ORGANO-ELECTRONIC TECHNOLOGY FOR INTEGRATED HIGH FUNCTIONALITY DEVICES

by

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ABSTRACT

Electrochromic (EC) materials can utilize the movement of ions to control optical absorption and electronic conduction. Combining this with the optical control afforded by photoconductor (PC) materials enables the fabrication of devices where electrons, ions and photons can be used in concert to provide unique functionality.

This thesis describes research into combining the features of electrochromic and photoconductive materials in an enabling technology by utilizing compatible components to allow fabrication of complex electronic, photonic and ionic systems. All materials explored are either organic or organic/inorganic hybrids capable of being deposited using simple printing techniques. Conducting polymers were chosen to produce structures that function as active electrolytic devices allowing electronic and ionic control of currents while simultaneously providing optical output via electrochromism. Poly(3,4-ethylenedioxythiophene) (PEDOT) is the primary active electrochromic material used for fabrication and measurements. A custom screen printing system was designed to fabricate circuits quickly and easily on rigid or flexible substrates.

A material model is presented to explain the percolation conduction in poly(styrenesulfonate) (PSS) template-doped PEDOT and the multiple ion intercalation required for electrolytic switching. Based on this and measured results from test structures, device models were developed to accurately simulate the dynamic response of

arbitrary device structures. This allows the design and fabrication of integrated circuitry with any degree of complexity.

To provide optical input a printable photoconductor material has been developed and investigated. This is an organic/inorganic hybrid using a polyester matrix host material and cadmium sulfide (CdS) active material *in-situ* doped with CuCl₂. The system is novel in that it works well as a photoconductor, having a current ratio of $>10^3$, without requiring sintering or any other high temperature processing step and is a printable as a polymer thick film (PTF).

The technology developed in the course of the work is particularly useful in applications where distributed processing of input information is required. Since the elements are capable of simultaneously sensing and processing optical, electronic and ionic stimuli a wide range of possibilities are available. Current target areas are artificial retinas, complex neural simulators and biosensor arrays.

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LIST OF SYMBOLS AND ACRONYMS

χ	Electrical susceptibility
ϵ_0	Permittivity of free space
ϵ_r	Relative permittivity
ϕ	Total potential
ϕ_{ext}	External potential
ϕ_{ind}	Induced potential
γ	Activity coefficient
η	Packing fraction
λ_D	Debye length
μ	Chemical potential
μ_e	Electron mobility
μ_h	Hole mobility
μ_m	Magnetic susceptibility
ρ	Total charge density
ρ_{ext}	External charge density
ρ_{ind}	Induced charge density
σ_e	Electron conductivity
σ_h	Hole conductivity
σ_{ion}	Ion conductivity
σ^d	Diffuse layer charge density
σ^i	Specifically absorbed ion charge density
σ^E	Electrode charge density
σ^S	Solution charge density
τ	Relaxation time
ω_p	Plasma frequency
ATO	Antimony tin oxide
c_i	Concentration of i^{th} species
C_{dl}	Double layer capacitance
CGL	Charge generation layer
CNN	Cellular neural network
CTL	Charge transport layer
CVD	Chemical vapour deposition
D_e	Electron diffusivity
DOF	Depth of focus
e	Electron charge
E	Expectation value
EC	Electrochromic, ethylene carbonate
E_F	Fermi energy

E_m	Mobility edge energy
F	Faraday's constant
FTO	Fluorine-doped tin oxide
FWHM	Full-width at half-maximum
G	Gibb's free energy
HMO	Hückel molecular orbital theory
HOMO	Highest occupied molecular orbital
IHL	Inner Helmholtz layer
IPE	Ideal polarized electrode
IR	Infrared
ITO	Indium tin oxide
k_0	Fermi-Thomas wave vector
k_F	Fermi wave vector
LUMO	Lowest unoccupied molecular orbital
m	Electron mass
M	Molarity (moles/litre)
MIT	Metal to insulator transition
n	Electron density
NIL	Nanoimprint lithography
OHL	Outer Helmholtz layer
OLED	Organic light emitting diode
OFET	Organic field effect transistor
p	Hole density
p_c^B	Bond percolation threshold
p_c^S	Site percolation threshold
PAN	Poly(acrylonitrile)
PANI	Polyaniline
PC	Photoconductor, propylene carbonate
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEGDA	Poly(tetraethylene glycol diacrylate)
PEO	Poly(ethylene oxide)
PDMS	Poly(dimethylsiloxane)
PMMA	Poly(methyl methacrylate)
PPy	Polypyrrole
Pr	Probability
PSS	Polystyrenesulfonate
PSSA	Polystyrenesulfonic acid
PTF	Polymer thick film
PVdF	Poly(vinylidene fluoride)
PVdF-HFP	Poly(vinylidene fluoride-hexafluoro propylene)
PVP	Poly(vinyl pyrrolidone)
q^E	Electrode charge
q^S	Solution charge
R	Universal gas constant
RT	Room temperature
RTIL	Room temperature ionic liquid

s_i	Stoichiometric coefficient of i^{th} species
SPE	Solid polymer electrolyte
t_i	Transference number of i^{th} species
t_+	Transference number cation
t_-	Transference number anion
T_0	Temperature coefficient for variable range hopping (VRH)
TCO	Transparent conducting oxide
TMO	Transition metal oxide
tpi	Threads per inch
U	Applied potential
U^θ	Standard cell potential
UV	Ultraviolet
Var	Variance
VCCS	Voltage controlled voltage source
VRH	Variable range hopping
z	Coordination number
z_i	Charge state of i^{th} species

1 INTRODUCTION

There are many types of electronic, optoelectronic and ionic devices available today that are used in a variety of products that enhance our daily lives. For example, electronics has produced transistors, integrated circuits, microprocessors; from optoelectronics there are diode lasers, flat-panel displays, digital camera sensors; ionics has enabled development of batteries and automatic analysis for health care. Unfortunately, the technologies used for these applications are often rigid and incompatible, making them difficult and expensive to integrate into complex solutions. The work presented in this thesis combines these disparate areas into a cohesive technology allowing the exploitation of their combined functionality. To this end, conducting and non-conducting polymers have been used, often in concert with inorganic materials as composites, to form printable devices on flexible or hard substrates.

Since the discovery of electrical conduction of polyacetylene in 1977 [1][2] it has been found that most organic conducting polymers exhibit electrochromism. Along with the change in optical absorption, the conductivity of many of these polymers is also altered reversibly by electrochemical means. The electrolytic intercalation of ionic species into the polymer can be used to either dope an undoped material or compensate a material that has been previously doped. By altering the level of doping, the conductivity of the materials can be varied over many decades. Devices that effectively act as

“electrolytic transistors” can be fabricated using this effect where the polymer “channel” conductivity is adjusted by applying a potential to a counter-electrode with a liquid, gel or solid electrolyte bridge to the channel. The electrolytic transistor was first investigated and patented by John Bardeen in the 1950s [3]. The basic operation of polymer implementations of such transistors and related structures has been examined in the past [4][5][6] and interesting results on planar devices have been demonstrated [7][8][9][10] during the progress of this work. If the material used for the electrolytic transistor is electrochromic, the state of the channel can be monitored optically by the change in the absorption spectrum. This coupling of optical absorption to the conduction state has never been used to add functionality to the device. In general, it is possible to monitor the conduction state of any segment of electrochromic material optically so the simple transistor configuration greatly limits utility.

Devices that make use of electrolytically controlled conduction and optical absorption form the basis of this work. Some background into the materials used and the effects produced are outlined below. The fabrication, measurement, modelling and simulation of test structures, individual devices and simple circuits form the bulk of this thesis. In addition, to add optical sensing capability, the use of a printable photoconductor has been investigated. The background and results of research into the operation of this device are also presented.

The methods developed in this work have allowed the fabrication and accurate modelling of devices that are able to interact through electronic, ionic and optical means. It is important to note that these methods are not limited to simple two and three terminal devices but can be used for large, complex, multiply-interacting, nonlinear structures.

The technology has been extended with the addition of printable hybrid photoconductive (PC) layers allowing the use of embedded optical inputs as well as EC-gated optical receptors.

1.1 Overview of Technologies

The real strength in using "soft material" technology is the broad functionality and compatibility that can be achieved. This is to some extent intrinsic to this class of materials but it is also a result of the ability to engineer their structure and functionality. Organic materials and polymers in particular, are easily adapted by changing groups – either in-line or side-groups – to alter their behaviour in any number of ways. These alterations can be structural, chemical, electronic, optical, or any combination. The possibilities are endless.

The tree in Figure 1-1 displays the breadth of functionality inherent to electronically controlled soft materials. Within this group are included both organics and organic/inorganic hybrids. In particular using inorganic nanoparticles in an organic matrix can yield many benefits. The matrix may just be a structural material or could provide charge transport or other properties that add to its utility. The upper branch of the tree contains electrolytic devices and is the focus of this work.

Although only part of the upper route has been explored in this work, the methods that have been developed can be extended to most of the tree.

Figure 1-1 “Organo-Electronic” Application Tree

The "organo-electronic" material systems and applications above use electrical signals to control other electrical, ionic and optical signals, and optical signals to control electrical and ionic signals. In addition to this, there are also “organo-photonic” systems in which optical signals are used to control other optical systems. A corresponding application tree is illustrated in Figure 1-2. Although the fabrication methods used in this thesis can be applied to these systems, and they could be used to provide additional functionality, their pursuit is outside the scope of the present work.

Figure 1-2 “Organo-Photonic” Application Tree

1.2 Objectives – Research Goals

The main purpose of this research was to utilize the combined electronic, ionic and photonic properties of conducting organic materials and organic/inorganic hybrids to enable the fabrication of novel devices. Individual properties have been used in the past to make information displays, individual electrochemical transistors, ionic sensors, etc. but the real promise of these materials lies in the simultaneous application of their

strengths. A number of sub-goals were necessary to achieve this end. Primarily these have been:

- choosing or creating a suitable fabrication method
- choosing or creating a compatible material set that will allow the formation of suitable devices
- creating a set of compatible building blocks that can be assembled into useful functions
- selection of a suitable trial application
- fabrication and testing of devices, building blocks and trial application circuits

The chief materials being examined in this study are commercially available conducting polymers and nanoparticulate inorganic materials that can be dispersed in polymeric binders.

2 BACKGROUND

In this section, some of the required background for the work is covered briefly. First, some theoretical backing is provided in the areas of conventional electronic and ionic conduction, electrostatic screening, electrochemistry and conducting polymers. This is followed by a review of the major materials groups that have been used in this study. The reader is directed to the references for more extensive coverage of these areas.

2.1 Transport Effects in Electronic and Ionic Materials

2.1.1 Electrical Transport

Electrical transport is a general name given the movement of charged carriers through a medium. Numerous conditions affect the motion of the carriers and many processes may be involved so it is beyond the scope of this thesis to cover them all in detail. There are two fundamental forms of single charged particle transport: band transport and hopping transport. Band transport is the main conduction process in crystalline metals and semiconductors where mutual interaction between the atoms causes bands to form from the individual atomic orbitals. In these bands the carriers are delocalized and not associated with any particular lattice site. Hopping transport

dominates conduction in highly disordered systems where the carriers are localized. There are many systems that fall in between these two extremes and can be influenced by both band and hopping mechanisms. This can occur through a homogeneous distribution of localized sites or separate regions of crystallinity and disorder. The latter is the case with conducting polymers, which will be covered later. Here we will review the theory of conduction in purely crystalline systems (section 2.1.1.1) and homogeneously disordered systems (section 2.1.1.2). The effect of diffusion is added in section 2.1.3.

2.1.1.1 Electrical Conduction in Crystalline Materials

The Drude model, covered in section 2.1.1.1.1, is a simple model describing electronic drift in a metal under the influence of an electric field. This model treats the electrons in the metal as a free electron gas. Energy bands are next introduced to account for differences between conduction properties in metals, insulators and semiconductors. Following this, some modifications to the Drude model are presented that are required due to quantum-mechanical effects and band conduction in semiconductors. Conduction processes specific to organic systems will be covered with the materials to which they apply in section 2.2.

2.1.1.1.1 Drude Theory of Metals

Electrical drift current is caused by the movement of electrons in a material under the influence of an electrical field. The Drude theory of drift conduction in a metal is

simple but still widely used [11]. The valence electrons are treated as a gas of free electrons around the fixed positively charged nuclei. Because damping forces such as scattering that are proportional to the velocity, the motion of the electrons under the influence of an electric field are only accelerated until they reach a terminal drift velocity, v_d . Under these conditions the terminal velocity of the electron will be

$$\vec{v}_d = -\frac{e\tau}{m}\vec{E} = -\mu_e\vec{E} \quad (2.1)$$

where e = electron charge, m = electron mass,
 τ = relaxation time, μ_e = electron mobility

The relaxation time τ , can be interpreted as the average time between scattering events.

The current density due to this movement of electrons is then

$$\vec{J}_e^{drift} = -ne\vec{v}_d \quad (2.2)$$

where n = electron density

Combining (2.1) and (2.2) yields

$$\vec{J}_e^{drift} = \left(\frac{ne^2\tau}{m} \right) \vec{E} = \sigma_e \vec{E} \quad (2.3)$$

where σ_e = electrical conductivity

which is Ohm's law. In addition, since the electron mobility μ_e is defined by (2.1) we have

$$\sigma_e = ne\mu_e \quad (2.4)$$

In a conductive media with no free charge the wave equation is given by

$$\bar{\nabla}^2 \bar{E} - \epsilon\mu_m \frac{\partial^2 \bar{E}}{\partial t^2} - \sigma_e \mu_m \frac{\partial \bar{E}}{\partial t} = 0 \quad (2.5)$$

Therefore, if the applied field is varying in time, such as that produced by an electromagnetic wave,

$$\bar{E} = \bar{E}_0 e^{i(\omega t - \bar{k} \cdot \bar{r})} \quad (2.6)$$

with an effective wavelength long compared to the electronic mean free path then

$$-k^2 + \epsilon\mu_m \omega^2 - i\sigma_e \mu_m \omega = -k^2 + \epsilon\mu_m \omega^2 \left(1 - \frac{i\sigma_e}{\epsilon_0 \omega}\right) = 0 \quad (2.7)$$

so that the conductivity can be incorporated into a complex relative dielectric constant

$$\begin{aligned} \nabla^2 \bar{E} &= -\frac{\omega^2}{c^2} \epsilon_r(\omega) \bar{E} \\ \text{where } \epsilon_r(\omega) &= 1 - \frac{i\sigma_e(\omega)}{\epsilon_0 \omega} \end{aligned} \quad (2.8)$$

The equation of motion with linear damping for the electron is

$$m \frac{d\vec{v}}{dt} + \frac{m\vec{v}}{\tau} + e\vec{E} = 0 \quad (2.9)$$

The electron velocity induced by the E-M field will be

$$\vec{v}(t) = \vec{v}(\omega) e^{i(\omega t - \vec{k} \cdot \vec{r})} \quad (2.10)$$

Therefore, the frequency dependent velocity will be given by

$$\begin{aligned} i\omega \vec{v}(\omega) + \frac{\vec{v}(\omega)}{\tau} + \frac{e\vec{E}}{m} &= 0 \\ \rightarrow \vec{v}(\omega) &= -\frac{e\tau}{m(1+i\omega\tau)} \vec{E} \end{aligned} \quad (2.11)$$

This means the dependence of current density on the electric field will be

$$\vec{J} = -ne\vec{v} = \frac{ne^2\tau}{m(1+i\omega\tau)} \vec{E} \quad (2.12)$$

Therefore, the frequency-dependent conductivity is

$$\sigma_e(\omega) = \frac{\sigma_{e0}}{1+i\omega\tau}, \text{ where } \sigma_{e0} = \frac{ne^2\tau}{m} \quad (2.13)$$

and the complex relative dielectric constant becomes

$$\varepsilon_r(\omega) = 1 - \frac{i\sigma_{e0}}{\varepsilon_0\omega(1+i\omega\tau)} \quad (2.14)$$

And if the frequency is sufficiently high so that

$$\omega\tau \gg 1 \quad (2.15)$$

then the relative dielectric constant can be approximated by

$$\varepsilon_r(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2} \quad (2.16)$$

where

$$\omega_p^2 = \frac{\sigma_{e0}}{\varepsilon_0\tau} = \frac{ne^2}{\varepsilon_0m} \quad (2.17)$$

is known as the plasma frequency. When $\omega < \omega_p$ the dielectric constant is real and negative so the field decays exponentially in the metal and no wave can propagate.

2.1.1.1.2 Energy Bands

The Drude model of free electrons works well under most circumstances for a metal but fails to provide any insight into the difference between metals, insulators and

semiconductors. It also fails to account for some aspects of conduction. To explore this difference and have a better understanding of conduction, energy bands need to be introduced.

When a crystal is formed from a material, it involves the bonding together of many atoms in a uniform array (at least locally). This bonding involves sharing electrons between the atoms involved. Every atom, or molecule, has a set of quantum-mechanical orbitals at different energy levels associated with it. Depending of the number of electrons the atom possesses, these levels will be filled to a given energy level at low temperatures and this is called the valence orbital (or, as we will see, it is sometimes called the Highest Occupied Molecular Orbital or "HOMO"). The first unfilled state may have the same energy as the valence level if there are an odd number of electrons or it will be at a higher energy if an even number of electrons is present. As more atoms are added and they become closer together as the crystal is formed, the individual levels for each atom spread out and become bands. The band corresponding to the valence orbital is called the "valence band". The band associated with the next highest energy orbital is termed the "conduction band". In the crystal, if the primitive cell has an odd number of electrons then there will be available states at the same energy as the valence orbital and no available states will exist for an odd number.

For a material with an odd number of electrons per primitive cell there are unfilled states and the electrons are free to move. This type of material is a metal. If there are an even number of electrons per primitive cell but the valence and conduction bands overlap in energy then a "semi-metal" is formed. Semi-metals behave similarly to metals but tend to have lower conductivities. If the number of electrons is even and the band do

not overlap then an "energy gap" or "band gap" exists between the top of the valence band and the bottom of the conduction band.

The energy at which the probability of orbital occupation would be 50% if an available orbital existed is called the "Fermi energy" (E_F). For a metal or semi-metal, the Fermi level lies within one or more bands so there will be electrons at this energy. For insulators and semiconductors, however, the Fermi level will always lie in the energy gap between the valence and conduction bands. For three-dimensional crystals, the Fermi level can be generalized to a "Fermi surface" in momentum (p) space [or, equivalently, wave vector (k) space].

The conductivity in metals increases with decreasing temperature right down to a finite residual conductivity at $T = 0$ K. Because the conduction band is only partially full, there are mobile carriers available at all temperatures and thermal electron scattering is reduced with decreasing temperature. For semiconductors the thermal scattering is also reduced but as the temperature approaches zero the number of available carriers also goes to zero. Therefore at $T = 0$ K semiconductors become insulators. The only difference between crystalline semiconductors (e.g. silicon, germanium, gallium arsenide, etc.) and crystalline insulators (e.g. diamond, sapphire, quartz, etc.) is the energy required to generate mobile carriers because of the size of the band gap.

2.1.1.1.3 Some Quantum Mechanical Considerations for a Metal

A slightly more rigorous quantum mechanical treatment of the problem of DC conduction in metal yields a slightly different result than treated above. This is mainly

due to band filling and the particular aspects of the crystal structure. If we make the simplifying assumption of a spherical Fermi surface then we can still use the form of (2.3) for the DC conductivity if we replace the electron mass m with the electron "effective" mass m^* and use the density of available carriers about the Fermi surface $n(k_F)$ for n [12].

$$\sigma = \frac{e^2 \tau}{m^*} n(k_F) \quad (2.18)$$

where k_F is the wave vector at the Fermi surface

The carrier density at the surface of the Fermi sphere is

$$n(k_F) = 2 \cdot \left(\frac{4\pi}{3} k_F^3 \right) / (8\pi^3) \quad (2.19)$$

since each state is associated with a k -space volume of $8\pi^3$ and can have two spins.

2.1.1.1.4 Conduction in a Crystalline Semiconductor

As discussed in 2.1.1.1.2, most metals have a partially filled electronic band structure so that there are mobile carriers right down to $T = 0$ K. For a semiconductor the valence band is filled and the conduction band is empty at $T = 0$ K so it becomes an insulator as this temperature is approached. At any finite temperature, there are some electrons available in the conduction band due to electrons that have been ionized from the lattice or impurity atoms. In the valence band, there are lattice atoms that have been

ionized to the conduction band or impurities. These missing electrons in the valence band act like positively charged pseudo-particles and are called holes. We need to take both kinds of carriers into account to find the total conductivity of the semiconductor. If the density of available electrons in the conduction band is n and the density of holes in the valence band is p then the conductivity of the semiconductor is

$$\sigma_{tot} = \sigma_e + \sigma_h = ne\mu_e + pe\mu_h \quad (2.20)$$

The values for n and p are equal for a semiconductor with no impurities, which is called an intrinsic semiconductor. In an extrinsic semiconductor, impurities have been added to increase the n or p carrier density – this is termed doping.

In semiconductors the carrier velocity, and hence current density, is proportional to the electric field only at relatively low fields. At high fields, band transfer and velocity saturation effects cause the linearity to break down. Therefore (2.20) is only valid over a limited range of applied electric field outside of which Ohm's law (in it's linear form) can no longer be used.

2.1.1.1.5 Polarons

Heretofore our discussion has assumed a rigid lattice of atoms and any interaction of the carriers with the underlying structure has been ignored. In materials with band conduction the screening of the electrons (see section 2.1.4) greatly reduces this interaction. The movement of the lattice ions by passing electrons causes an apparent

increase in electron mass for these materials. Because of the relative strength with which the electrons are bonded to the core atoms, this effect is smaller in covalently bonded crystals and larger in ionic crystals. If an individual electron can be identified as being associated with a bound lattice deformation this combination is known as a polaron [13].

Polarons are normally discussed as being one of two classes, large or small. Electrons in a band form large polarons and the strain field they cause in the lattice is distributed over many lattice sites. Small polarons are more tightly bound to a single lattice ion and the transport mechanism for these is most often by hopping (see section 2.1.1.2).

Polarons play a major role in carrier transport in conducting polymers, which is discussed later in section 2.2.

2.1.1.2 Electrical Conduction in Homogenously Disordered Materials

In disordered materials, at least some of the charge carriers are localized to binding sites. For these bound carriers to move under the application of an external electric field requires a different mechanism than drift. This mechanism is called hopping. The conductivity due to hopping goes to zero as the temperature goes to zero because of the localization of the charge carriers to certain positions in the material. As the temperature is reduced the probability of a hop from one site to another is reduced until finally at $T = 0$ K there is no transport at all. At finite temperatures, the carriers use thermal energy from the surrounding material in the form of phonons to allow them to hop. Hopping conductivity goes up with temperature because the availability of phonons

is higher. Conventional materials such as doped and amorphous semiconductors often show conduction through hopping at low temperatures because they have localized states randomly scattered within the band gap at energies close to the Fermi level. At higher temperatures, band transport dominates conduction so the hopping is not apparent.

2.1.1.2.1 Anderson Localization

Anderson [14] first studied the delocalization of carriers in disordered materials and its effect on their mobility. He used a tight binding model with energy wells of random depths over a fixed range ΔV as illustrated in Figure 2-1. These random depth wells caused by the disorder scatter electrons reducing their mean free path. The electron becomes localized when the mean free path is reduced to close to the lattice spacing distance. Whether this reduction and subsequent localization occurs depends on the position of the Fermi level relative to the energies of the wells. If the Fermi level lies high enough, sufficient delocalization occurs to allow band transport and the material is effectively a metal. If the Fermi level lies low enough, the electrons are effectively localized and the material is an insulator. The transition energy between these two cases is commonly called the mobility edge. If a material initially acting like a metal changes, under some applied condition such as temperature or pressure, so that the mean free path of the electrons drops down to the average lattice spacing this is known as a metal to insulator transition (MIT).

Figure 2-1 Potential energy of an electron in the Anderson model (after Mott [15]).

2.1.1.2.2 Mott Variable Range Hopping (VRH)

If the Fermi level is below the mobility edge conduction can occur through two different mechanisms. It is possible to have thermal activation over the mobility energy to achieve band transport giving an activated conductivity dependence of

$$\sigma = \sigma_0 e^{-(E_m - E_F)/kT} \quad (2.21)$$

where E_m is the energy of the mobility edge. Alternatively, if other sites have available states with energies close to the electrons energy then thermally activated hopping can occur. While studying the problem of conduction in glasses containing isolated carrier sites Mott [16] realized that, although it may seem intuitive that hops will occur to the closest neighbours, more distant sites are more likely to have available states at the right energy. This led to the development of the theory of variable range hopping (VRH) in

which the temperature dependence of conductivity does not follow the simple activation form of (2.21). Mott found that for VRH in three dimensions the conductivity was given by

$$\sigma = \sigma_0 e^{-\left(\frac{T_0}{T}\right)^{1/4}} \quad (2.22)$$

This form was then generalized for d dimensions [17] [18] as

$$\sigma = \sigma_0 e^{-\left(\frac{T_0}{T}\right)^{\frac{1}{1+d}}} \quad (2.23)$$

There has been considerable controversy over this temperature dependence of hopping conductivity. Efros and Shklovskii [19][20] have claimed that due to interaction between electrons a soft gap in the density of states appears near the Fermi level of disordered systems. This has become known as the Coulomb gap [21] and causes the temperature dependence of the conductivity to take the form

$$\sigma = \sigma_0 e^{-\left(\frac{T_0}{T}\right)^{1/2}} \quad (2.24)$$

for three dimensional systems. Mott strongly dismissed this argument and although there are still backers on both sides of the controversy most have sided with VRH and conduction obeying (2.30) is normally considered to be quasi-1D VRH.

