Ionically-Coupled Non-Linear Variable Resistors for Neuromorphic Applications

by

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Abstract

A means of simulating and fabricating memristor-like non-linear resistors for use in large arrays to form cellular neural networks is developed and investigated. The device is based on the action of ion intercalation of lithium ions into PEDOT:PSS active layers causing resistance to increase, similar to a memristor. A simple model is developed and implemented in SPICE to predict device behaviour, and a fabrication technique to rapidly create such a device by hand is detailed. Device testing confirmed the non-self-crossing hysteresis behaviour at a frequency of 10 Hz given a sinusoidal input. These results are compared to the aforementioned simulations as well as previous measurements performed in the group on similar devices, and are shown to be reasonably accurate.

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Abbreviations and Symbols

I Electric Current [A]

φ Magnetic Flux Linkage [Wb, V-s]

q Electric Charge [C]

V Electric Potential [V]

CNN Cellular Neural Network

DUT Device Under Test

nn-H Nearest-Neighbour Hopping

PC Propylene Carbonate

PEDOT Poly(3,4-ethylenedioxythiophene)

PEDOT:PSS Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate)

PET Polyethylene Terephthalate

VCCS Voltage-Controlled Current Source

VRH Variable Range Hopping

Chapter 1

Introduction

1.1 Objectives

The primary objective of the work in this thesis is to create a simple and efficient method to simulate ionically-coupled, non-linear devices with reasonable accuracy that could be scaled up for use in modelling larger, more complex neuromorphic circuits, as well as to verify the accuracy of these simulations via the fabrication and testing of these devices.

1.2 Outline

A brief background relating to cellular neural networks, the discovery and creation of the memristor are discussed in Chapter 2. In addition, a look into memristor-like devices is presented, followed by a background of some of the more significant materials used in this thesis. Chapter 3 investigates the device structure of memristor-like devices and how it can be developed into a practical mathematical model which can be implemented in a reasonably accurate, if approximated, manner. A method for fabricating these devices is presented in Chapter 4. The results of these simulated

models are discussed in Chapter 5 and their usefulness determined through comparison to results from previous work within the research group. Next, a practical method for fabricating these devices is presented using simple methods to create large memristor-like devices. Finally, the structure and operation of several promising devices is evaluated, and the behaviour of these devices is compared to the previously developed simulation for validation.

Chapter 2

Background

In the following sections, an introduction to cellular neural networks is presented, followed by a discussion of their applications. A particular emphasis is placed on their role as neuromorphic networks, as the devices investigated for this thesis are ultimately intended to function as elements in such a network. A discussion of non-linear elements follows as a means to demonstrate practical examples of useful CNN cells. Subsequently, conductive polymers and their usefulness in creating non-linear elements is also presented.

2.1 Cellular Neural Networks

A cellular neural network, or CNN, is a multidimensional array of mainly identical dynamical systems called “cells”. Each cell is restricted to interactions only within its own local space within a finite radius, typically referred to as “nearest neighbour” interactions. Additionally, all state variables in the CNN are continuous signals [1]. Cells can only communicate with distant cells in an indirect manner by propagating their input through their nearest neighbours and allowing each cell to process the data independently, based on how the CNN is programmed. Figure 2.1(a) shows the

general form of a nearest-neighbour CNN. In Figure 2.1(b), a symbolic notation for a computing cell is presented where the state of the cell, X_{ij} , is influenced by I_{ij} which is a summation via Kirchoff's Current Law of the nearest-neighbour contributions. Stationary and time-varying input signals are denoted by U_{ij} and $u_{ij}(t)$ respectively, and y_{ij} represents the output of the cell at position (i, j) .

Figure 2.1: Connectivity in a rectangular CNN (modified from [2]).

The set of parameters, arranged in matrices, that define a CNN of any size are shown in (2.1), where $\dot{\mathbf{x}}$ is array for the time derivative of $\mathbf{x}$.

$$\dot{\mathbf{x}} = -\mathbf{x} + \mathbf{A}\mathbf{y} + \mathbf{B}\mathbf{u} + \mathbf{U} \quad (2.1)$$

A template is what is used to program the interactions between a cell and its adjacent cells and is known as the “cloning template” [2]. For example, the cloning template that would describe a basic cell in a simple grid arrangement with connections to its eight nearest neighbour cells is given in (2.2), where matrices $\mathbf{A}$ and $\mathbf{B}$ describe the feedback and feedforward templates, respectively, for any one cell in the network.

$$\mathbf{A} = \begin{bmatrix} a_{i-1,j-1} & a_{i,j-1} & a_{i+1,j-1} \\ a_{i-1,j} & a_{i,j} & a_{i+1,j} \\ a_{i-1,j+1} & a_{i,j+1} & a_{i+1,j+1} \end{bmatrix}, \quad \mathbf{B} = \begin{bmatrix} b_{i-1,j-1} & b_{i,j-1} & b_{i+1,j-1} \\ b_{i-1,j} & b_{i,j} & b_{i+1,j} \\ b_{i-1,j+1} & b_{i,j+1} & b_{i+1,j+1} \end{bmatrix} \quad (2.2)$$

Upon receiving an external input, each cell will process the stimuli it detects as well as the output of its nearest neighbours, and will propagate its resultant signal to each of its own nearest neighbours, which will themselves repeat the process until the edge of the network is reached. In this way, a CNN will always settle to a specific steady state after receiving an input. A global effect is reached through several iterations of the local filter for a cell, through what is known as the “propagation property” [3].

2.1.1 Applications of Cellular Neural Networks

Due to their parallel structure, CNNs can process certain types of data very quickly. This makes them particularly competent at several specific applications. One of the most evident, and commonly explored, is image processing [4]. Another common application of the cellular neural network is a class of electronic network referred to as a neuromorphic network. A neuromorphic network is designed to emulate the architecture and operation of biological systems [5]. These systems include such human equivalences as the retina of the eye [6] or the neurons in the brain [7].

2.2 Non-Linear Resistive Elements

One type of device that is particularly well-suited for use as a cell unit in a CNN is the memristor, since it fulfils the necessary requirements of CNN elements, such as being continuous, dynamic devices that can be arranged into a multidimensional

array and only require connections to their nearest neighbour cells. Non-linearity is also a necessary feature for CNN cells that memristors inherently possess.

2.2.1 Memristors

A memristor is a passive, two-terminal circuit element. It was first posited by Dr. Leon Chua in an article in 1971 [8]. The basis of his argument for the existence of the memristor (so named as a portmanteau of “memory” and “resistor”) was that there were six mathematical relations relating pairs of the four fundamental electronic circuit variables: voltage v , current i , charge q , and magnetic flux linkage φ . Two of these pairs are time dependent, one defining the concept of flux and the other the concept of induction. Of the four remaining relations, three of them define the three common passive devices (resistor, capacitor, and inductor), leaving one relationship without a corresponding device. These relationships are summarized in a visual form in Figure 2.2.

