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2005 J. Phys.: Condens. Matter 17 2919

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A lattice gas approach to conduction in organic material

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Received 29 November 2004, in final form 28 February 2005

Published 29 April 2005

Online at stacks.iop.org/JPhysCM/17/2919

Abstract

The current–voltage relationship of organic diodes that are used as organic light emitting devices is reported. Charged molecules are created at the electrodes by an oxidation/reduction reaction. The charge moves across the material by an electron transfer mechanism from a charged molecule to a neutral molecule. The charges are described by a lattice gas because there is a low concentration of charges. The concentration of charged molecules at the electrode is governed by the Nernst equation and is coupled to the equations of transport. The concentration of charge is determined by a competition between charge creation and charge transport. The applied voltage creates the charge at the electrodes and causes charge transport. The graphical analysis results in the charge density and current density as a function of the applied voltage and the dependence of the current density on both temperature and device thickness.

Nomenclature

μ	Chemical potential
$\tilde{\mu}$	Electrochemical potential
μ^0	Chemical potential of pure substance
ΔG	Gibbs free energy
k	Boltzmann constant
q	Charge of an electron
ϵ_0	Permittivity of free space
ϵ	Dielectric constant
T	Temperature
n	Number of electrons transferred in the reaction
j	Current density
ρ	Number density of charged molecules

ρ_0	Number density of charged molecules at electrode
ρ_m	Number density of neutral molecules
u	mobility
$E(x)$	Electric field
L	Length of device
ϕ	Emf required to form the charges at the electrode
ΔV	Voltage required to transport the charges
V_t	Total applied voltage across the device ($V_t = \phi + \Delta V$)

1. Introduction

In 1987 Tang and VanSlyke reported on the phenomenon of light emission by passing an electrical current across an organic bilayer system [1]. These devices became known as organic light emitting diodes (OLEDs). The devices displayed unidirectional current flow and an exponential current–voltage (i – v) curve although there was a significant negative curvature in the $\log i$ versus v plot. The devices exhibited a rapid degradation in light emission (30% loss in 10 h) followed by a much slower decay. Light emission was also observed in polymer systems [2].

Several models are used to explain the charge injection and conduction in the devices. One is a Schottky model in which the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the organic molecule are regarded to be analogous to the conduction and valence bands of a semiconductor [3, 4]. A barrier is argued to form due to the mismatch between the Fermi level of the metal contact and the HOMO or LUMO ‘band’. A second model that has been applied to polymer systems is a Gaussian disorder model in which the i – v relationship is determined by bulk transport [5–7]. The current is space charge limited with an exponential field dependent mobility.

Light emission from a solution containing organic molecules has also been observed. This is known as electrochemically generated chemiluminescence. In this process, an electric current is passed between metal electrodes through a solution containing organic molecules. Radical cations are formed at the anode while radical anions are formed at the cathode. Subsequent recombination of the anions and cations in solution yields an excited state from which there is emission of light. Organic molecules that have been used include rubrene [8] aromatic amines, nitriles, nitro and polycyclic compounds [9]. It should be noted that these aromatic molecules are identical in composition to those in OLEDs. Further, the same rapid degradation in emissive properties (50% degradation in 50 h) followed by a much slower emission degradation was also observed in these systems [10].

While the majority of theories describing OLEDs stem from the application of band structure, it is the goal of this paper to describe how electrochemical processes can describe the conduction mechanism in OLEDs.

The essential features of the model are described in section 2. The chemical potential of the lattice gas and the electrochemical potential with a local electric field are presented in section 3. The emf required to form the charges at the electrodes is given in section 4. The charge transport described in section 5 results from electrostatic effects. The current–voltage relation in section 6 is obtained from the derived charge density by minimizing the voltage with respect to the concentration of charged ions at the surface for a fixed current density. The graphical analysis in section 7 results in plots of the charge density and current density as a function of the potential and the current density as a function of both temperature and device thickness. Finally, the discussion in section 9 relates the calculated results with properties of OLEDs and previous models of conduction. The conclusions are given in section 10.

2. Description of the model

In order to understand the conduction process in OLEDs we must find a model that is consistent with the chemical and physical properties of the material in question. The organic systems are molecular crystals with a typical molecular weight that is between 200 and 500 g mol⁻¹. The forces holding the molecules together are weak van der Waals forces, not the strong metallic or covalent bonding that is typical in metals and semiconductors. While models abound using band theory to describe the conduction process in organic material, these in the strictest sense are only analogies. The valence electrons are not free to flow between molecules as they are in metals and semiconductors. As such, descriptions involving electron and hole conduction in pseudo conduction and valence bands are questionable.

Our starting point is the electrochemical oxidation/reduction reaction of organic molecules. It is known that the kinetics of aromatic electrochemical reactions are extremely facile compared with inorganic electrochemical reactions [11]. As such, the processes are generally limited by thermodynamic rather than kinetic factors. The difference between an electrochemical cell and conduction in OLEDs is the fact that the conduction occurs in the solid state in the latter. Therefore the transport of charges does not occur via diffusion and mass transport of solvated charged ions. Since there is no electrolyte to compensate for charge imbalance, electrostatic effects must also be addressed. The model of the current–voltage behaviour is determined by the thermodynamic consideration for the creation of charged molecular species at the electrode surface and the subsequent transport of the charges to the counter-electrode via a series of electron transfers between molecules.