2.1.2 Ionic Transport in Electrolytic Solutions

The motion of ions in electrolytes can be treated in an analogous way to the "sea of electrons" in a Drude metal with extensions added for the multiple types of charge carriers. Only a brief summary of the simplest treatment is outlined here. It is normally assumed that we are dealing with dilute solutions of a binary electrolyte (only one type of anion and one type of cation). As in the electronic case of section 2.1.1 we will again investigate conduction. The study of the AC behaviour of electrolytic and electrochemical systems as a function of the frequency of an applied electric field is called impedance spectroscopy and is beyond the scope of this summary. More details on impedance spectroscopy can be found in a reference such as Macdonald [22].

Diffusion effects are added in section 2.1.3 and convection within the liquid electrolyte will also be mentioned briefly there.

2.1.2.1 Ionic Conduction

Ionic drift, or migration, current is caused by the movement of ions in a material under the influence of an electrical field. The ions in an electrolyte are more analogous to carriers in a semiconductor than electrons in a metal since we always need to deal with at least two species: cations carrying a positive charge and anions carrying a negative charge. In general, several different singly or multiply charged species of ion may be

present. For dilute solutions, the ions can be treated as a gas of non-interacting ions with both positively charged cations and negatively charged anions free to move throughout the electrolyte. The solvent causes viscous damping forces proportional to the velocity of the ions. This means that the motion of the ions under the influence of an electric field is only accelerated until they reach a terminal velocity, just as in the case of electrical conduction. Therefore the current will again be directly proportional to the field so

$$\vec{J}_{ion}^{drift} = \sigma_{ion} \vec{E} \quad (2.25)$$

where σ_{ion} = ionic conductivity

this is Ohm's law for ionic conduction and is valid for electrolytes in the absence of concentration gradients. The conductivity of the solution is given by

$$\sigma_{ion} = F^2 \sum_i z_i^2 \mu_i c_i \quad (2.26)$$

where F = Faraday's constant (C/mole)

z_i = charge state of the i^{th} species

μ_i = mobility of the i^{th} species

c_i = concentration of the i^{th} species

This is just a generalized form of (2.4) and (2.20) used for metals and semiconductors respectively that includes an arbitrary number of charged particles contributing to the conduction. In this case, the conventional constants and nomenclature appropriate for electrochemical systems have been used.

2.1.2.1.1 Transference Numbers

The equation for ionic conductivity above (2.26) is a summation over all the species contributing to the current. For a specific species, j , the fraction of the total current being carried is given by

$$t_j = \frac{z_j^2 \mu_j c_j}{\sum_i z_i^2 \mu_i c_i} \quad (2.27)$$

This is called the transference number and the sum over all the species carrying current is unity. If we are dealing with a simple binary electrolyte then (2.27) reduces to simply

$$t_+ = \frac{z_+ \mu_+}{z_+ \mu_+ - z_- \mu_-} = 1 - t_- \quad (2.28)$$

where t_+ = cation transference number

t_- = anion transference number

μ_+ = cation mobility

μ_- = anion mobility

where z_- is negative since it is the number of equivalent protonic charges. It is clear that an electrolyte with small mobile cations and large anions, like a typical polyelectrolyte, will have a cationic transference number close to unity.

2.1.3 Diffusion Effects

In all ionic and electronic systems with or without an applied electric field, diffusion will also be present due the thermal motion of the ions or carriers and their environment. This will tend to reduce any concentration gradients present, including those in uncharged particles. For a single type of carrier in isolation (electrons of charge $-e$ in this case) the current density due to diffusion is given by Fick's first Law

$$\vec{J}_e^{diff} = eD_e \vec{\nabla} n \quad (2.29)$$

where $\vec{J}_e^{diff}$ = electron diffusion current density,

e = electron charge,

D_e = electron diffusion constant,

n = electron carrier concentration

(for uncharged particles of concentration c , the particle flux F is given by $\vec{F} = -D\vec{\nabla}c$).

For non-steady-state diffusion the net change of carrier concentration at a point in space must be balanced by its divergence so

$$\frac{\partial n(x,t)}{\partial t} = \frac{\vec{\nabla} \cdot \vec{J}_e^{diff}(x,t)}{e} \quad (2.30)$$

Combining (2.29) and (2.30) produces Fick's second Law

$$\frac{\partial n(x,t)}{\partial t} = \bar{\nabla} \cdot (D_e \bar{\nabla} n(x,t)) \quad (2.31)$$

and if D_e is independent of position then

$$\frac{\partial n}{\partial t} = D_e \bar{\nabla}^2 n \quad (2.32)$$

For low concentrations, it is usually assumed that separate species do not interact so it is valid to treat them separately, and that the flux components from drift and diffusion are independent. For a pure electron conductor this will give an overall current density of

$$\bar{J}_e^{tot} = \bar{J}_e^{drift} + \bar{J}_e^{diff} = e(n\mu_e \bar{E} + D_e \bar{\nabla} n) \quad (2.33)$$

For ionic systems, since we are normally dealing with liquid electrolytes, we may also need to include a term for convection. The total current density for each species i in and electrolyte will therefore be

$$\begin{aligned} \bar{J}_i^{tot} &= \bar{J}_i^{drift} + \bar{J}_i^{diff} + \bar{J}_i^{conv} \\ &= Fz_i \left(-Fz_i \mu_i c_i \bar{E} - D_i \bar{\nabla} c_i + c_i \bar{v}_{electrolyte} \right) \end{aligned} \quad (2.34)$$

where $v_{electrolyte}$ is the velocity of the electrolyte due to convection. The conventional electrochemical nomenclature defined in (2.26) has again been used.

2.1.4 Screening Effects

Screening was first investigated in the seminal paper of Debye and Huckel [23] focusing on the interaction of ions in solution and is covered by most texts on solid-state physics (e.g. [24], [11]). Screening is caused by the redistribution of mobile charges in response to other fixed or mobile charges. The charges involved can be electronic, ionic or a combination of both of these. For the purposes of this work, our interest will be restricted to situations where the structure of the environment can be ignored. This will be the case in an electron gas (and real conductors if the periodic background potential can be neglected) and most electrolyte solutions. We will first deal with the electron gas.

If we were to place a single positive charge in an electron gas then it would attract electrons from the locality that would tend to shield it reducing the range of its electric field. The potential ϕ^{ext} that is produced by this positive charge alone is given by Poisson's equation

$$\nabla^2 \phi^{ext}(\vec{r}) = -\frac{\rho^{ext}(\vec{r})}{\epsilon_0} \quad (2.35)$$

where $\rho^{ext}(\vec{r})$ is the charge density related to the single particle. The potential generated by all of the charged particles in the region, the fixed charge and screening electrons, will also be governed by Poisson's equation for the total charge density $\rho(\vec{r})$

$$\nabla^2 \phi(\vec{r}) = -\frac{\rho(\vec{r})}{\epsilon_0} \quad (2.36)$$

where

$$\rho(\vec{r}) = \rho^{ext}(\vec{r}) + \rho^{ind}(\vec{r}) \quad (2.37)$$

and $\rho^{ind}(\vec{r})$ is the charge density that is induced by the presence of $\rho^{ext}(\vec{r})$.

We now assume, that the potential due to the added charge is related to the total potential by:

$$\phi^{ext}(\vec{r}) = \int \epsilon(\vec{r}, \vec{r}') \phi(\vec{r}') d\vec{r}' \quad (2.38)$$

Since the electron gas is uniform before the insertion of the extra charge it cannot matter the absolute position where the charge is placed so

$$\epsilon(\vec{r}, \vec{r}') = \epsilon(\vec{r} - \vec{r}') \quad (2.39)$$

and we have

$$\phi^{ext}(\vec{r}) = \int \epsilon(\vec{r} - \vec{r}') \phi(\vec{r}') d\vec{r}' \quad (2.40)$$

Through the Fourier convolution theorem (2.40) implies that the transforms are related by

$$\phi^{ext}(\vec{q}) = \varepsilon(\vec{q})\phi(\vec{q}) \quad (2.41)$$

If we assume that the field is sufficiently weak that the screening is linear ($\rho^{ind}(\vec{r}) \propto \phi(\vec{r})$) this also implies that the Fourier components of the induced charge density are linearly related to the potential

$$\rho^{ind}(\vec{q}) = \chi(\vec{q})\phi(\vec{q}) \quad (2.42)$$

Taking the Fourier transforms of the Poisson equations in (2.35) and (2.36) yields

$$q^2 \phi^{ext}(\vec{q}) = \frac{\rho^{ext}(\vec{q})}{\varepsilon_0} \quad (2.43)$$

and

$$q^2 \phi(\vec{q}) = \frac{\rho(\vec{q})}{\varepsilon_0} \quad (2.44)$$

Combining (2.37), (2.41), (2.42), (2.43) and (2.44) gives us the result that:

$$\varepsilon(\vec{q}) = 1 - \frac{\chi(\vec{q})}{\varepsilon_0 q^2} \quad (2.45)$$

There are two common approximations used for the value of $\chi(\vec{q})$ - the Fermi-Thomas approximation, which was developed in relation to the electron gas in a metal, and the Deybe-Huckel approximation, which was developed to explain the shielding due to ions in an electrolyte. In both cases, it is assumed that there is linear screening, $\rho^{ind}(\vec{r}) \propto \phi(\vec{r})$, and (2.45) is rewritten as:

$$\varepsilon(\vec{q}) = 1 + \frac{k_0^2}{q^2} \quad (2.46)$$

Using this form, a single point charge of Q will have the field given by:

$$\phi^{ext}(r) = \frac{Q}{4\pi\varepsilon_0 r} \quad (2.47)$$

so

$$\phi^{ext}(q) = \frac{Q}{\varepsilon_0 q^2} \quad (2.48)$$

and in total

$$\phi(q) = \frac{Q}{\epsilon_0 q^2 + k_0^2} \quad (2.49)$$

Finally, Fourier transforming (2.49) to return to real space

$$\phi(r) = \frac{Q}{4\pi\epsilon_0 r} e^{-k_0 r} \quad (2.50)$$

and this is just standard Coulombic potential with an exponential damping factor. It is called the screened Coulomb potential.

The value for k_0 will not be derived here but it is called the Fermi-Thomas wave vector in electronic theory. Throughout the above analysis, it has been assuming that we were dealing with an electron gas in steady state but this fact has not actually been used. In most cases, the analysis is equally applicable to freely mobile ions in an electrolyte and again we will end up with the screened coulomb potential (2.50). By convention, for ions in electrolyte the exponential constant is changed to $\lambda_D = 1/k_0$ and it is called the Debye length.

2.1.5 Electrochemical Effects

The devices at the focus of this work are different from most conventional electronic and optical components in that they employ electrochemical effects. Because of this consideration must be given not only to conventional systems (materials and their

interfaces) such as conductors, semiconductors and insulators but also to electrolytes and the interfaces between these and the former classes of materials. It is beyond the scope of this document to give a comprehensive backing in the theory of electrochemistry and the reader is referred to the general references [25][26][27]. The following reviews some of the basic concepts useful in the understanding of this work and is largely derived from the aforementioned references.

Figure 2-2 Typical electrochemical cell with two electrodes.

In an electrochemical system, there will normally be two or more electrodes with an intervening electrolyte, as illustrated in Figure 2-2. Electrochemical processes in the system can be controlled by applying appropriate electrical potentials to the electrodes. Depending on the magnitudes of these applied potentials and the nature of the electrodes and electrolyte, in addition to ion transport oxidation and reduction reactions can be induced. In most instances, these will occur at different electrodes and, hence, be separated physically – at any rate electrochemical reactions can only occur at the electrolyte/electrode interface. Within the overall system, both conservation of charge

and electroneutrality must be maintained. In order to have electroneutrality in the electrolyte we must have:

$$\sum_i z_i c_i = 0 \quad (2.51)$$

where the sum is over all ionic species i in solution and c_i and z_i are the concentration and charge number of species i , respectively.

If there are species being produced at the electrodes then their production must conform to Faraday's law (2.52), which relates the rate of reaction to the net current through the system.

$$m_i = -\frac{s_i M_i I t}{nF} \quad (2.52)$$

Where m_i is the mass of species i produced by a reaction in which its stoichiometric coefficient is s_i and n electrons are transferred, M_i is the molecular weight, F is Faraday's constant (=96487 Coulomb/mole) and the current times time $I \times t = Q$, the total charge. The signs of the s_i are determined to satisfy the overall reaction equation in the form

$$\sum_i s_i R_i^{z_i} \leftrightarrow n e^- \quad (2.53)$$

where the R_i are the symbols for chemical formulae for reacting species i .

Reactions governed by Faraday's law (2.52) require charges to be transferred across the electrode-electrolyte solution interface. These reactions are called *faradaic processes*. There are also conditions under which the electrode-solution interface will show a range of potentials where no charge-transfer reactions occur because they are thermodynamically or dynamically unfavourable. Other processes such as adsorption and desorption can still occur and altering the potential or composition can change the interface. These are called *nonfaradaic processes*. In this work, we have been primarily interested in using nonfaradaic processes and have always attempted to avoid charge-transfer reactions in the electrolyte.

2.1.5.1 The Nernst Equation

Let us now concentrate on a system limited to two electrodes one on the "right" and one on the "left" with an electrolyte between. We would like to know what reactions, if any, will happen if we simply short the two electrodes together. This will be determined by the electrochemical potentials of the constituents, which are thermodynamic properties of these materials. The overall energy change for the reaction is given by the change in Gibbs free energy at each electrode interface, called a half-cell reaction (2.54).

$$\Delta G = \left(\sum_i s_i \mu_i \right)_{right} - \left(\sum_i s_i \mu_i \right)_{left} \quad (2.54)$$

where G is the Gibbs free energy, μ_i is now the electrochemical potential of species i , and s_i is the stoichiometric coefficient. For negative ΔG electrons will spontaneously flow from left to right, which means that the right electrode is the more positive and has the lower electrochemical potential for the electrons.

Instead of shorting the electrodes and allowing the reaction to take place, we could also attach an external potential across the electrode and adjust it such that no net spontaneous reaction will occur. At this applied potential, U , no current will flow through the cell and this is called the equilibrium or open-circuit potential. It is related to Gibbs free energy by

$$\Delta G = -nFU \quad (2.55)$$

(again n electrons are transferred and F is Faraday's constant).

The electrochemical potential of a species may be related to its molality m_i (moles of species per kilogram of solvent) and its activity coefficient γ_i by

$$\mu_i = \mu_i^\theta + RT \ln(m_i \gamma_i) \quad (2.56)$$

where, μ^θ is independent of concentration, R is the universal gas constant and T is temperature. If we can assume that the activity coefficients for all of the constituents are unity, then (2.54) becomes the Nernst equation (2.57).

$$U = U^{\theta} - \frac{RT}{nF} \ln \left(\prod_i m_i^{s_i} \right)_{right} + \frac{RT}{nF} \ln \left(\prod_i m_i^{s_i} \right)_{left} \quad (2.57)$$

In this equation U is the total cell potential and U^{θ} is the net standard cell potential of both half-cells. The Nernst equation relates the equilibrium potential to the concentration of reactants and products for a system. This is important in many areas such as the potential generated by batteries and the potential required in the electrochemical refining of metals. Note that even in cases where the cell is balanced (both half-cells are the same material systems) and $U^{\theta} = 0$, an electrochemical potential can still be present due to the difference in concentrations of the species. This work concentrates on the use of such balanced cells. As stated previously we wish to avoid any reaction that changes the nature of the constituents in our system. Even completely reversible reactions can change the physical structure of materials and have detrimental effects. It is very important that the charge state of the ions in solution be not changed, only their distribution within the electrodes and electrolyte.

2.1.5.2 The Double Layer

If no charge-transfer can occur at the electrode-electrolyte interface regardless of the externally imposed potential then the electrode is called an ideal polarized electrode (IPE). There are no real IPEs but some systems act like them over a limited range of applied potential. The operation of systems in this study has been limited to this range for

the materials chosen, when possible. Even when choosing materials that give a wide IPE range, contaminants that are present may undergo reactions that can poison the system so attention to cleanliness and purity can also be very important.

Since charge cannot cross the interface of an IPE it accumulates on both sides to balance the applied voltage in the same manner as a conventional capacitor. This relationship is governed by the standard linear capacitor equation

$$Q = CV \quad (2.58)$$

where Q is the charge in coulombs, C is the capacitance in farads and V is the applied voltage in volts. Experimentally the electrode-solution interface has been shown to act like a capacitor and obeys (2.58) in the nonfaradaic range of operation. At a given potential there will be a charge q^E on the electrode and a charge q^S in the solution in the interface region. The polarity of these charges will depend on the potential across the interface and the composition of the solution. The charges must always be balanced to maintain local neutrality, $q^E = q^S$. The same is true of the other electrode region (the other half-cell) with the signs of the charges reversed. The charges in the electrode and solution are close to the physical interface and are often quoted as charge densities, $\sigma^E = q^E / A$ and $\sigma^S = q^S / A$ respectively. The structure made up of all of the species present at the interface is called the electrical double layer and is characterized at a given potential by its double layer capacitance, C_{dl} .

Most of the study of the double layer has been on electrochemical cells with metal electrodes and an aqueous electrolyte – usually using a mercury drop electrode and

simple salt (such as potassium iodide, KI) solution. The results of this work indicate that the interface may be viewed as being made up of "layers" as shown in Figure 2-3.

Figure 2-3 Proposed model for the double-layer region of an electrochemical electrode-solvent interface.

The layer closest to the electrode is made up of solvent molecules and perhaps other species that are said to be specifically adsorbed to the electrode surface. This is called the compact, Helmholtz or Stern layer. The "inner Helmholtz plane" (IHP) is defined as the average position of the electrical centres of the specifically adsorbed ions and is at a distance of x_{IHP} from the electrode surface. The total charge density due to these specifically adsorbed ions is σ^i . Solvated ions can only come as close as the "outer Helmholtz plane" (OHP), which is defined as the closest approach distance for their electrical centres. Since the attraction to the electrode of these ions is purely electrostatic and independent of their chemical nature they are said to be non-specifically adsorbed. These solvated ions are the closest of a distribution of similarly solvated ions extending out into the solution due to the balance between the electrostatic attraction and their

thermal motion. This is called the diffuse layer and has a total excess charge density of σ^d . Therefore, the total excess charge density in the solution, which must be balanced in the electrode, is given by (2.59).

$$\sigma^S = \sigma^i + \sigma^d = -\sigma^E \quad (2.59)$$

The thicknesses of the layers are typically quite small with the inner and outer Helmholtz layers being angstroms thick. The diffuse layer depends on the total ionic concentration in the electrolyte and is typically nanometers to tens of nanometers with concentrations in the range of 1M down to 10^{-3} M (M = moles/litre). Figure 2-4 illustrates the variation in potential through the double layer - ϕ_S is the potential in the bulk solution.

Figure 2-4 Potential profile across the double-layer region.

2.2 Conducting Polymers

Since the discovery of electrical conduction in polyacetylene in 1977 by Shirakawa *et al* [28], the field of conducting polymers has progressed at a rapid and accelerating pace. The relative conductivities of various materials are compared in Figure 2-5. Note that polymers span the whole range – almost 25 orders of magnitude.

Figure 2-5 Conductivities of conducting polymers relative to other common polymers and inorganic materials. (After Moliton and Hiorns [29] .)

Many different polymers have been discovered that possess the ability to be semiconducting or conducting when properly prepared. Figure 2-6 illustrates the chemical structure of some the more popular materials. In all cases, the conduction along the polymer chains is a result of their conjugated π -orbitals (see section 2.2.1.1 below).

Figure 2-6 The chemical structures of some common conducting polymers. (a) *trans*-polyacetylene (*trans*-PA), (b) poly(*para*-phenylene) (PPP), (c) poly(phenylenevinylene) (PPV), (d) polyaniline (PANI), (e) polypyrrole (PPy), (f) polythiophene (PT), (g) poly(3,4-ethylenedioxythiophene) (PEDOT).

This type of bonding allows the delocalization of the electrons along the polymer chain since there is continuous orbital overlap. Removing π -electrons effectively dopes the polymer *p*-type leaving free states to allow current to flow. To form an *n*-type conducting polymer we would need to add electrons to the π^* -orbitals, which would otherwise be

empty. The most common conducting polymers are *p*-type, the ability to produce *n*-type being rare. Conduction between polymer chains is thought to be most often due to hopping transport. The overall mobility that is achievable with available conducting polymers is still quite low at about 0.1-1 cm²/V-sec with the highest values being for highly structured, monodispersed oligomers such as pentacene.

In this section, the properties of polyacetylene will first be briefly outlined as a prototypical conducting polymer to illustrate how conduction arises. Following this a summary of some important aspects of polyaniline, polypyrrole, polythiophene will be described as these materials, and/or their derivatives, could be potential candidates for use in this work. Finally poly(3,4-ethylenedioxythiophene), which is a variant of polythiophene, is studied in some detail as it is the active material used in the majority of device implementations.

2.2.1 Polyacetylene

As mentioned in the introduction, polyacetylene (PA) was the first discovered and has the simplest structure of the conjugated conducting polymers. For this reason, it will be used to explain how conduction arises in this class of materials. The all-*trans* state of polyacetylene is illustrated in Figure 2-7 below illustrating the σ and π bonding in the plane of the page (note that hydrogen bonds are suppressed in the drawing). This is shown as a fully "dimerized" chain meaning that the identical repeat unit is two C-H groups since the positions of the single and double bonds are fixed. There is another degenerate *trans* state, which simply has the order of the single and double bonds

reversed relative to this. The reason for this dimerization is what is known as the Peierls instability [30] (see section 2.2.1.2) preventing the π electrons from being evenly distributed, which would have resulted in a repeat unit of one C-H monomer.

Also shown in Figure 2-7 is the structure of *cis*-polyacetylene. In this form, the bonding meanders and there is greater difference in bond lengths between single and double bonds. The *trans* isomer is more thermodynamically stable than the *cis* isomer. At room temperature, there is a slow *cis*-to-*trans* conversion but this can be accelerated by annealing the polymer at 150-200 C [31]. Doping will also cause this transformation so the transport properties of doped PA are almost always measured in the *trans* form.

Figure 2-7 *Cis*- and *trans*- isomers of polyacetylene.

2.2.1.1 Conjugation

A conjugated molecule is covalently bonded with alternating single and double bonds. In the case of organic molecules, these single and double bonds are linking carbon atoms. This can be understood by investigating how the single and double bonds are

related to the atomic and molecular orbitals of the constituents. The simplest double-bonded organic molecule, ethylene $\text{H}_2\text{C}=\text{CH}_2$ (Figure 2-8), can be used to illustrate this.

Figure 2-8 The molecular structure of ethylene, $\text{H}_2\text{C}=\text{CH}_2$.

The carbon atoms in the ethylene molecule are sp^2 hybridized. The sigma bonding is arranged of the sp^2 - sp^2 overlap between the two carbon atoms forming the double bond, and the four single bonds resulting from the sp^2 - s overlaps between the sp^2 orbitals of the carbon atoms and the s orbitals of the hydrogen atoms. All the σ bonds (C=C and C-H) are in the same plane and on each carbon atom is a $2p_y$ orbital lying perpendicular to this plane (see Figure 2-9).

Figure 2-9 Bonding of ethylene. The sigma bonds are shown as ovals between atoms and are all in the same plane. The black/white $2p_y$ orbitals are perpendicular to the sigma bond plane (black on top, white on bottom) and each contains a single electron.

The two $2p_y$ atomic orbitals on the carbon atoms can overlap to form π molecular orbitals. To determine the energies and shapes of the resulting orbitals it is often assumed that the electrons in the π bonds are influenced by the pre-existing, static σ bonding framework but do not significantly affect it. This is the basic assumption used in Hückel molecular orbital theory (HMO) [32] [33]. An energy level diagram, as generated by the Hückel approximation, for the π molecular orbitals is illustrated in Figure 2-10. The central, dotted line in the drawing corresponds to the energy of the isolated $2p_y$ atomic orbitals. The lower energy level in the diagram is called the π bonding orbital and the higher energy π orbital is the π^* anti-bonding orbital. (Note that the σ bonds also have possible σ^* anti-bonds but we have implicitly assumed that the entire σ structure is bonding and stable.)

Figure 2-10 Energy level diagram for the π molecular orbitals in ethylene.

If the energy of the isolated $2p_y$ atomic orbitals is α , then according to the Hückel approximation the π bonding orbital will have an energy that is lower in energy by a value called β and the π^* anti-bonding orbital will be higher in energy by the same magnitude. The signs in the diagram are chosen as shown since, by convention, β is negative ($\beta \approx -38 \text{ kcal/mole}$ for ethylene) [34].

Each of the two atomic $2p_y$ orbitals contains one electron so on forming the π bonding orbital both electrons occupy the same combined orbital with opposite spins. The total energy of the ethylene molecule is therefore lowered by 2β , β for each electron, relative to the energy with the original two $2p_y$ orbitals making it more stable.

The π bonding and anti-bonding orbitals are illustrated in Figure 2-11(a) and Figure 2-11(b), respectively. It is clear from the diagram that in the bonding state the π electrons are "delocalized" in a molecular orbital over both carbon atoms. The energy of the system relative to the separate $2p_y$ orbitals is lowered by this delocalization.

Figure 2-11 Pi orbitals for ethylene. (a) π bonding orbital (b) π^* anti-bonding orbital.

If we now expand our ethylene molecule by adding a central $=\text{HC}-\text{CH}=$ section we get the slightly larger molecule of 1,3-butadiene, as shown in Figure 2-12. As in the case of ethylene, 1,3-butadiene has a σ bonded framework all in the same plane and each of the carbons has an additional $2p_y$ atomic orbital out-of-plane. These four out-of-plane orbitals can overlap, as did the two out-of-plane orbitals in ethylene, to form π bonds.

