Abstract

Polymer light emitting electrochemical cells (LECs) are solid-state devices containing an active layer blend of luminescent polymer, ion transport material and salt sandwiched between two electrodes. They operate on the principal of in situ electrochemical doping. Doping entails the injection of electronic charge from the electrodes, causing the reduction/oxidization of the luminescent polymer, and accompanied by charge compensation through the redistribution of salt counter-ions. Due to the high conductivity of the doped polymer, a fully turned on LEC has a dramatically reduced contact and bulk resistance. This gives the LEC certain intrinsic advantages such as balanced charge injection, low operating voltage and high quantum efficiencies, even when stable metal or symmetric electrodes are used. These properties have led to the popular assumption that the electrode work function is not a critical device parameter for LEC operation.

In this thesis, I describe my original research to determine how the electrode composition influences LEC performance. A series of sandwich and planar configuration LECs with various electrodes on identical MEH-PPV (poly[5-(2-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene]):PEO (poly ethylene oxide):LiTr (Lithium trifluoromethanesulfonate) based films are constructed. I demonstrate that the doping profile, doping propagation speed, emission zone shape, emission zone location, electro-luminescence (EL) turn-on, and EL efficiency are all strongly affected by the choice of electrode materials. LECs with asymmetrical electrodes optimized for both electron and hole injection result in the best overall performance.

Using an optimized electrode configuration, I am able to realize extremely large crown ether based planar LECs. MEH-PPV: dicyclohexano-18-crown-6 (DCH18Cr6): LiTr and 108GE:DCH18Cr6:LiTr devices with various symmetric and asymmetric electrode configurations were constructed, where 108GE is the fluorene copolymer poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-co-(2-methoxy-5-(ethylhexyloxy)-1,4-phenylene)]. I demonstrate
and image the first ever crown ether-based planar LECs with millimeter inter-electrode spacing. Due to minimal phase separation, crown ether-based LECs display highly uniform doping propagation and very smooth emission zones. Junction relaxation, de-doping and reverse bias operation experiments are also presented, and results compared to behavior in PEO based LECs. Additionally, I demonstrate that crown ether-based LECs do not exhibit frozen junction behavior at room temperature.
Co-Authorship

Some of the experimental results in Chapter 3 have been published in Advanced Materials [1] (Published online July 14th 2008 in advance of print). Figures are created by the author unless otherwise cited.
I would like to thank my supervisor Dr. Gao, without his guidance and support this project would have never happened. A special thanks to Jay Weymouth for helping me with the MATLAB® code needed to analyze the photographs in chapters 3 and 4, and Paul Pavese for helping me with my revisions. I would also like to thank all my friends and family for their support during my time here at Queens University.
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<td>108GE</td>
<td>Poly-((9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-co-(2-methoxy-5-(ethylhexyloxy)-1,4-phenylene))</td>
</tr>
<tr>
<td>DCH18Cr6</td>
<td>Dicyclohexanon-18-crown-6</td>
</tr>
<tr>
<td>DMP</td>
<td>Dimethyl Phthalate</td>
</tr>
<tr>
<td>EL</td>
<td>Electro Luminescence</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>LEC</td>
<td>Light-emitting Electrochemical Cell</td>
</tr>
<tr>
<td>LED</td>
<td>Light-emitting Diode</td>
</tr>
<tr>
<td>LiTr</td>
<td>Lithium Trifluoromethanesulfonate</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Poly-(5-(2-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene)</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly-(ethylene oxide)</td>
</tr>
<tr>
<td>PFU</td>
<td>Poly-(furan)</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLED</td>
<td>Polymer Light-emitting Diode</td>
</tr>
<tr>
<td>PPP</td>
<td>Poly-(p-phenylene)</td>
</tr>
<tr>
<td>PPS</td>
<td>Poly-(phenylene sulphide)</td>
</tr>
<tr>
<td>PPV</td>
<td>Poly-(p-phenylene vinylene)</td>
</tr>
<tr>
<td>PPY</td>
<td>Poly-(pyrrole)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
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<td>-------------</td>
</tr>
<tr>
<td>PTP</td>
<td>Poly-(thiophene)</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions Per Minute</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet Radiation</td>
</tr>
<tr>
<td>UVA</td>
<td>Ultra Violet Radiation (long wavelength 400 nm – 315 nm)</td>
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Chapter 1 Introduction

1.1 History of Organic Light-Emitting Devices

In the past twenty years, organic light-emitting devices have been the subject of intensive research, fuelled by the prospect of achieving low cost devices with good stability and performance. These devices could, in principle, feature some of the key advantages of plastics, such as low weight and flexibility unavailable to current lighting and display technology. Research in this field has focused on understanding the underlying physical mechanisms governing the device behavior and the achievement of comparable device performance with that of existing inorganic semiconductor based devices.

Organic electro-luminescence (EL) or the creation of light via electrical excitation in organic molecules was originally demonstrated by Bernanose in 1955 [2]. These devices featured organic films of gonacrin, brilliant acridine orange E or carbazole mounted on cellulose then sandwiched between aluminum and mica electrodes. When subjected to a 2000 V, 50 Hz alternating electric potential, light was observed. The 1960’s saw continued research by Pope, Helfrich and Schneider using anthracene crystals [3-5]. Upon application of sufficient voltage bias a blue light could be observed emanating from the crystals, which was identified as the fluorescence of anthracene [5]. Electroluminescence from non crystalline organic materials including amorphous polymers was also observed during this time period with weak emission stimulated by high voltage alternating potentials [6, 7] by Hartman and Armstrong and emission near break down conditions with fixed potentials [8] by Darveniza.
In the 1960’s researchers began to delve into the practical applications of organic electroluminescence as many organic molecules show very high fluorescence quantum efficiencies in the visible spectrum. The construction of anthracene based diodes [5, 9, 10], see Figure 1.1, appeared promising. However, these devices required high driving voltages \(~100\) V to achieve sufficient charge injection; therefore, the power conversion efficiency was always very low \(~0.1\%\) W/W rendering them impractical for consumer applications. In 1987 Tang and VanSlyke created organic double-layered devices, consisting of one luminescent layer (8-hydroxyquinoline aluminum (Alq₃)) the other an aromatic diamine hole transporting layer. The active double layer was sandwiched between a transparent indium tin oxide (ITO) anode and a low work function cathode (magnesium/silver alloy) to facilitate electron injection. As the injected electrons could not pass through the diamine layer, charge recombination was forced at the interface of the two organic materials and the device efficiency increased. An external quantum efficiency of 1 % (photons emitted per electron injected), luminous efficiency of 1.5 lm/W and brightness >1000 cd/m² were achieved at driving voltages below 10 V [11].