The mathematical relations not yet assigned to a passive device are what define the memristor, summarized in (2.3).

$$d\varphi = M dq \quad (2.3)$$

Equation (2.3) can also be used to relate the voltage and current through a “charge-controlled” memristor, as shown in (2.4). A similar relation is valid for a “flux-controlled memristor”.

$$v(t) = M(q(t))i(t), \quad M(q) = \frac{d\varphi(q)}{dq} \quad (2.4)$$

M is a function of charge and represents the “memristance” of the device. From

Figure 2.2: Visualization of the four fundamental circuit elements and their relationships [9].

this, it can be seen that a memristor with constant current will simply be a resistor. The $i - v$ characteristic for a sinusoidal input to a typical memristor generally takes the form of a frequency dependent Lissajous figure [10]. This shape is often described as a “pinched hysteresis” curve. There are two types of hysteresis loops, referred to as “self-crossing” and “not self-crossing” [11]. An example of the self-crossing pinched hysteresis curve characteristic of a memristor is shown in Figure 2.3. Along with the concept of the memristor, Chua also proposed several practical circuit realizations of the memristor using the existing passive elements combined with active components.

In 1976, Chua published a follow-up paper which expanded the definition of memristors to include what he named “memrsitive systems” [10]. This definition included any device or system whose characteristics were similar to that of the memristor, though they cannot be accurately modelled strictly with classic memristor theory.

Figure 2.3: An example of a self-crossing hysteresis loop (modified from [11]).

These systems were defined by state equations, shown in (2.5), where u and y represent the input and output of the system, and x represents the state of the system.

$$\begin{aligned} \dot{x} &= f(x, u, t) \\ y &= g(x, u, t)u \end{aligned} \tag{2.5}$$

These state equations can be used to describe far more systems than those represented in the original article.

2.2.2 The First Memristors

The first discrete, passive, 2-terminal devices that were claimed to be memristors were developed by HP Labs in 2008. The device is based on dopant movement in a 5 nm titanium dioxide active layer sandwiched between two metal contacts [12]. The device is a semiconductor of thickness D between two metal contacts, in which there are two variable resistors in series. One resistor is the area of the film that has a high concentration of dopants, and is labelled R_{ON} . The other region, having low dopant concentration, is labelled R_{OFF} . This structure is shown in Figure 2.4, where the

doped region is R_{ON} and the undoped region is R_{OFF} .

Figure 2.4: Simplified device structure of HP memristor (from [12]).

Applying a voltage across the device moves the boundary between the two regions by causing the dopants to drift through the material. Using standard ion drift equations and device dimension and fitting them into the memristive system state equations, an expression for the memristance of this structure is obtained, as shown in (2.6).

$$M(q) = R_{OFF} \left(1 - \frac{\mu_V R_{ON}}{D^2} q(t) \right) \quad (2.6)$$

where μ_V is the average ion mobility. The state variable for the equation represented by the dopant distribution term is, naturally, bounded between 0 and the device thickness, D . This restricts the device operation and defines the “memristor regime”, outside of which the device cannot be considered a memristor. As long as the device is operated within these bounds, a symmetrical, double loop hysteresis $i-v$ curve is seen as the result of a sinusoidal input. As it should, the hysteresis loop becomes narrower as frequency is increased, ultimately reaching a linear relationship.

2.2.3 Memristor-like Devices

There has been some level of controversy regarding HP’s 2008 announcement of their discovery of the memristor. Primarily, the arguments centre on the fact that HP’s

memristive devices do not interact in any meaningful way with magnetism, and that Chua’s original paper implied that this magnetic interaction was significant as part of the device’s operation [13]. Some claim that these resistive memory elements are simply a broader category of device that the memristor would then fit somewhere within. These arguments have been refuted by Chua, who claims that all two-terminal resistance switching memory devices are memristors [14]. It is generally accepted, however, that the devices discussed in 2008 at least fall within the more general classification of memristive systems.

2.3 Conductive Polymers

This section discusses some of the materials used in the construction of the devices created for this thesis. It will focus on the conductive polymer PEDOT:PSS and discuss the mechanism of conduction therein, before discussing dynamic doping of the material.

2.3.1 PEDOT:PSS

Bayer AG research laboratories developed a water-soluble polyelectrolyte called Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonic acid) (abbreviated PEDOT:PSS) in the 1980s. It has been found to have a wide array of applications, from antistatic layers for photographic films, to electroluminescent displays, to organic transistors [15]. Part of the reason why PEDOT:PSS has seen so many applications is that it can be incorporated into a design process in a wide variety of ways including: screen-printing, ink jet printing, spin coating, and vacuum deposition [16].

The PEDOT chain can lose an electron from the EDOT monomer to take on a positive charge, becoming what is known as a polycation. The PSS chain forms

a polyanion by losing a hydrogen atom from its SO_3H group. The PSS polyanion can oxidize an EDOT monomer, creating an ionic bond between them and thereby p-doping the PEDOT chain. This bonding structure is shown in Figure 2.5.

Figure 2.5: Ionic bonding structure of PEDOT chain (bottom) and PSS backbone (modified from [17]).

In addition, it is possible to use a PSS backbone as a template to grow PEDOT on, as EDOT monomers oxidize and bond onto it, attaching the two polymers and resulting in a p-doped, conductive final product. The PEDOT does not form a continuous polymer bond along the entire length of the PSS backbone, however. Instead it forms segmented chains of PEDOT intermittently attached along the length of the PSS backbone, as can be seen in Figure 2.6(b) [15]. Since these sections of PEDOT:PSS are doped, they form conductive sections capable of accepting electrons from other conductive sections. Lengths of PSS with sporadically bonded PEDOT can then be immersed in water, allowing them to exist in a liquid film, suitable for various deposition techniques, as seen in Figure 2.6(d).

Figure 2.6: Templated PEDOT:PSS and its formation into a film.

- (a) Chemical structure of ionically bonded PEDOT:PSS.
 - (b) Segments of PEDOT interspersed along the PSS backbone.
 - (c) Water saturated, entangled PSS chains forming larger, amorphous particles.
 - (d) Larger particles of tangled PEDOT:PSS chains creating a consistent film.
- (with permission from [18])

2.3.2 Charge Transport in PEDOT:PSS

A PEDOT:PSS film can be visualized as an irregular composition of conductive and less conductive regions. The conductive regions are where there is a large concentration of PEDOT-rich particles, whereas the non-conductive regions are primarily composed of only the PSS backbone material [19]. Charge transport in this material is heavily dependent on the transport of charge within and between these regions. The conductivity, then, is strongly based on the ratio of PEDOT to PSS (i.e. the density of PEDOT-rich areas) [20]. In a similar manner, the conductivity of the film can also be reduced by adding other non-conductive material to the film [21]. The conductivity can also be affected by other factors, such as a different backbone polymer, the level of doping added to the film, as well as the type of ion used to dope the film.

The morphology of conductive polymers makes it difficult to accurately model exactly how charge travels through the material. The charge transport models of

traditional inorganic crystalline semiconductors or metals do not apply to the amorphous and random nature of conjugated polymers [21]. Electrons in those materials do not undergo a significant amount of scattering as they travel through the material, and as a result the electrons in those materials travel in a delocalised (i.e. free to move throughout the material) manner. This disorderly nature of conductive polymers means that electron scattering becomes a significant factor when considering the nature of electron movement through the material. Generally, electrons in a conductive polymer are no longer delocalised and become bound within a certain region of the material.

