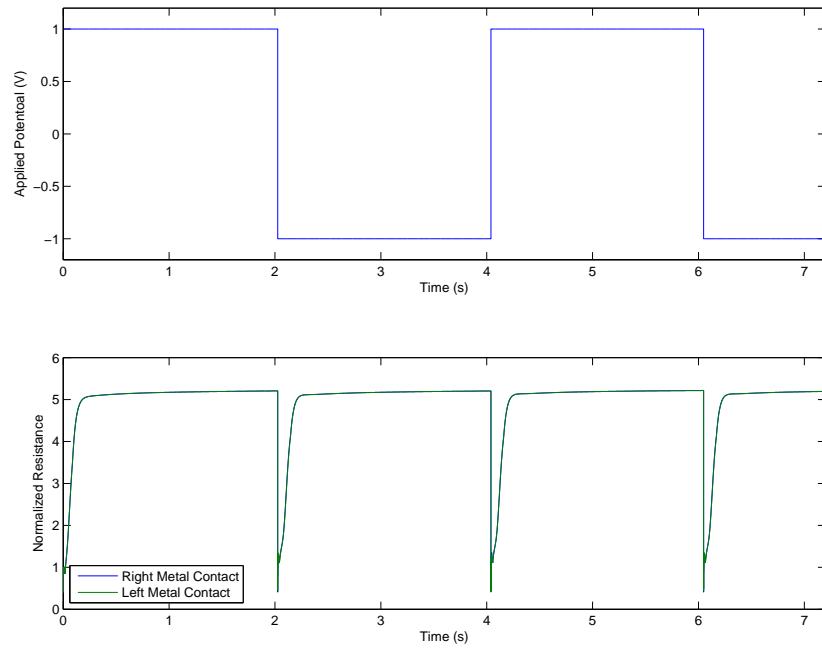


FIGURE 6.7

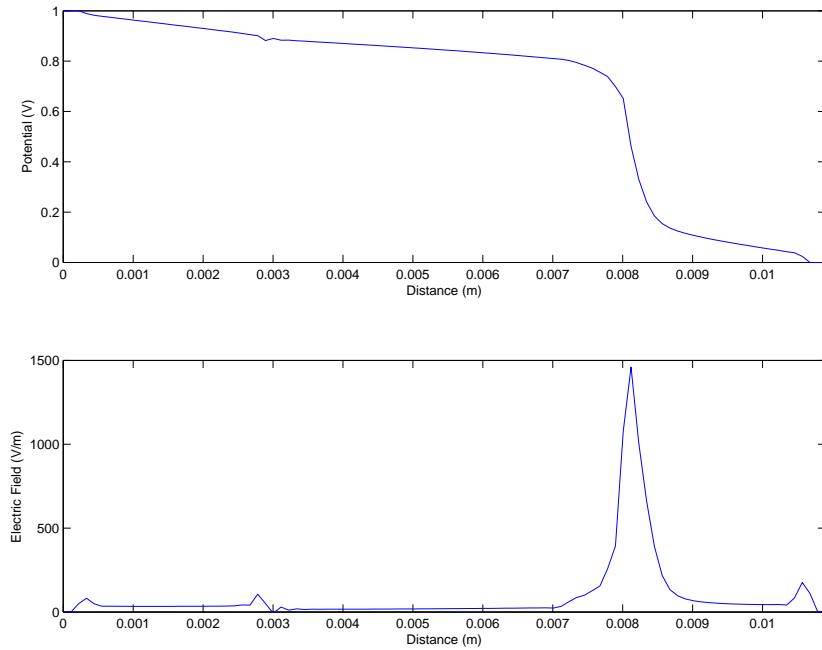


FIGURE 6.8

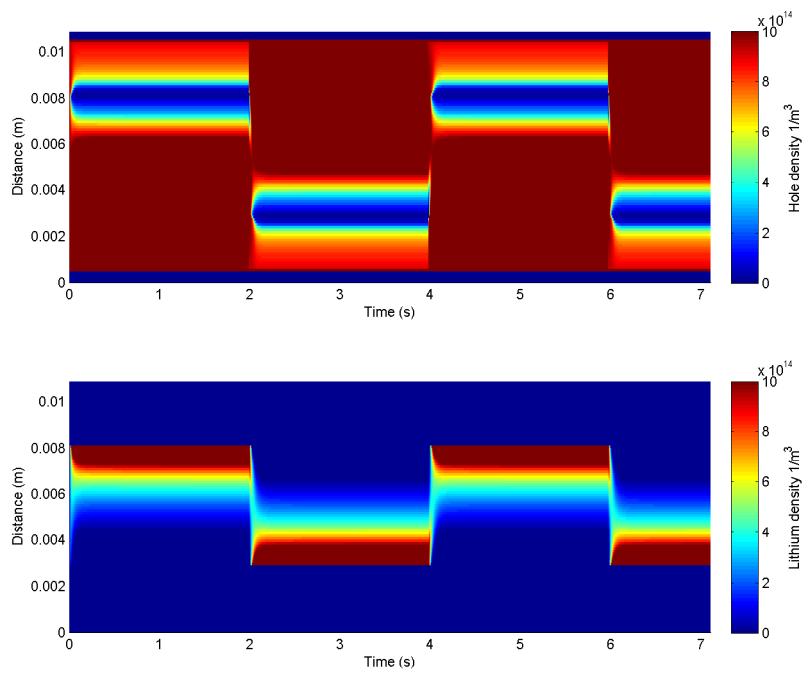


FIGURE 6.9

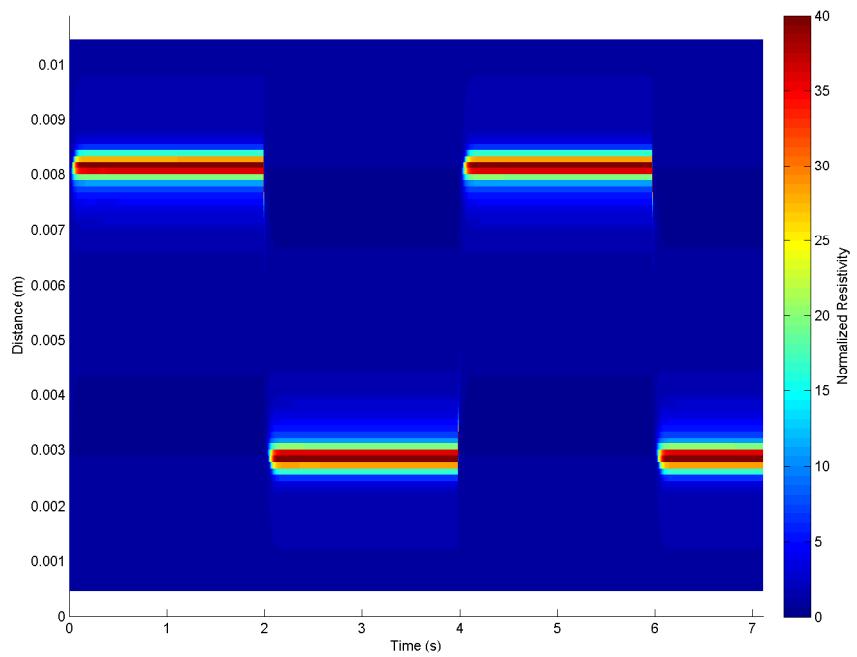


FIGURE 6.10

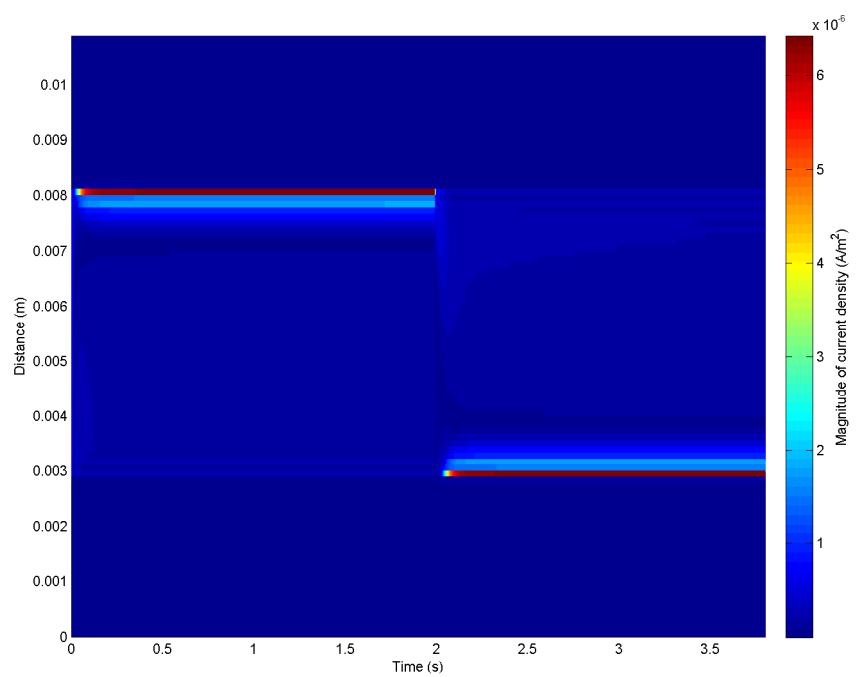


FIGURE 6.11

6.3 2-D Memristor Simulation Using a Sinusoid

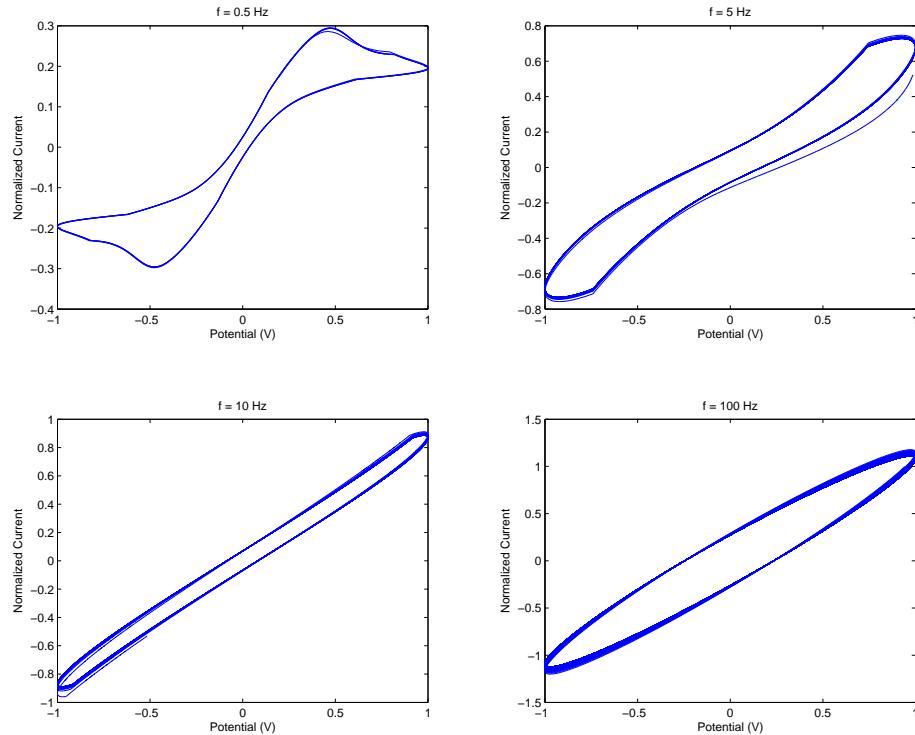


FIGURE 6.12

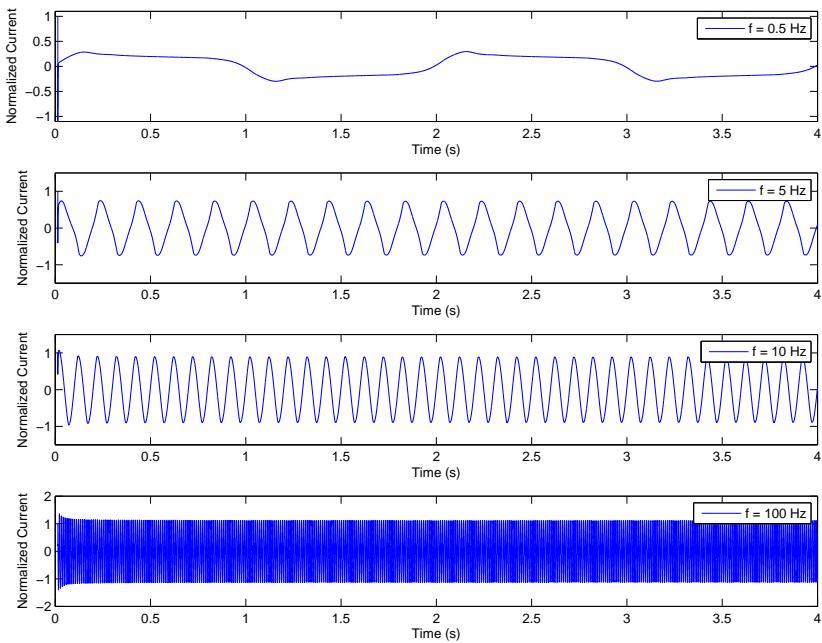


FIGURE 6.13

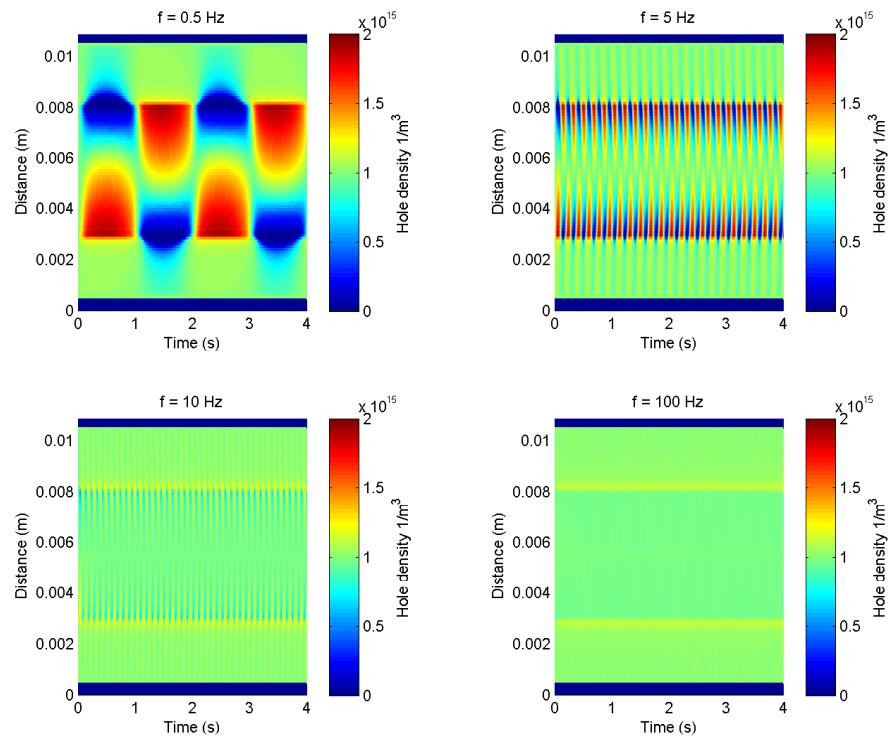


FIGURE 6.14