This mechanism is not completely new. In 1986, Abkowitz described conduction of tetraphenyldiamine in polycarbonate films [13]. In the article, the author stated that it is now generally accepted that charge transport is an electric-field driven sequence of redox processes involving neutral molecules and their charged derivatives. Further, it was stated that electron transport consisted of the electron transfer between anion radicals and neutral molecules, while hole transport involves electron transfer from a neutral molecule to its radical cation. Finally, he stated that it is the chemical nature of a given charge transport molecule which determines the sign of unipolar transport. The above statements reflect an electrochemical approach to transport. While the term ‘hole transport’ is used, it clearly does not imply a semiconducting band theory meaning of the term ‘hole’.

It is apparent that current flows through the device; hence charge must traverse the material. The material does not possess intrinsic charges and as such the charges must be created at the electrodes. Here at the electrode surface radical cations and anions are formed. The electric charge is then transferred from molecule to molecule across the material. The energy required to form the ions is determined by the electrochemical potential. The current–voltage curve results from the resultant of charge creation and charge transport.

The device consists of an organic material between a negative cathode and positive anode. A voltage is applied across the device and current flows between the metallic electrodes. Charge is transferred between the contacts and the organic molecules by an electron transfer reaction. Electrons are transferred from the cathode in a reduction process or moved to the anode via oxidation. Both or one of the processes takes place depending on the organic molecules that are present. This process requires a redox potential of several volts. The charge is delocalized over the aromatic molecule and not localized to one atom such as in an ionic crystal. Also, there is a low concentration of ions with a density of about 1 part in 10⁶.

The charge moves across the material by an electron transfer process. Aromatic organic molecules are unique in that the π electrons are delocalized over the entire ring structure. Thus, all π electrons are shared within the molecule. Removing or adding an electron from

a molecule results in a much smaller change between the initial and final nuclear positions of the atoms than in corresponding inorganic systems; therefore, the overlap of the electron wavefunction between the oxidized and reduced species is much higher than in inorganic systems. It is known that the rate of electron transfer depends on the overlap of electron wavefunctions between the neutral and oxidized or reduced species. As such, the electron transfer rate in aromatic organic molecules is orders of magnitude greater than in inorganic electrochemical species [12]. This theory is applied to both homogenous electron transfer and heterogenous electron transfer. Homogenous electron transfer is when an electron is transferred between neutral and oxidized or reduced species. Heterogenous electron transfer describes the oxidation or reduction of the molecule at the electrode. The theory of electron transfer has been worked out by Marcus [14, 15], Levich [16] and others [17].

While the electron transfer theory is general, in application the kinetics of the current–voltage relationship is usually given by the Butler–Volmer relation of electrochemistry. This phenomenological model accounts for kinetic effects associated with the electron transfer at the electrodes. In the limit of very facile kinetics, the equation reduces to the Nernst equation. Since the rate of electron transfer in aromatic systems is orders of magnitude greater than in inorganic electrochemical systems, the Nernst equation is a valid starting point for describing not only systems at equilibrium but also systems in the steady state in which current flows.

The applied voltage is partitioned between the redox potential and the potential across the device. It should be noted that the electric field, charge gradient and density of charges at the electrodes are not independent of each other. The applied voltage is partitioned in many ways depending on the material parameters, geometry and current driven through the device. The applied voltage creates the charges and drives the current.

A lattice gas is used to determine the chemical potential of the radical ions. The lattice gas is based upon the assumption that a particle can occupy any site on a lattice with equal probability. In the system, the radical ion can spontaneously transfer charge to any molecule around it. While there exist electrostatic interactions between the charged molecules, the concentration of charged molecules is so dilute that it does not appreciably affect the number of states that are accessible; therefore, the charge has an almost equal probability of occupying any site on the lattice.

This chemical potential is used to calculate the energy required to create charges at the electrode surface. The transport of charges is due to the electric field, which is considered in section 5.1. The solution to the charge transport involves solving the equation of continuity subject to Gauss' law. The current at each point in the device must be constant, because in steady state there is no charge accumulation.

The applied voltage is the sum of the potential required to transport the charge plus the voltage required to create the charges at the electrodes. The concentration of charged ions at the electrode surface, which is the boundary condition, is determined by minimizing the total applied potential for a given current.

In order to get a better feeling for the dynamics within the system a simplification is employed to elucidate the dynamics. If the current density is large and the mobility small the equations imply that the charge density is nearly constant across the material. Using this simplification, an analytic expression for the current–voltage curve is derived.