Organic films require specialized fabrication techniques such as thermal vapor deposition [11] that do not translate well to large-scale production. In contrast, the production of amorphous polymer films, which can readily be spin coated from solution, are easily scaled up through the use of existing manufacturing techniques available in the plastics industry. In the 1980’s, Partridge created the first polymer light-emitting diodes run at low voltages. These were fabricated using a polyvinylcarbazole film with a polyvinylcarbazole/tin-pentachloride hole injecting cathode and a cesium electron injecting anode. The first layer was produced via slow evaporation of cross-linked polyvinylcarbazole/tin-pentachloride from a solution of dichloromethane. Next the light-emitting layer of polyvinylcarbazole was spin coated on top [12]. The device emitted blue light and had current densities up to 1000 A/m² [12-15]
A major breakthrough came in 1990, when Burroughes et al. introduced polymer light-emitting diodes (PLEDs) based on films of amorphous semiconducting luminescent conjugated polymers [16]. Conjugated polymers have intrinsically good charge transport when compared to many other available organic materials [17-22]. The typical PLED consists of a polymer film
sandwiched between a transparent ITO hole injecting anode and an electron injecting cathode. The anode transparency allows light created in the device to escape. During operation, charges are injected from the anode and cathode by tunneling through the energy barriers at the polymer/electrode interface. These barriers are dependant on the electrode work function and existence of interfacial states (layers between the polymer and electrode) [23]. To maximize the EL, there must be not only efficient, but balanced hole and electron injection. Therefore these devices are sensitive to the film thickness and require small charge injection barriers at both electrodes. This is achieved by using very thin films and matching the work function of the cathode with the polymer’s lowest unoccupied molecular orbital (LUMO) and the anode with the polymer’s highest occupied molecular orbital (HOMO). Unfortunately, this requires the use of low work function cathode materials such as an alkali earth metals [24]. These metals are highly reactive in air and water, which make large-scale device manufacturing problematic. Much research and effort has focused on the optimization of these devices to achieve more efficient charge injection from the electrodes, higher charge carrier mobility and enhancement of radiative versus non radiative decay [25-29].

An answer to the charge injection challenges faced in the PLED was introduced in 1995 by Pei et al. [30]. This was the polymer light-emitting electrochemical cell (LEC). LECs are solid state devices consisting of an active layer blend (luminescent polymer, a salt and an ion transport material) sandwiched between two electrodes. Two models exist describing the operation of the LEC. The first proposes that, upon application of sufficient voltage, electrochemical doping occurs within the active layer, where doping in a polymer system refers to an electrochemical redox reaction, followed by the compensation of electronic charge through the redistribution of salt counter ions. N-doping occurs at the cathode and p-doping at the anode; the doped regions propagate through the bulk of the film and eventually meet to form a p-n junction,
where electroluminescence results from the radiative recombination of the injected electrons and holes in the junction region [31-34]. Since the doped polymer is highly conductive there is efficient and balanced charge injection [35]. The second model suggests that no electrochemical doping occurs. However, the ions present in the electrolyte enhance charge injection by the formation of space charges close to the electrodes [36, 37]. Both models support the observation of the accumulation of anions and cations at the electrodes upon turn on and light emission at low voltages with little dependence on the inter-electrode spacing or composition, for all colors of light.

Despite their intrinsic advantages, LECs are subject to several disadvantages such as: slow response time, poor stability at high operating voltages, hysteresis and bipolarity (the polarity of the junction is reversed under reverse bias). The solutions to many of these problems came in the form of the “frozen junction” LECs, introduced in 1997 by Gao et al.; in these devices, the light-emitting p-n junction is established then “frozen” by cooling below the glass transition temperature of the ion conducting polymer, thereby freezing all further ionic motion [38, 39]. Once the junction is fixed, the device can be operated like a traditional inorganic semiconductor LED, with almost instantaneous turn on, diode rectification and uni-polar light emission. Unfortunately, these frozen junction LECs are operated at 100 and 200 K, making them commercially impractical. The devolvement of room temperature frozen junction LECs was reported by Yu. et al. in 1998 [40], however our recent work (see Chapter 4) suggests these devices may not truly be frozen.

The end goal of efficient and practical LECs ready for consumer use will only be realized through an understanding and appreciation of the underlying physical mechanisms responsible for their behavior. In our research, the use of planar/sandwich structure LECs in combination with powerful experimental techniques such as time-lapse fluorescence imaging is used to collect data
during device operation. To give the reader a deeper understanding of the research presented in the following chapters, we use the following sections to expand upon conjugated polymers, organic electrolytes, doped polymers and the details of LEC operation focusing on the electrochemical doping model.

1.2 Fundamentals

1.2.1 Conjugated Polymers

In saturated carbon-based polymers, all electrons are in a bound state and cannot contribute to conduction, therefore these materials are electrically insulating. In comparison, conjugated polymers, which are characterized by an alternating single bond, double bond structure along the polymer backbone exhibit semiconducting behavior. Carbon atoms in the conjugated polymer backbone are sp\(^2\) hybridized and have a trigonal planar geometry. Of the 4 valence electrons available to each carbon, 3 are occupied in sigma-bonds formed between the hybridized orbitals of two neighboring carbon atoms and a hydrogen atom. The 4\(^{th}\) valence electron contained in the unhybridized p\(_z\) orbital is used to form π-bonds between the neighboring carbons. Along the polymer backbone, these molecular π-orbitals overlap leading to the formation of a delocalized π-band. It is through this band that conduction occurs [17-22] as per Figure 1.2
Examination of the electronic structure of conjugated polymers suggests metallic behavior should be observed as the delocalized orbitals have finite density of states at the Fermi level. Such a metallic polymer would have a half filled band with all carbon-carbon bonds having partial double bond character and equal length [20]. However, this is not the case because of Peierl’s instability, which states that a one dimensional system (long carbon chain) with incompletely filled bands distort to form a gap at the Fermi level [41]. In the case of conjugated polymers, a dimerization distortion occurs where neighboring CH groups move towards each other forming alternating double bonds (short) and single bonds (long) lowering the energy of the system which makes the semi-conducting state more energetically favorable than the metallic
one. The semiconducting nature of these polymers was first reported in 1961 by Hatano et al.[42].