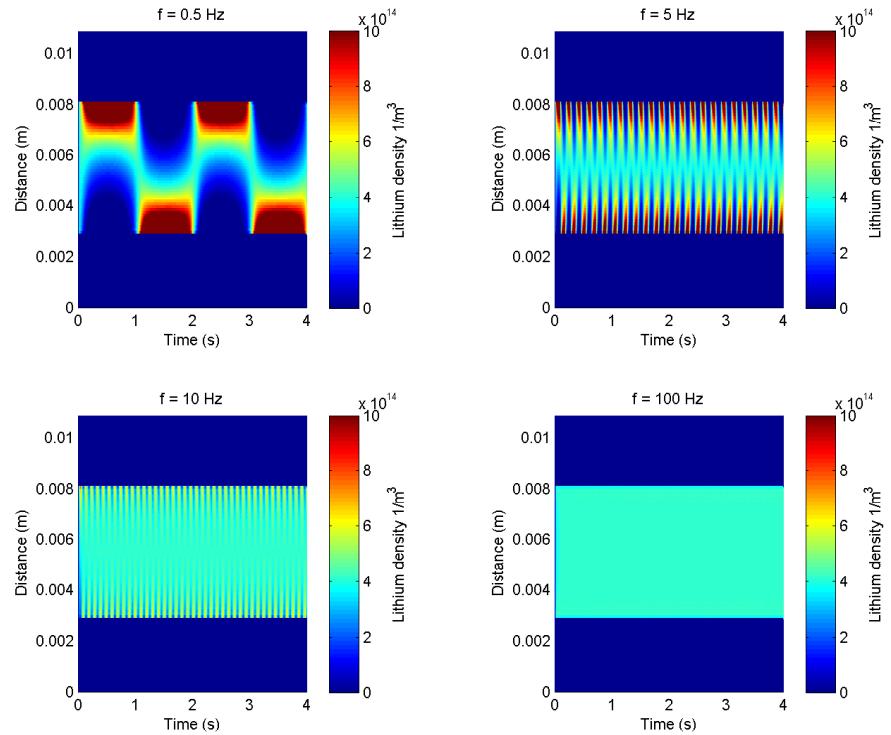


FIGURE 6.15

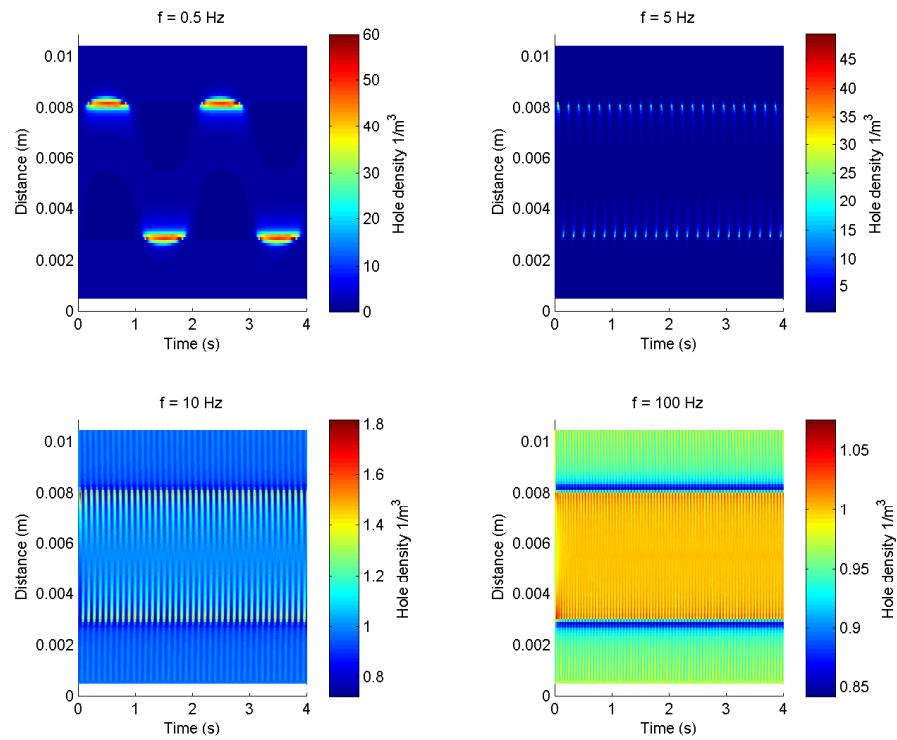


FIGURE 6.16

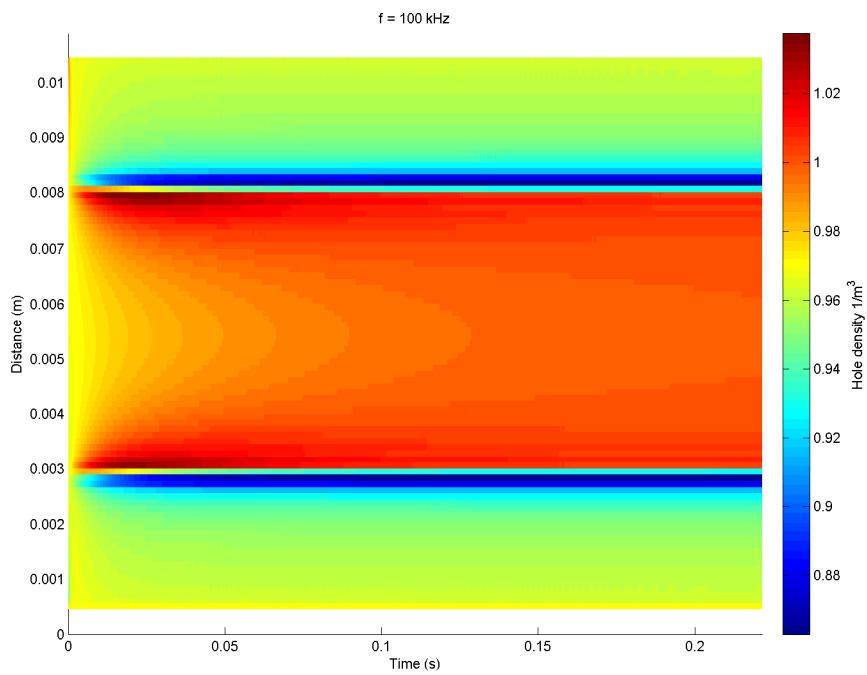


FIGURE 6.17

6.4 Experiment vs. Simulation

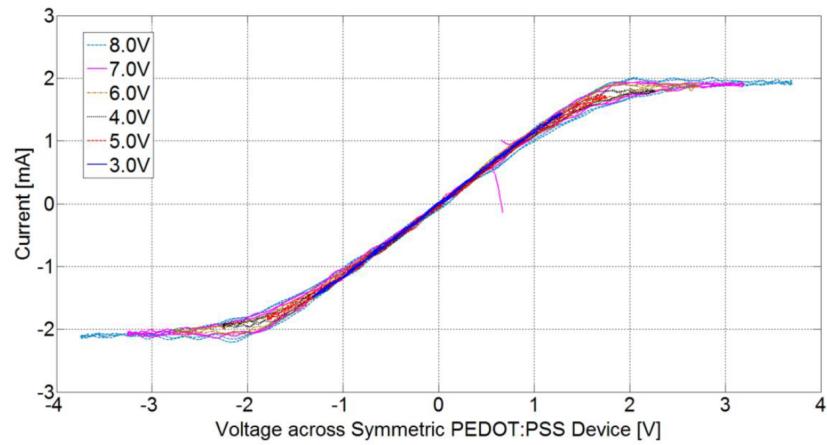


FIGURE 6.18

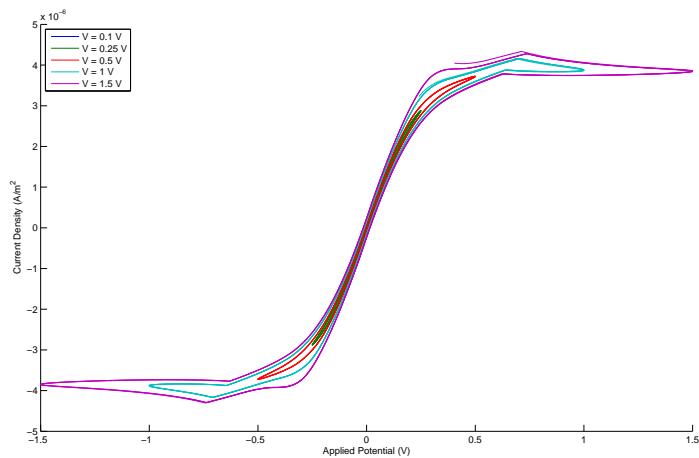


FIGURE 6.19

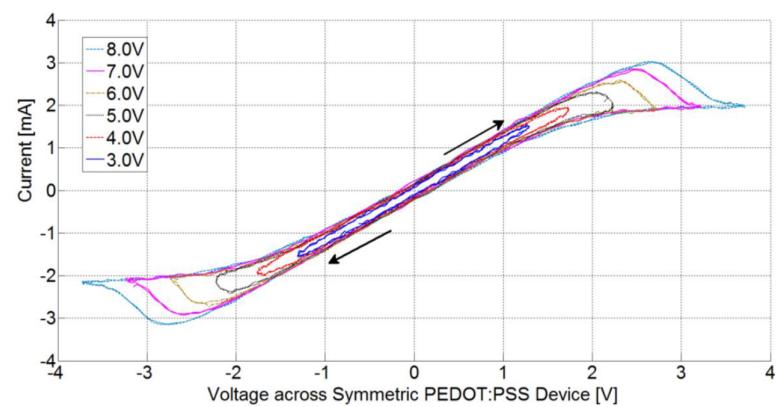


FIGURE 6.20

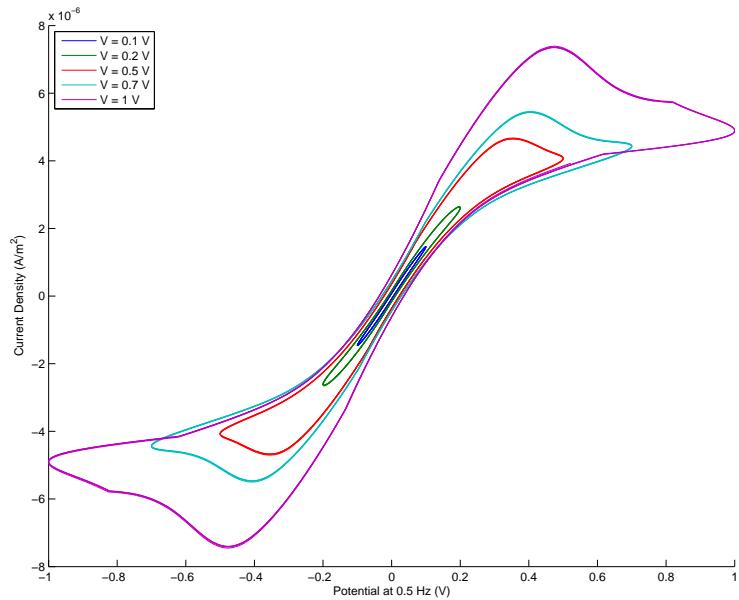


FIGURE 6.21

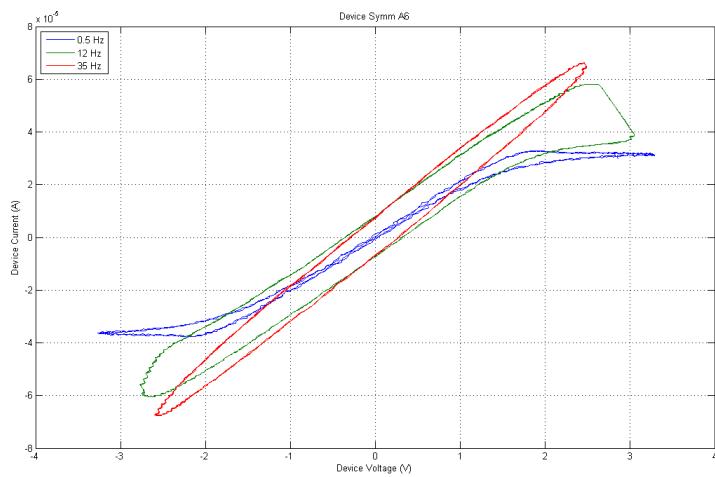


FIGURE 6.22

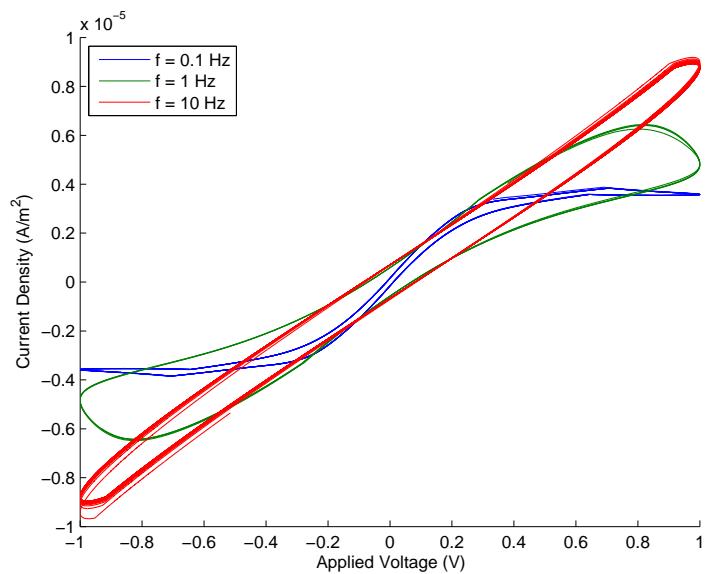