3. Chemical potential

Organic molecules in the condensed phase constitute a molecular crystal with strong intramolecular covalent bonding within the molecule and very weak intermolecular van der Waals forces between the molecules. Due to this weak bonding the electronic energy levels

do not extend to neighbouring molecules as in a metal. However, it is known that the charge on a molecular ion can spontaneously transfer from one molecule to another via a series of electron transfers [18]. The entropy associated with the possible ways the charges can be placed leads to a lattice gas description of the system. The chemical potential (μ) is thus given by equation (1).

$$\mu = \mu^0 + kT \ln \frac{\rho}{\rho_m}. \quad (1)$$

The chemical potential is the Gibbs free energy per molecule. In equation (1), ρ is the density of charged molecules, while ρ_m is the density of all molecules. μ^0 is the Gibbs free energy of the pure substance. When the molecule is charged, an electric potential alters the chemical potential. This electrochemical potential $\tilde{\mu}$ includes both the chemical potential and the effect of the electric potential (V) at that region of space. In equation (2), nq is the charge of the charged species.

$$\tilde{\mu} = \mu^0 + kT \ln \frac{\rho}{\rho_m} + nqV. \quad (2)$$

This chemical potential can also be derived as an extension of electrochemistry or from general statistical mechanical considerations. While the chemical potential is known as the dilute solution approximation in chemistry, it is known as a lattice gas in physics. Since the equations of electrochemistry stem from the same basic form of the chemical potential, the subsequent analysis bears a similar resemblance to electrochemistry.

A chemical potential of the form (2) is typical of many electrochemical systems. For example, Bernard *et al* [19] describe a mean-field kinetic lattice gas model of electrochemical cells having an electrochemical potential given by equation (3). Such an expression represents a generalized potential for species α at lattice site k . Here p_k^α represents the probability that species α occupies lattice site k and ϵ represents the energy of interactions between the chemical species (α, β).

$$\tilde{\mu}_k^\alpha = - \sum_{\beta} \sum_a \epsilon^{\alpha\beta} p_{k+a}^\beta + kT \ln p_k^\alpha + q^\alpha V_k. \quad (3)$$

The double sum is over all species β and neighbouring lattice sites a . The model that is currently under investigation is one in which the concentrations of charged species are very dilute because the cations and anions are surrounded by a sea of neutral molecules. Since the concentration of charged molecules is very small, the double sum is independent of k and results in a constant. This returns us to the original form of equation (2).

The essential difference between electrochemistry and the current analysis is that in an electrochemical cell no net electric charge exists between the electrodes. Further, the electric field between the electrodes is rather small. As such, the nqV term in the chemical potential does not have a significant effect in electrochemical systems. There exists in the system under consideration added coulombic interactions due to the space charge between the electrodes. This additional energy depends upon the charge distribution within the device. This added term will be accounted for when the voltage required to transport the charges is considered.

4. Charge creation at the electrodes

The emf required to form the charges at the electrodes will be evaluated now. The emf is derived by determining the energy required to form the charged species at the electrodes. At the anode radical cations are formed, $A \rightarrow A^+ + e^-$, while at the cathode radical anions are formed, $A + e^- \rightarrow A^-$. A represents any molecule that can be oxidized or reduced. The net

reaction is $2A \rightarrow A^+ + A^-$. The number densities of the species A^+ , A^- and A are ρ_{A^+} , ρ_{A^-} , ρ_n respectively. The Gibbs free energy change ΔG given in equation (4) is the difference in the chemical potential of the products and the reactants.

$$\Delta G = \mu_{A^+} + \mu_{A^-} - 2\mu_A. \quad (4)$$

The chemical potential for each species is represented by the lattice gas formula given by equation (1). The chemical potential of the pure substance (μ^0) for each chemical species can be combined into a single term $\Delta\mu^0$. This term represents the free energy change when the concentrations of the reactants and the products are equal. The log terms of equation (1) can also be combined to form a single term. This treatment follows the standard derivation used in chemical thermodynamics [20].

$$\Delta G = \left(\mu_{A^+}^0 + kT \ln \frac{\rho_{A^+}}{\rho_m} \right) + \left(\mu_{A^-}^0 + kT \ln \frac{\rho_{A^-}}{\rho_m} \right) - 2 \left(\mu_A^0 + kT \ln \frac{\rho_n}{\rho_m} \right) \quad (5)$$

$$\Delta G = \Delta\mu^0 + kT \ln \frac{\rho_{A^+} \rho_{A^-}}{\rho_n^2}. \quad (6)$$

The free energy ΔG is related to the emf ϕ required to form the charges.

$$\Delta G = -nq\phi. \quad (7)$$

The number of electrons transferred to a single molecule in the reaction is represented by n , q is the magnitude of the charge of an electron, and ϕ is the emf required to form the charge density at the electrodes. In our model, one electron is transferred to each molecule and hence $n = 1$. In addition the vast majority of molecules are neutral; hence, $\rho_n \approx \rho_m$. Combining equations (7) and (6) with $\rho_n \approx \rho_m$ results in the Nernst equation (8).

$$\phi = \phi^* + \frac{kT}{nq} \ln \left(\frac{\rho_{A^+} \rho_{A^-}}{\rho_m^2} \right). \quad (8)$$

The cell or redox potential represented by ϕ^* is a constant for a given chemical reaction. Equation (8) implies that the density of charged molecules increases exponentially with voltage.