The result is that the conductivity model of conductive polymers is dominated by charge hopping effects [21]. This effect is known as Variable Range Hopping (VRH). It has been shown that the primary charge transport mechanisms in spin-coated PEDOT:PSS is three dimensional VRH and nearest-neighbour hopping (nn-H), depending on whether the charges are travelling within PEDOT-rich regions or between them [22].

2.3.3 Doping PEDOT:PSS

One trait which conductive polymers share with traditional semiconductors is the ability to be either p-doped (by losing an electron) or n-doped (by gaining an electron), greatly affecting their overall conductivity [21]. In PEDOT:PSS, the presence of dopants adding or removing electrons from the ionic bond between the PSS backbone and PEDOT sections results in the creation of a quasi-particle known as a bipolaron [23]. Bipolarons are the result of a pair of polarons, themselves a pair of solitons, which are created when an electron is removed from a polymer chain and a hybrid bond is created to accommodate this change, manifesting physically as a “kink” in the polymer chain. These quasi-particles are mobile along the polymer chains as well

as between chains, so inter-chain conductivity remains the primary means of charge movement in a doped polymer.

Dopants can add or remove this charge via reduction or oxidation reactions, respectively, not by the addition of an impurity as in the case of crystalline semiconductors. These types of reactions are referred to as “redox” reactions.

A conductive polymer can be doped through a variety of means, including chemically, electrochemically, through photoinducing, and charge injection. The doping method used for this thesis was electrochemical doping. Electrochemical doping, in its simplest form, can be implemented in a very similar manner to the process of electro-plating. Two electrodes are placed into a solution of electrolyte, forming a circuit through the electrolyte. A potential is then applied across the electrodes and the cations and anions from the electrolyte separate and begin moving towards the electrodes. The electrode with the higher voltage, the cathode, attracts the anions whereas the lower potential electrode, the anode, draws the cations towards it. Depending on the type of doping desired, the polymer is placed on the corresponding electrode to have the appropriate type of ions drawn into it and cause redox reactions, doping the material. This process of reversibly inserting ions into a solid without affecting the structure is known as “intercalation” [24].

In the case of PEDOT:PSS, the PSS monomers drop their hydrogen atom, becoming PSS^- , and oxidizing the PEDOT chain by forcing it to lose an electron and become p-doped, as seen in (2.7). The doped PEDOT^+ and PSS^- counter ion then ionically bond to form stable PEDOT:PSS.

This doping of PEDOT^+ can be reversed by introduction of a cation such as Li^+ .

The cation breaks the ionic bond between PEDOT⁺ and PSS⁻ and the PEDOT⁺ gains an electron and becomes dedoped, while the Li⁺ cation neutralizes the PSS⁻ polyanion. Thus it can be said that the Li⁺ cation reduces the PEDOT⁺, as is shown in (2.8) [23].

These redox reactions can be applied dynamically to a section of conductive polymer by applying a potential across a section of PEDOT:PSS that is adjacent to mobile ions, intercalating Li⁺ cations into the PEDOT:PSS and dedoping part of it. As the potential changes, so does the doping level, thus introducing a non-linear history aspect to what is otherwise a simple strip of conductive material. This principle forms the basis for the devices used in this thesis.

Chapter 3

Modelling & Simulation

In this chapter, a brief summary of the methods being implemented for modelling non-linear resistive devices is provided. An overview of other simulation work in this research group follows before a discussion of the methods implemented for this thesis.

3.1 Device Structure

The intended structure of the memristor-like device is very simple and straightforward. This structure is demonstrated in Figure 3.1; a single strip of conductive polymer (grey) is connected lengthways between two electrodes (black).

Figure 3.1: General structure and lumped elements model of non-linear resistor.

The conductive polymer is immersed in ion-rich electrolyte and a path to intercalate ions is available. The electrodes are isolated from the electrolyte such that the only path from electrode to electrolyte is through the conductive polymer.

3.2 Model Development

The model and simulation method designed to simulate the devices in this thesis were based on the model and simulation method developed for a PEDOT:PSS-based dual-line transistor device, which used the same materials and electrochemical doping technique that was previously studied within the research group [18]. This transistor device works as an effective basis for a model of the non-linear resistors in this thesis because the geometries are highly similar. The development of a model for the dual-line device inevitably develops a model for a single line of conductive polymer surrounded by electrolyte.

In order to get an accurate model for the device, a lumped components equivalent circuit was developed, shown in Figure 3.2. It can be seen that, since the non-linear resistor device is simply a single strip of conductive polymer surrounded by electrolyte, the lumped element model for the dual-line device can easily be applied to the single line. This single line lumped element model is shown in Figure 3.1.

In this model, R_{ec} is the distributed resistance of the conductive polymer element, R_{ion} represents the resistance associated with the movement of ions in the electrolyte, and C_{dl} is the distributed “double layer” capacitance that is the result of the interaction of the conductive polymer and electrolyte boundary, particularly the tendency for ions of opposing charge (with respect to the electrode) to be near the electrode due to the applied voltage.

The next step in developing the model was based on curve-fitting and parameter

Figure 3.2: Lumped elements model of dual-line transistor device (with permission from [18]).

extraction of the dual-line transistor's conductivity response, which can be seen in Figure 3.3. The linear portion of the transfer characteristic can be given by (3.1).

A sigmoid curve was chosen to emulate the measured data, as shown in (3.2), where G is the conductance of the material segment, G_0 is the maximum conductance, G_{min} is the minimum conductance, C_{dl} is the double layer capacitance of the material segment, Q_{dl} is the charge intercalation parameter, V_{dl} is the voltage across the double layer capacitance (i.e. the potential difference between the conductive polymer and the electrolyte solution), and V_{off} is the offset voltage at $\frac{G_0}{2}$.

$$Q_{acc} = V_{app} \times C_{dl} \quad (3.1)$$

$$G = \frac{G_0}{1 + e^{\frac{C_{dl}}{Q_{dl}}(V_{dl} - V_{off})}} + G_{min} \quad (3.2)$$

Generally, G_{min} is small compared to G_0 , and thus can usually be ignored. Neglecting G_{min} , (3.3) is the result. This equation characterizes the variable conductivity

Figure 3.3: Measured conductance of dual-line device compared to modelled curve (with permission from [18]).

(or inversely, resistance) of a square of material and forms the basic building block used to simulate the non-linear resistors developed in this thesis.

$$G = \frac{G_0}{1 + e^{\frac{C_{dl}}{Q_{dl}}(V_{dl} - V_{off})}} \quad (3.3)$$

3.3 Simulation

In order to generalize the geometry this model can be applied to, it is useful to separate the model into an electronic layer, which is made up of any active or passive electronic components, and an ionic layer which is made up of the electrolyte and any other ionic components. These layers interact with each other via the double layer capacitance at the boundary of the polymer and the electrolyte. In addition, potentially any geometry can be simulated by using the basic electronic layer model

as a square, and connecting several squares to each other and to ionic layers.