The energy or band gap in the semiconducting conjugated polymer system is the difference between the HOMO (highest occupied molecular orbital) or $\pi$-bond and the LUMO (lowest unoccupied molecular orbital) or $\pi^*$-bond. In analogy to inorganic semiconductors, the $\pi$-bond pays the role of valence band and the $\pi^*$-bond becomes the conduction band. This energy gap varies from 0.8 - 4 eV depending on the polymer in question and encompasses the entire visible spectrum.

Due to their quasi-one dimensional structure, these polymer semiconductors are fundamentally different than conventional inorganic semiconductors. Weak inter-chain bonding allows the insertion of dopant molecules in the structure while the strong intra-chain carbon bonds ensure the integrity of the polymers. In inorganic semiconductors, charge is transported via electrons in the conduction band and holes in the valence band [17]. However in conducting polymers the chain structure leads to strong coupling of the electronic states causing conformational excitations such as solitons, polarons and bipolarons; these quasi particles are the charge carriers [17] which are more localized than in traditional semiconductors as they are confined to a single polymer chain [23].

The discussion of charge carriers must be divided into two distinct cases: polymers with a degenerate ground state such as trans-poly acetylene and those with non degenerate ground state such as PPV poly (p-phenylene vinylene) [17, 19, 20] as in Figure 1.3. In the degenerate case, charge is carried via neutral or charged solitons which create electronic states mid gap, as in Figure 1.4. These suppress inter-band transitions while those involving solitons become more favorable [17]. The soliton is not confined to a single carbon atom but has a sphere of influence
of approximately seven times the lattice constant and an effective mass of $6m_e$ [43], where $m_e$ is the mass of an electron.

Figure 1.3 Ground States of Various Polymers. A) The two degenerate ground states of trans-poly acetylene B) lower energy aromatic non-degenerate ground state of PPV C) higher energy quinoid state of PPV.

Figure 1.4 Solitons. The illustration shows the energy states caused by a) neutral b) positively charged c) negatively charged solitons and their associated chain defects on trans-poly acetylene.

In the non-degenerate case, neutral polarons, which are pairs of one negatively and one positively charged solitons, are the energetically favored carriers. Polarons carry both charge and
spin and form two energy states which are distributed symmetrically about the center of the energy gap, see Figure 1.5. Bipolaron charge carriers which become common at high levels of doping are pairs of polarons, and bipolarons have no spin [41]. Charge storage in conjugated polymers in polaron and bipolaron states is always energetically favored over occupation of extended band states [44].

![Figure 1.5 Polarons](image)

Figure 1.5 Polarons. This illustration shows the energy states and associated chain defects of a) negatively charged polaron b) positively charged polaron. When positive and negative polarons meet they form polaron excitons, the singlet is shown in c).

Understanding the intrinsic semiconducting nature of the individual polymer molecules is important, however it does not necessarily give us insight into the conductivity of polymer films, where there are thousands of intertwined polymer molecules. Here charge carriers are not truly confined to exist only on one chain as there is an inter-chain conduction. Carriers “hop” between chains where hopping is ‘phonon-assisted quantum mechanical tunneling’ [19], or tunnel between conducting segments separated by less conducting regions [41]. Hopping is a temperature dependant process. Therefore, unlike metals, an increase in the ambient temperature enhances the polymer film conductivity. Inter-chain interactions become very important as even weak chain
coupling can ensure the diffusion of charge carriers from one chain to the next [41]. If the degree of orientation in a polymer film is high, there may be “\(\pi-\pi\) stacking”, where the \(\pi\)-bonds of neighboring polymer chains lie directly on top of one another to form a lamella structure of two-dimensional conjugation, greatly enhancing film conductivity [45]. Other important factors include the conjugation length, doping level, anisotropy and for alternating current voltages the frequency [19]. Conjugation length is the average distance between chain conjugation defects. Roth et al. demonstrated for poly acetylene, a decrease in conjugation length from 100 Å to 10 Å decreased the conductivity by approximately 8 orders of magnitude [19]. Meanwhile, the conductivity can be increased by doping (adding impurities) with oxidizing/reducing agents or donor/acceptor radicals [22]. Anisotropy refers to polymer chain alignment within the film. The conductivity is greater if polymer chains are aligned parallel to, rather than perpendicular to, the direction of conduction. In the case of alternating potentials, the conductivity of these polymers shows an approximate linear dependence on the applied frequency [19].

1.2.2 Doping

The term doping commonly refers to the addition of impurities to an inorganic semiconductor system to change the electrical properties of the native material, this may come as the addition of hole (p-doping) or electron (n-doping) donor materials. In a similar fashion, a conducting or semi-conducting polymer molecule may be doped by the addition of oxidizing/reducing agents or donor/acceptor radicals [22]. These can include organic dopants, polymeric dopants or inorganic salts easily dissociated into free ions. Doping of polymers is usually achieved by direct exposure of the macromolecule to a dopant in gas or solution phase, or
by electrochemical redox reactions. Less common methods can include, self doping, radiation induced doping and ion exchange doping [22].

The LEC operates based on electrochemical doping. Upon the application of a sufficient bias, the polymer film is oxidized or reduced and subsequently p- or n-doped when counter ions from the electrolyte enter the polymer. P- and n-doping of the same luminescent polymer occurs simultaneously within the device, eventually creating a light-emitting p-n junction. The dopant counter ions do not chemically react with the polymer backbone by breaking covalent bonds. Instead, the ions are inserted between the polymer chains and can be easily removed by reversing the polarity of the applied bias.

Upon doping, conjugated polymers undergo a gradual semiconductor to metal transition [19, 20]. This was first demonstrated by Heeger et al. in 1977 with the halogenation of polyacetylene (CH)_x, the most basic conjugated polymer. Pristine films were exposed to either bromine or iodine gas, and the resulting doped films with compositions (CHBr_{0.05})_x and (CHI_{0.22})_x showed conductivities of 0.5 Ω^{-1} cm^{-1} and 38.5 Ω^{-1} cm^{-1} respectively. These results demonstrated a 4 to 7 orders of magnitude increase in the conductivity [46]. Later that year similar research by Shirakawa demonstrated films of polyacetylene doped with arsenic pentafluoride (AsF_5) with measured conductivities of 560 Ω^{-1} cm^{-1} [47]. These are compared to typical polymer conductivities of approximately 10^4 to 10^{14} Ω^{-1} cm^{-1} and typical metal conductivities of 10^4 to 10^6 Ω^{-1} cm^{-1} [17, 47] as shown in Figure 1.6. The charge carrier concentration that results from doping these polymers is directly proportional to the concentration of the dopant. Many other conjugated polymers may be chemically or electrochemically doped include poly (p-phenylene) (PPP), poly (phenylene) sulphide (PPS), poly pyrrole (PPY) poly thiophene (PTP) poly furan (PFU) and their derivatives.[17].
Doping in conjugated polymers is fundamentally different than that of inorganic semiconductors. In the latter, doping causes localized states near the conduction or valence band. However, in the conjugated polymer system through the reduction or oxidization of the polymer molecule, there is the formation of additional soliton, polaron or bipolaron states near mid gap [17, 22]. Eventually, upon heavy doping these broaden to form polaron or bipolaron bands and the result is a “metallic” polymer.