5. Derivation of charge transport

The charges that have been created at the surface of the electrode move from molecule to molecule to the counter-electrode surface. For simplicity, only the motion of carriers with the same charge will be considered. The positive charges are assumed to move under the applied field while the anions remain stationary. In general the current density (j) is proportional to the gradient of the electrochemical potential (equation (9)) [21]. This approach follows other methods used to describe conduction in electrochemical cells [19].

$$j \propto \nabla \tilde{\mu} = \frac{\partial}{\partial x} \left[\mu^0 + kT \ln \frac{\rho}{\rho_m} + qV \right] = \left[\frac{kT}{\rho} \frac{\partial \rho}{\partial x} + q \frac{\partial V}{\partial x} \right]. \quad (9)$$

There are two terms in equation (9) that drive the current. The first term is proportional to the gradient of the charge density, while the second is proportional to the gradient of the voltage. These two terms will be denoted as the electrochemical and electrostatic terms, respectively.

In the electrostatic process the steady state motion of the charge is driven by the electric field between the electrodes. Due to the uncompensated charges on the molecule, the transport is dominated by space charge effects. In the electrochemical process, charge is driven by virtue of the concentration gradient of charged molecules within the material. Both effects contribute to the overall conduction process.

5.1. Electrostatic transport of charges

Electrostatic effects driving the conduction will be considered now. Steady state continuity implies that the current is a product of the charge density and the electric field assuming that the mobility is constant. The mobility is designated by u to distinguish it from the symbol used for the chemical potential. The standard solution of space charge limited currents has the Dirichlet boundary condition that the electric field goes to zero at the electrodes. However, this implies that the concentration of ions at the electrode surface goes to infinity at $x = 0$. If there are no other factors affecting conduction, allowing $E = 0$ at the boundary minimizes the voltage required to drive charges across the material. Since the field varies as the square root of x while the charge density varies as the inverse of the square root of x , allowing $E = 0$ while the charge density goes to infinity at the boundary yields a finite current. However, due to the aforementioned electrochemical factor the derivative of the charge density can also drive the current. This would lead to an infinite chemical potential gradient driving an infinite charge density giving an infinite current. Further, due to the Nernst equation (8), maintaining an infinite charge density at the electrode requires an infinite voltage. Since this is unphysical we will apply Neumann boundary conditions $\rho(x = 0) = \rho_0$ at the boundary.

The current density is equal to the charge density times the mobility and the electric field.

$$j = q\rho(x)uE(x). \quad (10)$$

Since from Maxwell's equations $dE/dx = q\rho(x)/\epsilon\epsilon_0$ combining equation (10) with Maxwell's equations leads to equation (11).

$$\frac{dE}{dx} = \frac{j(x)}{uE(x)\epsilon\epsilon_0}. \quad (11)$$

Integrating equation (11),

$$\int E(x) dE = \int \frac{j(x)}{u\epsilon\epsilon_0} dx.$$

Substituting the equation of continuity (10) into Gauss' law (11) leads to a differential equation. Solving the differential equation we obtain equation (12). The charge density at the boundary (ρ_0) determines the integration constant. For clarity and to simplify the equations the variable x_c is introduced.

$$E(x) = \sqrt{\frac{2j}{\epsilon\epsilon_0 u}}(x + x_c) \quad \rho(x) = \frac{\rho_0}{\sqrt{1 + \frac{x}{x_c}}} \quad x_c \equiv \frac{\epsilon\epsilon_0 j}{2uq^2\rho_0^2}. \quad (12)$$

The potential difference ΔV required to drive the current across the device length (L) is

$$\Delta V = \int_0^L E(x) dx = \frac{2}{3} \sqrt{\frac{2j}{\epsilon\epsilon_0 u}} [(L + x_c)^{3/2} - (x_c)^{3/2}]. \quad (13)$$

There are several important limits that need to be considered. x_c defines a length scale over which the charge density drops to $1/\sqrt{2}$ of its initial value. If we let x_c go to zero, the density of ions at the surface (ρ_0) goes to infinity at $x = 0$. Equation (13) then reduces to the classic Child's law result of equation (14). As such, the above relation is a general space charge equation for which Child's law is a particular solution.

$$\lim_{x_c \rightarrow 0} \rho(x) = \frac{1}{q} \sqrt{\frac{\epsilon\epsilon_0 j}{2ux}} \quad \lim_{x_c \rightarrow 0} \Delta V = \frac{2}{3} \sqrt{\frac{2jL^3}{\epsilon\epsilon_0 u}}. \quad (14)$$

It is not necessary for the charge density to actually go to infinity to arrive at the classical space charge result. If the inequality of equation (15) holds, then x_c becomes negligible compared to L in equation (13).

$$\rho_0 \gg \frac{1}{q} \sqrt{\frac{j\epsilon\epsilon_0}{2uL}} \quad (15)$$

Another important limit occurs if we let x_c go to infinity. The charge density becomes constant across the material and the voltage required to drive the charges reduces to Ohm's law. This can be derived by taking a Taylor expansion of equation (13) if $x_c \gg L$.

$$\lim_{x_c \rightarrow \infty} \rho(x) = \rho_0 \quad \lim_{x_c \rightarrow \infty} \Delta V = \frac{jL}{uq\rho_0}. \quad (16)$$

The voltage in (16) is the potential difference required to drive the charges from the anode to the cathode.

6. Current–voltage relationship

It is now time to determine the i – v relationship. Consideration must be given to the voltage required to maintain the charge density at the electrodes and the voltage required to drive the current. If the mobility is sufficiently low and the current density is sufficiently high the space charge limit equation (12) reduces to an ohmic result (16). In this limit the electrochemical term drops out since the charge density is uniform ($\rho(x) = \rho_0$). The mobility of carriers in an organic material is several orders smaller than that in metals and semiconductors and therefore equation (16) can accurately describe certain systems.