The key component used to simulate the electronic layer blocks is a voltage-controlled current source (VCCS) with a custom gain or transconductance expression, as shown in Figure 3.4. This element can be used to convert the voltage across the double layer capacitance into the conductivity for a short section of conductive polymer material. Combining this VCCS element with the lumped-element model previously established, a complete model for simulation is formed. This simulation cell for a one-dimensional conductive polymer element is shown in figure 3.5.

Figure 3.4: Voltage-controlled current source with custom gain expression (with permission from [18])

This cell can be used to represent a short section of conductive polymer that is surrounded by electrolyte solution. By connecting several 1D elements in series, a long strip of conductive polymer surrounded by electrolyte can be simulated. This cell can be expanded to a two-dimensional version that can be used to emulate virtually any geometry that can be constructed out of these standardized squares of material, and is shown in Figure 3.6.

The only remaining aspect of the device to simulate is the electrolyte surrounding the device. Given that the interaction between the device and the electrolyte is already defined by the VCCSs, all that needs to be done is to account for the resistance due to ion mobility. Thus, the electrolyte can be incorporated into the circuit as simple

Figure 3.5: One-dimensional conducting polymer cell with two dimensional ionic connections (with permission from [18])

Figure 3.6: Two-dimensional conducting polymer cell with two dimensional ionic connections (with permission from [18])

resistors that connect to the ionic layer connections of the previously defined cells. To simplify simulation, several standard blocks representing common R_{ion} configurations are added, with examples of what is contained in these blocks shown in Figure 3.7.

Figure 3.7: Several common configurations for ionic resistance blocks (with permission and modified from [18])

These elements can all be assembled into one circuit whose layout can accurately model the single-line variable resistor device used for this thesis. This circuit is shown in Figure 3.8. The sub-blocks for each component in the simulation were implemented by netlists which can be found in Appendix A. The variable values shown in Table 3.1 were used for all simulations in this chapter. These values were determined via parameter extraction to accurately represent the active material.

3.4 Simulation Results

In order to obtain the optimal response, a sinusoidal input with an amplitude of 5 V was applied while the frequency of the input signal was swept across a range of 0.1 Hz

Figure 3.8: Complete circuit schematic to simulate a strip of conductive polymer surrounded by electrolyte.

Table 3.1: Variable values used in non-linear resistor simulations.

Variable	Value
R_{ec}	200 Ω
R_{ion}	200 k Ω
R_{leak}	$1 \times 10^{15} \Omega$
Q_0	10 μC
C_0	20 μF
V_{th}	0 V

to 100 Hz to determine the frequency which gives the best response. In this case, the best response is determined by the widest hysteresis loop, since that indicates more non-linearity and more significant memory effects. The plot of the $I - V$ curves for all tested frequencies is shown in Figure 3.9.

From this figure, it can be seen that the most non-linear response occurs with an input frequency of 10 Hz. Due to this, all future simulations will be using an input frequency of 10 Hz in this chapter. Figure 3.10 shows the basic response of the device given a 10 Hz sinusoidal input with an amplitude of 5 V. In addition, arrows have been added to the figure to show the movement of the signal over time. It is clear that this hysteresis effect is of the “not self-crossing” type. Also of note is the small curve on the inside of the loop in the first quadrant. This loop is due to a “start-up” effect as the ion intercalation is not as fast on the first cycle.

The most relevant point of comparison for the results of these simulations would be a master’s thesis previously completed in this research group in which similar non-linear devices were constructed and tested [25]. Their structure was similar enough that the behaviour of the devices should be very similar, but there will be some differences as the physical dimensions of the devices are different. Thus, the simulation

Figure 3.9: Frequency sweep results for the one-line non-linear resistor model.

Figure 3.10: Simulation results of non-linear resistor device given a 10 Hz sinusoidal input of amplitude 5 V.

results will be compared primarily on a behavioural level.

For comparison, Figure 3.11 shows the measured results for a symmetrical PE-DOT:PSS device with an input of a sinusoid of varying amplitudes and a frequency of 100 mHz.

Figure 3.11: I-V curves measured across a non-linear resistor device at a frequency of 100 mHz with varying amplitude [25].

Figure 3.12 shows the simulation results for the same type and range of input as Figure 3.11. Both figures demonstrate a linear region from approximately -1.5 V to 1.5 V, and the simulated data matches the measured data quite well. However, the simulated data clearly deviates from the measured data as the input voltage increases beyond approximately ± 2 V. As it approaches total saturation, the resistance of the device should stop changing, reaching either maximum or minimum resistance. It is reasonable to conclude that the curve-fitted model does not properly account for long-term saturation or de-saturation of ions at high voltages and low frequencies. This is reasonable since the model is only partially empirical. At higher frequencies,

Figure 3.12: Simulation results for varying amplitudes of a sinusoidal input of frequency 100 mHz.

the model will continue to remain valid for high voltages as the device will never be completely saturated or de-saturated since the voltage changes too quickly. This can be inferred by comparing higher frequency measurements of the devices at the same amplitudes to equivalent simulations.

Figure 3.13 shows the measured data for a symmetrical non-linear resistor device across the same range of input amplitudes as previously discussed, but at a frequency of 1 Hz. Figure 3.14 shows the simulated results for the same conditions.

From these figures, it can be seen that the simulated and measured data have very good correlation within the bounds of ± 3 V. Beyond this threshold the shape of the curve remains reasonably accurate, although it again fails to account for the

Figure 3.13: I-V curves measured across a non-linear resistor device at a frequency of 1 Hz with varying amplitude [25].

Figure 3.14: Simulation results for varying amplitudes of a sinusoidal input of frequency 1 Hz.

total saturation or de-saturation of the device channel. As long as the device is used within these bounds, however, the model remains accurate and provides insight into the overall behaviour of the device.

Figure 3.15 shows the measured response of a symmetric non-linear resistor for various frequency sinusoidal input signals at an amplitude of 3 V. Figure 3.16 shows the simulation results for a similar set of frequency variants at an amplitude of 5 V. It can be seen that the curves have very similar characteristics, and that those characteristics vary in a consistent manner as the frequency is varied. These simulations are still somewhat rough estimates of idealized components, yet still provide useful insight into how the devices will behave with various input configurations. Later in this thesis, devices were developed which match the geometry in the simulations more accurately that will be compared to these simulated results again to ultimately gauge their accuracy.

Figure 3.15: I-V curves measured across a non-linear resistor device with varying frequency and a 3 V amplitude [26].

Figure 3.16: Simulation results for varying frequencies of a sinusoidal input of amplitude 5 V.

Chapter 4

Fabrication

The purpose of this chapter is to document the process that was used to realize the simulated device geometries from the previous chapter. First, the materials used to create the devices are described, followed by the step by step process used to fabricate a simple one-line strip of conducting polymer immersed in electrolyte solution. Next is a summary of the relevant physical parameters of the devices that were tested.

4.1 Materials

Previous work within this research group has focused on using PEDOT:PSS in an ink form that is suitable for screen-printing [25]. This is typically screen-printed onto a glass substrate. While accurate and versatile, this process requires the use of masks in order to be implemented. This requires time spent designing a mask, a method for creating a custom mask, as well as a screen-printing jig that allows for alignment of multiple layers. Masks were created by using a UV laser to precisely cure emulsion that had been deposited onto a metal wire screen.