1.2.3 Polymer Electrolytes
One of the primary components of the LEC film is the polymer electrolyte. To achieve successful doping, counter ions must possess enough mobility to redistribute and compensate the charge of the reduced/oxidized polymer. Polymer electrolytes, first studied in 1973 by Fenton et al. [48], are solid ionically conducting systems composed of salts dissolved in ion-coordinating macromolecules. The behavior of polymer electrolytes lies between that of solvent free ceramic/molten electrolyte systems, where ions move about freely, and liquid/gel electrolytes, where ions undergo long range motion while solvated by low molecular weight polar molecules. In polymer electrolytes, the mechanism for ionic motion is provided by local liquid-like relaxations at the atomic level while from a macroscopic perspective, they behave much like solids. These polymer salt systems can be amorphous, semi-crystalline or fully crystalline depending on the polymer in question. In general, the crystalline phases are insulating and ion transport is confined to the amorphous regions [49].

For a polymer to successfully serve as a host, it must exhibit the following features: atoms or groups with sufficient electron donor ability to effectively coordinate with the cations from the salt, low energy barriers to bond rotation so that the chain may undergo the local relaxations that allow ion mobility, and appropriate distances between coordinating centers [50]. In these systems, the cations form weak complexes with the polymer chains while the anions show little interaction. The transport of cations involves segmental motion of the host polymer, therefore conduction is strongly temperature dependant [51]. These structural relaxations provide opportunities for ions to move between suitable low energy sites, and they also aide the short range transport of ions as they are temporarily attached to the polymer chain. At temperatures below $T_g$, the glass transition temperature of the polymer, all chain motion ceases. However, conductivity is still observed in highly doped species through activated ion transitions between ion clusters [52-54]. Argumugam et al. demonstrated in mixtures of LiPF$_6$ and PEO at high salt
concentrations > 50:1 (PEO oxygen to Li) that cation diffusion coefficients were temperature independent [52]. In general, the conductivity of polymer electrolytes is molecular weight independent. Additionally, studies in PEO have shown above the critical chain entanglement limit of 3200 monomers, the $M_w$ has no significant effect on cation mobility [50].

Polymer electrolytes show fundamentally different behavior as compared to low molecular weight liquid based electrolytes. There is a lack of convective stirring, so that upon lengthy application of voltage, very stable concentration gradients may be established within a cell. For thin films, these gradients may traverse the entire film and may be responsible for significant diffusion transport of neutral ion pairs [55]. In a liquid electrolyte, ions move while surrounded by a shell of solvent molecules. The strength of solvent-ion bonds has little impact on the ion mobility. In the polymer system, it is clear that bonds between the ions and host polymer greatly affect mobility [50]. In liquid electrolytes and in the absence of ion association, which is the clumping of adjacent salt ions, the reduction of conductivity due to the presence of a secondary ions through coulombic attraction/repulsion interactions is second order in nature. In the polymer system, secondary ions have a more pronounced effect as they form transient crosslinks between polymer chains reducing segmental motion, thereby decreasing conductivity [50].
1.2.4 Crown Ether Electrolytes

In an LEC film, the more compatible the electrolyte with the luminescent polymer the more effectively charge can be delivered to the oxidized/reduced sites on the chain [56]. In general, luminescent polymers are non-polar while solid electrolytes tend to be polar, therefore mixtures of the two are prone to phase separation [56, 57]. The production of high quality films for good device performance can therefore be problematic, and the choices of luminescent polymers available to form compatible mixtures with common electrolytes are severely limited. The first LECs were all based on high molecular weight PEO:LiTr electrolytes. Despite careful fabrication procedures and judicious choice of solvents, many PEO based devices still show significant phase separation [31, 58-60]

Crown ethers, or cyclic polyethers, featuring large planar rings with oxygen atoms pointing inward, demonstrate effective ion transport properties (as shown in Figure 1.7), which has permitted the development of organic electrolytes [61, 62]. They follow the nomenclature of y-crown-x, where y is the total number of atoms in the ring and x is the number of oxygen. The small size and non-polar nature of crown ether molecules allows them to be easily miscible in the luminescent polymer matrix. Also, crown ethers form exceptionally stable and selective complexes with alkali metal ions. This process is a balance between the intrinsic affinity (the matching of cation size and the crown ether ring diameter and charge density on metal ions) and the influence of the solvent (desolvation of the metal ion and solvation of the complex) [63]. Selectivity is caused by the close-fitting of the alkali metal ion into the hole in the middle of the ligand, the optimum ring size being such that the cation just fits into the hole [63, 64]. Therefore, ring size 15-18 solvates Na+, 18 solvates K+ and 18-21 solvates Cs+. Cations that are too large for a specific crown may form double complexes with two rings [64].
In most crown ether complexes, the bonding between the cation and ring is too strong to allow cation conduction. Therefore, in crown ether electrolytes, a crown and cation is chosen with an intentional ring mismatch allowing the cation to “hop” from ring to ring [63, 65-68]. In LiTr-based electrolytes, dicyclohexanon-18-crown-6 (DCH18Cr6) demonstrated the best performance [51]. Variations between the conductivity of films made with crown ethers of identical ring size are dependant on the nature of the substituents attached to the ring. For example for LiTr-based electrolytes featuring DCH18Cr6 versus di-tert-butyl dibenz018-crown-6, reduced performance is observed in the latter case as the benzene side groups make the ring very rigid, hindering ion conductivity [56]. Despite this optimization, the conductivity of crown ether based electrolytes is much lower than PEO based systems [56].

Films cast from solutions of luminescent polymer, crown ether and an ionic salt demonstrate excellent morphology [51, 56, 69]. It has been shown that improving the phase morphology of the LEC film leads to improvements in device performance, enhancing both the quantum efficiency and response time [56, 58]. Work by Wenzl et al.[51, 69] suggests that there still is phase separation in crown ether based devices. However, in general, these phase separated
domains are smaller and more uniformly distributed throughout the bulk of the film than in PEO based devices. This leads to more intimate contact between electrolyte and polymer.