Figure 2-12 Structure of 1,3-butadiene.

These are further delocalized as the molecular orbitals span all four carbons in the lowest energy state. In this case, if we were to use the Huckel approximation to calculate the π orbital energies we end up with four levels as shown in Figure 2-13. For the lowest energy, the two bonding orbitals are filled each with two electrons of opposite spin. Now the energy will be reduced by

$$2(1.618\beta) + 2(0.618\beta) = 4.472\beta \quad (2.60)$$

since the lowest level is 1.618β below the $2p_y$ atomic orbital value and the next is 0.618β lower.

Not only is the energy lower than that for isolated $2p_y$ atomic orbitals for 1,3-butadiene it is also lower than that for two separate ethylene molecules, which would be 4β , as well. This extra level of stability is due to the further delocalization of the electrons and, in general, the longer the length of a conjugated molecule, the larger the degree of stabilization.

Figure 2-13 The four π molecular orbital energy levels for 1,3-butadiene.

The highest energy π -bonding orbital is often called the HOMO since it is the Highest Occupied Molecular Orbital in an unexcited molecule. Similarly, the lowest energy π^* -antibonding orbital is often called the LUMO since it is the Lowest Unoccupied Molecular Orbital in an unexcited molecule. As longer and longer polyene molecules are formed, the number of bonding and antibonding levels continues to increase and the levels get closer together until they approach a continuum for very long chains of polyacetylene (Figure 2-14). When the individual levels can no longer be discerned, the groups of levels are often referred to as "bands" in analogy to crystalline semiconductors. Those corresponding to π -bonding and π^* -antibonding are often called the HOMO (highest occupied molecular orbital) band and LUMO (lowest unoccupied molecular orbital) band, respectively.

Figure 2-14 Effect of the increasing length of polyenes on the molecular energy levels.

2.2.1.2 Peierls Instability

Peierls theorem [30] states that one-dimensional strings cannot be metals. As stated above this means that in Figure 2-15(a) the degenerate states A and B are stable but C is not leading to an effectively doubling the repeat unit (dimerization). This causes a double well potential to form with the π electrons localized in one of the two stable states at the minimums and the fully delocalized state at the central local maximum (Figure 2-15(b)). The bond distortion in the PA chain stabilizes the carrier localization. If the situation in C were possible, the bond lengths to neighbouring CH groups would be equal, there would be no bandgap and the PA would be a metal. In fact, due to the Peierls distortion, the bond lengths are different causing a bandgap to appear at $k = \pm \frac{\pi}{2a}$ as shown in band structure diagram, Figure 2-15(c). The case for a chain without dimerization is shown as the solid line having no bandgap.

Figure 2-15 Peierls instability in polyacetylene.

The generalized coordinate for the n^{th} carbon atom, u_n , is related to the effective single and double bond lengths, r_s and r_d respectively, by:

$$u_n = a(r_s - r_d) \quad (2.61)$$

From neutron diffraction [35] and electron diffraction [36] data the difference in the length of the single and double bonds in *trans*-polyacetylene has been found to be in the range $r_s - r_d = 0.006 \leftrightarrow 0.008 \text{ nm}$.

2.2.1.3 Su-Schrieffer-Heeger (SSH) Model

The most widely used theoretical model for conduction in polyacetylene is the Su-Schrieffer-Heeger (SSH) model [37][38], which has been used to accurately predict the measured electronic properties of polyacetylene. The SSH model assumes:

- (1) the existence of bond alternation (alternating single and double bonds) and
- (2) relative weak interchain coupling (quasi-one-dimensional behavior)

Figure 2-15(b) shows the energy perfect dimerized *trans*-polyacetylene with the dimerization coordinate u_n for degenerate ground states.

The Hamiltonian of a *trans*-polyacetylene can be described by the following:

$$\begin{aligned}
 H = & \frac{M}{2} \sum_n \dot{u}_n^2 \\
 & + \frac{K}{2} \sum_n (u_n - u_{n+1})^2 \\
 & - \sum_{n,s} [t_0 + \alpha(u_n - u_{n+1})] (c_{n+1,s}^+ c_{n,s} + c_{n,s}^+ c_{n+1,s}) \\
 & + U \sum_n (electron - electron)
 \end{aligned}
 \tag{ 2.62 }$$

where M is the mass of the CH group, K is the elastic constant of the σ -bond, $W (=4t_0)$ the width of the π -band, α is the electron-phonon coupling constant and the $c_{n,s}^+$ and $c_{n,s}$ are the fermion creation and annihilation operators for site n and spin s . The U is the Hubbard parameter for the on-site electron-electron interaction. The first three terms of the equation represent the kinetic energy, the elastic (phonon) energy and electron hopping respectively. The forth term corresponds to the correlation energy and if we assume no coupling ($U=0$) this simplifies to the SSH form:

$$H_{SSH} = H_{KE} + H_{ph} - H_{hop}
 \tag{ 2.63 }$$

Using this Hamiltonian, the predicted ground state energy and the density of states have been calculated. In addition, because of the ground state degeneracy, the predicted elementary excitation for carriers is a soliton [31][39].

The calculated energy structure and geometry for polyacetylene and a number of other conducting polymers, including polypyrrole and polythiophene described below, can be found in Salzner *et al* [40]. This study looks at the properties of short chains from monomers to hexamers as well as the long-chain polymer limit.

2.2.2 Carrier Transport in Polymers

There are two important elements to charge transport in conducting polymers: intrachain transport and interchain transport. Intrachain transport refers to conduction along the chain and is normally one-dimensional. Interchain transport is between chains and has a dimensionality determined by the relative configuration of the chains. In some cases, there is a third element, which is "intercable" transport, and this occurs when parallel chains crystallize into rope-like cables. The following sections contain a brief overview of intra- and interchain transport.

2.2.2.1 Intrachain Transport

Intrachain conduction in conducting polymers can itself be divided into two distinct forms depending on the ground state configuration of the polymer: degenerate

and non-degenerate. As discussed in section 2.2.1 *trans*-polyacetylene is the prototypical degenerate ground state conducting polymer. The fundamental carrier type in this kind of material is the soliton [31]. A soliton occurs by a flipping of configuration on the bonding from one degenerate form to the other at some point along the chain as shown in Figure 2-16.

Figure 2-16 Solitons in *trans*-polyacetylene (after [31]). (a) positively charged, spinless soliton (b) uncharged, spin $\frac{1}{2}$ solitons (c) negatively charged, spinless soliton.

In changing from one degenerate state to the other along the chain there needs to be a point in the transition where either state is equally likely. This suppresses the Peierls instability and there is no gap at this transition point. This is how the midgap state of the solitons shown in Figure 2-16 arises. The transition region would span several repeat units in a real chain.

To create a single soliton midchain the bond alteration on one of the sides must be flipped for the remainder of the chain which makes this unlikely. The alternatives are

either to generate solitons at the ends of chains or generate a pair of solitons. When a pair of solitons is generated, one is called a soliton and the other is an antisoliton because they can annihilate each other to restore the chain to its original form. Any of the solitons in Figure 2-16 can be generated in soliton-antisoliton pairs but they must of course conserve charge and spin.

Solitons on *trans*-PA chains in isolation do not interact, but the effect of surrounding chains and other influences can cause a charged, spinless soliton to pair with an uncharged soliton with spin to form a single compound particle. This composite particle has charge, spin and carries with it a deformation of the PA chain. In analogy to the solid-state particle of the same name, it is called a polaron. Figure 2-17 illustrates the structure of PA polarons and a number of particles that can be made from various combinations of solitons.

Figure 2-17 Various compound particle composed of solitons in *trans*-polyacetylene (after [31]).

In *cis*-PA, the ground state is non-degenerate; swapping single and double bonds changes the energy as shown in Figure 2-18. Because of the lack of symmetry, the formation of a soliton is not stable as a static entity. However, polarons are stable and mobile so are able to act as carriers in *cis*-PA. All the other conducting polymers we will discuss are also non-degenerate and so do not have stable soliton conjugation defects. Polyacetylene is unique in this respect.

Figure 2-18 Ground state energy of degenerate *trans*-polyacetylene versus non-degenerate *cis*-polyacetylene (after [31]).

Since the other conducting polymers are non-degenerate, the intrachain conduction mechanism is thought to be by polaron or bipolaron [41]. These particles have intergap states that occur in pairs in the gap as illustrated in Figure 2-19. The polaron states are closer the band edges than the bipolaron states, as shown. Without doping, there are generally no states within the gap. As doping is increased, the states appear and

under heavy doping, they broaden into bands within the gap. This band structure applies to all the conducting polymers are covered in this work as well as most others. The appearance of the states and bands within the bandgap causes a marked change in the absorption spectrum and is the source of electrochromism in these materials. When polaron states are present transition selection rules allow absorption to both the polaron states and full gap. When bipolaron states are present however the full gap transition is no longer allowed eliminating this absorption peak and replacing it with a much lower energy one.

Figure 2-19 Band structure of a polymer chain containing: (a) two polarons; (b) one bipolaron. (after [41]).

In all cases of intrachain transport (solitons, polarons, bipolarons) the movement of a conformational change accompanies the motion of carriers along the polymer chain. This means that the maximum rate of charge transfer through the chain is going to be limited to the speed of sound in the chain.

2.2.2.2 Interchain Transport

Chain-to-chain transport in conducting polymer is accomplished through hopping (and/or perhaps resonant tunnelling [42] or fluctuation-assisted tunnelling [43]). In any case, the characteristic conductivity relationship is almost always experimentally found to follow Mott's variable range hopping (VRH) equation (2.23) with d falling somewhere between 1 and 3 . As stated in section 2.1.1.2.2, there has been some controversy over the underlying physics. Most experimental and theoretical analysis indicates that quasi-1D VRH is most likely to be the most prevalent transport mechanism [44] [45] [46] [47] [48].

2.2.3 Polyaniline (PANI)

Another popular conducting polymer that is commercially available is polyaniline (PANI) [49]. It was the first conducting polymer to be available in large quantities as a dispersion or dispersible solid [50]. Polyaniline is a phenylene-based polymer that has a chemically flexible -NH- group separating phenylene rings in a polymer chain. It typically polymerizes by the oxidation of aniline under acidic conditions and has been known as aniline black since 1862. It was investigated fairly thoroughly in the early 1900s, but its resurrection had to wait for the discovery of metal-like conductivity in iodine-doped polyacetylene in 1977. This sparked renewed interest into many conducting polymers including PANI [51].

The synthesis of polyaniline is carried out using either chemical or electrochemical oxidation of aniline under acidic conditions. The electrochemical method allows the production of uniform thin films. The smallest repeat block is a C_6H_4-NH unit (shown in Figure 2-6d) having a mass of about 91 Daltons. Low-temperature polymerization has been used to generate very long chains having weights of greater than 4×10^5 g/mole. Various substitutions can be made to form complex molecular structures with branching, honeycombing, etc.

Polyaniline is a conducting polymer that has four distinct states: fully reduced, partially oxidized (acid), partially oxidized (base), and fully oxidized as shown from (a)-(d) in the oxidation-reduction diagram in Figure 2-20. In the fully reduced polyleucoemeraldine (LE) state (clear or yellowish in colour), the nitrogen possesses three bonds in addition to two unbound electrons. During oxidation, one of these electrons is lost leaving the nitrogen with a net positive charge; this charge can be balanced by the introduction of a counter anion into the polymer. In this partially oxidized (i.e. doped) state, the polyemeraldine salt (ES) is most transmissive in the green region of the visible spectrum. The polyemeraldine salt is the only conducting form of polyaniline. As the film is further oxidized, a second electron as well as a proton is ejected. This so-called polyemeraldine base (EB) is non-conductive and blue in colour. The fourth, fully oxidized state of polyaniline is known as the pernigraniline base (PNB) state and is not normally used, as it is non-conducting and nonreactive. Because of the protonation-deprotonation mechanism, electrochemical cycling works best in an acidic medium. The proton-rich environment provides the necessary proton gradient to reduce the polyaniline from the blue, non-conductive base back to the green, conductive acid.

The conductivity achieved in polyaniline can be greater than 100 S/cm [52][53]. The band gaps for the states has been measured and calculated [54] to be about 3.6-3.8 eV for LB, 1.7-2.5 eV for PNB and 1.5 eV for ES.

Figure 2-20 Forms of polyaniline. (a) Leucoemeraldine (LB), (b) conducting emeraldine (emeraldine salt) (ES), (c) emeraldine base (EB), (d) pernigraniline (PNB).

There are many possible application areas for polyaniline. Commercial applications to date have included:

- Antistatic coatings
- EMI and microwave shielding
- Electrostatic loudspeakers
- Batteries

In addition, polyaniline it is also under investigation for use in [51]:

- electrochemical actuators
- electroluminescent devices
- electrochromic applications (devices, smart windows)
- biosensors (enzymatic electrodes)
- inhibiting corrosion
- etc.

The conductivity of PANI can be controlled electrolytically and it is electrochromic. It can therefore be used as a controlled conductance channel material whose conductance state can be monitored optically. It also has very high conductivity when properly doped so may also be useful as a printable electronic interconnect. It is available in a number of forms of dispersion, including one that is template-doped by polystyrene sulfonate (PSS).

2.2.4 Polypyrrole (PPy)

Polypyrrole is also a popular conducting polymer that has found some commercial success. It was first polymerized in 1916 through oxidation with hydrogen peroxide to form "pyrrole black". Electrochemical formation of highly conducting films in the late 1970s caused renewed interest. The chemical structure of polypyrrole is illustrated in Figure 2-21.

Figure 2-21 Chemical structure of (a) pyrrole and (b) polymerized polypyrrole chain.

Polypyrrole is one of the most studied conducting polymers and conductivities of >500 S/cm have been obtained [55]. Many different variations have been made by adding substituted groups to change its properties, combining it with other monomers to form copolymers and using it in composites. It is the most popular material for constructing electroactive polymer actuators [56][57] and has found many other applications such as [58]

- Antistatic coatings
- EMI and microwave shielding
- Conductive textiles
- Capacitors
- Polymer batteries
- Electroplating
- Catalysts

- Gas separation membranes
- etc.

A recent aging study [59] has shown very encouraging results in degradation of the conductivity of PPy over a twenty-year time span.

2.2.5 Polythiophene (PT)

Polythiophene has a similar structure to polypyrrole with the N-H substituted with sulphur. Thiophene was known in the 1800s in both monomer and short-chain oligomer forms. The synthesis of conducting films of long-chain polythiophene began in the early 1980s [60]. It is a very stable polymer, even in the neutral state and many derivatives have been produced including poly(3,4-ethylenedioxythiophene) (PEDOT) described in detail below. The chemical structure of polythiophene is illustrated in Figure 2-22.

Figure 2-22 Chemical structure of (a) thiophene and (b) polymerized polythiophene chain.

Polythiophene has been extensively studied and conductivities of up to 5500 S/cm have been obtained in regioregular, head-to-tail coupled polythiophenes [61]. Its various forms have been used extensively in the study of organic field-effect transistors (OFETs). In particular, monodispersed oligothiophenes, such as sexithiophene [62], have shown high mobility when used as a channel material. As in the case of polypyrrole, many different variations have been made by adding substituted groups to change its properties, it has been combined with other monomers to form copolymers and used in composite materials. It has had little success as a commercial material in its original form but the derivative PEDOT, described below, has been one of the most successful conducting polymers available.

2.2.6 Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)

One of the most widely used conducting polymers manufactured to date has been the polythiophene derivative PEDOT:PSS. This material was originally developed by Bayer [63][64][65] and is now available through a variety of suppliers. The chemical structure is shown in Figure 2-23. It is formed by polymerizing templated EDOT monomers along a PSS backbone chain.

The PEDOT is doped *in situ* by a transfer of charge between the PEDOT and PSS chains, which are then held together through ionic bonding. About 40% of the PSS chains are used to template the PEDOT as shown in Figure 2-24(b).

Figure 2-23 PEDOT:PSS Chemical Structure

Its most commonly available form is a water-based printable ink, called Bayer "Baytron P", which contains dispersed gel particles of many PEDOT:PSS chains. The particles have diameters of about 100nm and a concentration of about 1.2% in aqueous dispersion. After printing, these particles coalesce to form a continuous film (Figure 2-24).

PEDOT has a non-degenerate ground state and because of this the carrier properties are not dominated by soliton conduction, as is the case of polyacetylene. As described in section 2.2.2.1, in nondegenerate ground-state polymers polarons and bipolarons are the chief agents of transport and the electronic structure of these for PEDOT are shown in Figure 2-25 [66]. The vertical lines show the possible electronic

transitions. The lines with x are for transitions that are not allowed because of symmetry or the dipole selection rule [67]. $P_1 = \omega_1$, $P_2 = \omega_2 - \omega_1$, and $BP_1 = \tilde{\omega}_1$. (Here P means polaron and BP means bipolaron.) The small arrow stands for an electron with a spin (either up or down). From this diagram, it is clear where the electrochromic behaviour arises and how it is linked to the conductivity.

Figure 2-24 PEDOT:PSS aqueous dispersion as a printable ink gel. The templated PEDOT:PSS and its formation into a film. (a) doped PEDOT chain ionically attached to the PSS backbone. (b) short PEDOT chains grown in-situ on long PSS chains (c) water saturated coils that are dispersed to become processable (d) deposited film of dispersed PEDOT/PSS particles.

There has been a great deal of effort in studying the conduction of PEDOT:PSS and in almost all cases, experimental results show a very good agreement with theory for one-dimensional variable range hopping [68][69][70]. Although when spin casting is used to deposit the material the effect is to produce some anomalous anisotropic behaviour [71][72]. It seems most likely that this behaviour is due to the way the casting technique affects the phase segregation of PEDOT and PSS producing asymmetric islands of higher conductivity.

Figure 2-25 Band structure, optical absorption spectra and electronic structure of polarons and bipolarons in PEDOT (from [66]).

The most common early applications of PEDOT:PSS were [73]:

- antistatic coating for photographic film and antistatic component bags
- electrode material for solid electrolyte capacitors
- transparent conductors for display applications
- etc.

The use of PEDOT is now ubiquitous in the fabrication of numerous organic devices. In organic light emitting diodes (OLEDs), it has long been used as a coating over the indium-tin-oxide (ITO) transparent conductor as a planarizing and high work

function hole conducting layer [74]. Recently it has been found that the work function can be reduced to about 3.8 eV [75] so its use at the OLED cathode may also be possible. It is also used extensively in organic field effect transistors (OFETs) both for electrodes [76] as well as the active channel material [77][78]. With the rising interest in photovoltaic devices it has been finding utility as a hole conductor in dye sensitized solar cells [79][80].

2.3 Electrochromics

Electrochromism is used to describe materials and devices that change their optical absorption or reflection spectrum with some type of applied electrical stimulus. It was originally used for materials that have changes in the visible portion of the spectrum, which is why "chromism" is used, but the term is now generally used for changes at almost any wavelength. In most cases, the change in spectral properties is due to a reversible, electrochemical electron transfer causing an alteration in the absorption bands of the material. The first electrochromic (EC) materials discovered were inorganic and these have been studied extensively over the past few decades [81][82][83]. More recently, it has been found that most conducting polymers also exhibit electrochromic behaviour [84][85][86][87] and this has led to resurgence in interest and a flurry of activity.

There have been a number of applications for electrochromics over the past several years including:

- variable transmittance windows for energy-efficient buildings[88][89]
- adjustable reflectance rear-view mirrors in luxury automobiles[89][90]
- adjustable sunglasses
- displays for watches and other applications[90]

These have been based on inorganic materials and achieved limited commercial success. The problems have been mainly due to cost, complexity, limited lifetime because of cyclicality issues and lack of ruggedness normally attributed to the use of an electrolyte layer. There has also been recent interest in using electrochromics for controlling near infrared (IR) light for optical communications [91][92][93][94] and far IR (thermal)[95] and microwaves for military applications [96][97][98].

Figure 2-26 Typical thin film electrochromic device structure (after [99]). The EC layer(s) could be organic or inorganic or a combination of the two.

2.3.1 Inorganic Materials

As discussed above, inorganic materials were the first electrochromic materials to be discovered. The most studied of these have been the transition metal oxides (TMOs) [100][101]. Nickel, molybdenum, vanadium, iridium, cobalt, ruthenium and others have been used but the most popular of these has been tungsten oxide (WO_3), which will be covered in more detail below. Typically, the TMO EC materials are used as thin films covering a transparent conducting oxide (TCO) layer [102][103] that is usually indium-tin oxide (ITO) [104] but could also be antimony-tin oxide (ATO), fluorine-doped tin oxide (FTO) or some other variant. The conducting layer could also be a non-transparent, conducting material such as gold or carbon, depending on the application. There are many methods used to deposit the thin films – evaporation, sputtering, chemical vapour deposition (CVD) and sol-gel all being popular.

The other major family of inorganic electrochromic materials are the iron hexacyanoferrates [105][82][85]. The most common of these is Prussian blue (PB): $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]^-$, but the family also contains the variants Prussian green (PG), Prussian white (PW) and Prussian brown (PX). Prussian blue has often been used as the counter electrode in tungsten oxide systems since it is anodically colouring while the WO_3 colours cathodically. When used in a thin film cell in this results in maximizing the contrast ratio since both films will be coloured or bleached under the same biasing conditions

2.3.1.1 Tungsten Oxide (WO₃)

The first discovered and one of the most widely studied electrochromic materials is tungsten oxide (WO₃) [106]. As in most electrochromic materials, the optical properties of the WO₃ change when cations are intercalated into the material or are extracted from it. This process is illustrated schematically in (2.64)

with $M = H, Li, Na, \dots$. In reality the details of the process are more complex than this since the tungsten oxide is actually substoichiometric and there are always hydration effects involved.

It is thought that the electrochromism arises because the electrons entering the WO₃ complex cause some of the tungsten to change charge state from W⁶⁺ to W⁵⁺ changing the optical properties [107][108].

In addition to being electrochromic tungsten oxide also shows a large change in conductivity as a result of ion intercalation [109]. This makes it a possible candidate for an inorganic active material for electrochromic devices. The availability of nanocrystalline material [110] has also made it possible to prepare nanocomposite WO₃/polymer inks that are printable. Deposited films of nanocrystalline tungsten oxide have shown very promising characteristics [111][112][113].

2.3.2 Organic Materials

There are many organic materials that are electrochromic [87][86]. In fact, most intrinsically conducting polymers are also electrochromic. The reason for this is evident from the basis of conduction in these materials when they are doped [114]. Doping causes polaron states to be formed within the band gaps of the polymers. These states allow absorption of photons at energies where they formerly would have been transparent. This causes a change in the absorption spectrum. Hence the act of reversibly doping and dedoping these materials through electrochemical means will normally also cause an electrochromic change.

A wide variety of electrochromic polymers has been reported in the literature [115][116][117][84][87] with many different colour variations, speeds, stabilities, etc. Although many of these would also be suitable for application in this work, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most studied and is commercially available in a number of forms and hence serves as the backbone of this work.

2.4 Electrolytes

There are a number of different classes of electrolyte that can be used in electrochromic devices. All of these have their own strengths and weaknesses so the choice of material will always be a compromise. The main types are:

- liquid electrolyte (aqueous or non-aqueous)
- gel electrolytes
- solid electrolytes
- polyelectrolytes

Each of these classes is described in more detail below. In most cases, we have to choose what the ionic species are and what the matrix material will be. The goal is to find the best combination of ionic suitability, material stability, ease of fabrication, safety and environmental impact for a given application.

2.4.1 Ionic Suitability

A number of factors determine the suitability of the ionic species used in an electrolyte. In some cases, the choice of the cation or anion (or both) will be fixed because they are inherent to the function (i.e. if the goal is making a sensor for specific ions or ion products of a reaction). In most circumstances, however, it will be advantageous to choose a high mobility cation since that will largely determine the speed of operation of the devices. In systems where there are several active ionic species, there may be utility in using varying mobilities to differentiate between species. The availability of ion-selective membranes to separate multiple species may also have an impact.

For the devices of main interest for this work, we are reliant on the intercalation of cations into conducting polymer materials so we will be most interested in using salts with small, monovalent cations.

2.4.2 Liquid Electrolytes

Liquid electrolytes are typically made up of one or more solvents into which one or more materials have been dissolved that dissociate to produce mobile ions. There are two basic types of electrolyte, true electrolytes and potential electrolytes. True electrolytes are formed from materials that are already composed of ions even in their solid state. The interaction with the dissolving solvent just serves to disperse these ions. When melted these become a pure ionic liquid with ionic conduction even in the absence of solvent (see sections 2.4.2.1 and 2.4.2.2 below). What we normally think of as salts, such as NaCl, are true electrolytes. Potential electrolytes, on the other hand, do not show significant ionic conduction in the pure liquid state. The components are not ions but non-ionic molecules. This type of material requires a reaction with the solvent used to generate the free ions. Most bases and organic acids are examples of where this is true.

2.4.2.1 Ionic Liquids (Molten Salts)

Ionic liquids are comprised solely of dissociated ions with no intervening solvent. These materials exhibit a high conductivity, molten sodium chloride is typical of this

class and at a temperature of 1173K has a conductivity of 3.9 S/cm. (the melting temperature of NaCl is 1074K). Many other molten salts are ionic liquids and they typically liquefy in the range of 400-1100K. At even higher temperatures, molten oxides, silicates, borates and phosphates become conductive ionic liquids.