In this thesis a different method was chosen in order to accelerate the process and potentially skip these tedious and possibly expensive steps altogether. The solution

was to simply purchase PEDOT:PSS that had already been coated onto a polyethylene terephthalate (PET) substrate, maintaining both the flexible and transparent nature of the PEDOT:PSS. Since the substrate is a polymeric plastic, it is possible to simply cut out a section of material from the large roll and use that as the active device channel.

The material used for this was Orgacon EL-350/175 [27]. This provides an even layer of PEDOT:PSS on 175 μm PET base with a resistance of 350 Ω/sq . The silver ink used to connect the contact pins to the conductive polymer was Dupont 5028 silver conductor [28]. In order to give the device structure, and to isolate the connection pins and silver ink from the electrolyte solution (due to corrosive effects resulting from their interaction), two different UV curable epoxies were used. One was low viscosity and was primarily used for connecting parts; the second was highly viscous and was used to form device structures. The epoxies used were Norland Optical Adhesive 81 and 68, respectively [29, 30]. The electrolyte used for this work was previously mixed lithium perchlorate (LiClO_4) in propylene carbonate with a concentration of 1.0 M.

4.2 Fabrication Steps

In order to be functional, the devices must be a single strip of conductive polymer connected to usable electrodes, with free access to a reservoir of electrolyte material. In order to achieve this, a standard pin header of four pins was used, and the two pins in the middle were removed. This header is then affixed to a small glass substrate using the NOA 81 UV epoxy such that the remaining two pins extend out into the middle of the glass. Next, a strip of PEDOT:PSS-coated PET of appropriate dimensions is placed between the pins and the glass, such that the length of the strip connects the two pins together. A cross-section of this step can be seen in Figure 4.1.

Figure 4.1: Cross-section of PEDOT:PSS on PET on a glass substrate with header pins as contacts.

The next step is to apply silver ink to the pins of the header such that they form a reliable electrical connection to the PEDOT:PSS channel. The entire device is then placed in an oven at 140 °C for approximately 6 minutes. This cures the silver ink so that it becomes solid while leaving the PEDOT:PSS unaffected due to the relatively low temperature. A cross section at this point in the process can be seen in Figure 4.2.

Figure 4.2: Cross-section of device in fabrication with silver ink applied to form reliable contact from pin to polymer.

After forming a continuous conductive path from pin to pin on the header, the next step is to insulate the pins and the silver to prevent them from contacting the electrolyte while simultaneously creating a raised ring of NOA 68 UV epoxy that creates a well to contain the electrolyte and keep it in contact with the device channel. The more viscous epoxy allows for some degree of shaping of the device well. The results of this step are shown in Figure 4.3. The epoxy is also transparent so it is cured throughout with the application of an intense UV light source. While the light source cures the epoxy most of the way, in order to form a lasting chemical bond with the glass, the epoxy must be left to cure in the open air for a week or placed into an oven at 50 °C for 24 hours [30].

Figure 4.3: Cross-section of device in fabrication where cured UV epoxy has been applied, insulating the contacts and forming the electrolyte well.

The final step is to deposit the electrolyte solution into the device well using a syringe, completing the device structure. Optionally, another layer of NOA 68 UV epoxy can be applied by depositing it on top of the electrolyte where it will remain long enough to be mostly cured by application of UV light. This allows for the electrolyte to be sealed in, creating a fairly robust device. The device can still

function completely normally without this seal. Figures 4.4 and 4.5 demonstrate these two steps of the process, respectively. A photo of a mostly completed device (all steps except electrolyte deposition) is shown in Figure 4.6.

Figure 4.4: Cross-section of device in fabrication where electrolyte has been deposited into the electrolyte well.

Figure 4.5: Final cross-section of device showing all applied materials including epoxy seal on top of electrolyte well.

Figure 4.6: Photo of a mostly complete device. The blue strip in the middle is the PEDOT:PSS channel; the header pins and cured silver ink are visible at either end of the PEDOT:PSS strip. The epoxy that forms the device well can also be seen surrounding the device. No electrolyte has been deposited yet.

4.3 Process Improvements

The most significant drawback with this process is that each step for each device is carried out entirely by hand. While this allows the process to be completed in a very reasonable amount of time, it introduces a potentially infinite number of possible errors and inconsistencies that can occur. Without modifying the process too heavily, a simple jig could be created with a cutout for the device channel which could be set atop the PEDOT:PSS strip and have the epoxy deposited around it. This would allow for much more consistent device active regions and significantly reduce the time needed to build the devices. Additionally, a punch could be created to cut out PEDOT:PSS strips of a consistent size.

Chapter 5

Testing & Results

This chapter will describe the equipment and methods implemented in the testing of the devices previously discussed and developed. A description and evaluation of each functional device will be covered in the subsequent section. The results of the testing will then be presented and interpreted, before being compared and validated based on new simulations and previous measurements for similar devices previously created in the research group.

5.1 Testing Setup

The setup to test the devices was very simple. An arbitrary function generator was used to provide a sinusoidal input capable of varying both amplitude and frequency. This was connected to a series resistor, which was then connected in series with the device under test (DUT) before completing the circuit and connecting to ground. Oscilloscope probes were then attached to the source node and the node between the sensing resistor and DUT. This circuit is shown in Figure 5.1. Doing this allows for determination of the current in the circuit by dividing the difference of these two voltages by the sensing resistance, thus enabling the creation of an I-V characteristic

plot. The sensing resistor was chosen to be $1\text{ k}\Omega$ such that it was large enough to provide a measurable amount of voltage difference as compared to the input signal, but not so large as to become a majority of the resistance in the circuit at any point in the sinusoidal cycle of the input. The measured value of the sensing resistor was $0.986\text{ k}\Omega$.

Figure 5.1: Test circuit configuration.

Table 5.1 shows a summary of the equipment used in the acquisition of the following data.

Table 5.1: Summary of equipment used in testing.

Device	Model
Multimeter	Tenma 72-2050
Oscilloscope	Tektronix TDS 3054
Voltage Probes	Tek 6139A
Function Generator	HP 33120A
Function Generator 2	Rigol DG1022

5.2 Results

This section will present the results of previously discussed testing methods when applied to each fabricated device that had a meaningful result. Many devices never functioned whatsoever due to issues in the fabrication process. Results of each functional device are presented, followed by a comparison to both expectations based on simulations as well as the previous tests of similar devices created in this research group.

5.2.1 Physical Properties

Two headers supporting five devices each were used in a breadboard to make connections and keep the devices stable while testing. The devices on each header, or “rail” were numbered from top to bottom with the pins on the left. Tables 5.2 and 5.3 contain the physical properties for the devices on rail 1 (R1) and rail 2 (R2), respectively. Note that the devices on rail 2 were intentionally designed with a gradually increasing width as device enumeration increases in order to investigate the effects of channel width.

Table 5.2: Physical device properties for Rail 1.