1.2.5 Salt Requirements

In order to demonstrate successful ionic conduction, the polymer/organic electrolyte must contain a salt or other ionic species. To ensure high ionic mobility, the salt will ideally form an amorphous phase with the host molecule and must have a low dissociation energy allowing its ions to be easily incorporated into the electrolyte [62, 70, 71]. In organic electrolytes, it is the cation which is solvated by the host molecule. The interactions between host molecule and cation can be described by the hard/soft acid base (HSAB) principal [72]. The strongest chemical interactions, and hence best solvation, occur when matching hard acid with hard base or soft acid with soft base. The classification is described as follows:

1) Acid:
   a. Hard: Small cations with strongly bound valence electrons for example alkali earth metals; and
   b. Soft: Large cations with weakly bound/easily polarizable valence electrons such as: Au+, Ag+ (partially filled d- or f- orbitals).

2) Base:
   a. Hard: Ligands that are non-polarizable and highly electronegative such as ether oxygens; and
   b. Soft: Easily polarizable ligands such as thiolates (RS⁻).
Hard/hard interactions are primarily ionic and soft/soft interactions are primary covalent. In polymer/organic solvent systems, anion stability requires adequate charge dispersion. Therefore, the anion will ideally be a large polyatomic molecule with delocalized charge [72]. These can be either hard or soft bases.

1.3 The Polymer Light-emitting Electrochemical Cell

1.3.1 Operational Principals

LECs are light-emitting solid state devices featuring an active layer blend of conjugated luminescent polymer, ion transport molecule and salt sandwiched between two electrodes [30, 73, 74]. The LEC works on the principal of the in situ electrochemical doping of the luminescent polymer initiated by the application of an external voltage. Doping consists of an electrochemically induced redox reaction, followed by charge compensation by nearby ions of opposite sign [30, 32, 33, 35, 38, 39, 51, 74-77].

Upon application of a voltage bias, anions and cations from the electrolyte begin to accumulate at the electrodes. These form an electric double layer which lowers the charge injection barrier [78], as in Figure 1.8.A. At an applied voltage threshold of \( E_g/e \), where \( E_g \) refers to the \( \pi-\pi^* \) energy gap of the semi-conducting polymer, and \( e \) is the elementary charge of an electron, the onset of electronic charge injection is observed at each electrode [56, 78-80]. Holes introduced from the anode oxidize the polymer while electrons from the cathode reduce the luminescent polymer. The film remains electrically neutral as cations and anions in the electrolyte move to compensate the injected charges. This ionic redistribution during doping
leads to the generation of a small but measurable ionic current [74]. The polymer near the cathode becomes n-doped and the polymer near the anode becomes p-doped (Figure 1.8.B). P- and n-doping are intimately linked processes [78, 81], where one does not occur without the other. The exception is certain situations at $V_{\text{applied}} < E_g/e$, where unipolar doping is observed [78]. Doping dramatically increases the conductivity of the polymer causing it to undergo a gradual semiconductor to metal transition [17, 19-22, 41]. Due to the polymer’s increasing conductivity, ohmic contact begins to form at the polymer/electrode interface, further enhancing charge injection, which in turn further enhances the doping process.

P- and n-doping exhibit different velocities due to different cation and anion mobilities [77]. Despite n-doping involving the insertion of cations into the polymer matrix, its velocity is dictated by the anion’s mobility as they must move out of the way to allow n-doping to occur. Similarly, p-doping velocity is dictated by cation mobility. The p- and n-doped regions propagate through the bulk of the film eventually meeting to form a p-n junction [32] where EL then results from the radiative recombination of injected electrons and holes [31-34], as shown in Figure 1.8.C. After the junction forms, the current will now consist of ionic (doping) and electronic (recombination/diffusion) components. The current, doping level and emission zone intensity increase dramatically [32]. Upon the completion of doping, the device brightness reaches a maximum and the current plateaus. The current is now primarily electronic in nature [33]. Eventually these devices fail either due to overdoping [82] or break down of the luminescent polymer.
Figure 1.8 LEC Operation. A) Upon initial application of a voltage bias the cations and anions move towards the electrodes, forming electric double layers, which reduce the barrier for charge injection. B) At $V > E_g/e$ charge injection and electrochemical doping commences. C) The two doping fronts meet and form a p-n junction or “emission zone” where holes and electrons recombine in a radiatively.
At the junction, both singlet (S=0) and triplet (S=1) polaron-excitons are formed by the meeting of two spin ½ polarons (holes and electrons). Singlet excitons relax in a radiative manner, emitting light via fluorescence. The wavelength of the emitted light is dictated by the $\pi-\pi^*$ energy gap of the luminescent polymer. The triplet excitons usually decay via non-radiative processes, with the exception of rare triplet-triplet annihilation and intersystem crossing (spin flipping). Triplet phosphorescence in conjugated organic systems at room temperature is rare [83] unless a phosphorescent sensitizer is added to the mix [84].

### 1.3.2 LEC vs. PLED

LECs and PLEDs both feature conjugated luminescent polymers; however, they have very different operational mechanisms. The active layer of a PLED is pristine luminescent polymer [16]; there can be no electrochemical doping and charges must be directly injected into the polymer’s LUMO or HOMO. Ideally, these energy levels will be perfectly matched to the electrode work functions leading to efficient and balanced charge injection. However, in reality, finite energy barriers of unequal magnitude exist at both the anode and cathode. To minimize the barriers, a low work function cathode such as an alkali earth metal [23, 24] and a high work function anode must be used. In comparison, there is ohmic contact at the LEC polymer/electrode interface due to the high conductivity of the doped polymer, thereby minimizing the significance of the electrode composition. Therefore, LECs have intrinsically balanced hole and electron injection and higher quantum efficiencies [75].

PLEDs are very sensitive to the inter-electrode spacing, and must have thin active layers or the series resistance of the device quickly becomes too large for efficient charge injection [23].
Charge capture in such thin layers is problematic. One of the carriers must have much lower mobility than the other, to ensure sufficient local charge density to allow charges to pass within a collision radius of each other [23]. The use of double layer structures that introduce artificial barriers for charge transport has been very effective at controlling and balancing electron and hole injection [11]. Unfortunately, this makes the device architecture and consequent manufacturing more complex.