This leads to an ohmic voltage drop across the bulk of the sample $\Delta V = jL/q\rho_0u$. The total potential for a given current is the sum of the emf required to create a given charge density at the electrodes given by the Nernst equation (8) and the voltage to transport the charges. An additional voltage representing the electrostatic energy associated with the charge distribution also needs to be accounted for. If the positive charge is uniformly distributed in the material and an equal amount of negative charge resides near the counter-electrode there is an electrostatic voltage of $q\rho_0L^2/\epsilon\epsilon_0$. The total voltage V_t for a given current is the sum of these three voltages given by equation (17).

$$V_t = \phi^* + \frac{kT}{nq} \ln \frac{\rho_0}{\rho_m} + \frac{q\rho_0L^2}{\epsilon\epsilon_0} + \frac{jL}{q\rho_0u}. \quad (17)$$

The first two terms are the voltage required to create the charge density at the surface (Nernst equation), ρ_0 is the density of charged molecules and ρ_m denotes the density of neutral molecules. The third term is the voltage required to overcome electrostatic repulsions which the Nernst equation does not include. The fourth term is the voltage required to move the charges across the material.

It should be noted that the added electrostatic field affects the charge distribution and causes deviations from a constant charge density. However, if the electrostatic voltage is less than the voltage required to transport the charges (the third term is much less than the fourth term in (17)) then this electrostatic field can be treated as a perturbation. A more general expression will be given in a subsequent publication. A non-uniform distribution of the charge density will affect the specific equation representing the electrostatic repulsions; however, a similar expression relating the electrostatic voltage with the charge density and device thickness will be obtained.

It is assumed that the current is transported by a single carrier. This can occur when the mobility of one charge type (positive or negative) is much greater than the other. Alternatively,

it can occur with only a single charge type in the material. Either possibility leads to a similar expression given by equation (17).

There is now an optimization condition; while it requires more voltage to create a higher density of charges, the ohmic voltage is reduced by an increase of charges. As such the density of charged ions will depend on the applied current. In order to determine the current–voltage behaviour, we need to know the density of charged molecules as a function of current.

For a given applied voltage, equation (17) defines the charge density and current density. It is necessary to determine the charge density, as the charge density and current are not independent of each other. The voltage and hence the power dissipated within the material goes through a minimum at a certain charge density. Since nature chooses the path of least resistance, the charge density is determined by the density which minimizes the power dissipation. This follows from the example given by Feynmann, who stated that the current is determined so as to minimize the rate at which heat or energy is generated in the material [22]. As such the concentration of charged ions at the electrode surface is determined by minimizing the voltage with respect to charge density at a fixed current density.

$$\begin{aligned} \frac{dV_t}{d\rho_0} &= \frac{qL^2}{\epsilon\epsilon_0} + \frac{kT}{nq\rho_0} - \frac{jL}{q\rho_0^2u} = 0 \\ \rho_0 &= \frac{\epsilon\epsilon_0}{2qL^2} \left[-\frac{kT}{nq} + \sqrt{\left(\frac{kT}{nq}\right)^2 + \frac{4jL^3}{\epsilon\epsilon_0u}} \right]. \end{aligned} \quad (18)$$

The reason for this minimum is that there is an opposition between electrostatic forces attempting to expel all charges from the material and resistive forces impeding the motion of charges. If the charge density is less than the charge density at the minimum, it requires less force to increase the charge density than to drive current through the material. Likewise, if the charge density exceeds the value at the minimum, electrostatic forces exceed resistive forces, and charge is expelled from the medium. As such the charge density lies at equilibrium at the energy minimum in steady state.

If the charge density is uniform across the material or has only a small change as a function of distance, the charge density that minimizes the voltage as a function of current results in a quadratic expression which can be solved analytically. The model assumes that the mobility of one of the carriers dominates the transport.

7. Graphical analysis

The above equations (17) and (18) will be solved with the following parameters: $L = 100$ nm, $u = 1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $T = 300$ K, $\rho_m = 2 \times 10^{21} \text{ cm}^{-3}$, $\epsilon = 1$, $\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$. The numerical values of the mobility, thickness and number density of the material are parameters that are typical of organic materials used in OLEDs. Graphs of the charge density and current as a function of the applied voltage are shown in figures 1 and 2. A redox potential (ϕ^*) of 3.0 V, which is a typical value in organic material is assumed in the following graphs.

As we can see in the first graph (figure 1), the charge density rises exponentially at low applied voltage and tapers off at higher voltages. The initial increase arises from the first term (Nernst equation) where the charge density increases exponentially with voltage. As more charge is injected into the system the third electrostatic term in equation (17) impedes further creation of charges. As such the charge density does not increase significantly with increasing potential. The charge density levels off at about $5.4 \times 10^{16} \text{ cm}^{-3}$. This value is much smaller than the number density of neutral molecules (number of molecules per unit volume). Thus our approximation that the number of neutral molecules is constant is justified.