Device	Width (mm)	Length (mm)	Dry Resistance (k Ω)
D1	1.34	8.47	2.90
	1.13		
D2	1.32	8.75	5.83
	1.43		
D3	1.50	7.99	2.89
	1.58		
D4	1.61	7.85	4.27
	1.47		
D5	1.33	8.05	2.563
	1.47		

Table 5.3: Physical device properties for Rail 2.

Device	Width (mm)	Length (mm)	Dry Resistance (k Ω)
D1	1.76	7.82	2.174
	1.91		
D2	2.10	7.83	2.060
	1.88		
D3	2.15	7.49	1.270
	2.29		
D4	2.46	7.53	1.439
	2.47		
D5	3.56	7.68	1.298
	3.60		

5.2.2 Device Functionality

This section contains a device-by-device presentation of results of testing as well as a brief discussion of any inconsistencies or oddities in the resulting waveforms and their potential causes. One particularly useful aspect of the devices investigated in this thesis is their predisposition to electrochromativity [31]. As ions intercalate into the PEDOT:PSS film and dedope it, the optical absorption spectrum for the material is changed [18]. This results in an apparent blue opacity property and provides the unique opportunity to determine a significant amount of information about the functionality of the device from simple visual inspection using a microscope.

This property of organic conducting polymers is used extensively to understand abnormalities in the devices fabricated for this thesis, and is highlighted in device photos by a red rectangle for this chapter. The method for observation of this effect in this thesis was to apply a constant voltage across the device using a battery pack with two 1.2 V batteries connected in series. The voltage was applied across the device in both directions for observation of the electrochromic properties at both ends of the device. This effect is due to the presence of positively charged ions intercalating into the material, and thus will be observed on the device terminal that is connected to the negative side of the batteries.

Device R1D1

Device R1D1 was one of the most promising devices during initial testing. Figures 5.2 and 5.3 show a clean, straight edge at both ends of the device, resulting in a uniform cross-sectional resistance and good symmetry. It is a little difficult to see the change in opacity in Figure 5.3, however it is noticeable as a blue discolouration beneath the reflection on the left of the device when compared to the photo with no applied potential.

Figure 5.2: Side by side of device R1D1 with positive voltage applied to the left electrode with respect to the right electrode (top) and with no applied voltage (bottom).

The results of this symmetry can be seen in the voltage response of the device in Figure 5.4. The same or very similar curve shape is seen on both ends of the device (i.e. at both high and low potential). Figure 5.5 shows a zero-crossing hysteresis loop with wide opening at either end. As expected, it is also highly symmetrical.

Figure 5.3: Side by side of device R1D1 with positive voltage applied to the right electrode with respect to the left electrode (top) and with no applied voltage (bottom).

Figure 5.4: Voltage over time for device R1D1 at 10 Hz and 5 V amplitude.

Figure 5.5: I-V curve for device R1D1 at 10 Hz and 5 V amplitude. Arrows indicate signal change with respect to time.

The current of the device remains low until the input voltage reaches about half of its maximum value, at which point it increases rapidly. At approximately 4 V, the resistance begins to increase and the current starts to drop off again while voltage continues to increase. As the voltage reaches its maximum value, the current has returned to being low and stays there until high negative voltage is reached, at which point the other end of the device begins to get dedoped by intercalating ions and the process repeats for the negative half-cycle. This exact behaviour is not quite the expected result, as can be seen if compared to Figure 3.10. The transitions from high resistance to low resistance are far more abrupt than predicted. This is most likely due to the relatively high voltage input of the device. In the past, it has been demonstrated that voltages beyond 2 V can cause reactions in the polymer other than the desired and reversible redox reactions that can permanently affect conductivity [25]. The data in Figure 5.5 were acquired shortly after the voltage had been applied and as such it is likely that the polymer had not yet significantly degraded, but was showing first signs of the degradation. This effect is the likely cause of the close match between the two voltages measured. The degradation would cause a much higher resistance on the device channel and result in a much smaller differential voltage detected across the sensing resistor. Shortly after these data were collected, the device ceased conducting entirely, appearing for all intents and purposes as an open circuit. Later visual inspection of the device using a microscope yielded no discernible visible changes.

Device R1D2

Figures 5.6 and 5.7 indicate device R1D2 to be working well, visually. The dedoped region is quite large for both ends of the device, as well as reasonably even across the device. The large mark on the left side of the device is an area where some of the UV epoxy ran underneath the device before being cured, and does not affect the operation of the device.

Figure 5.6 shows device R1D2 with a DC potential applied across the device from its left side (positive) to its right side (negative), and shows a change in the colour and transparency of the material, indicating an intercalation of ions. Figure 5.7 shows the same device with the potential applied in the other direction.

Figure 5.6: Device R1D2 with positive voltage applied to the left electrode with respect to the right electrode (top) and without (bottom).

Figure 5.7: Device R1D2 with positive voltage applied to the right electrode with respect to the left electrode (top) and without (bottom).

Figure 5.8 shows the measured voltage response of the device for an AC sinusoidal input of frequency 10 Hz and amplitude 3 V. Figure 5.9 shows the I-V curve for the device, exhibiting a non-crossing hysteresis characteristic, as expected. The hysteresis loop is very similar to the response measured for device R1D1, except that it never quite crosses zero. Inspecting the ion intercalation area in Figures 5.6 and 5.7 shows that it makes up the majority of the device channel. Only a very short length of the device is not dedoped. As a result, many of the Li^+ ions remain in the PEDOT:PSS film perpetually, preventing the curve from reaching zero. At a lower frequency, the loop would become zero-crossing again as the additional time would allow ions to be expelled from the PEDOT:PSS.

Figure 5.8: Voltage over time for testing of device R1D2 at 10 Hz, 3 V amplitude.

Figure 5.9: I-V curve for R1D2 at 10 Hz. Arrows indicate signal change over time.

Device R1D4

Device R1D4 also has a clearly defined active region with good electrode isolation from the electrolyte. Figures 5.10 and 5.11 show these properties. Note that the left side of the device is somewhat close to the electrode, as can be seen in 5.11.

Figure 5.10: Device R1D4 with positive voltage applied to the left electrode with respect to the right electrode (top) and without (bottom).

Figure 5.12 shows the voltage change on the device over time, where it can be seen that the signal is not perfectly symmetrical. Looking at the I-V curve in Figure 5.13 better demonstrates this inconsistency. A possible cause of the sudden changes in current at high voltage could be due to intercalated Li^+ ions migrating through the PEDOT:PSS layer and reaching the electrode due to the shorter distance between the electrode and the electrolyte. The issue is almost assuredly due to the geometry of the device, as no similar inconsistency can be seen on the other side of the hysteresis

loop since the epoxy barrier separating the electrode from the electrolyte is greater.

The response remains a valid non-self-crossing response for a non-linear resistor device. Once again, the slow rate of ion movement prevents the loop from crossing through zero.

Figure 5.11: Device R1D4 with positive voltage applied to the right electrode with respect to the left electrode (top) and without (bottom).

Figure 5.12: Voltage over time for testing of device R1D4 at 10 Hz, 3 V amplitude.

Figure 5.13: I-V curve for device R1D4 at 10 Hz.