As in LECs, electrons and holes meet to form polaron-excitons in the active layer of the PLED. These excitons can be triplets (S=1) or singlets (S=0), with only singlets relaxing in a radiative manner. PLEDs have a fast response times as there is no junction to form. The emission color of the PLED is dictated by the choice of polymer. Unfortunately, each unique macromolecule will have slightly different HOMO and LUMO levels, implying the need to optimize the PLED’s electrodes for each color [75]. PLEDs currently have greater stability and longer lifetimes than LECs as they do not suffer from overdoping induced failure. Instead, the primary failure mechanism is photo-oxidization of the luminescent polymer caused by the ingress of oxygen or water through pin holes in the cathode or encapsulation material [23]. Some of the major differences and similarities of LECs and PLEDs are summarized in Table 1.1.
<table>
<thead>
<tr>
<th>Property</th>
<th>PLED</th>
<th>LEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active layer composition</td>
<td>Conjugated polymer</td>
<td>Blend of conjugated polymer and electrolyte</td>
</tr>
<tr>
<td>Sensitivity to active layer</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>thickness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sensitivity to electrode work</td>
<td>High</td>
<td>Relatively low</td>
</tr>
<tr>
<td>function</td>
<td></td>
<td></td>
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<tr>
<td>Quantum Efficiency</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Operating Voltage</td>
<td>High for wide gap material</td>
<td>Low</td>
</tr>
<tr>
<td>Response speed</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Light-emitting region</td>
<td>Wide</td>
<td>Narrow</td>
</tr>
<tr>
<td>Lifetimes</td>
<td>&gt;10,000 hrs</td>
<td>&lt;1,000 hrs</td>
</tr>
</tbody>
</table>

Table 1.1 Comparison of PLED and LEC Characteristics. Adapted from Q. Sun et al. [85]

1.4 The Planar LEC

Due to the high conductivity of doped conjugated polymers, LECs are extremely insensitive to inter-electrode spacing and can be operated in open planar configuration [32], see Figure 2.1. This architecture, although of limited commercial value, is very attractive to the researcher as it allows the direct observation of the active layer during operation providing unprecedented spatial and temporal resolution. Some other advantages include, less electrode induced charge absorption and EL quenching, also the polymer chains can be mechanically aligned in the direction of current flow [86]. First demonstrated by Dick et al. in 1996 [74], the utility of the first planar LECs were limited, due to their micrometer inter-electrode spacing [74, 78]. Recently, these devices have been demonstrated in extremely large planar form [33, 35, 87, 88] with the largest having an inter-electrode spacing of 11 mm [32]. To turn on these extremely large devices in a timely manner, a high operational voltage is required as the initially undoped film possess a large series resistance [88].
A powerful technique used to study planar configuration LECs is time-lapse fluorescence imaging. A material that demonstrates EL must also exhibit photoluminescence (PL). PL is the process whereby irradiation by incident light causes the material to remit light of longer wavelength via fluorescence or phosphorescence. PL is a more efficient process than EL, since electron/hole pairs are formed in close proximity making radiative recombination favorable [77]. An undoped LEC film exhibits strong PL under UV illumination. Upon doping, the PL is strongly quenched due to the formation of additional energy states within the band gap of the polymer, even at levels well below changes observable by optical absorption [32, 74]. A time-lapse digital camera connected to a 10X optical microscope, is sufficient to capture high-resolution images of the planar LEC. Through observation of PL, PL quenching and EL, the n- and p-doping velocity, uniformity, density, and relaxation as well as emission zone shape/position may be studied [32, 33, 35, 87]. This technique cannot be used in sandwich configuration LECs as the device thickness is typically on the order of the wavelength of visible light [35].

The use of extremely large planar LECs has allowed detailed study of the doping process. It was determined through direct observation that p- and n- doping fronts propagate at constant velocity until they meet to form a p-n junction [33]. Additionally, these velocities demonstrate a linearly dependence on the applied voltage and exponential dependence on temperature [88]. Small but constant redox induced currents were measured in the devices during doping, suggesting that prior to junction formation, the redox reactions occur mainly near the doping frontiers [33]. Following junction formation, it was observed that the current and doping level increase dramatically and is visible by an increasing level of PL quenching in both the p- and n-doped regions [33].
Photographs of the emission zone show it represents only a small region of the active film ~5-10% of its absolute size [87]. This zone has a very jagged shaped caused by phase separation in the LEC blend [87] or electrode imperfections and generally forms closer to the cathode [32, 33, 77, 78] as seen in Figure 1.9. Its relative position may be adjusted by the choice of salt [77]. The off center position was originally thought to be a product of the mobility asymmetry of holes and electrons in the luminescent polymer matrix but is actually due to uneven p- and n- doping velocities [32]. The more centered the emission zone the greater the device stability and efficiency [77].

![LEC Emission Zone](image)

Figure 1.9 LEC Emission Zone. An photograph of the emission zone in a MEH-PPV/PEO/LiTr blend LEC. The electrodes have been shown in false color for clarity.

LEC s are frequently operated in what is known as dynamic junction mode. Upon removal of the applied bias, light emission ceases, and the p- and n- doped regions retreat until eventually undoped equilibrium is restored. In large planar LECs, this is observed by the distinctive retreat of PL quenching and the formation of a bright, undoped (unquenched) intrinsic region where the junction used to be. When reverse bias is applied to a dynamic junction LEC, doping quickly
retreats and will reemerge from the opposite electrodes, eventually forming a new emission zone [33, 34]. It is observed that p-doping retreats more slowly than n-doping. This doping/relaxation process may be cycled many times [38].

Unfortunately the dynamic junction is the cause of many of the LECs intrinsic disadvantages, such as slow response times and poor stability caused by overdoping (degradation) when the device is operated at voltages above the electrochemical stability threshold of the polymer/electrolyte/electrode [39, 40]. In 1997 Gao et al. introduced “frozen junction” LECs. Here, the junction is formed at elevated temperatures, then the device is quickly cooled below the lowest thermal transition of the ion conducting material, thereby freezing ionic motion; bias can now be removed and the junction will not relax [38]. These frozen junction LECs in extremely large planar form have been used to demonstrate controlled doping relaxation. Here a freeze, thaw, freeze process is used to generate a small intrinsic region between the p- and n-doped regions, causing dramatic increases in EL efficiency [89]. Unfortunately, early frozen junction LECs were run at temperatures below 200 K making them somewhat impractical for consumer applications. In 1998 Yu et al reported room temperature frozen junction LECs based on crown ether electrolytes [40]. However due to the low ionic mobility of LEC crown ether blends, inter-electrode gaps in planar configuration exceeding 50 μm have never been demonstrated [86].
1.5 Scope and Motivation