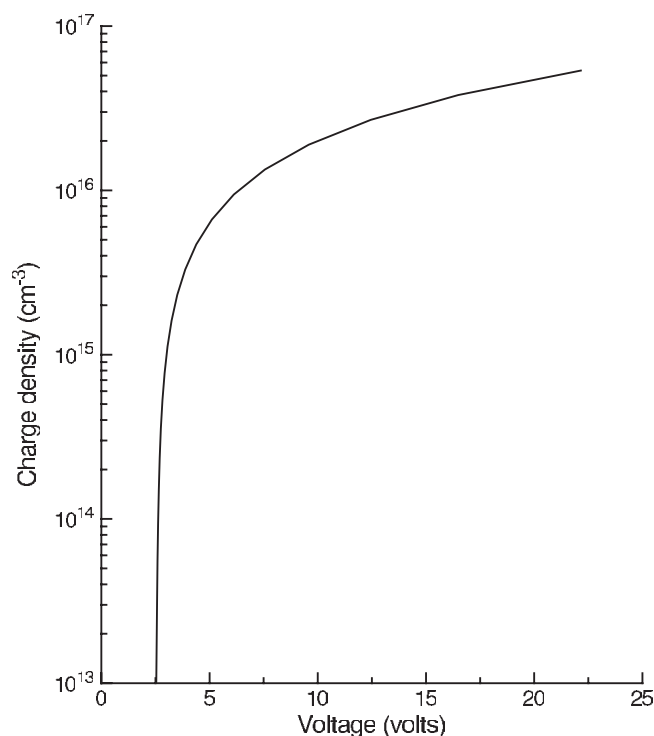


Figure 1. Charge density versus applied voltage (equation (18)). $\rho_m = 2 \times 10^{21} \text{ cm}^{-3}$, $T = 300 \text{ K}$, $u = 1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $L = 100 \text{ nm}$, $\phi^* = 3.0 \text{ V}$.

Figure 2 shows the current as a function of applied voltage. The current at first increases exponentially with applied voltage and then begins to increase at a rate that is more quadratic in nature. As the current increases, the system can either increase the number of charges or increase the speed at which they cross the material. At low applied voltages it is easier to create more charges, as the charges increase exponentially with voltage. As the current increases, the electrostatic term inhibits further increase of charges. Therefore more voltage is used to drive the charges across the material, leading to electrostatic limitation of the current.

There is negligible current and charge for voltages less than 2–3 V. In this range the voltage is less than the redox potential, and significant numbers of charged molecules are not generated. The sole effect of a change in the redox potential is to shift the curves to higher or lower potential. This is taken into account in electrochemistry by subtracting the redox potential of a molecule from the applied voltage to form the overpotential. It is not used here.

The dependence of current and voltage upon temperature can also be investigated. Using the same equations the current–voltage behaviour as a function of temperature can be calculated. Since the equation determines the voltage at fixed current densities, it is necessary to interpolate the values to obtain the current at fixed applied voltages. The current at a fixed voltage is then plotted as a function of temperature (figure 3). The current increases linearly with temperature in the temperature range 260–360 K.

As a final analysis, the current–voltage behaviour for different thicknesses is also examined. By varying the thickness of the device we obtain a series of curves (figure 4). As the thickness increases, the voltage required to obtain a fixed current also increases.

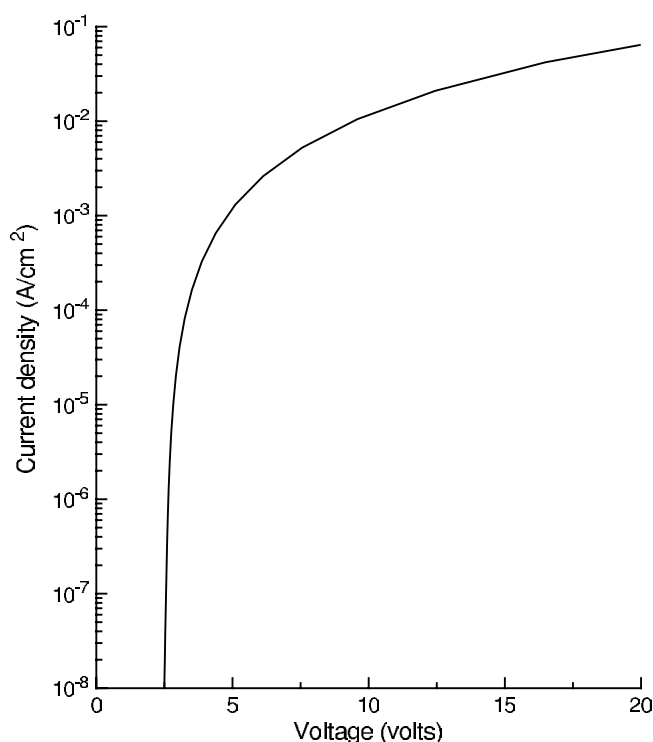


Figure 2. Current density versus applied voltage (equation (17)). $\rho_m = 2 \times 10^{21} \text{ cm}^{-3}$, $T = 300 \text{ K}$, $u = 1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $L = 100 \text{ nm}$, $\phi^* = 3.0 \text{ V}$.

To summarize the results of charge transport, the following properties are predicted.