2.4.2.2 Room Temperature Ionic Liquids (RT Molten Salts)

Room temperature ionic liquids (RTIL) are salts having a melting point at or below room temperature. This new class of liquid has unique and interesting properties and have found applications in a wide variety of areas. Unfortunately, these materials invariably have large, organic cations making them usually unsuitable for use in this work.

2.4.3 Gel Electrolytes

Gel electrolytes are composed of a linked matrix of material, giving physical structure, interstitially filled with a liquid electrolyte. The saturating electrolyte is composed of one or more salts dissolved in one or more solvents. Plasticizer materials are also often added to adjust the physical characteristics of the overall blend. Gel electrolytes are used in many applications but most of the recent research has been pertaining to lithium-polymer batteries. Since the gel formation necessarily results in

large increase in the bulk viscosity one of the big trade-offs here is ionic mobility, which is normally lowered as a result.

There have been a large number of polymer matrix materials investigated in recent years. The most popular of these have been poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVdF) and poly(vinylidene fluoride-hexafluoro propylene) (PVdF-HFP). Their properties are outlined in Table 2-1 below [118].

	Polymer matrix material	Abbr.	Conductivity (S/cm)
1	poly(ethylene oxide)	PEO	$10^{-8} - 10^{-4}$ (non-gel @ 40-80°C) to 7×10^{-4} as plasticized gel @25°C
2	poly(acrylonitrile)	PAN	$>2.0 \times 10^{-3}$ as plasticized gel @25°C
3	Poly(methyl methacrylate)	PMMA	$>5.0 \times 10^{-3}$ as plasticized gel @25°C
4	poly(vinylidene fluoride)	PVdF	$>1.7 \times 10^{-3}$ as plasticized gel @30°C
5	poly(vinylidene fluoride-hexafluoro propylene)	PVdF-HFP	As high as 10^{-2} as plasticized gel @25°C

Table 2-1 Common host polymers for gel electrolytes.

Table 2-2 lists some high conductivity gel electrolytes used for lithium batteries [119] (EC-ethylene carbonate, PC-propylene carbonate, PAN-poly(acrylonitrile), PEGDA-poly(tetraethylene glycol diacrylate), PVP-poly(vinyl pyrrolidone). The composition numbers quoted are molar percentages and conductivities were measured using the complex impedance technique. Sometimes the term "solid polymer electrolyte" (SPE) is used for these types of materials but we will restrict the use of the word "solid" for materials not bearing liquid solvents.

	Electrolyte	Conductivity (S/cm)			
		-10 C	0 C	20 C	50 C
1	38%EC/33%PC/21%PAN/8%LiClO ₄	1.1 x 10 ⁻³	1.2 x 10 ⁻³	1.7 x 10 ⁻³	3.5 x 10 ⁻³
2	42%EC/36%PC/15%PAN/7%LiCF ₃ SO ₃	4.0 x 10 ⁻⁴	6.0 x 10 ⁻⁴	1.4 x 10 ⁻³	2.2 x 10 ⁻³
3	63%EC/13%PC/16%PAN/1%PEGDA/8%LiClO ₄	4.0 x 10 ⁻⁴	6.0 x 10 ⁻⁴	1.2 x 10 ⁻³	3.0 x 10 ⁻³
4	68%EC/15%PC/3%PEGDA/14%LiClO ₄	1.2 x 10 ⁻³	2.1 x 10 ⁻³	4.1 x 10 ⁻³	8.0 x 10 ⁻³
5	35%EC/31%PC/24%PVP/10%LiCF ₃ SO ₃	4.0 x 10 ⁻⁵	1.3 x 10 ⁻⁴	5.0 x 10 ⁻⁴	1.0 x 10 ⁻³

Table 2-2 Conductivities for some high conductivity gel electrolytes for lithium battery applications.

2.4.3.1 Composite Polymer Electrolytes (CPE)

Recently it has been discovered that adding a quantity of ceramic filler material can actually improve the properties of polymer gel electrolytes [120]. The original fillers used were alumina (Al₂O₃) in PEO and since then many different materials have been tested with micro- and nano- sized particulates. There are two ways in which the filler can enhance the conductivity – passively and actively, depending on the material. The passive interaction is the frustration of the crystallization process in the polymer host causing it to remain amorphous at lower temperatures than would otherwise be the case. Ionic mobility through the amorphous material is higher than when it is crystalline. Active interactions can also occur if the nature of the particle material allows it to partake in the ion transport.

2.4.4 Solid Electrolytes

True solid electrolytes, inorganic or organic, are of limited interest as their conductivity at room temperature is always very low, typically $< 10^{-8}$ S/cm. There are some applications either where speed is not a problem, some electrochromic "smart window" uses for example, or when high temperatures can be tolerated, e.g. high temperature fuel cells.

2.4.5 Polyelectrolytes

Polyelectrolytes are a special class of electrolyte in which at least one type of ion is a polymer. Normally these are polymers with small ions as the counter-ion and either the cation or anion can be the polymer. The doping anion for PEDOT:PSS is polystyrene sulfonate (PSS) and various polyelectrolytes based on PSS have been used in this work. In particular we have used polystyrene sulfonic acid (PSSA) and the lithium (PSS:Li) and sodium (PSS:Na) substituted forms as electrolytes.

2.5 Photoconductors

There are many different ways of sensing optical signals. Most are based on solid-state semiconductor materials. These may be formed as crystalline or amorphous devices.

Silicon, germanium, III-V and II-VI compound semiconductors and, recently, some organic materials are commonly used. These materials can be used to fabricate junction devices, which use the depletion region of a diode to separate photon-generated electron-hole pairs, or photoconductors in which the photons generate free carriers increasing the conductivity of the material.

Since photons are required to generate carriers in a photoconductor, they are insulators when not illuminated. In a semiconducting photoconductor, the carriers can be generated in two ways [121]. In an intrinsic photoconductor, an absorbed photon generates an electron-hole pair that are separated by the applied field and act as carriers. In this case, the conductivity is just due to the increase in the number of carriers. In an extrinsic photoconductor, photons either ionize a valence electron to trap level in the band gap or ionize a trap level to the conduction band. In either case, a single carrier is generated. To maintain electroneutrality the generated carrier will be available for conduction for the lifetime of the trapped carrier. Depending on the relative value of the transit time to the lifetime a net photoconductor gain can result. Whether the photoconductor has gain or not, the response is typically linear with optical input so the photoconductor acts as an optically controlled resistor.

Most of the research and development into photoconductors has been aimed at the photosensitizing coating in xerographic applications such as photocopiers and laser printers. These require specific properties such as a low lateral conductance to maintain resolution that are at odds with use in this work. This is particularly true of organic photoconductors [122] [123] that are generally designed to use separate charge generation layer (CGL) and charge transport layer (CTL). The other option is to use an

inorganic photoconductor but since a screen printable low temperature solution is required and there has been no work done in this area. The available information pertains mostly to sintered thick film cadmium sulphide and cadmium selenide devices [124] [125] [126] or thin film vacuum deposited devices [127] [128] [129].

3 AREAL PROCESSING

3.1 Device Fabrication Methods

There are two main techniques used to form patterns of some material or materials on a substrate. These are

- 1) deposit a layer of material over a surface and use a patterning technique to remove the areas that are not required, or
- 2) transfer the material directly to the substrate using a patterned transfer instrument or direct writing

The first of these is the method used by conventional microlithography and the second covers most forms of conventional ink printing. This work is based on using "functional inks" to form active and passive devices so it has concentrated mostly on the second technique. Another emerging area uses the transfer of material at the molecular level and is can achieve nanoscale deposition and patterning.

This section is divided into three parts. The first two briefly outline conventional microlithography and soft nanolithography. The third covers a number of forms of ink printing technology in more depth since this seems to be the clear direction forward for

printed electronics. These use additive techniques on a variety of flexible substrates at relatively low resolution, which is aligned with the goals of this work.

3.1.1 Conventional Microlithography

Conventional microlithography is primarily based on transferring "patterns" to either to a substrate directly or some material that has been deposited on the substrate. This is normally done by coating the substrate with a photosensitive material (called photoresist) which can itself be patterned by appropriate illumination and development. The pattern can be written optically through a photomask or directly by scanning an electron beam or laser over the areas to be illuminated. There are many excellent reference books covering all aspects of microlithography, e.g. [130].

Because modern semiconductor fabrication requires high resolution, repeatability and reliability conventional lithography normally has high demands such as

- vacuum deposition equipment
- high material purity
- extremely low particulate levels
- high level of cleanliness
- limited substrate sizes for ultimate resolution (although display manufacturers are pushing the limit here)

It is also more conducive to batch processing and rigid substrates than roll-to-roll processing of flexible materials although roll-based vacuum coating systems are common. The cost of a state-of-the-art semiconductor fabrication facility or a large area display manufacturing system is very high so the entry cost into such a technology is often a barrier.

There is the argument that the high demands are the result of having an extremely high resolution, high density electronic technology which could be downgraded to make it more affordable and reduce the required cleanliness. It is still unlikely though that this is a viable way to achieve roll-based or continuous sheet processing of flexible circuits. Even large display manufacturers, although still using conventional lithography for backplane patterning, are turning to other methods such as ink-jet printing for some manufacturing steps [131].

3.1.2 Soft Nanofabrication Techniques

A group of methods known as "soft" nanofabrication are becoming popular because of their capability to form structures with very small features, approximately ~20 nm [132] [133]. They all use a rigid master as the pattern source.

Nanoimprint lithography (NIL) transfers the pattern directly to a softer material layer, such as a polymer, deposited on a substrate. The master is pressed into the film, normally under heat and pressure causing the pattern to be imprinted. A variation on this

is to use a photocurable polymer that is flash-cured with the master in contact (or just after contact release).

There are also a number of methods that transfer the pattern from the master to an elastomeric stamp made from a material such as poly(dimethylsiloxane) (PDMS) [134]. This soft stamp is then used, in a method similar to pad printing or offset gravure (see section 3.1.3.4), to transfer a material print the pattern to a substrate. Depending on the details, this is called microcontact printing or nanocontact printing or nanotransfer printing, etc. This method can also be used to transfer molecular inks that alter the surface energy in conjunction with selective wetting techniques to transfer patterns that would otherwise be very difficult to achieve [135] [136] [137].

The resolution achievable by these techniques is very impressive and they are capable of large areas with the appropriate mastering. Although the capabilities provided are not necessary for this work at present. The reader is directed to the references, and in particular the review articles [132] [133], for more detailed information on this important emerging field.

3.1.3 Printing Techniques

The ability to automatically reproduce text began in the 1450s with the invention of the Gutenberg press. This used movable type that picked up ink on its moulded face and transferred it to sheets of paper. Although it became more and more mechanized over time, this method continued to be the dominant printing technology for about five

centuries. Most of the more modern techniques, which are outlined below, use some form of lithography to produce a master that is then used to transfer complete page or multi-page images onto a substrate. They are also able to print colour by overlaying multiple ink layers so have at least rudimentary alignment abilities.

In choosing a printing technique for devices, we need to choose a method able to deposit the materials with dimensional and positional accuracy. We would like to quickly:

- apply an accurate volume of ink over a given area to yield a known and repeatable layer thickness
- accurately define the geometry of the patterns on the layers with high resolution
- repeatably deposit layers relative to each other to achieve accurate registration

We will look at six of the most commonly used printing techniques below. The first three, offset lithography, flexography and gravure, are patterned plate processes and are commonly used in high-speed roll and continuous sheet-feed applications. The other three, pad/imprint, ink jet and screen-printing are more batch oriented.

3.1.3.1 Offset Lithography

Since the 1950s offset lithography has been the most popular printing process for paper publications and is also used for other materials such as cardboard, plastic, and

metal films. It is very mature, fast and accurate and is cheap for high volume printing applications.

An aluminium plate is used to bear the image to be transferred. It is coated with a hydrophobic photopolymer that is patterned with the image. The actual process employed is the differential wetting of water between this photopolymer and the oxide present on the surface of the aluminium. The plate is then dampened with water that wets the aluminium oxide but leaves the photopolymer dry. When ink is then applied, it will not stick to the wet areas but adheres to the photopolymer. The ink is then transferred from the primary plate to an intermediate transfer agent called a "blanket". The blanket serves to reduce the amount of water transferred to the final substrate and is also somewhat conformal under pressure allowing printing on non-uniform surfaces. This process is illustrated in Figure 3-1. Water-free printing is also possible using another material for the background, such as silicone, to which the ink will not adhere.

Figure 3-1 Continuous sheet feed offset lithography process.

Although the resolution and accuracy of deposition are both very good, the amount of ink that can be transferred is fixed and limited. In addition, the range of suitable viscosities and surface energies for the inks are constrained making it more difficult to apply existing materials.

3.1.3.2 Flexography

Flexographic printing is similar to offset but the ink is deposited directly from the photopolymer (or some other flexible, patterned surface coating material) to the substrate material. To ensure that ink is only coated on the photopolymer relief a metering roll called the Anilox roll is used. It is arrayed with indentations in a regular pattern that fill with ink from the fountain roll (or sometimes using an ink reservoir with a doctor blade to remove the excess) and transfers the ink in accurately metered amounts to the plate. In this way, the ink only contacts the relief and leaves the background bare. The process is shown in Figure 3-2.

The resolution of flexography is necessarily lower than offset printing since it is limited both by the resolution of the image written to the plate and the structure of holes in the Anilox roll. The flexibility and softness of the plate materials and the fact they are in direct contact with the substrate is also detrimental to both resolution and accuracy. However the volume of ink deposited can be controlled to some extent by the depth of the holes in the Anilox roll and a wider range of viscosities is possible than with offset printing.

Figure 3-2 The flexographic printing process.

3.1.3.3 Gravure

In gravure, printing an engraved cylinder is used rather than forming a roll by bending a flat plate as in the previous techniques. Because there is no plate joint, printing can be truly continuous with no dead space. The cells engraved in the drum are filled with ink by being immersed in a reservoir and a doctor blade is used to remove the excess. The substrate is passed between the engraved cylinder and a backing impression cylinder with a high contact pressure causing the ink to be transferred.

The engraving uses a pattern of cells to hold the ink that can be of varying surface area and depth. This allows the volume of deposited ink to be varied over a reasonable range. As with flexography, the use of cells limits the ultimate resolution but since the transfer surface is hard and high-resolution laser engraving can be used the limitation is not as severe.

Figure 3-3 The gravure printing process.

3.1.3.4 Pad Printing

Pad or imprint printing is an offset technique that is similar in theory to gravure (and is also called "offset Gravure"). Instead of a cylinder, it uses an engraved flat plate. The plate is filled with ink and the excess is removed with a doctor blade. An elastomeric pad is then pressed or rolled over the plate surface picking up the patterned ink. The pad is then moved over the substrate and pressed or rolled on it transferring the ink image.

This technique requires careful control of the ink properties but high resolutions can be obtained. In addition, non-uniform substrates can be coated and even fairly complex shapes can be accommodated through appropriate design of the elastomer transfer stamp.

Figure 3-4 Pad or imprint printing process.

3.1.3.5 Inkjet

Inkjet printing has gone through a lot of development over the last couple of decades. Initially this was in the area of paper printing but more recently, the versatility of this technique has attracted a lot of interest for solution-based deposition. There are three main types of inkjet print heads available – thermal drop-on-demand, piezoelectric drop-on-demand and electrostatically controlled continuous drop. In the case of the

continuous drop print head, the ink drops are electrically charged and then deflected into a gutter if they are not to be deposited. A typical printer arrangement is illustrated in Figure 3-5. Normally one or more print heads will be rastered along one axis while the substrate or printhead carrier travels along the other.

Figure 3-5 Drop-on-demand inkjet printing system.

The resolution and accuracy of the drop-on-demand systems is quite good but the main drawback is the difficulty in preparing suitable ink formulations, which can be complex and costly to develop.

3.1.3.6 Selective Wetting

Selective wetting is not really a printing method on its own but rather a technique used in conjunction with other coatings. The idea is identical to that in the coating of the offset lithographic plate. Variations in the relative surface energies between the inks and previously deposited layers are varied to cause the ink to preferentially wet and hence coat certain areas. This technique has been used to fabricate some of the devices studied in this work and is described in detail in section 4.1.

3.1.3.7 Screenprinting

Screenprinting uses a fine mesh covered with photoemulsion. The desired image is optically transferred to the photoemulsion, which is then developed leaving open mesh only where ink is to be deposited on the substrate and cured emulsion everywhere else. The screen is placed a fixed distance above the substrate and the pattern is flooded with ink on the other side. A squeegee is drawn across the back side forcing the screen into contact with the substrate and simultaneously depositing ink through the open mesh as shown schematically in Figure 3-6.

Screenprinting allows for the widest variety of ink properties and enables the largest variation in film thickness of all the techniques covered. All types of inks – thermal curing, ultraviolet (UV) curing, electron-beam curing or even materials that are

not to be cured at all – can be used in a screenprinting system. This high degree of flexibility is why this method was chosen for most of the fabrication work in this thesis – the details of the system used and the results are presented in section 4.2.

Figure 3-6 System for screenprinting.

The main drawbacks to screenprinting are the resolution obtainable, which is about 25 μm (see section 4.2.4), and the speed of printing. Neither of these limitations has been an important factor in this work.

3.2 Printable Materials

A number of different materials have been used as screen printable inks in this work. Some of these have been commercially available materials that have been adjusted by the manufacturer to be suitable. For others, in order to be used as a screenprintable ink the materials had to be adjusted in viscosity and solid content to form an ink that had a suitable consistency and would form a layer of the proper thickness. A number of these materials are outlined in the sections below.

3.2.1 Controlled Conduction ("Semiconductor")

These materials are the same as the electrochromic polymer materials outlined in section 3.2.2. The focus of the work was mainly PEDOT:PSS but other conducting polymers, such as polyaniline and polypyrrole, were tried and operated with some success. A number of composites were also formulated and tested, again with some success.

3.2.2 Electrochromic

A number of different electrochromic materials were used in the fabrication of the devices. Primarily studied were:

- polythiophene (Baytron-P, etc.)
- polyaniline (Ormecon, etc.)
- nanoparticulate inorganics in polymer (WO₃, CeO₂, etc.)

Of these Baytron-P, which is a polythiophene derivative, poly(3,4-deoxythiophene), templated along a polystyrene sulphonate chain, was found to be the most suitable for use. It is available in many forms including a screen-printable ink or precoated onto flexible polymeric film.

3.2.3 Photoconductors

The current application requires the photoconductor to be used as an optical input device so it needs to have a sufficient change in conductivity to be sensed by the active devices being used. Therefore, in the "on" state it should be able to have similar conductivities as the channel conductivities of the electrolytically controlled device. In addition, in order to be compatible with the rest of the process it should be screen printable and not require any high temperature processing.

There are two routes to making printable photoconductors – all polymer or polymer/inorganic hybrid. In some respects, the former route would be the most desirable but, as discussed in section 2.5, it can only be used in cases when the overall conductivity can be low. Printable photoconductive inks have been fabricated but they all require sintering in order to be useful [124] [125] [126]. Even so, the hybrid approach has proven to be more useful in generating higher photoconductivity. The results of developing a

polymer thick film (PTF) ink based on cadmium sulphide (CdS) and cadmium selenide (CdSe) are presented in section 4.3.2.

3.2.4 Electrolytes

One of the key elements of electrolytic devices is the electrolyte. The electrolyte needs to be chosen to be stable, have high ion mobility (or appropriate for the application) and, preferably, be applied as a “solid” to allow overcoating and encapsulation. A number of different types of electrolyte have been used in this work. The primary types examined are:

- Li salts
- other salts (Na, K, Ca)
- acids
- ionic liquids (RT molten salts)
- matrix (liquid, gel, solid)

For initial testing of fabricated structures, liquid electrolytes were often used. Typically, this would be lithium perchlorate dissolved in propylene carbonate sometimes with the addition of ethylene carbonate as well. Some preparation and testing using this electrolyte with Kynar polyvinylidene fluoride (PVdF) as a solid polymer electrolyte (SPE) matrix material was also carried out.

As a liquid electrolyte, ionic liquids can also be used. These are room temperature molten salts, have extremely low vapour pressure, and so can be left exposed for extended periods.

3.2.5 Conductors

In some cases, the doped conducting polymer can be used dry as a conductor but for other applications, we require materials with different properties. There are number of materials that can be used in a variety of circumstances:

- silver – general purpose, high conductivity but sensitive to contamination to electrolytes and degradation by them
- gold – good conductivity and electrochemically stable but expensive
- platinum – similar to gold but can also act as a catalyst
- carbon – reasonable conductivity, electrochemically stable, cheap but more difficult to contact to than the metals
- antimony-tin-oxide (ATO)/ indium-tin-oxide (ITO) – fairly low conductivity but translucent so can be used where optical signals are required to pass

3.2.6 Dielectrics/Encapsulants

To complete the process materials are needed to separate and encapsulate the active and conductive inks. These should normally be impermeable to any overprinted

inks, solvents, moisture, electrolytic ions, etc. It is especially critical to have an electrolyte encapsulant that will prevent the loss of solvent from the electrolyte since this will usually lead to a marked reduction in ion mobility over time.

4 DEVICE FABRICATION

There have been many different methods used in recent years to apply patterned active polymeric materials to a variety of substrates. These include standard lithography techniques used in conventional microcircuits as well as printing methods such as gravure, ink jet, pad printing, etc. There are two main techniques that have been used to fabricate devices in this work. The first is "Channel Casting", which was used for early devices, and is described in Section 4.1 below. Screenprinting has been used for the bulk of the work since it is relatively insensitive to ink properties and allows a common technique to be used for all applied layers on a variety of substrates.

4.1 Channel Casting

Channel casting is essentially a differential wetting technique, as illustrated in Figure 4-1. A substrate is chosen that is wetted easily by the material that is to be deposited. This can be accomplished by choosing a suitable substrate material or, if this is not possible, applying a surface preparation step (oxygen plasma, etc.) or wettable coating. A material that is not wettable is then applied in areas that are to be excluded from the coating. The substrate can then be dip-coated and the material to be coated will only adhere in the desired channels.

For this work the coating material was an aqueous suspension so the wettable and unwettable areas were hydrophilic and hydrophobic, respectively.

Figure 4-1 Channel Casting technique for the electro-active polymer followed by silver contact formation and electrolyte cell construction.

As shown, the contacts to these simple devices were added by simply masking the active area and using the same channel delineation to pattern silver polymer thick film

(PTF) ink. The structure was then baked, lidded using a glass cap and epoxy seal, and filled with electrolyte.

For patterning, an 80 μm thick “blue film” channel mask on a glass substrate was used for casting of the electrochromic aqueous dispersion. ("Blue film" is a flexible polymer film with a low-tack adhesive designed not to leave a residue when removed. It was meant to be applied to the back side to secure wafers during singulation operations such as sawing or dicing. It is also available with UV release adhesives for applications requiring that there be no removal force.) The relative surface energies between the materials cause the channels to fill uniformly yielding the generation of repeatable films.

The surface profile for a cast channel was measured using a KLA/Tencor P-10 surface profilometer and is shown in Figure 4-2.

Figure 4-2 Profilometry of dry channel-cast PEDOT film

Note that the 80 μ m thick wet 1.2% PEDOT:PSS aqueous dispersion results in a dry film of an average thickness of about 1 μ m, as expected. The "ears" at the edges of the channel are caused by non-180° contact angle and subsequent accumulation during drying. It is difficult to get much larger than a 110° receding contact angle when using aqueous solutions so, although it may be possible to reduce these somewhat, they cannot be completely eliminated.

A completed version of a simple test structure device is illustrated in Figure 4-3. It consists of a T-structure, which will be detailed later in the measurement and simulation sections, along with a simple channel to form a "T-bar". This was used for measurements of the individual structures and the interactions between them.

Figure 4-3 Completed version of simple T-structure device with additional line (to form T-bar) before filling with electrolyte.

4.2 Screen Printing Equipment Design and Implementation

4.2.1 Overall System Design

A custom screen printing system was designed and built to facilitate the simple fabrication of multi-layer organic and hybrid devices with rapid design turn-around. This system is comprised of two main elements custom designed for this application: 1) a direct-write, flying spot laser screen writer and 2) a screen printer; both of which are described in detail below. These two elements were designed to be used together. They allow the printing of multiple layers without requiring alignment marks and active or passive alignment between printing layers. This was accomplished by mounting the framed screens in frameholders incorporating accurate alignment pins. Both the laser screenwriter and screenprinter use corresponding precision sockets to ensure accurate and repeatable positioning on each unit. Using this system the overall accuracy and repeatability has been both calculated and measured to be better than $\pm 25\mu\text{m}$. The print area is nominally 50mm x 50mm but can be easily extended to 75mm square or round if required.

4.2.2 Screen Writer

4.2.2.1 Design

The direct screen writer is a custom flying spot system that was designed to use a General Scanning MiniSAX VM500 dual-axis galvo scanner assembly and a Power Technologies PPMT25/5231 405 nm gallium nitride (GaN) diode laser. A block diagram and photograph of the system are shown in Figure 4-4 and Figure 4-5 respectively. The scanner controller is sent commands under software control by a computer running Agilent Virtual Engineering Environment (VEE). Digital outputs on the controller are used to modulate the laser output in precise synchronization with the motion of the mirrors.

Figure 4-4 Block diagram of direct screen writer system illustrating the main components.

4.2.2.2 Implementation

The physical structure for the writer was built using an extruded aluminium structural system from 80/20 Inc. The extruded beams were mounted on a 12-inch square optical base plate for stability. This allowed the integration of a solid base combined with the ability to integrate the required optical components. Precision optical positioning components were used for the laser beam positioning and steering in the writer.

Figure 4-5 Direct screen writer with blank and patterned screens in alignment frames. The inset shows assembly with screen in place.