FIGURE 6.23

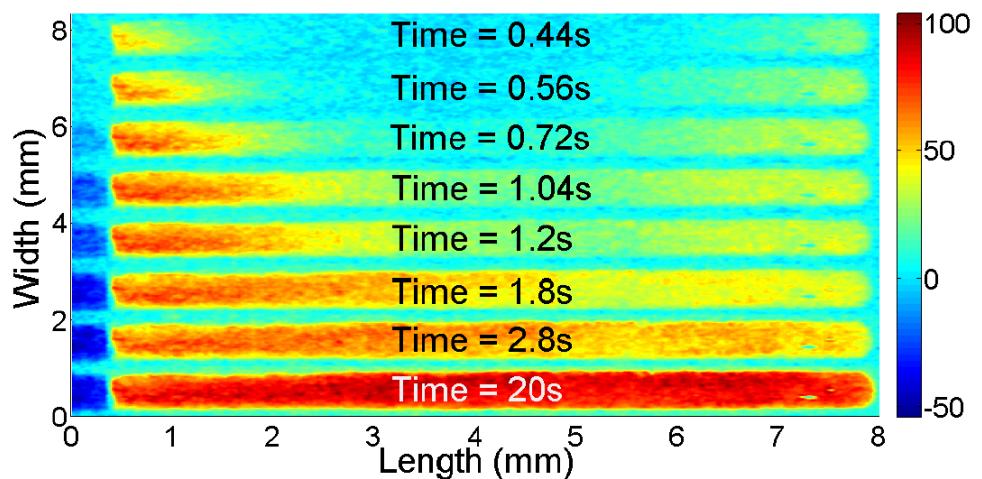


FIGURE 6.24

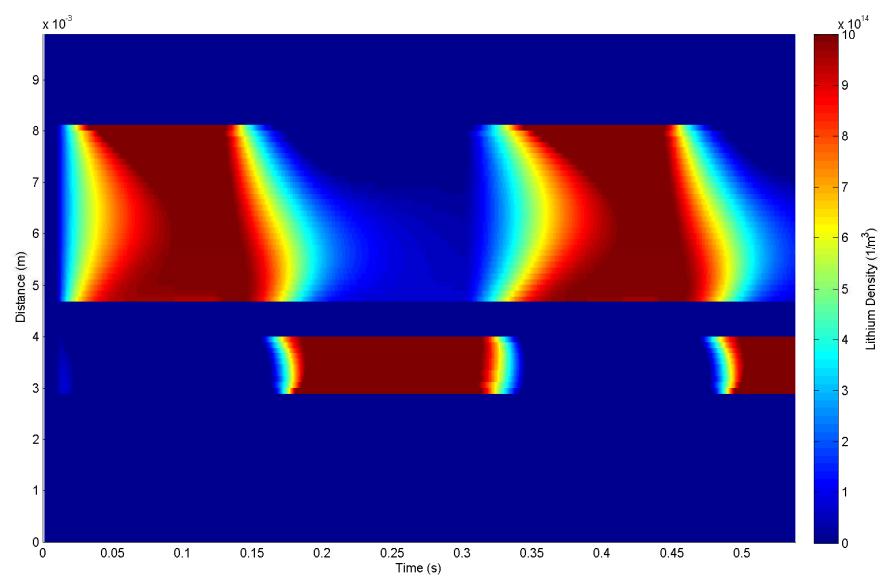


FIGURE 6.25

Chapter 7

Conclusion

The purpose of this thesis was to create a memristor model for computer simulation. We were able to model the change in conductivity through the movement of lithium and undoping of PEDOT. The transient simulation results match experimental data visually for both single channel and notched memristor. Although our simulation matched with the experimental data