Device R1D5

It is clear from Figure 5.14 that device R1D5 will not work in the expected manner. The opacity and colour change caused by intercalated ions indicate that there is a direct connection from the right electrode to the electrolyte solution, despite the majority of that end of the device being acceptable. Figure 5.15 indicates that the other end of the device should function normally as expected. While not an ideal device, it can still serve as an interesting case study for unexpected effects or possibly even identifying future manufacturing defects.

The effect of this fabrication error can be seen clearly in both Figures 5.16 and 5.17. In Figure 5.16, at the positive end of the sinusoid, the non-linearity inherent in the system is evident, whereas as at the negative end there is no such non-linearity, only a voltage drop as though there is a series resistance. This is further demonstrated in Figure 5.17 where the classic open hysteresis loop that can be expected from these devices is seen, but only on the positive half of the sinusoid input. For the negative half, it functions as a basic resistor. Looking closely, there is a very minor non-linearity in the form of a very narrow hysteresis loop, but it is narrow enough to approximately be just a constant resistance. This correlates with the fabrication error. The devices on R1 were connected to the test circuit (Figure 5.1) such that the right electrode was connected to the voltage source, and the left electrode to ground. Ions intercalate on the side of the device that is at the lower resistance. So then it would be reasonable that the negative half of the cycle would be the one affected by the fabrication error, since that's the half of the cycle where ions would intercalate in that region.

Figure 5.14: Device R1D5 with positive voltage applied to the left electrode with respect to the right electrode (top) and without (bottom).

Figure 5.15: Device R1D5 with positive voltage applied to the right electrode with respect to the left electrode (top) and without (bottom).

Figure 5.16: Voltage over time for testing of device R1D5 at 10 Hz, 3 V amplitude.

Figure 5.17: I-V curve for device R1D5 at 10 Hz.

Device R2D2

Device R2D2 is the first device in the second rail of devices that were intentionally fabricated with increasing widths so as to investigate the effects of wider device channels. Figures 5.18 and 5.19 summarize the fabrication of the device. The electrodes are well isolated, and the ion front is uniform so the device should operate in the expected manner.

Figure 5.18: Device R2D2 with positive voltage applied to the left electrode with respect to the right electrode (top) and without (bottom).

Figure 5.19: Device R2D2 with positive voltage applied to the right electrode with respect to the left electrode (top) and without (bottom).

Looking at Figures 5.20 and 5.21, however, it is obvious that the device is not operating ideally. The behaviour of the device is similar to that of device R1D5, in that it appears to operate normally on one half of the waveform but is nearly a regular resistor for the other half. Unlike R1D5, there is no readily apparent reason for this behaviour. It is possible that the device was permanently changed due to high voltages from previous tests. Devices on R2 were connected into the test circuit in the opposite configuration to the devices on R1. This means that the lack of response in the negative cycle is most likely a result of some problem with the left side of the device. Regardless, this one half of the device is enough to draw conclusions from

since the devices are symmetrical.

Figure 5.20: Voltage over time for testing of device R2D2 at 10 Hz, 3 V amplitude.

Figure 5.21: I-V curve for device R2D2 at 10 Hz.

Figure 5.22: I-V curve for device R2D2 at 20 Hz.

The width of the device seems to affect the shape of the hysteresis loop and the degree of non-linearity. Figure 5.22 shows a far more similar hysteresis response to that of device R1D5 for device R2D2 running at 20 Hz.

Device R2D3

Device R2D3 was the result of several mistakes in fabrication being accounted for. The splatter from the application of the silver ink was accommodated by expanding the region insulated by epoxy, as shown in Figures 5.23 and 5.24. This resulted in a device with a particularly short active channel. Due to the inconsistent deposition of epoxy, and the wide device channel, the active area is wider than it is long.

Figure 5.23: Device R2D3 with positive voltage applied to the left electrode with respect to the right electrode(top) and without (bottom).

Figure 5.24: Device R2D3 with positive voltage applied to the right electrode with respect to the left electrode (top) and without (bottom). In the top half of the photo, a needle was used to distort the top of the electrolyte and reduce the shine so that the ion front could be seen.

This resulted in a hysteresis loop that did not come close to closing on itself or crossing zero. In addition, since the Li^+ ions did not need to move around very much in the material, the device is not exceptionally non-linear. Though it does still display expected characteristics, they are less pronounced, as seen in Figures 5.25 and 5.26.

Figure 5.25: Voltage over time for testing of device R2D3 at 10 Hz, 2.5 V amplitude.

Figure 5.26: I-V curve for device R2D3 at 10 Hz.

Device R2D4

Device R2D4 is the widest device that was able to be fabricated by hand. Beyond this width, there was not sufficient space between the active layer and the pin header to create a proper epoxy well. The device otherwise has standard device properties, as can be seen in Figures 5.27 and 5.28.

Figure 5.27: Device R2D4 with positive voltage applied to the left electrode with respect to the right electrode (top) and without (bottom).

Figure 5.28: Device R2D4 with positive voltage applied to the right electrode with respect to the left electrode (top) and without (bottom).

Again, this device seems to exhibit the previously established characteristic where it is functional for one half-cycle but not the other as shown in Figures 5.29 and 5.30. As before, this is probably due to a combination of factors. The lack of non-linear response on the positive cycle seems to indicate some flaw with the right side of the device. This could be due to the proximity of the device active region to the electrode on the right side.

Figure 5.29: Voltage over time for testing of device R2D4 at 10 Hz, 2.5 V amplitude.

Figure 5.30: I-V curve for device R2D4 at 10 Hz.

5.3 Simulation and Measurement Comparison

This section will compare the measured response of devices to the simulation model implemented earlier in this thesis. It is reasonable to assume that these simulations will be reasonably accurate, as they were shown to match previously measured data quite well in Chapter 3. Since the majority of the testing of these devices was performed in regimes that avoided saturation, the part of the model that is most prone to error should not affect the results.

The schematic test bench that was used for the proceeding simulations is given in Figure 5.31. The only notable difference between this schematic and Figure 3.8, used previously, is accounting for the sensing resistor that would need to be used to measure the fabricated devices.

The first comparison to make is the behaviour of the devices given various frequencies of input signals. Figures 3.9 and 3.16 show composite plots of simulations of the devices with a wide range of frequencies in the ideal simulation environment. Figure 5.32 shows a similar range of frequencies simulated, but passed through a $986\ \Omega$ sensing resistor, as was the scenario in measurement. It can be seen that the devices in the simulation become far more linear and display much less hysteresis than devices in the idea simulation. Comparatively, Figure 5.33 shows measured data for device R2D2 with a range of frequency inputs. Device R2D2 was selected for comparison, as the part which functioned as expected worked quite well, and other, more ideal devices had ceased functioning. It was discovered that any voltage above approximately 2 V will permanently degrade the device if applied for more than a few seconds.