Control software was written such that any bitmapped image from the computer can be reproduced as a raster image in the plane of the sensitized screen. Multilayer images can then be generated corresponding to the device layers using layout or drawing software and transferred to emulsion-coated screens that will be self-aligned when printed. The optical free aperture of the scanning system is $a = 4$ mm and the distance to the target plane is about $f = 200$ mm as shown in the diagram in Figure 4-6. Assuming that the optical system is diffraction-limited with a Gaussian beam profile of diameter $D = 3$ mm and $\lambda = 405$ nm, the full-width at half-max (FWHM) optical spot size in the plane of the screen will be

$$\begin{aligned}
 w_{FWHM} &= 0.59 \cdot 2w_0 & (4.1) \\
 &= 0.59 \cdot \left(\frac{4\lambda}{\pi} \right) \left(\frac{f}{D} \right) \\
 &= 0.59 \cdot \left(\frac{4 \cdot 405 \times 10^{-9}}{\pi} \right) \left(\frac{200 \times 10^{-3}}{3 \times 10^{-3}} \right) \\
 &= 20.3 \mu\text{m}
 \end{aligned}$$

where w_0 is the size of the Gaussian beam waist [138]. The corresponding depth of focus (DOF) is given by

$$\begin{aligned}
 z_{DOF} &= \left(\frac{8\lambda}{\pi} \right) \left(\frac{f}{D} \right)^2 & (4.2) \\
 &= \left(\frac{8 \cdot 405 \times 10^{-9}}{\pi} \right) \left(\frac{200 \times 10^{-3}}{3 \times 10^{-3}} \right)^2 \\
 &= 4.58 \text{ mm}
 \end{aligned}$$

Writing in the screen emulsion is normally limited to the central 50 mm x 50 mm area so the maximum curvature at the edges will be

$$\Delta z_{\max} \approx 25 \left(\frac{25}{200} \right) \quad (4.3)$$

$$= 3.13 \text{ mm}$$

This is well within the DOF so will yield only a small impact on the system resolution. There should not be any appreciable degradation over the 50mm square field.

Figure 4-6 Optical path design for the rastering screen writer.

Figure 4-7 is a photograph of a section of screen showing the pattern for the active layer of a simple dual-line transistor structure. The edge definition of the emulsion pattern clearly shows the system to be capable of at least the quality expected from the calculated resolution.

Figure 4-7 A section of a printing screen showing the patterned emulsion for the active layer for two transistor devices with different channel dimensions. In this case 200 thread/inch screen has been used. (a) 125 μm x 1000 μm channel with 150 μm gap, as drawn. (b) 250 μm x 1000 μm channel with 250 μm gap, as drawn.

After writing the printed area of the screen (normally 50 mm x 50 mm), this area is masked and the exterior emulsion is crosslinked using a 365 nm UV flood from a mercury arc lamp. The flood system (Figure 4-8) is also used when the pattern to be printed is provided on a conventional contact mask (up to 5"x5").

Figure 4-8 Ultraviolet flood system used to crosslink border emulsion or do exposures using contact masks.

Finally, the exposed screen is developed to remove uncrosslinked emulsion and dried. Once the screen is dry, a blanket flood can be used to maximize the durability of the emulsion, particularly if it is to be used for many print cycles.

4.2.3 Screen Printer

4.2.3.1 Design

The custom screen printer designed and built to match the direct screen writer is a simple manual drawbar design as shown in Figure 4-9. It uses the same precision socket mechanical alignment as the writer ensuring accurate alignment of multiple printed layers. The squeegee is 75 mm wide to print a nominally 50 mm square area. The substrates used can be hard or soft. They are mounted on a vacuum holder with alignment pins that is vertically adjustable to allow changing the substrate-to-screen snap off height. Optionally, a spring-loaded flood bar can be used to prespread the ink on the screen when required.

To print multiple layers, a batch of substrates are sequentially mounted in registration with the alignment pins and printed. For layers employing thermoplastic inks the substrates are then transferred to a vacuum oven, typically set to 130 C, after printing to be cured. UV inks are cured either individually *in situ* or as a batch using a mercury arc lamp.

4.2.3.2 Implementation

In the same manner as the screen writer, the physical structure for the printer was built using an extruded aluminium structural system from 80/20 Inc. Again, the extrusions were mounted on a 12-inch square optical base plate for stability. In this case, the base needed to be integrated with the required moving components. These were the clamshell, which was used to bring the printing mechanism in contact with the screen, and the squeegee and flood drawbars. A precision vertical optical positioning stage was used for substrate height positioning in the printer.

Figure 4-9 Assembled screen printer. The substrate sits on an adjustable height stage to set the appropriate "snap off" gap between it and the screen.

4.2.4 Evaluation

A number of tests were run to verify the resolution of both the screen writer and the screen printer. In all cases, the results showed that the targets of overall resolution and accuracy of approximately $\pm 25\mu\text{m}$ were consistently met. Figure 4-10 is an example of a test screen sequence used to set the laser power and pulse length to give the optimum emulsion exposure.

Test Charts Setting Screen Emulsion Exposure

Figure 4-10 Screen writer test screens for setting emulsion exposure time.

To test the layer-to-layer alignment accuracy for the laser writer three separate patterns were written on the same screen emulsion using the interspersed squares as shown in Figure 4-11 (a), (b) and (c). Between writes, the screen was removed from the write, installed in the printer, removed from printer and then reinstalled in the writer. The final result for the completed screen after development is shown in Figure 4-11 (d) with a close-up of a group of four squares in Figure 4-11 (e).

Figure 4-11 Squares test. (a) Initial written pattern of frame and squares (b) second interspersed squares overlay (c) third interspersed squares overlay (d) photograph of final screen pattern (e) close-up of a group of emulsion squares.

The thread pitch of the screen is 200 tpi and the squares have as-drawn dimensions of 50 mils on a side with 20 mil separations. The overall alignment of the squares is about $\pm 25\mu\text{m}$ so this will undoubtedly be the limiting factor if layer-to-layer alignment is critical.

4.3 Device Design & Evaluation

4.3.1 Device Structures

Using the screen printing system described above, the stated resolution and dimensions and the types of inks available are the only limits on the device structures that are possible. In this work we have made a number of structures based on simple lines of active material that are used both as controlled conductance "channels" and controlling electrodes. The interaction is due to movement and intercalation of ionic species due to the relative potentials applied to the lines. We have also incorporated:

- hybrid metal/polymer inks to form interconnections and pads
- polymer dielectrics for isolation and protection
- electrolytes for ion supply and transport
- epoxy encapsulation for sealing

The structures of some of the particular devices that have been fabricated are described below.

4.3.1.1 Simple Structures

The simple structures initially made used the "selective wetting" method of fabrication. They are single channel devices, as shown in Figure 4-1, and the T-structure as illustrated in Figure 4-1 and Figure 7-1. These devices used a liquid electrolyte and were normally capped with a glass lid to prevent evaporation as shown in Figure 4-3.

4.3.1.2 Electrolytic "Transistors"

The simple dual-line, symmetric transistor structures are formed using a three-layer process:

- 1) print PEDOT:PSS ink on glass or polymeric substrate
- 2) print silver colloid ink to form conductors
- 3) print dielectric overcoat with electrolyte and pad windows

Each printing step is followed by a thermal cure in a vacuum oven at 130C. The active conducting polymer material used is Agfa Orgacon EL-P3040 PEDOT:PSS ink formulated specifically for screen printed applications. The silver ink is DuPont 5028 and the dielectric is DuPont 5036, both from their polymer thick film (PTF) line of materials. The printed layer lay-up is illustrated in Figure 4-12.

Figure 4-12 Printed three-layer stack for a simple dual-line transistor structure. The substrate is first printed with the PEDOT:PSS layer followed by the textured silver/polymer layer and dielectric overcoat.

After the three layers are printed, the electrolyte is added through the window in the dielectric overcoat that provides access to the active lines. The electrolyte is then encapsulated by applying a UV-curable epoxy dome over the top of the electrolyte. Plane and cross-sectional schematic diagrams of the device are shown in Figure 4-13.

Figure 4-13 Schematic diagram of completed dual-line transistor device. (a) plane view illustrating overall structure. (b) cross-section of central region showing electrolyte and epoxy encapsulant over the active lines.

A photomicrograph and the results of surface height measurement of a device using a Wyko optical profilometer are presented in Figure 4-14 below. Devices shown were fabricated using 200 tpi polyester screens. The edge “scalloping” is due to the thread pitch. Thread densities of up to ~500 tpi are available for improved transfer fidelity. As shown in the fabrication section above, the screen emulsion pattern resolution was >1000 dpi. The lines (or channels) in the device shown are approximately 125 μ m x 1000 μ m overall with a 150 μ m gap. The active portion of the lines, however, is limited to a section about 500 μ m long by the electrolyte window as shown in the profilometer y-profile. The profilometer x-profile indicates the lines have a meniscus-like cross-section with a maximum thickness of approximately 500nm. These values are consistent with the deposition parameters and solid content of the ink as well as post-processing resistance measurements.

Figure 4-14 Photomicrograph and optical profilometry measurements of a dual-line transistor device. (a) photomicrograph (b) pseudo-colour profilometer image (c) cross-sectional profilometer measurements

A photograph of a complete, operating device is shown in Figure 4-15.

Figure 4-15 Complete operating dual-line transistor device. For this particular design, the $125\mu\text{m}$ lines are spaced with a $250\mu\text{m}$ gap. The clear dome is the epoxy encapsulant. The colouring of the active material will be addressed in the device operation section.

4.3.1.3 Other Structures

Almost any arrangement of active polymer, passive polymer, interconnect metal, electrolyte and encapsulant can be fabricated using the techniques that have been outlined. These include single devices, multiple devices and complex integrated structures. The interconnection and control through electronic and ionic means can be arranged to perform many interesting functions. One such device is the three-line structure shown in Figure 4-16 below.

Figure 4-16 Simple three-line device structure that allows the implementation of a 2-input NOR function.

Later, in the section outlining experimental results we will describe how this structure can be used as simple 2-input NOR gate and present operational results. Since the interaction between separated segments of active material is through the interaction of ions and the potential distribution on these segments, the fabrication of devices of arbitrary complexity can be accomplished.

4.3.2 Photoconductor Implementation

A powder of inorganic photoconductor, such as cadmium sulphide (CdS) or cadmium selenide (CdSe), can be used as a photoconductor if it is made into a paste and sintered onto some form of substrate. Here we describe a method of using a CdS powder

and a polymeric binder to form a photoconductor that does not require sintering and can thus be used with temperature sensitive substrates. This allows the addition of photosensitive elements to flexible circuits and other temperature sensitive substrates such as circuit boards, etc.

Cadmium sulphide (CdS) powder was purchased from Aldrich. The powder was examined using a scanning electron microscope (SEM) to determine the particle sizes. From the SEM photographs in Figure 4-17 the particles range from $\sim 500\text{nm}$ up to $\sim 2\mu\text{m}$.

Figure 4-17 SEM photographs of cadmium sulphide powder used in polymer thick film printable photoconductor ink.

To determine the crystallinity of the powder X-ray diffraction (XRD) was used. The results shown in Figure 4-18 indicate that the powder is crystalline with the narrow peaks indicative of the large crystal size measured from SEM photographs.

Figure 4-18 X-ray diffraction results for cadmium sulphide powder.

To prepare a printable ink the CdS powder was mixed with screen printable polymer base (Dupont 3571) and solvent to maintain an appropriate consistency. The ink was then coated onto 25 mm round glass cover slips and cured at 130 C for 15 min. Silver contacts were then added about 1 mm apart over the CdS ink and cured once again. A prepared "smudge test" sample is shown in Figure 4-19.

Smudge test samples with varying concentrations of CdS in polymer binder were prepared and tested for photoconductivity using an Agilent 4155 semiconductor parameter analyser and 20 W halogen lamp for illumination. The as received CdS showed no photoresponse at any filling level.

Figure 4-19 "Smudge test" sample for evaluating CdS photoconductor inks.

Next doping with copper chloride (CuCl_2) was attempted by dissolving varying quantities of dopant in the polymer base before adding the CdS. This proved effective, photosensitive smudge samples were produced, and a number of experiments were performed to optimize the doping level.

Once the photoconductor ink had been optimized, screens were designed to make interdigitated samples to increase the conductivity. One is shown in Figure 4-20.

Figure 4-20 Interdigitated CdS photoconductor element.

5 ELECTROLYTIC DEVICE OPERATION

The devices that have been fabricated in this work operate through the control of the doping level, and consequently the conductivity, of a section of a film of conducting polymer by controlling the relative potential of a neighbouring piece of the same material. The applied potential causes a movement of charge between the two through the external circuit. The resultant electric field in the electrolyte moves cations to the electron-rich line and anions to the one that is positively charged. The material that intercalated the cations has the conducting polymer portion reduced to the neutral, non-conducting state. This process is illustrated for PEDOT:PSS in Figure 5-1.

Figure 5-1 Intercalation of cations (M^+) from the electrolyte causes the normally doped, conducting PEDOT to be reduced to the non-conducting state.

In general, this process can be characterized by (5.1) below.

where: CP – conducting polymer

PE – polyelectrolyte template used for doping (5.1)

M – cation

In all the cases of interest in this work, the active materials were doped conducting polymers with a polyelectrolyte backbone. Although normally so, the materials used for different electrodes are not necessarily the same and it may be advantageous in some situations to use different materials to adjust thresholds or sensitivity values. In all cases however, we use materials that are capable of ion intercalation and release in a balanced "push-pull" configuration such that the number of ions intercalated and released by all electrodes is balanced. Otherwise, the resulting local potentials may cause irreversible electrochemical reactions to occur degrading the devices.

From Figure 5-1(a), we can see that in the initial, doped state the PEDOT acts as the polycation to the PSS polyanion forming a one-dimensional organic salt. In the absence of the PEDOT, the PSS would exist as polystyrene sulfonic acid (PSSA) in aqueous solution. When the PEDOT:PSS is formed the PEDOT takes the place of some of the hydrogen sites in the PSSA. The level of doping, i.e. the fraction of PEDOT doping sites actually oxidized, determines the intercalation required to neutralized the conducting polymer to the insulating state (Figure 5-1(b)). In an unbiased device overall neutrality must be maintained and when it is biased the charges, both electronic and ionic, will redistribute to balance the applied potential.

For the case where the two arms of a balanced, symmetric device have less than half of the saturated doping level then, as we apply a potential, ions are released from one arm and an equal number will be intercalated in the other. When the bias is reversed, the opposite movement of ions will occur. During initial cycles, some of the cations will be protons released from the material of the positively charged arm causing it to become more highly doped. For subsequent cycles, the ions may be metal ions or protons depending on the composition of the electrolyte.

If the doping level of the active material is higher than half the saturation level then there needs to be another process at work to balance the charge at the positive electrode. What this will be depends on the structure of the arm material and the size and mobility of the anions in the electrolyte and solvent used for the electrolyte. In general, we can have:

- release of protons from the PSS backbone further from away the PEDOT segments
- intercalation of anions from the electrolyte in the material
- accumulation of anions from the electrolyte close to the material

In most cases, all of the above will be present to some extent. We expect the first process to dominate when PEDOT:PSS is used with aqueous or "wet" electrolytes having relatively large or immobile anions.

5.1 Material Conductivity

The two-line balanced device illustrated in the drawing in Figure 4-13 and photomicrograph in Figure 4-15 was used for conductivity measurements. The device was fabricated as described above. The active sections were two lines of screen-printed PEDOT:PSS and these were contacted using a composite thermoplastic polymer/silver ink deposited in a similar manner. These layers were then overprinted with a protective polymer dielectric layer leaving windows for the pads and conducting polymer lines. The active area window was then filled with electrolyte and overcoated with a UV curable epoxy.

To adjust the intercalation of ions a DC bias was applied between the two lines. Simultaneously a small AC voltage signal was applied across one of the lines and the resultant current monitored to measure the conductivity through the line. The results of the measurements of this device are plotted in Figure 5-2. These results are consistent with other measurements of the variation of the material conductivity of PEDOT with de-doping found in the literature [139][140].

Since the device is symmetric, the conductivity curve for the other "channel" is just the mirror image of this about zero volts, where they cross. From the curve we see that unbiased, both arms had a conductance of $32.5\mu\text{S}$. When a negative bias was applied, the doping level was enhanced by increasing the oxidization of the PEDOT raising the conductivity to a maximum of $37\mu\text{S}$. Under positive bias, it was possible to reduce the conductivity to less than $0.1\mu\text{S}$ at a maximum bias of 2 volts. This yields a raw ON/OFF

ratio about 400 but, as evident in the photomicrograph of figure 9, less than half of the channel is being modulated so eliminating this part will bring the real ratio up to about 1000. This is typical for most of the devices measured and a conductivity range of five orders of magnitude can be achieved.

Figure 5-2 Plot of measured conductance of dual-line "transistor" device illustrating the qualitatively sigmoid-like behaviour.

Caution is required in using the conductivity curve in estimating how close the material doping is to saturation. A zero-crossing at high conductivity does not necessarily mean that the doping is close to saturation. In the conducting state, because the material is composed of isolated conducting polymer islands in an insulating matrix, the overall conductivity will be dominated by the island-to-island hopping conduction. The individual PEDOT chains are several units long but because of the large conjugation length do not need to be doped to saturation to achieve an intrachain conductivity that is high compared to the interchain, hopping conductivity. This means that even after the

conduction saturates there needs only to be about one dopant per chain leaving many dopant sites available to store cations. The effect of this multi-ion doping on the percolation conduction is studied in depth in Section 6.1.2.

5.2 Electrochromic Response

In addition to a change in conductivity with the level of ion intercalation, most conducting polymers experience a change in their optical absorption spectra. This electrochromic response has been measured for PEDOT:PSS over the same range of potential as in the case for conductivity. This response, measured using a Perkin-Elmer Lambda 900 UV-vis-IR spectrophotometer, is plotted in Figure 5-3.

Figure 5-3 Change in the optical absorption spectrum of PEDOT:PSS as a function of bias for a balanced electrolytic cell (170 nm of Baytron P on 100 $\Omega/\square$ ITO).

For this measurement the PEDOT:PSS was deposited as a 170nm thick layer on a $100\Omega/\square$ ITO coated glass slide and measured in a wet cell.

This electrochromic response is also evident in the photograph of a dual-line device under operating conditions in Figure 4-15.

Figure 5-4 Sequence of photographs showing the variation in optical absorption of an electrochromic transistor device under operating conditions.

In this case, the relative bias between the two arms is 1.5 volts. The change in the absorption properties in the visible spectrum is clearly evident. The sequence of photographs in Figure 5-4 illustrates the change in the relative absorption of the arms with applied bias appropriate for actual operation of a device. We can see that the conduction state of the channel can be easily monitored via the relative optical properties of the active material. This is a powerful feature of these materials and enables their operation in devices that simultaneously take advantage of the optical, electronic and ionic properties.

6 MODELLING & SIMULATION

6.1 Material Modelling

Processible, predoped conducting polymer materials are now commonly formed using a polyelectrolyte backbone as a template material. This results in the conducting portion of the material being composed of a distribution of relatively short-chain oligomers with a corresponding distribution of saturated doping levels. In this section, we investigate the effect of the resulting distribution of short-chain oligomers on the conduction properties of such materials by treating the individual chains as switchable conducting island sites in a percolation matrix. The effect of selective ionic doping compensation of the sites through cation intercalation was investigated through computer simulation and measurement.

6.1.1 Percolation Theory

Percolation theory deals with the clustering properties in networks of "entities". These "entities" can either be "sites", as in the case of a flat of eggs where each position may or may not be filled, or "bonds", as for a metal screen with the wires between crosses that may or may not be present. These are called site-percolation and bond-percolation,

respectively, and have somewhat different properties. The difference between the two is the relative effect of filling or emptying a site or bond as illustrated in Figure 6-1 (a) and (b) respectively. In both cases shown the arrays are 50% occupied. At this filling level, we are still below the percolation threshold p_c^S , for site percolation but exactly at the threshold for bond percolation p_c^B . The percolation threshold is the filling level at which continuous clusters start spanning the grid. The lattice shown is a simple square lattice but any other form can be used, including random networks, in any number of dimensions.

Figure 6-1 Small two-dimensional percolation matrices. (a) site percolation (b) bond percolation.

The percolation thresholds and packing fractions for a number of two- and three-dimensional lattices and coordination numbers are presented in Table 6-1 [141].

	Coordination number	Packing fraction	Percolation threshold		Critical bond number	Critical volume fraction
			Bonds	Sites		
Lattice	z	η	p_c^B	p_c^S	zp_c^B	ηp_c^S
Honeycomb	3	0.61	0.6527...	0.70	1.96...	0.427
Square	4	0.79	0.5000...	0.59	2.00...	0.466
Triangular	6	0.91	0.3473...	0.5000...	2.08...	0.455...
Tetrahedral (diamond)	4	0.34	0.39	0.43	1.56	0.143
Simple cubic	6	0.52	0.25	0.31	1.50	0.161
Body centered c.	8	0.68	0.18	0.24	1.44	0.163
Face c.c. (h.c.p)	12	0.74	0.12	0.20	1.44	0.148

Table 6-1 **Thresholds for site and bond percolation on regular two- and three-dimensional lattices (numbers suffixed with ... are exact).**

Percolation theory has many interesting applications and it has been used to explain some of the aspects of the conduction in conducting polymer devices in Section 6.1.2 below. A good introduction to percolation theory can be found in Stauffer and Aharony [142].

6.1.2 Percolation Conduction in Templated Conducting Oligomers

There have been numerous studies of percolation conduction through many types of homo- and heterogeneous media [143] [144] [145]. In recent years there has been a great deal of research into conducting polymers and a large number have been developed for use in a variety of different areas such as anti-static coatings, organic transistors, organic light emitting diodes (OLEDs), etc.. As discussed in Section 2.2.6, a novel method for producing processible, predoped conducting polymer materials and making

then available as either aqueous or solvent-based dispersions has been recently developed by Bayer. This method uses a host polyelectrolyte chain, such as polystyrenesulfonic acid (PSSA), as a template for the growth of the conducting polymer, e.g. poly(3,4-ethylenedioxythiophene) (PEDOT), which is then formed into a printable dispersion. This was shown for Bayer's "Baytron P" in Figure 2-24.

The resultant conducting oligomer chains are ionically bonded to the polyelectrolyte due to electron transfer. This means that the backbone also acts as a dopant since it (normally) accepts electrons from the highest occupied molecular orbital (HOMO) of the chain leaving it p-doped. Studies have indicated that the oligomers grown in this way are relatively short with their length depending on the synthesis conditions. For commercially available Bayer "Baytron P" material they seem to vary between 1000 and 2500 Daltons or lengths of about 8 to 16 monomer units [146]. As formed, each of these doped oligomer chains can act as a conductive island capable of accepting electrons from neighbouring chains. When they are undoped, however, the HOMO levels are filled and there are no available states so that they cannot accept charge transfer from the HOMO levels of neighbours and conduction is blocked. The chains are short relative to the conjugation length so they will remain strongly conducting even when only singly ionized. This means that the conductivity of the material will be dominated by the interchain hopping conduction and largely independent of any changes in intrachain conductivity due to doping level. This means that the chains can be treated as switchable conduction sites that are "on" if they are doped at any level between a single carrier and being fully saturated (doping = number of units) and are "off" only if they are completely de-doped and the HOMO is filled. In the following sections, a simple percolation

conduction model is presented for the electrolytically controlled response of devices fabricated from such templated conducting polymers. This work helps to explain the underlying mechanism responsible for their characteristic behaviour and guide material selection and future development. Comparing the simulation results to measurements presented in section 5.1 shows that the modelled response follows the experimentally determined sigmoid-like characteristics and that results corresponding to one-dimensional conduction most closely match measurement. This is consistent with quasi-1D conduction mechanisms that are generally accepted to occur in PEDOT:PSS though these have not fully explained to date, as discussed in section 2.2.6.

6.1.2.1 Assumptions

A number of simplifying assumptions have been made in the implementation of the model system. The system has been represented as a simple N -dimensional (ND) regular array of nodes which has been investigated starting with $N = 2$ then followed by $N = 3$ and $N = 1$. The electronic transport has been assumed to occur as a site-to-site mechanism with fixed conductance between sites. The sites are physically related to the individual oligomer chains and the conductance between sites to the interchain conduction mechanism. In all cases, it has been assumed that the conduction is dominated by the interchain portion and that the intrachain conduction is a small factor. This has been assumed true regardless of the level of doping of the chain i.e. as long as the HOMO 'band' has at least one open state we will assume the site is available. Since the chains are

relatively short in comparison to the conjugation length and the interchain mechanism is an average hopping conduction, this is likely a valid assumption.

The process modelled is the change in the conductance of a section of material as ions are electrolytically intercalated to compensate the doping. This process is illustrated in Figure 5-1 for a short, doubly-ionized segment on one electrode with an identical compensated segment at a complementary counter-electrode. With a voltage applied between the two electrodes, electrons are transferred between the chains and cations are intercalated from the electrolyte to balance the charge.

It has been further assumed that the intercalated ions are distributed randomly when compensating the available doped sites as a potential difference is applied between the electrodes. No consideration has been given to the ion and charge dynamics and it has been assumed that there is no ion diffusion between chains. Finally, there has not been any differentiation between oligomer length and saturated doping level and it has been assumed that we are always starting from the fully saturated state when at maximum conductance.

6.1.2.2 Two-Dimensional Conductivity Simulation

6.1.2.2.1 Monodispersed Oligomers

We first investigate the properties of a two-dimensional (2D) system in which all of the oligomer chains have been grown to the same length on the template chains (although this is impractical in practice). The effect of changing the ratio of a

combination of conducting and non-conducting materials on the conductivity of the mixture [147][148][149] is a problem that has been previously studied in the literature. This is normally used to model the behaviour of conducting composites and corresponds to a special case of the current problem restricted to singly ionized conducting oligomers (although these studies relate to initial mixing ratios rather than switching the conductivity of internal sites). We first address the simulation of this case.