this model requires more work and can be improved through better numerical schemes, physical models and thorough experimentation. There are also few limitations of this model due to its size and physical features.

In terms of numerical methods there are a few down sides of using finite difference. The simulation for this device was done in 2-D instead of 3-D. This did not cause a lot of problems in our case since the structures we used were quite simple and produced reasonable results in 2-D. Unfortunately getting a transient response for devices using finite difference is computationally expensive. Even though we had a 100x100 grid, which is quite coarse, the simulation time was not less than 3 hours on a computer with multiple cores. Addition of another 100 points for a third dimension will make this simulation at least a 100 times longer. This makes 3-D simulations impractically long and very hard to test and optimize.

Another fundamental issue with this simulation arises from debye length. Maximum grid size in finite difference depends on the debye length, which is at least 5 or 6 orders of magnitude smaller than the device size. This means that we need at least 10^5 points in each direction in order to simulate this device. At this point the simulation becomes

impossibly long so we had to compromise by either reducing the device size or carrier density.

The model we have developed is quite open for improvements on carrier transport models. A constant bulk mobility was used for holes in this model which is not the case in an actual device. Holes move from site to site via hopping. Addition of lithium into PEDOT not only reduces the number of available holes but also decreases the number of possible sites through holes can move. A variable range hopping mechanism and thermal effects can be added into this model for a more complete simulation. Also PEDOT:PSS is a disordered material and the way it was deposited on a substrate can make a big difference on hole movement. Anisotropic hole mobility can be implemented in order to account for this issue.

Overall we have showed that it is possible to simulate a memristor using a simple finite difference method which can be very useful model in understanding the way ions and holes move in PEDOT. Our results show a very promising start for a vast research and development opportunities on memristor and polymer conductors.

Appendix A

Title 1

Appendix B

Title 2

Appendix C

Title 3

Bibliography

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