- (i) When the thickness or current density is small the current varies exponentially with voltage.
- (ii) At higher currents the log current versus voltage curve exhibits a negative curvature. The current varies quadratically with voltage at high currents.
- (iii) At a fixed applied voltage the current increases linearly with increasing temperature.
- (iv) As the device thickness increases, the voltage required to obtain a constant current also increases.

Several simplifications have been used to obtain an analytical expression for the current–voltage characteristics. However, the above four properties are fundamentally linked to the basic physics regarding the creation of the charges, the electrostatic interactions of the charges and the transport of the charges across the material. The exact form of the charge distribution will affect the term used in representing the electrostatic repulsion. This will change the numerical value of the equations but not the qualitative behaviour.

8. Thickness effect

A further approximation can show why the current–voltage curves appear quadratic when the film thickness is large. In equation (18) it is possible for $4jL^3/u\epsilon\epsilon_0$ to be much greater than $(kT/q)^2$. If the film thickness is 100 nm, the mobility $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and current density $10^{-8} \text{ A cm}^{-2}$, then the voltage corresponds to 6.7 mV. Since kT/q is only 25.4 mV at room temperature, it does not require a large increase in thickness or current density for

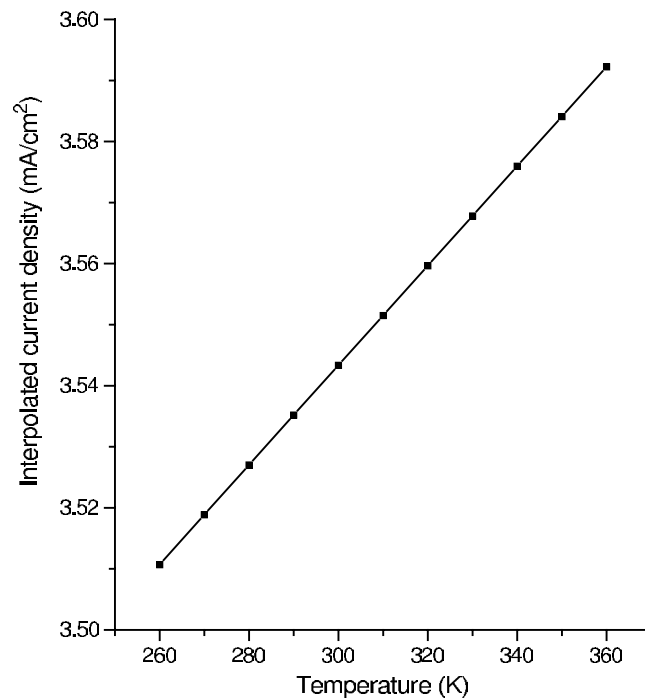


Figure 3. Current density versus temperature, at 8 V applied voltage.

the second term to dominate. When this is true, the charge density is given by equation (19). The term in the square root is the charge density, while $1/q$ times the quantity is the number density of charges. Substituting this result back into equation (17) yields, after simplification, equation (20).

$$\rho_0 = \frac{1}{q} \sqrt{\frac{j\epsilon\epsilon_0}{uL}} \quad (19)$$

$$V_t = \phi^* + \frac{kT}{q} \ln \frac{1}{\rho_m} \sqrt{\frac{j\epsilon\epsilon_0}{uL}} + 2L \sqrt{\frac{jL}{u\epsilon\epsilon_0}}. \quad (20)$$

The two different limits are seen easily now. If the thickness is sufficiently small the second term dominates, and a current that depends exponentially on voltage is obtained. At the other limit when the thickness of the film is large, the third term dominates, yielding a current that depends quadratically on the voltage and is inversely proportional to the cube of the thickness. This is a space charge regime.

9. Discussion

It has been found that the behaviour of organic light emitting diodes exhibits the four properties mentioned in section 7. The negative curvature in the log current versus voltage plots are evident in these systems [1, 23]. The linear temperature behaviour is also observed [23]. Finally, it is observed that the voltage required to drive current in the device increases with thickness [23]. This of course would not occur if the current were limited by a Schottky barrier. While it is generally observed that thin films (100 nm) exhibit a pseudo exponential current versus voltages behaviour, quadratic behaviour is observed for thicker films [13, 24]. This is in agreement

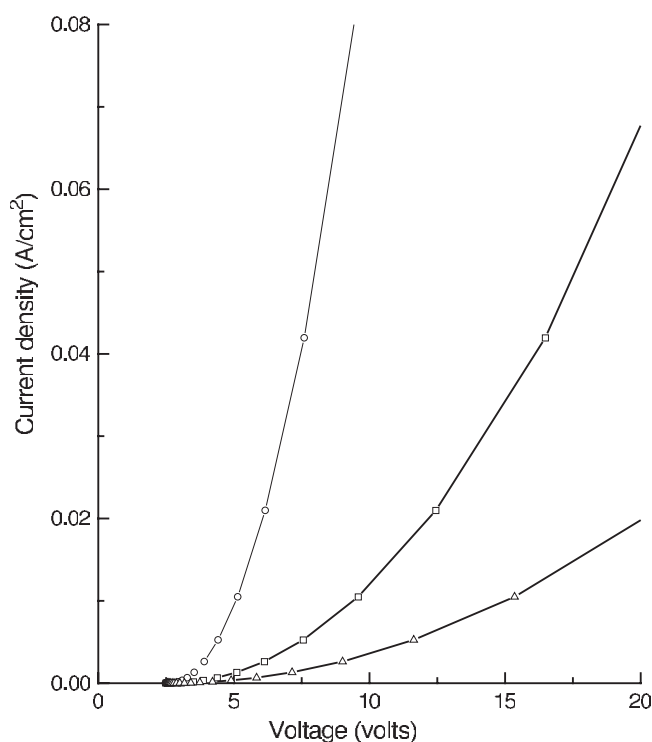


Figure 4. Current density versus applied voltage for different device thicknesses. (○) $L = 50$ nm, (□) $L = 100$ nm, (△) $L = 150$ nm.