For an array of $N \times M$ sites all the sites initially provide conduction and then each site is turned off at random to simulate the random intercalation of ions which compensate the pre-doped monomer segments (in this special case only one ion is required to block a site by not having any available states at that site). In order to achieve a completely random order of turning off the sites a method due to Newman and Ziff [150] has been used. This is accomplished by creating a vector having a length equal to the total number of sites to be modelled and then filling the sites from the first with a random site greater than or equal to the current site and then swapping the two sites. This process is then repeated for every element. The appendix illustrates the method in more detail.

The 2D model grid is setup as illustrated in Figure 6-2. A general square array is shown but for the simulations here we have made all of the interconnecting resistors in the network equal although there will naturally be a distribution of chain separations and resultant effective hopping resistances. In addition, or perhaps as part of this, the distribution of the number of neighbours will also require consideration (effective coordination number). For the present, both of these are averaged to the uniform grid

approximation with equal resistances and a coordination number of four for internal nodes in the 2D case.

Figure 6-2 Grid setup for two-dimensional percolation simulation. The sites, S_{xy} are treated as switches that connect the four incoming connections unless completely de-doped. Inset shows an arbitrary internal node.

Once the random site intercalation order has been determined as outlined above, the effect of intercalating the ions on the overall conductivity of the grid is calculated. This is done by simply alternating between two steps:

- 1) *turn off a site (or a group of sites)*
- 2) *calculate the new conductivity of the array*

Step 2 is accomplished by assuming constant conductivity connecting sites and balancing the current at each site using an iterative technique (equivalent to using finite differences to solve Laplace's equation for the grid). The process is repeated for each ion intercalation step. The simulated results for an average of ten runs on a 25 x 25 grid are presented in Figure 6-3 as the single ion curve. This can be compared to the work of Last and Thouless, which reports on the effect of punching holes at random in sheet of conducting paper [144]. Although the situations are slightly different since their experiment used completely randomly placed holes rather than turning off points on a regular grid, the results are very consistent. These results are also in line with other theoretical treatments of electrically conductive mixtures from the literature [149].

Note that, as shown in Figure 6-3, an effective medium approximation [145]

$$\begin{aligned}\sigma(x) &= \sigma_0 \left\{ 1 - \frac{1}{2} \pi \left[1 - (1-x)^2 \right] \right\} \\ &= \sigma_0 \left(1 - \pi x + \frac{1}{2} \pi x^2 \right)\end{aligned}\tag{6.1}$$

matches the simulated conductivity very well for single ion intercalation at low levels (high conductivity).

Figure 6-3 Change in conductivity of template-doped conducting oligomer material as a function of ion intercalation for monodispersed chains of length ℓ (25 x 25 grid averaged 500 times).

To extend the analysis to multiply ionized, monodispersed oligomers multiple independent 2D random intercalation order layers are generated each using the same method as above. The layers are then shuffled and the same procedure as before is applied for determining the conductivity (alternatively, a single randomized vector that is n -times the single layer length could be used for n layers, but when polydispersion is considered later the layers will not all be filled). Since it is assumed that the interchain conductance dominates, the site remains "on" until it is fully compensated. The results for various levels of ionization are shown in addition to the singly ionized case in Figure 6-3. Note that the shape changes to a more S-shaped (or sigmoid) curve and the effective media approximation can no longer be used at any point. We now have a transfer

characteristic that is well saturated in the "on" and "off" states with a well-defined transition between.

6.1.2.2.2 Binomial Distribution of Oligomer Lengths

As previously discussed, as-grown conductive chains are not monodispersed as in the situations treated above. A method is needed to generate a representative random distribution of oligomer lengths to simulate the actual, polydispersed nature of PSS templated growth. The simplest way to accomplish this is to add monomers to random sites in the 2D array until the desired number is reached. The resulting distribution of oligomer lengths will follow a binomial distribution

$$\Pr(X = i) = \binom{n}{i} p^i (1 - p)^{n-i} \quad (6.2)$$

where n is the total number of monomers added, i is the final chain length and p is the probability of adding a monomer to a particular site. This distribution has an expectation value and variance of

$$\begin{aligned} E(X) &= np \\ Var(X) &= np(1 - p) \end{aligned} \quad (6.3)$$

And this can be used to calculate the average distribution exactly. For small p , which will be the case since this is the probability of a particular site being occupied

when one monomer is added; this can be closely approximated with a Poisson distribution

$$\Pr(X = i) = \frac{(np)^i}{i!} e^{-np} \quad (6.4)$$

and for this case

$$E(X) = Var(X) = np \quad (6.5)$$

And if np is sufficiently large, this is closely approximated by a normal (Gaussian) distribution

$$\Pr(X = i) \approx \frac{1}{\sqrt{2\pi np}} e^{-(i-np)^2/(2np)} \quad (6.6)$$

where again:

$$E(X) = Var(X) = np \quad (6.7)$$

Using the exact binomial distribution on a 2-D 25 x 25 site array, the probability of adding a monomer to a given site is

$$p = \frac{1}{25 \times 25} = 0.0016 \quad (6.8)$$

The resulting distributions for mean oligomer lengths of 1, 3, 6 and 12 units calculated by using these lengths as the expectation values np , are shown in Figure 6-4.

Figure 6-4 Binomial distributions for oligomer length using expectation values of 1, 3, 6 and 12 units.

The calculated relative conductances using these distributions rather than monodispersed chains are plotted in Figure 6-5.

Figure 6-5 Change in conductivity of template-doped conducting oligomer material as a function of ion intercalation for binomially distributed chain lengths (25 x 25 grid averaged 500 times).

6.1.2.2.3 Stacked geometric distribution of oligomer lengths

There are some problems with the binomial method of building up the oligomer chains. For short average chain lengths, the probability of having an empty site is large causing the unintercalated, fully saturated conductivity to be low. This also goes against the initial definition of the sites being conductive islands by allowing "non-sites" that can never be turned on. In addition, the variance in chain length is quite large, significantly larger than that seen in real material that has been synthesized. This is likely because of the higher likelihood of adding to an existing chain than nucleating a new one on the template. To solve these issues an alternative method of populating the sites has been used that provides the characteristics that we desire. This is accomplished by again

randomly filling layers as was done in previous sections, and outlined in the Appendix, but reducing the fraction of sites that are filled at each step up to the maximum oligomer length. This "site stacking" method is illustrated for a small grid in Figure 6-6.

Figure 6-6 "Site stacking" a 2-D grid to form a distribution of site doping levels that is representative of a PSS templated PEDOT oligomer material.

The shortest length is unity up to a maximum length of L so each site has at least a single monomer associated with it. L is chosen to be large enough so that the probability of adding monomers at this stage will be small (this is just a computational limit where the distribution will be truncated so, ideally, it will have no effect on the outcome). If the

fraction of the total sites $\mathcal{N}$, added at stage n is X_n , then the number of sites having m "monomers" is, on average, given by $\mathcal{N}_m^n$ in the recursion relation

$$\mathcal{N}_{m+1}^{n+1} = (1 - X_n)\mathcal{N}_{m+1}^n + X_n\mathcal{N}_m^n \quad \text{for } n \geq m, n \geq 1, m \geq 0 \quad (6.9)$$

where

$$\mathcal{N}_1^1 = \mathcal{N} \quad (6.10)$$

$$\mathcal{N}_0^n = 0$$

$$\mathcal{N}_m^n = 0 \quad \text{for } n < m$$

If the added fraction is reduced by the same ratio, X , for each stage $n > 1$ then

$$X_n = X^n \quad \text{for } n \geq 0 \quad (6.11)$$

and the recursion relation becomes

$$\mathcal{N}_{m+1}^{n+1} = (1 - X^n)\mathcal{N}_{m+1}^n + X^n\mathcal{N}_m^n \quad (6.12)$$

where again

$$\mathcal{N}_1^1 = \mathcal{N} \quad (6.13)$$

$$\mathcal{N}_0^n = 0$$

$$\mathcal{N}_m^n = 0 \quad \text{for } n < m$$

The resulting distribution is bounded since no site can have less than one or greater than n "monomers". The total number of monomers at stage n will be:

$$\sum_{i=0}^n X_i \mathcal{N} = \mathcal{N} \sum_{i=0}^n X^n \quad (6.14)$$

and for "large" n ,

$$\sum_{i=0}^n X^n \approx \frac{1}{(1-X)} = \alpha \quad (6.15)$$

In addition, for large n and "reasonably large" α , the distribution becomes approximately Gaussian, which should accurately model the actual distribution of oligomer lengths and/or ionization distributions. For large n

$$\mathcal{N}(m) = A e^{-\frac{\left(m - \frac{1}{(1-X)}\right)^2}{\left(\frac{1}{(1-X)}\right)}} = A e^{-\frac{(m-\alpha)^2}{\alpha}} \quad (6.16)$$

The constant of proportionality is

$$\begin{aligned} \int_0^n A e^{-\frac{(m-\alpha)^2}{\alpha}} dn &= \mathcal{N} \\ A \sqrt{\pi \alpha} &\approx \mathcal{N} \\ A &\approx \frac{\mathcal{N}}{\sqrt{\pi \alpha}} \end{aligned} \quad (6.17)$$

So that, finally we have simply

$$\mathcal{N}(m) \approx \frac{\mathcal{N}}{\sqrt{\pi\alpha}} e^{-\frac{(m-\alpha)^2}{\alpha}} \quad (6.18)$$

this corresponds to a probability distribution of

$$\Pr(X = m) \approx \frac{1}{\sqrt{\pi\alpha}} e^{-(m-\alpha)^2/\alpha} \quad (6.19)$$

which has expectation value and variance

$$\begin{aligned} E(X) &= \alpha \\ \text{Var}(X) &= \frac{\alpha}{2} \end{aligned} \quad (6.20)$$

This is similar to the large number Gaussian approximation for the binomial distribution but has a variance that is smaller by a factor of two. Figure 6-7 compares the calculated oligomer length distribution curves for $n = 100$, $X = 0.917$ ($\alpha = 12$) with the statistical distribution averaged 50 times. Notice that the distribution is still slightly skewed with respect to the corresponding Gaussian since the low end is bounded and the finite values of n and α . In any case, the fit to the Gaussian is still very good, even for such a modest value of α .

Figure 6-7 Comparison of stacked geometric distribution and the Gaussian approximation with $\alpha = 12$.

The actual range of lengths in commercially available material (Bayer's Baytron P PEDOT-PSS) has been reported to be about 6-18 repeat units [146]. As shown in Figure 6-8 of the distributions from the recursion relation (6.12), setting $\alpha = 12$ produces a well-confined distribution with an appropriate variance for that range.

Figure 6-8 Stacked geometrical distributions for oligomer length using expectation values of 1, 3, 6 and 12 units.

Using these distributions the effect of ion intercalation on a 2D array was again calculated using the same technique as previously described. The results of these simulations are illustrated in Figure 6-9. There is little evident qualitative change in the curves from the monodispersed case due to the dispersion of lengths about the expectation value. For larger values of α there is little quantitative difference as well.

Figure 6-9 Change in conductivity of template-doped conducting oligomer material as a function of ion intercalation for 2D stacked geometric distributed chain lengths with the given values for alpha (25 x 25 grid averaged 500 times).

6.1.2.3 Three-Dimensional Conduction Simulation

In the 2D simulations above it has been assumed that the coordination number for the sites is fixed at four. Actual devices will naturally be three-dimensional objects and the effect of moving to three dimensions was tested by increasing the coordination number (and connectivity) to six in a 3D simple cubic grid. (Other values for the average coordination number and connectivity for a given system could also be used.)

The implementation of a three dimensional simulation is a simple extension of the 2D technique used above. The size of the random filling vector is simply increased and

folded again in the vertical direction. Calculating the conductivity is again done by iteratively balancing individual site currents where the bulk sites have six contributing neighbour sites. The same stacked geometric distribution as above was used with a thickness of 10 units to give an overall array of 25 x 25 x 10 sites. The resultant conductivity curves are illustrated in Figure 6-10.

Figure 6-10 Change in conductivity of template-doped conducting oligomer material as a function of ion intercalation for 3D stacked geometric distributed chain lengths with the given values for alpha (25 x 25 grid averaged 50 times).

Except for the differences in the thresholds, which is to be expected, the features of the curves are very similar to their 2D counterparts.

6.1.2.4 One-Dimensional Conduction Simulation

Another interesting case can be investigated by reducing the connectivity. In this case, we lower the coordination number to two to represent a one-dimensional system. If the direction of connectivity points from one contact to the other then we essentially end up with filaments between the contacts as illustrated in Figure 6-11. In this case, the conductivity of any filament abruptly drops to zero as soon as sufficient ion intercalation has taken place to fully compensate any site along its length.

Figure 6-11 Grid setup for one-dimensional percolation simulation. As in the 2D case, the sites, S_{xy} are treated as switches that connect the two incoming connections unless completely depopulated. Inset shows an arbitrary internal node.

In this case, since the filaments act as switches and are either "on" or "off", we could just test for continuity instead of balancing currents. For consistency however, we have chosen to use the same method (and the same code) as in the two and three-dimensional cases. The results of the simulations are presented in Figure 6-12. Again, we have used the same stacked geometric size distribution for the oligomers.

Figure 6-12 Change in conductivity of template-doped conducting oligomer material as a function of ion intercalation for 1D stacked geometric distributed chain lengths with the given values for alpha (25 x 25 grid averaged 1000 times).

Note that the 1D filament array behaves slightly differently than averaging individual filaments. This is because the whole array is filled randomly and ions continue to be intercalated into filaments, which have already stopped conducting but still have active doping. The results of the alternative case of the conductivity resulting from averaging single filaments are presented in Figure 6-13. Since with one ion per site a

single filament will always be turned off with the addition of a single ion, the case of $\alpha = 1$ is trivial.

Figure 6-13 Change in conductivity of template-doped conducting oligomer material as a function of ion intercalation for a single filament of stacked geometric distributed chain lengths with the given values for alpha (25 site filament averaged 100,000 times).

Although the 1D curves are quantitatively different from in 2D and 3D, the shapes are still well matched.

6.1.2.5 Effect of Grid Size on Simulated Conductivity

Grid sizes used in the simulations have been small relative to what would occur in an actual device. The effect of changing the size of grid on the characteristics of the conductivity curves has been tested by varying the number of sites. As shown in Figure

6-14, results for 2D grids indicate that only for very small grids is there any appreciable effect on the conductivity curves. Changes to the aspect ratio also have a negligible effect as long as the grid is large enough to make edge effects small.

Figure 6-14 Effect of 2D stacked geometric grid size on relative conductance for alpha values of 6 and 12. For grids with $M > 10$ and $N > 10$ there is little dependency on grid size.

This insensitivity to grid size is of course not true for 1D simulation of either arrays or individual filaments. The effect of filament length on conductivity for different oligomer lengths is illustrated in Figure 6-15. In this case the fraction of the intercalated charge relative to the total dopant level that is required to reduce the average filament conductivity to one half is plotted as a function of filament length. Clearly, for a filament length of unity in all cases an intercalation fraction of one is required to switch the conduction off since with a single site there will always be an abrupt transition when α ions have been intercalated. Also for infinite lengths, the fraction must asymptotically

approach zero. From these curves, it is apparent that there is significant variation in the channel conduction threshold with filament length and it is much more pronounced at shorter mean oligomer lengths.

Figure 6-15 Fraction of maximum intercalated ions required to cause a 50% drop in conductivity of template-doped conducting oligomer material for a single filament of stacked geometric distributed chain lengths with the given values for alpha.

6.1.2.6 Comparison with Experiment

The simulated percolation conduction effects of ion intercalation on channel conductivity are consistent with transfer characteristics measured using a fabricated electrolytic device (section 5.1) as well as data from the literature [151]. The sigmoid shape of the transition between the conducting and non-conducting states is qualitatively insensitive to dimensionality (or coordination number) and lattice parameters for 2D and

3D. One-dimensional simulation results bear the closest match to the measured transfer characteristics. This is consistent with recent transport studies in the literature [68] [69] [70] that indicate that conduction in the PEDOT:PSS system may be dominated by quasi-1D hopping. This work has focused on the analysis of a uniform grid or lattice of sites having a constant interconnection conductivity. In general, the treatment can be extended to include different conductivities and connectivity which may improve the accuracy in simulating variable range hopping (VRH) which is likely to be the actual conduction mechanism between islands [152] [44] [45] [46] [47] [48] .

It is important to note that, in the balanced devices that have been considered here, the conduction transition in the material is not due to saturation in doping or dedoping. In all cases, there are still sites available for cation intercalation after the conduction has reached a minimum and stored cations available for deintercalation when it has been maximized. This allows the use of a simple linear double-layer capacitance model to relating the stored charge to the applied voltage. It also validates direct comparison of the voltage dependent experimental results to the modelling of intercalated charge. This simple relationship has also been clearly observed for the case of balanced PEDOT:PSS supercapacitors by Gnosh and Inganas [153].

Although this discussion has been limited to the applicability of this work to a matrix of conducting oligomers, it can equally well be used to represent other similar systems. This includes longer conducting polymer chains with limited conducting segments due to doping nonuniformity, the doping/dedoping of inorganic semiconductor nanoparticles, or any other case where the conductivity of the site entities can be switched from below to above the interconnect conductivity by discretely adding or

subtracting charge via a secondary mechanism. Indeed this need not be limited to electronic and ionic systems, any system where multiple events are required to change the gating properties of the sites will be governed by the analysis we have outlined.

6.2 Device Modelling

As described above, the electrolytic devices we have fabricated operate through the intercalation and expulsion of cations from the channel material and the resulting change in conductivity due to doping compensation and redoping, respectively. This process is illustrated for a dual-line device in Figure 6-16 which is the macroscopic manifestation of Figure 5-1.

Figure 6-16 Equivalent circuit of a dual-line device using only lumped components.

The electrons deposited in the right-hand line by the applied potential cause the intercalation of sufficient cations to balance the charge. This effectively forms a double-layer capacitor between the electronic charge in the PEDOT and the ionic charge in the electrolyte. Similarly, for the left-hand line, the removal of electrons causes the expulsion of the required number of positive ions to balance the charge. This causes a redistribution of ions in the electrolyte and again effectively sets up a double layer capacitor between the now charged polyelectrolyte backbone and the conducting polymer. For modelling purposes, we assume that the double-layer capacitance formed at each line is the same, C_{dl} .

Between the electrolyte sides of these two capacitors, we have the resistance associated with the movement of ions in the electrolyte, R_{ion} . The value of this resistance will depend on the properties of the electrolyte such as the transference number and mobility of the ions, which in turn are dependent on material parameters like ion size, electrolyte viscosity, solvent polarizability and shielding effects. In addition, the cations will normally need to intercalate into the lines so that their mobility within the PEDOT:PSS will also influence the device operation.

Finally, there is a resistance associated with the transport of charge through the conducting polymer to the other plates of the capacitances, R_{ec} . This is a distributed resistance corresponding to the distributed double-layer capacitance. It is also dependent on the current doping level of the material.

6.2.1 Modelling the Transfer Response

At first it may seem that we cannot use linear charging with applied voltage and hence assume a constant value for the capacitance as in (6.21).

$$Q_{acc} = V_{app} \times C_{dl} \quad (6.21)$$

Although the conductivity of the material saturates in a nonlinear way at both the high and low ends of the conductivity-voltage curve this is not due to the number of available doping sites or available ions being depleted. Fortunately this is not the case, if it were then modelling would be quite difficult.

Because the material is composed of a matrix of isolated conducting particles interconnected by hopping conductivity, there will be a percolation transition to (almost) zero conductivity that will be reached at some applied potential as we turn off the conductivity of the islands (see Section 6.1.2). This will happen long before all the doping has been compensated so for the low conductivity end of the curve there should be no issue with site depletion.

As mentioned briefly above, each chain of PEDOT is several units long but the overall conductivity of the matrix is insensitive to doping at higher than the single ionization level because the dominant conduction mechanism is hopping between chains. This means that the conductivity will saturate long before the doping level is saturated

(this is explored in detail in see Section 6.1.2). Therefore, the high conductivity end of the curve also occurs during linear charge transfer.

It can therefore be concluded that in the region of interest of the transfer characteristic it can always be assumed that the charge will accumulate on the capacitor linearly with voltage as given in (6.21). This is further evidenced by the near ideal characteristics measured when PEDOT:PSS is used as a balanced, symmetric supercapacitor structure [153].

We know that physically the system relies on percolation conduction combined with controlled doping, but for the sake of modelling, the shape of the conductance curve, Figure 5-2, indicates that we should be able to use a sigmoid curve to generate a semi-empirical model. The function will take the form:

$$G = \frac{G_0}{1 + e^{\frac{C_{dl}}{Q_{dl}}(V_{dlc} - V_{off})}} + G_{min} \quad (6.22)$$

where:

G	conductance of material segment
G_0	maximum conductance
G_{min}	minimum conductance
C_{dl}	double-layer capacitance of material segment (one side)
Q_{dl}	charge intercalation parameter (charge for $G=G_0/[1+e]$)
V_{dlc}	voltage across double layer capacitor
V_{off}	offset voltage at $G_0/2$

The sensitivity parameter, C_{dl}/Q_{dl} , determines the abruptness of the transition. G_{min} is small compared to G_0 and can usually be ignored. The device measured in Figure 5-2 has some unswitched material as well the active region governed by (6.22) so to account for this we modify the equation, ignoring G_{min} , to be:

$$G_{total} = \left[R_{active} \left(1 + e^{\frac{C_{dl}}{Q_{dl}} (V_{dlc} - V_{off})} \right) + R_{unswitched} \right]^{-1} \quad (6.23)$$

Where R_{active} is the minimum resistance of the active segment and $R_{unswitched}$ is the resistance of the uncontrolled pieces. We assume that these two contributions are about equal. When we extract the two parameters from the transfer curve in Figure 5-2 the fitted curve is as shown in Figure 6-17.

Figure 6-17 Plot of measured conductance of dual-line "transistor" device with fitted semi-empirical curve overlaid.

The sigmoid curve provides an excellent fit to the data. As mentioned earlier, the offset is due to the initial doping level and could be adjusted during the synthesis of the material. The relative conductivity, G/G_0 , is fixed by the selection of the two parameters and we have no adjustable parameters once we have matched this curve. This will be true for any structure we choose to look at since these are fundamental material parameters that will be unaffected by geometry.

6.3 Topological Modelling

The dual-line structure that was modelled for data fitting in Figure 6-16 uses lumped elements except for the split access resistances. This was valid for this use because there was no applied bias through the lines and the structure was symmetric ensuring that each arm would be equipotential. For more complex biasing schemes or structure geometries, we must break things down into simple, roughly equipotential segments that will be combined for simulation. These segments, and the whole structure that results from their combination, are separated into two primary functional layers – the electronic layer consisting of the active and passive electronic components and the ionic layer consisting of the electrolyte and any ionic components. These two layers are connected only through the double layer capacitors at the conducting polymer/electrolyte interface.

6.3.1 Element Models

The basic component that we start with to generate circuit elements is a voltage-controlled current source (VCCS). Shown in Figure 6-18, this will translate the voltage that is calculated to appear across the double-layer capacitance into the conductivity for a small section of active material.

Figure 6-18 Voltage-controlled current source used to translate the voltage across the double-layer capacitance for a small segment of conducting polymer into its conductance.

Using this VCCS the simple lumped model we used to model the transfer characteristic of the dual-line device shown in Figure 6-16 can be represented as shown in Figure 6-19. This equivalent circuit was used to produce the simulated curve in Figure 6-17.

For the steady-state transfer function there will be no ion current so R_{ion} is irrelevant and the electrolyte plates of the capacitors can be considered to be directly connected. Since both of the VCCSs for each line are controlled by the same inputs, they will have equal conductance and just serve to average any voltage across the line. This is

adequate for the small-signal conductance transfer function but for most other cases, we will need to use an approach that is slightly more complex. Rather than developing a completely separate equivalent circuit for each configuration of materials, we have chosen to develop some standard cells. These can be interconnected and then simulated using a common time-domain circuit simulator, such as SPICE. The following sections describe some the cells.

Figure 6-19 Equivalent circuit for lumped dual-line device shown in Figure 6-16 that generated response in Figure 6-17.

6.3.2 General Two-Dimensional Electronic/Ionic Element

In most applications, we will be using a process that incorporates a layer of active material and an over-layer of electrolyte. Either or both of these layers may be arbitrarily patterned depending on the application. To simulate this case we need we will need a model for an element of a size where we can consider the conductivity of the material to be constant, and then interconnect these to match the geometry of the patterns of material

used. A 2-D element with connections available for neighbouring elements on four sides for both the electronic and ionic layers is presented in Figure 6-20.

Figure 6-20 Arbitrary 2-D node composed of an electronic layer and an ionic layer, each with four I/Os, connected by a double-layer capacitance.

The four VCCS components are all controlled by the same nodes so will have the same conductance. This model therefore just represents two finite element resistance elements in parallel with the resistance value of the electronic layer being controlled by interaction with the ionic layer through the double layer capacitance.

6.3.3 Other Two-Dimensional Elements

In addition to the general 2-D element above, several others are commonly required. Although all of these can be generated by using appropriate terminations on some of the ports of the general element, it is cleaner and more efficient to use these additional cells.

6.3.3.1 2-D Ionic Elements

For areas where the electrolyte layer exists with no underlying active layer, we use the single ionic layer element shown in Figure 6-21. This is just a simple square matrix finite element node.