Figure 5.33 actually shows considerably more non-linearity and hysteresis than the simulated data across a range of frequencies. This is most likely due to the fact that the fabricated devices had a higher average resistance value than those in simulation,

Figure 5.31: Simulation circuit schematic used for comparison to real device tests to account for sensing resistor.

which was around $2\text{ k}\Omega$, causing a proportionately larger input voltage to drop across the sensing resistor. In addition, the data captured for low frequencies (below 10 Hz) is significantly noisier than that of higher frequencies. This was due to a setting on the oscilloscope that causes the display to automatically sweep for data if the trigger condition was not found within a certain time frame. Unfortunately this problem was not realized at the time of measurement. The average behaviour of the signal remains valid. Comparing Figure 5.32 to 5.33, it is clear that their overall behavioural trends are the same. They both demonstrate a widening of the hysteresis loop around a certain frequency (approximately 10 Hz), which degrades at lower frequency to more of a sigmoid shape. They also both demonstrate that as the frequency increases, the devices become functionally equivalent to linear resistors as expected. This also matches reasonably well with the previous measurements within the group, seen in Figure 3.15.

As expected, the simulations and measured data across a frequency range match reasonably well, but not perfectly, particularly at lower frequency due to the lack of accounting for device saturation and de-saturation.

Figure 5.32: I-V characteristic curves for simulated devices with varying frequency inputs.

Figure 5.33: I-V characteristic curves measured on device R2D2 with varying frequency inputs.

The next point of comparison is the behaviour of the devices at a range of input signal amplitudes at a frequency of 10 Hz. Two devices were tested to compare this behaviour: device R1D5 and device R2D3. Figure 5.34 shows the simulated data for a device measured via a sensing resistor at several input amplitudes. Compared to Figure 5.35, a plot of the same input signal amplitudes measured over device R1D5, the behavioural match is quite strong. Device R1D5 also had hysteresis on only one half-cycle, but the comparison remains useful since generally speaking, the device would normally be symmetrical. The 4.5 V input amplitude I-V trace in Figure 5.35 was captured with the trigger setting unfixed, but even so, the average of the data correlates with the trend of a widening hysteresis loop that can be seen in both the simulated and measured data. There is once again some numerical mismatch due to the lack of compensation for the actual average resistance of the device as compared to the simulated device.

This match between measured and simulated data can also be seen readily for device R2D3. Figure 5.36 provides the simulated I-V traces for a device, and Figure 5.37 shows the measured data for the device across a range of input amplitudes. In this case, a properly symmetrical device was used to acquire the data. It can be seen that the data in the two figures matches incredibly well, apart from the anomaly in the shape of the waveform when maximum or minimum input voltages are reached on the measured device. This effect is likely an indicator of device breakdown. Only a few cycles could be captured at these higher voltages before the device would be destroyed. This also means that each higher voltage measurement is slightly affected by the previous ones as they would degrade the device for the few cycles they were applied. Prolonged application resulted in the device ceasing to conduct any current whatsoever.

Figure 5.34: I-V characteristic curves for simulated devices with varying voltage amplitude inputs to compare with R1D5.

Figure 5.35: I-V characteristic curves measured on device R1D5 with varying voltage amplitude inputs.

Figure 5.36: I-V characteristic curves for simulated devices with varying voltage amplitude inputs to compare with R2D3.

Figure 5.37: I-V characteristic curves measured on device R2D3 with varying voltage amplitude inputs.

Chapter 6

Conclusion

6.1 Summary

The objective of this thesis was to create a simple and efficient method to simulate ionically-coupled, non-linear devices with reasonable accuracy that could be scaled up for use in modelling larger, more complex neuromorphic circuits, as well as to verify the accuracy of these simulations via the fabrication and testing of these devices.

This work presented experimental results for the comparison and validation of a simplified, SPICE-based non-linear resistor model. Comparisons were drawn to validate the accuracy and range of a semi-empirical model that can be implemented using currently available simulation software and that uses significantly less computational resources than more complex models. A method of fabricating corresponding devices was also presented using commonly available and well-established materials.

These devices were tested and their functionality evaluated. The behaviour of these devices was discussed, and any abnormalities investigated. The functionality of the devices was then compared to that of the previously validated simulations, and strong correlations were found.

6.2 Future Work

Looking forward, parameter extraction should be performed on the devices to more closely relate the results of the simulations with those of the devices themselves. In addition, some level of granularity in the model would aid in the accuracy of its results. In addition, the process for fabricating these devices would benefit greatly from some level of automation. Consistency of device quality and yield are difficult factors to maintain high standards on when work of this scale is being performed by hand.

These devices have the potential to see a myriad of uses in the field of neuromorphic applications and CNNs. Development of these devices into cells that could be scaled into large matrices would be ideal next steps. Even the electrochromic aspects of these devices could be used, perhaps as a means of sensing the state of the device without the need of a probing or testing voltage. Neuromorphic networks using non-linear cells, such as the ones easily implemented by the devices studied in this thesis, are already being investigated for use in applications such as learning networks and networks that mimic the neural paths of human tissue such as the retina.

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Appendix A

SPICE Netlists for Simulations

This appendix provides the SPICE code used in Chapters 3 and 5 simulation blocks to simulate the memristor-like devices discussed in this thesis.

EL_Node_TL

```
* source EL_Node_TL
.SUBCKT EL_NODE_TL BI RI

R_EL_BI MI BI {Rion}
R_EL_RI MI RI {Rion}

.ENDS EL_NODE_TL
```

ELNode_T

```
* source ELNode_T
.SUBCKT EL_NODE_T BI LI RI

R_EL_BI MI BI {Rion}
R_EL_LI LI MI {Rion}
R_EL_RI MI RI {Rion}

.ENDS    EL_NODE_T
```

ELNode_TR

```
* source ELNode_TR
.SUBCKT EL_NODE_TR BI LI

R_EL_BI MI BI {Rion}
R_EL_LI LI MI {Rion}

.ENDS    EL_NODE_TR
```

ELNode_BL

```
* source ELNode_BL
.SUBCKT EL_NODE_BL TI RI

R_EL_TI TI MI {Rion}
R_EL_RI MI RI {Rion}

.ENDS    EL_NODE_BL
```

ELNode_B

```
* source ELNode_B
.SUBCKT EL_NODE_B TI LI RI

R_EL_TI TI MI {Rion}
R_EL_LI LI MI {Rion}
R_EL_RI MI RI {Rion}

.ENDS    EL_NODE_B
```

ELNode_BR

```
* source ELNode_BR
.SUBCKT EL_NODE_BR TI LI

R_EL_TI TI MI {Rion}
R_EL_LI LI MI {Rion}

.ENDS    EL_NODE_BR
```

EC_Node_H

```

* source EC_Node_H

.SUBCKT EC_NODE_H LR RR TI BI LI RI

G_EC_LR LR MR VALUE={V(LR,MR)/(Rec*(1+EXP(C0*(V(MI,MR)-Vth)/Q0)))}
G_EC_RR MR RR VALUE={V(MR,RR)/(Rec*(1+EXP(C0*(V(MI,MR)-Vth)/Q0)))}

R_EL_TI TI MI {Rion}
R_EL_BI BI MI {Rion}
R_EL_LI LI MI {Rion}
R_EL_RI RI MI {Rion}

CM MR MI {C0}

RMI MR MI {Rleak}

RLR LR MI {Rleak}
RRR RI RR {Rleak}

*.PARAM Rec=200 Rion=200*1E3 Rleak=1E15 Q0=0.00001 C0=0.00002

.ENDS EC_NODE_H

```