with the results of section 8. These results assume the charge density is uniform across the material. In general the charge density will decrease across the material. This modification will be considered in a subsequent publication.

Thus, the above theory represents a novel mechanism explaining conduction in organic material that does not rely on band theory to explain the charge transport. The conventional models in OLEDs use band theory and Schottky barriers to explain the exponential current–voltage behaviour, while others use space charge effects to explain a quadratic voltage dependence. The above theory shows that the two observations are not the result of separate mechanisms of carrier transport but rather two regimes of behaviour.

In addition, the above theory correctly predicts a linear variance of current at fixed field when the temperature is varied. Conventional models of OLED operation utilizing Schottky barriers predict an exponential temperature behaviour, while tunnelling models predict no dependence on temperature. Those models based upon space charge limited conduction require that the mobility must increase linearly with temperature to explain the observation.

Finally, the electrochemical properties of molecules can now be related to their use in OLED construction. Since it is the chemical nature of a given charge transport molecule which determines whether a molecule can be oxidized or reduced [13], it is possible to understand the polarized nature of OLEDs as observed by Tang [1] with an electrochemical interpretation. Oxine (8-hydroxyquinoline) is known to form radical anions [25], while triphenyl substituted amines (TPD) are known to form very stable radical cations [26]. The molecule tris-8-hydroxyquinoline aluminium (Alq) would therefore be reduced at the cathode, while TPD would be oxidized at the anode. Since Alq cannot be oxidized nor TPD reduced, reversing the

applied voltage would not lead to current flow. It should be noted that not all molecules would behave in a similar fashion. Rubrene is known to form stable cations and anions; hence, a bilayer device composed of molecules that could be both reduced and oxidized would not be polarized.

One aspect of the electrochemical model is that it assumes that the electrodes are inert. It is possible for chemical reactions to occur at the cathode because metals are reducing agents. It is known that most unsubstituted aromatic molecules form stable radical anions in solution when alkali metals are added. Hence metals with low reduction potentials, such as aluminium, magnesium and calcium, would undergo chemical reactions. Such processes are not considered in this paper.

The power of this model is its unifying nature. Currently, electrochemical processes describe light emission in solution of aromatic molecules, Schottky barriers describe the $i-v$ relation when the same molecules are in the solid phase, while a Gaussian disorder model describes conduction processes in polymer solid state devices. Using the above lattice gas model, all three can be treated by a single formalism. The exponential $i-v$ behaviour is not a result of barrier formation or exponential mobility but rather reflects the fact that there are no intrinsic charges to conduct the current. The charges must be electrochemically generated at the electrodes, and the ΔG of the chemical reaction is the origin of this exponential dependency. Further, as more current is driven in the system, more charge accumulates which increases the energy of radical ion formation. This is the origin of the negative curvature in the $\log i$ versus v plots. The current-voltage characteristics result as an interplay between charge creation and transport. The 'built-in' potential that is added ad hoc to the Schottky models of OLEDs can be interpreted as the cell or redox potential of the system.

Most importantly, the electrochemical model explains the material choice used in OLEDs. As stated by Abkowitz: 'It is thus the chemical nature of a given charge transport molecule which determines the sign of unipolar transport' [13]. In the current semiconductor approach to OLEDs, the theory is divorced from the material. Both n-type and p-type behaviour in semiconductors are achieved through impurity doping. If a band model is used to explain OLEDs, since all molecules possess both a HOMO and LUMO it is not apparent what causes a certain material to be a 'hole' conductor. It is interesting to note that the justification for Tang's designation that TPD is a hole conductor was the paper by Abkowitz. However clearly in Abkowitz' article 'hole' conduction is used to denote an electrochemical process. Such an explanation is incompatible with the band theory definition of a hole.

10. Conclusions

In conclusion, a novel lattice gas approach to conduction in organic material has been presented. In this model, charged radical cations and anions are formed at the electrodes. The $i-v$ behaviour results from a competition between charge creation and charge transport. A simplified solution to the current-voltage relationship is obtained that agrees qualitatively with the observed OLED behaviour. The model implicitly assumes that one charge dominates the transport, that the mobility is constant, and that the electrodes are inert. The charge density is assumed to be uniform in order to obtain a closed form solution. This limit is reasonable for certain device parameters. A more detailed approach involves solving the system accounting for both electrochemical and electrostatic effects.

Acknowledgments

The authors would like to thank Dr Randy Dumont in the Department of Chemistry at McMaster University for his valuable help and insight. The research was supported financially by the Natural Sciences and Engineering Research Council of Canada.

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