Figure 6-21 Ionic only 2-D node simply composed of a four resistor node.

In addition, there are the various boundary elements that are used on the edges of the electrolyte. These are illustrated in Figure 6-22.

Figure 6-22 Edge cells for areas with only electrolyte. (a) left side edge (b) top left corner edge (c) top to bottom single channel through. The other possible orientations, all 4 sides and corners and two throughs, are also included. Although the three above can be used as is for other orientations, having the orientations is cleaner.

6.3.3.2 2-D Electronic Elements

Similarly to above, areas may also exist where only the active layer exists with no electrolyte over layer. In these cases, we use the single electronic layer element shown in Figure 6-23. Again, this is just a simple square matrix finite element node.

In addition, there are the various boundary elements that are used on the edges of the conducting polymer layer. These are illustrated in Figure 6-24.

Figure 6-23 Electronic only 2-D node simply composed of a four resistor node.

Figure 6-24 Edge cells for areas with only conducting polymer. (a) left side edge (b) top left corner edge (c) top to bottom single channel through. The other possible orientations, all 4 sides and corners and two throughs, are also included. Although the three above can be used as is for other orientations, having the orientations is cleaner.

6.3.3.3 Specialized Electronic/Ionic Elements

In addition to the general 2-D electronic/ionic element, two specialized elements will be useful to avoid using complicated terminating configurations. The first is a one-dimensional line of active material with a one-dimensional electrolyte over-layer as shown in Figure 6-25. This allows us to simplify modelling the response of lines of active material under electrolyte where there are no neighbouring influences.

Figure 6-25 Model of an electronic/ionic 1-D node.

Finally, there are situations in which we have lines of active material, which can be treated as one-dimensional, overlaid with a 2D electrolyte layer allowing interaction with neighbouring active segments. This will normally be the case for the dual-line transistor devices previously discussed. A simplified model for a node of this type is illustrated in Figure 6-26.

Figure 6-26 Model of a one-dimensional electronic node overlaid with a two-dimensional ionic node.

6.3.3.4 Three-Dimensional Electronic/Ionic Elements

It is easy to extend our elements to the third dimension by simply adding the required z-axis components. Voltage-controlled current sources or resistors as required allowing layer-to-layer interaction for 3D structures.

6.3.4 Standard Cell Model of the Dual-Line Transistor

To put everything together some of the standard cells described above are connected to generate an overall model for the dual-line transistor structure that has been the focus of much of this work. To accurately model the effect of the potential

distribution, and hence intercalated charge and conductivity, along the lines they are broken up into four of the 1D electronic with 2D electrolyte elements shown in Figure 6-26. The effect of ionic interaction between lines is included by using the ionic-only nodes from Figure 6-21 between the lines and a variety of edge cells from Figure 6-22 to complete the electrolyte layer. The final equivalent circuit for the device includes fixed series resistors at the two ends of the channel segment to simulate the unswitched material not in contact with the electrolyte. The circuit, as entered for SPICE simulation, is shown in Figure 6-27. This includes the sources and loading that was used in the device measurements that will be described in the following section.

Figure 6-27 Schematic diagram for complete dual-line transistor structure ready for simulation.

7 DEVICE & CIRCUIT MEASUREMENTS

A number of simple device geometries have been fabricated and tested. In this section, the results of these measurements will be presented and in the next section, they will be compared to simulated results using the modelling presented in the previous section.

7.1 Simple T-Structure

We first present some results from measurements of a simple T-structure device illustrated in the diagram in Figure 7-1.

Figure 7-1 Simple T-structure device operates as a channel with a resistive tap.

The operation and theory of this device is relatively simple and it is useful to examine it first since it illustrates the operation of a single line (or channel) under bias without the complication of interference from surrounding influences. We will also present simulation results for the device in the next section. The dynamic transfer function for the device was measured using the test configuration illustrated in Figure 7-2.

Figure 7-2 Test configuration for measurement of dynamic transfer function of simple T-structure device.

The measured dynamic transfer characteristic of the T-structure or tapped-channel device with applied voltage amplitude of 2 volts and a frequency of 0.1 Hz are presented in Figure 7-3. The tap voltage saturates strongly under negative applied bias because cations from the electrolyte are intercalated into R_1 causing its resistance to go up relative to R_2 . This forms a partial rectifying effect and can be used for level shifting or frequency doubling applications. It also indicates that the channel current will saturate with applied

voltage when used in a transistor structure, in a similar manner to semiconductor field-effect transistors but for ionic rather than electronic reasons.

Figure 7-3 Measured dynamic transfer characteristic of tapped channel device. The applied signal, V_{app} , has amplitude of 2 volts and a frequency of 0.1 Hz.

7.2 Dual-Line Electrolytic "Transistor" Device

Next, we look at the main focus device of this work, the dual-line "transistor" structure. We have already studied the structure of this device extensively in the fabrication section. A device diagram and photograph of the device in operation have been presented in Figure 4-13 and Figure 4-15 respectively. We have measured the dynamic response of the device in a test configuration consisting of a square wave generator as the signal source driving the device connected as a simple inverter with the

output captured by a digital oscilloscope. Figure 7-4 provides a schematic of the test configuration.

Figure 7-4 Test configuration for simple dual-line transistor structure biased as an inverter.

The transistor operates like a P-channel depletion-mode device. The control input (gate) must be biased to a potential that is positive with respect to both channel terminals. The square-wave response is shown in Figure 7-5.

Under the bias and loading conditions that we have chosen the circuit is acting as an inverter with approximately unity gain. The rise and fall times are approximately 100 msec and 200 msec, respectively with the materials and configuration used.

Figure 7-5 Measured square wave signal response for dual-line transistor structure biased as a simple inverter.

There has been a significant amount of discussion about the stability of the response with this type of material over a large number of operational cycles. It is suspected that troubles with cyclicity stem from over-oxidation of the conducting polymers. Figure 7-6 shows the response of one of our dual-line device switched 100 times showing no degradation in the uniformity.

Devices have been run for much longer periods with no significant change in the response due to material degradation. Ultimately, after a long period of operation (at least several days), the speed of the encapsulated devices slowly and steadily declines. It is strongly suspected that this is due to loss of solvent from the electrolyte because of diffusion through the epoxy encapsulant causing a reduction in the ion mobility. This problem has not been observed when unencapsulated devices with liquid electrolyte are

used – these seem to have an indefinite lifetime if the electrolyte is replenished periodically.

Figure 7-6 Signal response for simple dual-line transistor structure biased as an inverter over 100 switches.

7.3 Simple 2-Input NOR Gate

The final device we will investigate is the simple NOR gate that we introduced in the fabrication section having a structure similar to that shown in Figure 4-16. This has the same structure as the dual-line device except that another identical line has been added. The two outside lines are used as controls and the centre line acts as the channel and is influenced by both of its neighbours. We have measured the dynamic response of this device using a similar test configuration as for the inverter with a second generator added as the signal source driving the second input. Again the output captured by a digital oscilloscope. Figure 7-7 provides a schematic of the test configuration.

Figure 7-7 Test configuration for simple 2-input NOR gate structure.

This device operates like a dual-gate P-channel depletion-mode transistor. The control inputs (gates) must both be biased to a potential that is positive with respect to both channel terminals. The square-wave response is shown in Figure 7-8.

For this device, in order for the channel to conduct and provide a "high" output, neither control line can cause cations to be intercalated into the channel. This will only occur when both are in the "low" state. Again, we have chosen the bias and loading conditions so that the circuit has approximately unity gain.

Figure 7-8 Measured signal response for simple 2-input NOR gate structure.

7.4 Photoconductor Response

The "smudge" tests described in section 4.3.2 were used to optimise the concentration of CuCl_2 in the polymer base to maximise the conductivity while maintaining a printable ink. The results are shown in Figure 7-9. The ratio of light to dark photoconductivity is almost 10^4 , which is excellent. This is an uncalibrated result with respect to the optical power but that seems to be the norm in this field. The photosensitivity is defined as $(\text{dark resistance})/(\text{photoresistance})$.

Figure 7-9 CdS/polymer thick film photoconductor smudge test optimization results.

The photoresponse for the screen printed interdigitated device is presented in Figure 7-10. Both light and dark curves are slightly superlinear. Although simply made these are relatively complex devices. There are many things to consider including how the doping is working, the silver to CdS contacts, the percolation conduction through the CdS/polymer hybrid, etc. More study will be needed to achieve a full understanding.

Figure 7-10 Interdigitated CdS/polymer thick film photoconductor cell response [device CdSPTF1(3,3)].

8 SIMULATION RESULTS

The following sections present the results of simulating the same circuits that we measured in the previous section using the models we have developed in Section 6. The parameters used for the dual line device are those extracted from the fit to the transfer characteristic shown in Figure 6-17.

8.1 Simple T-Structure Device

The circuit used to simulate the tapped-channel device is shown in Figure 8-1. This is simply two of the 1D electronic/ionic cells shown in Figure 6-25 in series, with a resistive tap, R_{tee} , attached where they are connected. A source is attached to one end of the line and the other end is grounded. The output voltage is monitored from the open end of R_{tee} .

Figure 8-1 Circuit schematic for simulation of the dynamic transfer function of the simple T-structure device.

Results of SPICE simulation of this circuit are presented in Figure 8-2. Comparing this to the measured curve in Figure 7-3 shows that the model we have developed accurately matched both the levels and hysteresis inherent in the response. The response to other signal amplitudes and frequencies are also well modelled.

Figure 8-2 Simulated dynamic transfer characteristic of tapped channel device. The applied signal, V_{app} , has amplitude of 2 volts and a frequency of 0.1 Hz.

8.2 Dual-Line Transistor Structure (Simple Inverter)

The circuit used to simulate the operation of a dual-line transistor biased as a simple inverter was shown previously as the schematic diagram in Figure 6-27. The circuit contains the structure itself, modelled as two four-segment 1D active lines overlaid with the electrolyte ionic-conduction layer, the passive access resistors on both

ends of the channel, a square wave voltage source and a load resistance. The circuit is designed to replicate the conditions present in the measurement configuration.

Figure 8-3 Simulated square wave signal response for dual-line transistor structure biased as a simple inverter.

The initial simulation results using the simple inverter circuit from Figure 6-27 are shown as the "Output A" trace in Figure 8-3. Comparing this to the measured response in Figure 7-5 indicated that, although most of the features such as the preshoots, rise time, fall time and approximate operating point are quite well modelled, the amplitude of the output is significantly larger than that measured. This presents a significant problem since the only parameters available are those extracted from Figure 6-17 and these are not adjustable. We know the transfer function from Figure 6-17 is well matched and T-structure simulation fits well so we would expect a good match for the dual-line transistor as well.

The solution to our problem lies in difference between the biasing methods used. In the previous cases, there was no net DC bias on the channel or conducting line, only small-signal or large-signal AC modulation. When a DC bias is applied to a line, cations are preferentially intercalated at more negative end due to the potential gradient along the line. This is not a bad thing; we want this to happen since it is what gives us saturating characteristics typical of transistor operation. Unfortunately, there is still a potential gradient in the line after it leaves the electrolyte window and goes under the dielectric layer. Cations from the electrolyte drift slowly in the line material under the dielectric where they have extremely low mobility and will now not respond to the applied signal. This process eventually comes to equilibrium for a fixed bias but it results in there being a significant reduction in the conductance of the line in a small region under the dielectric at the edge of the electrolyte window. This divides the output signal and causes the significant reduction in gain we see. Including this effect by adding a large resistance at the most negative end of the channel yields the "Output B" trace in Figure 8-3. Comparing this to the measured output in Figure 7-5 confirms that the match is now almost perfect.

The charge accumulation under the dielectric layer has been independently verified by single line DC conductivity measurements and the observation of the electrochromic darkening of the line material under the dielectric when bias is applied. A number of techniques are currently being investigating to reduce or eliminate this for cases where it is undesirable. It is also being characterized under different conditions to determine if it may be useful in some applications.

8.3 Simple 2-Input NOR Gate

The circuit used to simulate the operation of the simple 2-input NOR gate was generated by taking the schematic diagram for the simple inverter in Figure 6-27 and adding a third line by mirroring the "gate" segment at the top on the other side of the channel segment. The circuit contains the structure itself, with the three four-segment 1D active lines overlaid with the electrolyte ionic-conduction layer, the passive access resistors on both ends of the channel, two square wave voltage sources and a load resistance. We have also included the extra resistance due to the charge accumulation at the negative end of the channel to account for this effect. Again, the circuit is designed to replicate the conditions present in the measurement configuration. The results of the simulation are shown in Figure 8-4.

Figure 8-4 Simulated signal response for simple 2-input NOR gate structure.

Comparing these results to the measurements in Figure 7-8 shows close agreement for all aspects of the response and gives us confidence in the accuracy of the models.

9 FURTHER DESIGNS & APPLICATIONS

9.1 Design of "Smart" Structures

The devices presented in this work are interesting in their own right but really only become useful when incorporated into systems that are more complex. On their own, they are really just slow, wet "transistors" and slow, dry photoconductors. They have a very respectable on/off ratio of about 10^3 for both the ionically switched channel conductance of the PEDOT devices and the photonicallly switched channel conductance of the photoconductors. However, to make up for the lack of speed requires complexity or functionality that cannot be (or is difficult to) achieved in conventional ways. Therefore, capitalizing on the unique material interactions requires the incorporation of the properties of these devices into smart structures.

The work outlined in this thesis has provided the tools to close the design-simulation-fabrication loop of complex systems utilizing the building blocks provided. The ionic interaction between areas of material allows a natural coupling of the non-linear sigmoid conductivity response. To illustrate a more complex system we can use the arbitrary 2D modelling blocks shown in Figure 6-20 to simulate a large (10 x 10 elements) area of active material as shown in Figure 9-1.

Figure 9-1 Structure for simulation of 10 x 10 grid of active material.

The overlying electrolyte is held at ground around the edge of the material and a conductive ring attached at the edge is switched from -3 V to +2 V. The simulated dynamic response of this structure is plotted in Figure 9-2. The change in voltage is plotted for the connections between the elements along the dashed line at the centre of the array. The nonlinear interaction of the material causes a sharp moving wavefront to propagate front the edge of the region to the centre until all the material has been

switched to the voltage applied at the edge. This process is reminiscent of travelling wavefront propagation in other two-dimensional nonlinear systems such as cellular neural networks and reaction-diffusion systems.

Figure 9-2 Simulated voltage response of the array in Figure 9-1 at the vertical level indicated by the dashed line. The rows positions are given by the x-values.

9.2 Application to Cellular Neural Networks (CNNs) and Related Topics

The coupling of many neighbouring elements through a sigmoidal transfer characteristic is typical for the connection mechanism used in cellular neural networks [154] [155]. In particular, the ability to integrate areal optical input and output with

simple local interaction computing elements makes image processing tasks a strong possibility [156]. The printable photoconductive material developed in this thesis can be used to provide an optical input layer. The simplest implementation would be to use printed, continuous blanket layers of photoconductor, PEDOT:PSS and electrolyte as shown in Figure 9-3.

Figure 9-3 An example of a simple blanket layer EC-over-PC areal device configuration for optical processing.

In this configuration, the photoconductive layer provides the input for image data by allowing current to flow vertically in illuminated areas and the electrochromic layer applying a nonlinear threshold function. Overall, the expected response would be used for edge enhancement or detection. An impermeable, anisotropic conduction layer may be required between the EC and PC layers to block the transport of ions into the PC layer.

To fabricate a more standard CNN structure, the EC layer can be separated into elements that are interconnected with PC elements. The interaction "weights" are then

controlled by the optical signal striking the PC links. This slightly more complex configuration is illustrated in Figure 9-4.

Figure 9-4 Interspersed PC and EC to provide optical control of interconnect weighting of CNN array.

Finally, it is possible to construct much more complicated structures having multiple patterned layers utilizing non-linear interaction to achieve operations that are ever more complex (see Figure 9-5).

Figure 9-5 Complex, patterned multi-layer structure for optical information processing.

The type of nonlinear coupling discussed above can also be associated with reaction-diffusion computing and enzyme circuits [157] [158] [159]. Cellular automata are also based on this type of mutual coupling between neighbouring cells with well-defined rule sets. The implementation of such systems could lead to many applications and in a variety of directions, all interesting and novel.

10 CONCLUSION & SUMMARY

The long-term goal of this project is to investigate the application of electrolytic electrochromic devices to develop complex systems of interacting elements. The idea is to utilize the evolving temporal and spatial response of an array of devices as a parallel computational system. Interaction between cells (or contiguous regions) within the system is through the variation in concentration of ionic species in their environment, changes in electrical conductivity and optical absorption spectra. Stimuli can be applied electrically and/or optically and results can be read out by monitoring optical changes in the electrochromic polymer and electrical interface signals.

Before these complex structures could be designed and fabricated, the individual elements needed to be designed, made, measured and modelled. Even isolated devices have complex interactions between the electrochromic polymer, electrolyte and metal electrodes. A number of different materials and devices structures needed to be evaluated to determine the best combinations to use in the integrated designs.

The methods developed in this work have allowed the fabrication and accurate modelling of devices that are able to interact through electronic, ionic and optical means. These methods are not limited to simple two and three terminal devices but can be used for large, complex, multiply interacting, nonlinear structures. There are now models and

fabrication methods in place that will enable the accurate simulation and realization of these more complex structures.

In summary:

- a fabrication system has been developed to fabricate multilayer active polymeric and inorganic/organic hybrid materials
- balanced, ionically controlled conduction element have been designed, fabricated and demonstrated showing on/off conduction ratios of 10^3
- materials models have been developed that model the unique interaction in a multi-ion doped conducting island percolation system
- a system of elements have been designed that allow the simple simulation of arbitrary structures built with these materials
- a screen printable inorganic/polymer photoconductor process and device have been developed allowing low temperature integration of optical sensors with on/off ratios of $>10^3$
- a great deal of material evaluation has been done

And, of course, most of the real work never makes its way into the thesis...

10.1 Conference Presentations

S.P. McGarry, N.G. Tarr, "Polymer Technology Integrating Electronic, Ionic and Photonic Control - Electrochrotronics", 12th Canadian Semiconductor Conference, August 2005.

S.P. McGarry, N.G. Tarr, "Electrochrotronics: Highly Functional Devices Operating in Three Realms", 63rd Device Research Conference, June 2005.

S.P. McGarry, N.G. Tarr, "Electrolytic Polymer Active Devices", 61st Device Research Conference, June 2003.

10.2 Journal Submissions

S. P. McGarry, N. G. Tarr, "Modeling electrochemical control of percolation conductivity in short-chain templated conducting polymers", submitted for publication.

S. P. McGarry, N. G. Tarr, "Fabrication and modelling of screen-printed active electrolytic polymer devices", submitted for publication.

S. P. McGarry, N. G. Tarr, "Low-Temperature Inorganic/Organic Hybrid Photosensor for Flexible Substrates", to be published.

10.3 Related Publications

A. B. Froimovitch, S. McGarry, T. Smy, J. Fraser, "Ultrahigh Surface Area Anatase Thin Films by Direct Oxidation of Ti Film with Hydrogen Peroxide", *Electrochem. Solid-State Lett.*, **10** K11 (2007).

A. B. Froimovitch, S. McGarry, T. Smy, J. Fraser, "Surface Area Analysis of Low Temperature Nanostructured Anatase Films", 2006 MRS Fall Meeting, November 2006.

A. Tran, S. McGarry, S. Nicol, J. Wojcik, M.C.E. Yagoub, "Design of Highly Sensitive H-Field Probes for Near-Field EMC & HAC Assessment", IEEE ANTEM 2006 – 12th International Symposium on Antenna Technology and Applied Electromagnetics, July 2006.

APPENDIX

Array Randomizing Shuffle

The diagram below illustrates the method used to randomize the site ordering for a nine element 3x3 grid. It is a random pick full shuffle and ensures that all elements are unique. To extend the treatment to three dimensions requires simply extending the original array to the total number of elements and adding another level of folding.

	0	1	2
0	7	5	3
1	2	0	8
2	4	6	1

Finally, the vector is folded into the appropriate array shape required to represent the problem.

This method of shuffling the elements ensures that the filling of the array will be as random as the generator used to calculate the sequence.

REFERENCES

- [1] C.K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa and E.J. Louis, "Electrical Conductivity in Doped Polyacetylene", *Phys. Rev. Lett.*, **39**, 1098 (1977).
- [2] C.K. Chiang, Y.W. Park, A.J. Heeger, H. Schirakawa, E.J. Louis and A. G. MacDiarmid, "Conducting polymers: Halogen doped polyacetylene", *J. Chem. Phys.*, **69**, 5098 (1978).
- [3] H. Letaw Jr. and J. Bardeen, "Electrolytic Analog Transistor", *J. Appl. Phys.*, **25**, 600 (1954).
- [4] D. Ofer, R.M. Crooks and M.S. Wrighton, "Potential dependence of the conductivity of highly oxidized polythiophenes, polypyrroles, and polyaniline: finite windows of high conductivity", *J. Am. Chem. Soc.* **112**, 7869 (1990).
- [5] E.T. Turner-Jones, O.M. Chyan and M.S. Wrighton, "Preparation and Characterization of Molecular-Based Transistors with a 50-nm Source-Drain Separation with use of Shadow Deposition Techniques: Toward Faster, More Sensitive Molecule-Based Devices", *J. Am. Chem. Soc.*, **109**, 5526 (1987).
- [6] V. Rani, K.S.V. Santhanam, "Polycarbazole-based electrochemical transistor", *J. Solid State Electrochem.*, **2**, 99 (1998).
- [7] D. Nilsson, M. Chen, T. Kugler, T. Remonen, M. Armgarth and M. Berggren, "Bi-stable and Dynamic Current Modulation in Electrochemical Organic Transistors", *Adv. Mater.* **14**, 51 (2002).
- [8] S. McGarry and N. G. Tarr, "Electrolytic Polymer Active Devices", *61st Device Research Conference*, June 2003.
- [9] M. Chen, D. Nilsson, T. Kugler, M. Berggren, and T. Remonen "Electric current rectification by an all-organic electrochemical device", *Appl. Phys. Lett.* **81**, 2011 (2002).
- [10] S. McGarry and N.G. Tarr, "Electrochrotronics: Highly Functional Devices Operating in Three Realms", *63rd Device Research Conference*, June 2005.
- [11] N.W. Ashcroft and N.D. Merman, "Solid State Physics", (Holt, Rinehart and Winston, New York, NY, 1976).
- [12] N.F. Mott, "Conduction in Non-Crystalline Materials", 2nd Ed., (Oxford University Press, 1993).
- [13] N.F. Mott, "Polarons in crystalline and non-crystalline materials", *Adv. in Phys.*, **18**, 41 (1969).

- [14] P.W. Anderson, "Absence of Diffusion in Certain Random Lattices", *Phys. Rev.*, **109**, 1492 (1958).
- [15] N.F. Mott, "The Origin of Some Ideas on Non-crystalline Materials", *J. Non-Crystalline Solids*, **28**, 147 (1978).
- [16] N.F. Mott, "Conduction in Glasses Containing Transition Metal Ions", *J. Non-Crystalline Solids*, **1**, 1 (1968).
- [17] N.F. Mott, E.A. Davis, "Electronic Processes in Non-Crystalline Materials", 2nd Ed., (Oxford University Press, 1979).
- [18] W.F. Pasveer and M.A.J. Michels, "Understanding Mott's law from scaling of variable-range-hopping currents and intrinsic current fluctuations", *Phys. Rev. B*, **74**, 195129 (2006).
- [19] A.L. Efros and B.I. Shklovskii, "Coulomb Gap and Low Temperature Conductivity of Disordered Systems", *J. Phys. C*, **8**, L49 (1975).
- [20] A.L. Efros, "Coulomb Gap in Disordered Systems", *J. Phys. C*, **9**, 2021 (1976).
- [21] M. Pollak, "The Coulomb gap: a review, and new developments", *Phil. Mag.*, **65**, 657 (1992).
- [22] J.R. Macdonald, "Impedance Spectroscopy", (John Wiley & Sons, Inc., Hoboken, NJ, 1987).
- [23] P. Debye and E. Huckel, "Zur Theorie der Elektrolyte", *Phys. Z.* **24**, 185-206 (1923).
- [24] C. Kittel, "Introduction to Solid State Physics", 5th Ed., (John Wiley & Sons, Inc., Hoboken, NJ, 1976).
- [25] J. Newman and K.E. Thomas-Alyea, "Electrochemical Systems", 3rd Ed., (John Wiley & Sons, Inc., Hoboken, NJ, 2004).
- [26] J.O'M. Bockris and A.K.N. Reddy, "Modern Electrochemistry 1: Ionics", 2nd Ed., (Plenum Press, New York, NY, 1998).
- [27] A.J. Bard and L.R. Faulkner, "Electrochemical Methods: Fundamentals and Applications", (John Wiley & Sons, Inc., Hoboken, NJ, 1980).
- [28] A.G. Heeger, "Nobel Lecture: Semiconducting and metallic polymers: The fourth generation of polymeric materials", *Rev. Mod. Phys.*, **73**, 3 (2001).
- [29] A. Moliton and R. Hiorns, "Review of electronic and optical properties of semiconducting π -conjugated polymers: applications in optoelectronics", *Polym. Int.*, **53**, 1397 (2004).
- [30] R. E. Peierls, "*Quantum Theory of Solids*" (Oxford: Clarendon Press, 1955), p.108.
- [31] S. Roth and H. Bleier, "Solitons in polyacetylene", *Adv. in Phys.*, **36**, 385 (1987).
- [32] K. Yates, "*Hückel Molecular Orbital Theory*" (New York, NY: Academic Press, 1978).