1.5.1 Motivation

In the preceding introduction, I have shown that the fundamental operating mechanism of LEC is that of in situ electrochemical doping and the formation of a light-emitting p-n junction. As a result of doping, a fully turned on LEC has dramatically reduced contact and bulk resistance. This is responsible for the LEC’s extreme insensitivity to the inter-electrode spacing and a host of other unique device characteristics. Unlike PLEDs, LECs exhibit very low operating voltage and high quantum efficiency even when an air stable metal, such as aluminum, is used as an electron injector or when identical electrodes are used. This has led people to rule out electrode work function as a critical device parameter for LEC operation. Not surprisingly, upon review of the literature, we find very few investigations into the effects of electrode composition on LEC performance [90-96]. This belief, however, contradicts the very nature of electrochemical doping, which is central to LEC operation. In order for the luminescent polymer in an LEC to be electrochemically doped, two conditions must be met. First, there must be injection of electronic charges across the electrode interface that leads to the oxidation or reduction of the polymer. Second, there must be redistribution of counter ions in the polymer electrolyte that leads to the stabilization/compensation of the injected electronic charges. A doped polymer is electrically neutral but highly conductive due to the externally injected, stabilized excess charges. While we do expect charge injection into a highly doped polymer to be ohmic and therefore insensitive to electrode work function, this is not true during the turn on process of an LEC when the polymer film is highly insulating due to incomplete doping. We therefore postulate that the
electrochemical doping process could be very well injection-limited during the LEC turn on process, and as a result, highly sensitive to the composition of the electrode materials. *It is the purpose of this thesis to test this hypothesis by systematically studying the effect of electrode composition on the various LEC performance parameters.*

**1.5.2 Scope**

Chapter 2 gives a detailed description of the experimental methods used in this work. The experimental work involves the fabrication of polymer light-emitting electrochemical cells in both sandwich and planar configuration, as well as the testing of these devices using a variety of electrical and optical techniques. Also introduced in this chapter are major pieces of equipment and instruments central to the processing and testing of the devices.

Chapter 3 presents an investigation into the effects of electrode composition on LEC performance. A series of sandwich and planar MEH-PPV:PEO:LiTf LECs with various combinations of gold, calcium, silver and aluminum electrodes are constructed. The devices are characterized by time-lapse fluorescence imaging as well as current and electroluminescence intensity measurements. From the data, key performance parameters such as turn on speed, EL efficiency, doping propagation speed, emission zone position are determined and compared. Our results clearly demonstrate that nearly all aspects of the LEC operation are strongly affected by the choice of electrode materials. We discuss the observed effects and explain them in terms of the electrode work function difference, which affects doping initiation and all subsequent device behaviors.

Chapter 4 describes the realization of extremely large crown ether based planar LECs using the optimized electrode configuration developed in Chapter 3. LECs based on MEH-
PPV:DCH18Cr6:LiTr and 108GE:DCH18Cr6:LiTr with various symmetric and asymmetric electrode configurations are constructed. For the first time crown ether based planar LECs with millimeter inter-electrode spacing have been demonstrated and imaged. Due to minimal phase separation in the LEC film, crown ether based LECs display highly uniform doping propagation and a very smooth emission zone highly distinct from PEO-based LECs. Junction relaxation, de-doping and reverse bias operation experiments are also presented and results are compared to behavior in PEO based LECs.

Finally in Chapter 5 conclusions are drawn and some future work is outlined.
Chapter 2 Experimental Methods

2.1 Materials

2.1.1 Substrates

In this work, sapphire, ITO coated glass or ordinary glass substrates are used as a support medium for LECs. LECs are fabricated in either sandwich or planar configurations as per Figure 2.1. In the sandwich configuration, the active polymer layer is “sandwiched” between two conducting electrodes across which a potential is applied. One of these electrodes is transparent thereby allowing light created in the device to escape. The simultaneous requirement of transparency and electrical conductivity is satisfied with either glass coated with a thin semi-transparent metal electrode deposited via thermal evaporation or patterned ITO coated glass. For our experiments, 150 mm x 150 mm x 1.1 mm ITO coated (sheet resistance 20±5 Ω/square) Corning 1737 aluminisilicate glass plates were obtained from Delta Technologies Limited and subsequently cut into 15 mm by 15 mm squares. In comparison, the planar device has both electrodes deposited on top of the polymer film. The active area lies in the region of film between the two electrodes, and light is emitted normal to the surface without passing through one of the electrodes. In these devices, only the LEC film is in direct contact with the substrate. Synthetic sapphire squares, of dimensions 15 mm x 15 mm x 1 mm purchased from the Swiss
Jewel Company, make an ideal substrate as it is insulating, mechanically robust, chemically inert and transparent. All sapphire substrates are recycled and reused after thorough cleaning.

Figure 2.1 Planar and Sandwich Device Structures. An illustration depicting the two possible device configurations; sandwich devices represent the conventional architecture used in a majority of studies and planar devices which may have inter-electrode spacing of several millimeters allow the direct imaging of the dynamic LEC operating processes.
2.1.2 LEC films

The luminescent polymers used in this work are poly[5-(2-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV) and a fluorene copolymer (108GE, poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-co-(2-methoxy-5-(ethylhexyloxy)-1,4 phenylene)], both are end capped with dimethyl phthalate (DMP). These polymers were graciously provided by American Dye Source Incorporated. MEH-PPV is a conjugated polymer featuring a photoluminescent maximum of 585 nm (red/orange emitter) available in various molecular weights. In this study we used one batch with low molecular weight ($M_w$) (~500,000 g/mol) and one batch of high $M_w$ (~1,000,000 g/mol). In general, the higher molecular weight MEH-PPV produced films with superior morphology. By comparison, 108GE is a conjugated fluorene copolymer with a photoluminescent maximum of 539 nm (green emitter). The 108GE used in this work had $M_w$ of 157,000 g/mol with a polydispersity (ratio of $M_w$ to the number average molecular weight $M_n$) of 4.5. The structures of these two polymers are shown in Figure 2.2.
Figure 2.2 The Structure of Various Luminescent Polymers. The above figure shows the chemical structure of the two luminescent polymers used in this study; ADS108GE and MEH-PPV (ADS100RE). Both feature an alternating single and double bond structure along the polymer backbone, which through the overlap of adjacent π-bonds, allows the transport of electronic charge. The lipophilic side groups allow the polymer to dissolve in organic solvents.
Ion transport materials PEO with $M_w$ 2,000,000 g/mol, and DCH18Cr6 (mixture of cis-syn and cis-anti - cis-dicyclohexano-18-crown-6) were purchased from Sigma Aldrich as was salt Lithium trifluoromethanesulfonate (LiTr). Cesium perchlorate ($\text{CsClO}_4$) was obtained from Alfa Aesar. The structures of these materials are shown in Figure 2.3. Solvents used included reagent grade cyclohexanone, acetone and iso-propanol. All were purchased from Fisher Scientific while distilled water was obtained from an in house still.