- [33] A. Streitwieser, Jr., "Molecular Orbital Theory" (New York, NY: John Wiley & Sons, 1961).
- [34] T.H. Goodwin and D.A. Morton-Blake, "An Empirical Determination of the Hückel Parameter β and of the C-C and C-H Bond Energies in Aromatic Hydrocarbons", *J. Chem. Soc.*, 615-618 (1964).
- [35] C.R. Fincher Jr., C.-E. Chen, A.J. Heeger, A.G. MacDiarmid and J.B. Hastings, "Structural Determination of the Symmetry-Breaking Parameter in trans-(CH)_x", *Phys. Rev. Lett.*, **48**, 100 (1982).
- [36] J.C.W. Chien, F.E. Karasz and K. Shimamura, "Crystal structure of pristine and iodine-doped cis-polyacetylene", *Macromolecules*, **15**, 1012 (1982).
- [37] W.P. Su, J.R. Schrieffer, A.J. Heeger, "Soliton excitations in polyacetylene", *Phys. Rev. B*, **22**, 2099 (1980).
- [38] W.P. Su, J.R. Schrieffer, A.J. Heeger, "Solitons in polyacetylene", *Phys. Rev. Lett.*, **42**, 1698 (1979).
- [39] A.B. Kaiser, "Electronic transport properties of conducting polymers and carbon nanotubes", *Rep. Prog. Phys.*, **64**, 1 (2001).
- [40] U. Salzner, J.B. Lagowski, P.G. Pickup, R.A. Poirier, "Comparison of geometries and electronic structures of polyacetylene, polyborole, polycyclopentadiene, polypyrrole, polyfuran, polysilole, polyphosphole, polythiophene, polyselenophene and polytellurophene", *Synth. Met.*, **96**, 177 (1998).
- [41] J.L. Brédas and G.B. Street, "Polarons, Bipolarons, and Solitons in Conducting Polymers", *Acc. Chem. Res.*, **18**, 309 (1985).
- [42] V.N. Prigodin and A.J. Epstein, "Nature of insulator-metal transition and novel mechanism of charge transport in the metallic state of highly doped electronic polymers", *Synth. Met.*, **125**, 43 (2002).
- [43] M.C. Anglada, N. Ferrer-Anglada, J.M. Ribo and B. Movaghar, "Fluctuation-assisted transport in polymers", *Synth. Met.*, **78**, 169 (1996).
- [44] L. Zuppiroli, M.N. Bussac, S. Paschen, O. Chauvet and L. Forro, "Hopping in disordered conducting polymers", *Phys. Rev. B*, **50**, 5196 (1994).
- [45] V. N. Prigodin, "One-dimensional localization effects in three-dimensional structures of highly-conducting polymers", *Synth. Met.*, **84**, 705 (1997).
- [46] A.N. Samukhin, V.N. Prigodin, L. Jastrabík and A.J. Epstein, "Hopping conductivity of a nearly 1D fractal: A model for conducting polymers", *Phys. Rev. B*, **58**, 11354 (1998).
- [47] A.J. Epstein, W.-P. Lee, V.N. Prigodin, "Low-dimensional variable range hopping in conducting polymers", *Synth. Met.*, **117**, 9 (2001).
- [48] V.N. Prigodin, A.N. Samukhin and A.J. Epstein, "Variable range hopping in low-dimensional polymer structures", *Synth. Met.*, **141**, 155 (2004).

- [49] W.-S. Huang, B.D. Humphrey, and A.G. MacDiarmid, "Polyaniline, a Novel Conducting Polymer", *J. Chem. Soc., Faraday Trans. 1*, **82**, 2385 (1986).
- [50] B. Wessling, "Dispersion – The key tool for understanding, improving and using conducting polymers and organic metals", *Synth. Met.*, **152**, 5 (2005).
- [51] D.C. Trivedi, "Polyanilines", in *Handbook of Organic Conductive Molecules and Polymers*, Vol. **2**, ed. by H.S. Nalwa, (Chichester, UK, John Wiley & Sons, 1997).
- [52] A.B. Kaiser *et al*, "Comparison of electronic transport in polyaniline blends, polyaniline and polypyrrole", *Synth. Met.*, **84**, 699 (1997).
- [53] B. Wessling, "Progress in Science and Technology of Polyaniline and Polyethylenedioxythiophene", *Synth. Met.*, **135-136**, 265 (2003).
- [54] O. Kwon and M.L. McKee, "Calculations of Band Gaps in Polyaniline from Theoretical Studies of Oligomers", *J. Phys. Chem. B*, **104**, 1686 (2000).
- [55] M. Satoh, K. Kaneto and K. Yashino, "Dependences of electrical and mechanical properties of conducting polypyrrole films on conditions of electrochemical polymerization in an aqueous medium", *Synth. Met.*, **14**, 289 (1986).
- [56] E. Smela, O. Inganas, I. Lundstrom, "Conducting polymers as artificial muscles: challenges and possibilities", *J. Micromech. Microeng.*, **3**, 203 (1993).
- [57] E. Smela, "Microfabrication of PPy microactuators and other conjugated polymer devices", *J. Micromech. Microeng.*, **9**, 1 (1999).
- [58] J. Rodríguez, H.-J. Grande and T.F. Otero, "Polypyrroles: from Basic Research to Technological Applications", in *Handbook of Organic Conductive Molecules and Polymers*, Vol. **2**, ed. by H.S. Nalwa, Jon Wiley & Sons, Chichester, UK (1997).
- [59] H.L. Ricks-Laskoski and L.J. Buckley, "Twenty-year aging study of electrically conductive polypyrrole films", *Synth. Met.*, **156**, 417 (2006).
- [60] K. Kaeriyama, "Synthesis and Properties of Processable Polythiophenes", in *Handbook of Organic Conductive Molecules and Polymers*, Vol. **2**, ed. by H.S. Nalwa, (Chichester, UK, John Wiley & Sons, 1997).
- [61] R.D. McCullough, S.P. Williams, S. Tristram-Nagle, M. Jayaraman, P.C. Ewbank, and L. Miller, "The first synthesis and new properties of regioregular, head-to-tail coupled polythiophenes", *Synth. Met.*, **69**, 279 (1995).
- [62] G. Horowitz, X. Peng, D. Fichou, and F. Garnier, "The oligothiophene-based field-effect transistor: How it works and how to improve it", *J. Appl. Phys.*, **67**, 528 (1990).
- [63] A.G. Bayer, Germany, Patent US 4959430 (1990).
- [64] A.G. Bayer, Germany, Patent US 4987042 (1991).
- [65] G. Heywang and F. Jonas, "Poly(alkylenedioxythiophene)s - New, Very Stable Conducting Polymers", *Adv. Mater.*, **4**, 116 (1992).

- [66] J. Hwang, D.B. Tanner, I. Schwendeman and J.R. Reynolds, "Optical properties of nondegenerate ground-state polymers: Three dioxythiophene-based conjugated polymers", *Phys. Rev. B*, **67**, 115205 (2003).
- [67] H.W. Heuer, R. Wehrmann, and S. Kirchmeyer, "Electrochromic Window Based on Conducting Poly(3,4-ethylenedioxythiophene):Poly(styrene sulfonate)", *Adv. Funct. Mater.* **12**, 89 (2002).
- [68] J.Y. Kim, J.H. Jung, D.E. Lee and J. Joo, "Enhancement of the electrical conductivity of poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) by a change of solvents", *Synth. Met.*, **126**, 311 (2002).
- [69] J. Ouyang, Q. Xu, C.-W. Chu, Y. Yang, G. Li and J. Shinar, "On the mechanism of conductivity enhancement in poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) film through solvent treatment", *Polymer*, **45**, 8443 (2004).
- [70] S. Ashizawa, R. Horikawa and H. Okuzaki, "Effects of solvent on carrier transport in poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate)", *Synth. Met.*, **153**, 5 (2005).
- [71] A.M. Nardes, M. Kemerink and R.A.J. Janssen, "Anisotropic hopping conduction in spin-coated PEDOT:PSS thin films", *Phys. Rev. B*, **76**, 085208 (2007).
- [72] A.M. Nardes, M. Kemerink and R.A.J. Janssen, J.A.M. Bastiaansen, N.M.M. Kiggen, B.M.W. Langeveld, J.J.M. van Breeman and M.M. de Kok, "Microscopic Understanding of the Anisotropic Conductivity of PEDOT:PSS thin films", *Adv. Mater.*, **19**, 1196 (2007).
- [73] L.B. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J.R. Reynolds, "Poly(3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future", *Adv. Mater.*, **12**, 481 (2000).
- [74] A. Elschner, F. Bruder, H.-W. Heuer, F. Jonas, A. Karbach, S. Kirchmeyer, S. Thurm and R. Wehrmann, "PEDT/PSS for efficient hole-injection in hybrid organic light-emitting diodes", *Synth. Met.*, **111–112**, 139 (2000).
- [75] L. Lindell, A. Burquel, F.L.E. Jakobsson, V. Lemaur, M. Berggren, R. Lazzaroni, J. Cornil, W.R. Salaneck and X. Crispin, "Transparent, Plastic, Low-Work-Function Poly(3,4-ethylenedioxythiophene) Electrodes", *Chem. Mater.*, **18**, 4246 (2006).
- [76] F. Xue, Y. Su and K. Varshneyan, "Modified PEDOT-PSS Conducting Polymer as S/D Electrodes for Device Performance Enhancement of P3HT TFTs", *IEEE Trans. Elec. Dev.*, **52**, 1982 (2005).
- [77] S. Ashizawa, Y. Shinohara, H. Shindo, Y. Watanabe and H. Okuzaki, "Polymer FET with a conducting channel", *Synth. Met.*, **153**, 41 (2005).
- [78] Y. Saito, T. Kitamura, Y. Wada and S. Yanagida, "Poly(3,4-ethylenedioxythiophene) as a hole conductor in solid state dye sensitized solar cells", *Synth. Met.*, **131**, 185 (2002).

- [79] J.-G. Chena, H.-Y. Weib and K.-C. Ho, "Using modified poly(3,4-ethylene dioxythiophene): Poly(styrene sulfonate) film as a counter electrode in dye-sensitized solar cells", *Sol. Ener. Mat. & Sol. Cells*, **91**, 1472 (2007).
- [80] G. Liang, T. Cui, "Fabrication and characterization of poly(3,4-ethylenedioxythiophene) field-effect transistors", *Solid-State Elec.*, **48**, 87 (2004).
- [81] C.G. Granqvist, "Electrochromism and Electrochromic Devices", in *The CRC Handbook of Soli State Electrochemistry*, (The CRC Press, 1997).
- [82] P.R. Somani, S. Radhakrishnan, " Electrochromic materials and devices: present and future", *Mat. Chem. and Phys.*, **9299**, 1 (2002).
- [83] C.G. Granqvist, "Electrochromic Materials: Microstructure, Electronic Bands, and Optical Properties", *Appl. Phys. A*, **57**, 3, (1993).
- [84] K. Hyodo, "Electrochromism of Conducting Polymers", *Electrochim. Acta*, **39**, 265 (1994).
- [85] R.J Mortimer, " Electrochromic Materials", *Chem. Soc. Rev.*, **26**, 147 (1997).
- [86] M.-A. De Paoli, G. Casalbore-Miceli, E.M. Girotto, W.A. Gazotti, "All polymeric solid state electrochromic devices", *Electrochimica Acta* **44**, 2983 (1999).
- [87] R.J. Mortimer, "Organic electrochromic materials", *Electrochimica Acta* **44**, 2971 (1999).
- [88] R.D. Rauh, "Electrochromic windows: an overview", *Electrochimica Acta* **44**, 3165 (1999).
- [89] T.J. Richardson, "New electrochromic mirror systems", *Solid State Ionics*, **165**, 305 (2003).
- [90] D.R. Rosseinsky and R.J. Mortimer, "Electrochromic Systems and the Prospects for Devices", *Adv. Mat.*, **13**, 783 (2001).
- [91] Y. Qi and Z.Y. Wang, "Dendritic Mixed-Valence Dinuclear Ruthenium Complexes for Optical Attenuation at Telecommunication Wavelengths", *Macromolecules*, **36**, 3146 (2003).
- [92] J.D. Zhang, H.A. Yu, X.G. Wu, Z.Y. Wang, "Towards the improvement of attenuation range and response time of electrochromic polymer-based variable optical attenuators", *Optical Materials*, **27**, 265 (2004).
- [93] M.D. Ward, "Near-infrared electrochromic materials for optical attenuation based on transition-metal coordination complexes", *J. Solid State Electrochem.*, **9**, 778 (2005).
- [94] A.L. Dyer, C.R.G. Grenier, and J.R. Reynolds, "A Poly(3,4-alkylenedioxythiophene) Electrochromic Variable Optical Attenuator with Near-Infrared Reflectivity Tuned Independently of the Visible Region", *Adv. Funct. Mater.*, **17**, 1480 (2007).
- [95] P. Chandrasekhar, B.J. Zay, T. McQueeney, A. Scara, D. Ross, G.C. Birur, S. Haapanen, L. Kauder, T. Swanson, D. Douglas, "Conducting Polymer (CP)

- infrared electrochromics in spacecraft thermal control and military applications", *Synth. Met.*, **135-136**, 23 (2003).
- [96] T.L. Rose, S. D'Antonio, M.H. Jillson, A.B. Kon, R. Suresh and F. Wang, "A microwave shutter using conductive polymers", *Synth. Met.*, **85**, 1439 (1997).
 - [97] P.V. Wright, B. Chambers, A. Barnes, K. Lees and A. Despotakis, "Progress in smart microwave materials and structures", *Smart Mater. Struct.*, **9**, 273 (2000).
 - [98] R. Zhang, A. Barnes, K.L. Ford, B. Chambers and P.V. Wright, "A new microwave "smart window" based on a poly(3,4-ethylenedioxythiophene) composite", *J. Mater. Chem.*, **13**, 16 (2003).
 - [99] C.G. Granqvist, "Progress in electrochromics: tungsten oxide revisited", *Electrochimica Acta* **44**, 3005-3015 (1999).
 - [100] W.C. Dautremont-Smith, "Transition metal oxide electrochromic materials and displays: a review – Part 1: oxides with cathodic coloration", *Displays*, **3**, 3 (1982).
 - [101] W.C. Dautremont-Smith, "Transition metal oxide electrochromic materials and displays: a review – Part 2: oxides with anodic coloration", *Displays*, **3**, 67 (1982).
 - [102] H. Hosono, "Recent progress in transparent oxide semiconductors: Materials and device application", *Thin Solid Films*, **515**, 6000 (2007).
 - [103] C.G. Granqvist, "Transparent conductors as solar energy materials: A panoramic review", *Sol. Energy Mater. Sol. Cells* (2007), doi:10.1016/j.solmat.2007.04.031
 - [104] C.G. Granqvist, A. Hultaker, "Transparent and conducting ITO films: new developments and applications", *Thin Solid Films* **411**, 1 (2002).
 - [105] A.A. Karyakin, "Prussian Blue and Its Analogues: Electrochemistry and Analytical Applications", *Electroanalysis*, **13**, 813 (2001).
 - [106] S.K. Deb, "Optical and Photoelectric Properties and Color Centers in Thin-Films of Tungsten Oxide" *Phil. Mag.*, **27**, 801 (1973).
 - [107] S.-H. Lee, H.M. Cheong, J.-G. Zhang, A. Mascarenhas, D.K. Benson, S.K. Deb, "Electrochromic mechanism in α -WO_{3-y} thin films", *Appl. Phys. Lett.*, **74**, 242 (1999).
 - [108] S.-H. Lee, H.M. Cheong, C.E. Tracy, A. Mascarenhas, A.W. Czanderna, S.K. Deb, "Electrochromic coloration efficiency of α -WO_{3-y} thin films as a function of oxygen deficiency", *Appl. Phys. Lett.*, **75**, 1541 (1999).
 - [109] A. Georg, W. Graf and V. Wittwer, "Comparison of electrical conductivity and optical properties of substoichiometrically and electrochemically coloured WO_x films of different crystallinity", *Sol. Ener. Mat. and Sol. Cells*, **51**, 353 (1998).
 - [110] S.-H. Lee, R. Deshpande, P.A. Parilla, K.M. Jones, B. To, A.H. Mahan and Anne C. Dillon, "Crystalline WO₃ Nanoparticles for Highly Improved Electrochromic Applications", *Adv. Mater.*, **18**, 763 (2006).

- [111] I. Bedja, S. Hotchandani, R. Carpentier, K. Vinodgopal and P.V. Kamat, "Electrochromic and photoelectrochemical behavior of thin WO₃ films prepared from quantized colloidal particles", *Thin Solid Films*, **247**, 195 (1994).
- [112] P.V. Ashrit, G. Bader, V.-V. Truong, "Electrochromic properties of nanocrystalline tungsten oxide thin films", *Thin Solid Films*, **320**, 324 (1998).
- [113] N. Xu, M. Sun, Y.W. Cao, J.N. Yao, E.G. Wang, "Influence of pH on structure and photochromic behavior of nanocrystalline WO₃ films", *Appl. Surf. Sci.*, **157**, 81 (2000).
- [114] K. Yoshino, M. Onoda and T. Kawai, "Novel Optical Property of Conducting Polymer and its Application", *Optoelectronics*, **5**, 1 (1990).
- [115] A.A. Argun, P.-H. Aubert, B.C. Thompson, I. Schwendeman, C.L. Gaupp, J. Hwang, N.J. Pinto, D.B. Tanner, A.G. MacDiarmid and J.R. Reynolds, "Multicolored Electrochromism in Polymers: Structures and Devices", *Chem. Mater.*, **16**, 4401 (2004).
- [116] F. Carpi, D. De Rossi, "Colours from electroactive polymers: Electrochromic, electroluminescent and laser devices based on organic materials", *Opt. & Las. Tech.*, **38**, 292 (2006).
- [117] M. Fabretto, T. Vaithianathan, C. Hall, P. Murphy, P.C. Innis, J. Mazurkiewicz and G.G. Wallace, "Colouration efficiency measurements in electrochromic polymers: The importance of charge density", *Electrochem. Comm.*, **9**, 2032 (2007).
- [118] A. M. Stephan, "Review on gel polymer electrolytes for lithium batteries", *European Polymer Journal*, **42**, 21 (2006).
- [119] K.M. Abraham, M. Alamgir "Li⁺-Conductive solid polymer electrolyte with liquid-like conductivity", *J Electrochem Soc*, **137**, 1657 (1990).
- [120] A. M. Stephan, K.S. Nahm, "Review on composite polymer electrolytes for lithium batteries", *Polymer*, **47**, 5952 (2006).
- [121] S.M. Sze, "Physics of Semiconductor Devices", (John Wiley & Sons, 1981).
- [122] K.-Y. Law, "Organic Photoconductive Materials for Xerographic Photoreceptors", in *Handbook of Organic Conductive Molecules and Polymers*, Vol. **1**, ed. by H.S. Nalwa, (Chichester, UK, John Wiley & Sons 1997).
- [123] P. Strohriegl and J.V. Grazulevicius, "Photoconductive Polymers", in *Handbook of Organic Conductive Molecules and Polymers*, Vol. **1**, ed. by H.S. Nalwa, (Chichester, UK, John Wiley & Sons, 1997).
- [124] J.N. Ross, "Thick-film photosensors", *Meas. Sci. Technol.*, **6**, 405 (1995).
- [125] L.A. Patil, P.A. Wani, S.R. Sainkar, A. Mitra, G.J. Phatak and D.P. Amalnerkar "Studies on 'fritted' thick films of photoconducting CdS", *Mat. Chem. and Phys.*, **55**, 79 (1998).
- [126] D.P. Amalnerkar, "Photoconducting and allied properties of CdS thick films", *Mat. Chem. and Phys.*, **60**, 1 (1999).

- [127] Z.C. Huang, C.R. Wie, I. Na, H. Luo, D.B. Mott and P.K. Shu, "High performance ZnSe photoconductors", *Elect. Lett.*, **32**, 1507 (1996).
- [128] S.P. Lacour, S. Wagner, H. Prahlaad, R. Perline, "High voltage photoconductive switches of amorphous silicon for electroactive polymer actuators", *J. Non-Cryst. Sol.*, **338-340**, 736 (2004).
- [129] S.P. Lacour, H. Prahlaad, R. Perline, S. Wagner, "Mechatronic system of dielectric elastomer actuators addressed by thin film photoconductors on plastic", *Sens. and Actu. A*, **111**, 288 (2004).
- [130] J.D. Plummer, M.D. Deal and P.B. Griffin, "*Silicon VLSI Technology*", (Upper Saddle River, NJ: Prentice Hall, 2000).
- [131] C. MacPherson, M. Stainer, G. Yu, M. O'Regan, "Fabricating Full-Color OLED Displays Using Ink-Jet Printing", *Information Display*, 11, **16** (2003).
- [132] B. Michel et al, "Printing meets lithography: Soft approaches to high-resolution patterning", *IBM J. Res. & Dev.*, **45**, 697 (2001).
- [133] B.D. Gates, Q. Xu, M. Stewart, D. Ryan, C.G. Willson and G.M. Whitesides, "New Approaches to Nanofabrication: Molding, Printing, and Other Techniques", *Chem. Rev.*, **105**, 1171 (2005).
- [134] B.D. Gates, Q. Xu, J.C. Love, D.B. Wolfe and G.M. Whitesides, "Unconventional Nanofabrication", *Annu. Rev. Mater. Res.*, **34**, 339 (2004).
- [135] Y. Xiaa, D. Qinb and Y. Yin, "Surface patterning and its application in wetting/dewetting studies", *Curr. Opin. Coll. & Inter. Sci.*, **6**, 54 (2001).
- [136] M. Heule, U.P. Schönholzer and L.J. Gauckler, "Patterning colloidal suspensions by selective wetting of microcontact-printed surfaces", *Jour. Eur. Cer. Soc.*, **24**, 2733 (2004).
- [137] A. Benor, A. Hoppe, V. Wagner and D. Knipp, "Microcontact printing and selective surface dewetting for large area electronic applications", *Thin Solid Films*, **515**, 7679 (2007).
- [138] A. Yariv, "Optical Electronics in Modern Communications", 5th Ed., (New York, NY: Oxford University Press, 1997).
- [139] M.C. Morvant and J.R. Reynolds, "In situ conductivity studies of poly(3,4-ethylenedioxythiophene)", *Synth. Met.*, **92**, 57 (1998).
- [140] T. Johansson, L.L.A. Pettersson, O. Inganas, "Conductivity of de-doped poly(3,4-ethylenedioxythiophene)", *Synth. Met.*, **129**, 269 (2002).
- [141] J.M. Ziman, "Models of Disorder", 2nd Ed., p. 375, (London, Cambridge University Press, 1979).
- [142] D. Stauffer and A. Aharony, "Introduction to Percolation Theory", 2nd Ed., (London, Taylor & Francis Ltd., 1991).
- [143] J. W. Essam, "Percolation Theory", *Rep. Prog. Phys.*, **43**, 833 (1980).

- [144] B.J. Last and D.J. Thouless, "Percolation Theory and Electrical Conductivity", *Phys Rev Lett*, **27** 1719 (1971).
- [145] B.P. Watson and P.L. Leath, "Conductivity in the two-dimensional-site percolation problem", *Phys Rev B*, **9**, 4893 (1974).
- [146] S. Kirchmeyer and K. Reuter, "Scientific importance, properties and growing applications of poly(3,4-ethylenedioxythiophene)", *J. Mater. Chem.*, **15**, 2077 (2005).
- [147] S. Kirkpatrick, "Classical Transport in Disordered Media: Scaling and Effective-Medium Theories", *Phys. Rev. Lett.*, **27** 1722 (1971).
- [148] S. Kirkpatrick, "Percolation and Conduction" in *Rev. Mod. Phys.*, **45** 574 (1973).
- [149] F. Lux, "Models proposed to explain the electrical conductivity of mixtures made of conductive and insulating materials" in *J. Mater. Sci.*, **28** 285 (1993).
- [150] M.E.J. Newman and R.M. Ziff, "Fast Monte Carlo algorithm for site or bond percolation" in *Phys. Rev. E*, **64**, 016706 (2001).
- [151] G. Zotti, "Doping-level dependence of conductivity in polypyrroles and polythiophenes", *Synth. Met.*, **97**, 267 (1998).
- [152] S. Roth, H. Bleier and W. Pukacki, "Charge Transport in Conducting Polymers", *Faraday Discuss. Chem. Soc.*, **88** 223 (1989).
- [153] S. Ghosh, O. Inganäs, "Conducting Polymer Hydrogels as 3D Electrodes: Applications for Supercapacitors", *Adv. Mat.*, **11** 1214 (1999).
- [154] G. Manganaro, P. Arena and L. Fortuna, "Cellular Neural Networks: Chaos, Complexity and VLSI Processing", (Berlin, Springer-Verlag, 1999).
- [155] A. Slavova and V. Mladenov, "Cellular Neural Networks: Theory and Applications", (Nova Science Publishers, 2004).
- [156] T. Roska and A. Rodriguez-Vazquez, "Towards the Visual Microprocessor: VLSI Design and the Use of Cellular Neural Network Universal Machines", (John Wiley & Sons, 2001).
- [157] T. Aoki, M. Hiratsuka and T. Higuchi, "Enzyme transistor circuits", *IEE Proc. Circuits Devices Syst.*, **145** 264 (1998).
- [158] M. Hiratsuka, T. Aoki and T. Higuchi, "Enzyme Transistor Circuits for Reaction-Diffusion Computing", *IEEE Trans. Cir. Syst. I*, **46** 294 (1999).
- [159] M. Hiratsuka, T. Aoki and T. Higuchi, "Reaction-diffusion cellular automation using integrated microelectrodes", *Elec. Lett.*, **37** 87 (2001).