**Ion Conductors**

**Polyethylene oxide**

![Polyethylene oxide](image)

**Dicyclohexano-18-crown-6**

**Salts**

**Lithium trifluoromethanesulfonate**

![Lithium trifluoromethanesulfonate](image)

**Cesium Perchlorate**

![Cesium Perchlorate](image)

Figure 2.3 Chemical Structures of Electrolyte Ingredients.
Metallic electrodes in this work were all fabricated using thermal evaporation through shadow masks. Metals used in this process include 99% pure calcium (Ca) purchased from Sigma Aldrich and 99.99 % pure Chromium (Cr) pellets purchased 99.99% pure gold (Au), 99.99% pure silver (Ag) and 99.99% pure aluminum (Al) wire from the Kurt J. Lesker Company.

2.2 Device Processing

2.2.1 Substrate Cleaning and Preparation

All substrates were cleaned and prepared prior to use. The preparation method depends on the substrate in question. Substrate cleaning involves the use of chemicals that pose significant health risks, therefore all procedures were performed in a fume hood or glove box while wearing appropriate personal protective equipment as outline on the material safety data sheets.

Large plates of ITO coated glass 150 mm X 150 mm X 1.1 mm were patterned by placing strips of scotch tape at approximately 10 mm intervals. The substrate is coated with zinc powder and placed in a 37% HCl and distilled water bath. Through manual abrasion and chemical reaction the ITO in the exposed regions was removed. The etched sample was rinsed thoroughly with water and the tape removed leaving a patterned surface. The large plate was cut into smaller usable samples with a hand held glass cutter. Each sample had dimensions of approximately 15 mm x 15 mm. Samples were cut such that approximately half of the substrate was coated with ITO and the rest was exposed glass. Following cutting, the substrates were put into a clean teflon holder and sonicated in an acetone bath for 15 min. This was followed by 15 min of sonication in
an isopropanol bath. The substrates were then rinsed with fresh isopropanol and blown dry with oil free nitrogen gas. Finally they were placed in an Ultra Violet Ozone Cleaning Systems T10X10 UV ozone cleaner for 10 min before being transferred to the glove box for use.

Glass sheets were cut into 15 mm x 15 mm squares with a hand held glass cutter. The pieces were placed in a teflon sample holder and immersed/sonicated in an acetone bath for 15 min. This was followed by an additional 15 min of sonication in an isopropanol bath after which they were rinsed with clean isopropanol and blown dry with oil free nitrogen gas. Once dry the substrates were transferred to the UV ozone cleaner for 10 min. The clean samples were then transferred to the glove box.

Sapphire substrates were recycled and therefore, must be thoroughly cleaned between uses. Clean substrates were essential for obtaining reliable and repeatable experimental data. Organic surface contaminants may react chemically with the polymer film or electrode material while metallic/insulating particles may contribute to unusual film morphology and device performance. First, substrates were wiped with a lint free cloth and isopropanol to manually remove as much surface contamination as possible. They were then placed in a clean teflon substrate holder and were treated in the following chemical baths and rinses:

- Bath: Cyclohexanone 1: 15 min sonication.
- Rinse: Acetone followed by isopropanol
- Bath: Aqueous sodium hydroxide/ isopropanol, sonication: 15 min followed by ~1 hr soaking time to remove residual electrode material.
- Bath: Distilled water, 15 min sonication (to remove residual sodium hydroxide).
- Rinse: Acetone
• Bath: Cyclohexanone 1: 15 min sonication.
• Bath: Cyclohexanone 2: 15 min sonication.
• Bath: Cyclohexanone 3: 15 min sonication.
• Bath: Cyclohexanone 4: 15 min sonication.
• Bath: Acetone: 15 min sonication
• Bath: Isopropanol: 15 min sonication
• Rinse: isopropanol

After the final rinse, substrates were blown dry using oil free nitrogen gas. Substrates were subjected to a visual inspection and then they were transferred to the UV ozone cleaner for 10 minutes (final removal of any residual organics). Finally the clean substrates were transferred to the glove box and stored in a covered Petri dish for use.

2.2.2 Solutions

LEC films were spin cast from solutions containing a luminescent polymer, an ion transport material and a salt. First, individual master solutions of both luminescent polymer and polymer electrolyte were created. Luminescent polymer master solutions were created by weighing out an appropriate amount of MEH-PPV or 108GE into a vial, which was then carefully transferred into the glove box. Cyclohexanone was added into the vial to dissolve the contents. The polymer (g) to solvent (ml) ratio of MEH-PPV and 108GE solutions were 0.01 and 0.02 respectively. Next, the electrolyte master solution which contained the ion transport polymer/molecule and salt was created. Appropriate weights of each of the two materials were
weighed out in a vial and transferred to the glove box. Cyclohexanone was added such that the mass of ion transport material (g) to volume of solvent (ml) was equal to 0.02. All master solutions were allowed to stir for a minimum of 12 hours while being heated to 50 °C to ensure thorough dissolution and mixing of all components prior to use.

LEC solutions, which were used for spin coating, were created from the master solutions. An electrolyte and luminescent polymer solution were selected; a volume of each constituent was pipetted into a common vial such that the final mass ratio of polymer and ion transport material was identical. The LEC blend was allowed to mix on a magnetic stirring hotplate for a minimum of 12 hours prior to first use. The compositions and concentrations of test solutions used in this work are presented in detail in Table 2.1
<table>
<thead>
<tr>
<th>Name</th>
<th>Master Polymer Solution</th>
<th>Master Electrolyte Solution</th>
<th>Final Ratio and Composition</th>
<th>Mass Polymer (g)/ Volume Solvent (mls)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ø</td>
<td>1.00 % MEH-PPV in cyclohexanone $\text{M}_w$ n/a</td>
<td>1.99% PEO :LiTr in cyclohexanone $\text{M}_w$ PEO: 2,000,000 g/mol</td>
<td>5.1:5.1:1</td>
<td>0.67%</td>
</tr>
<tr>
<td>N</td>
<td>2.13 % ADS108GE In cyclohexanone $\text{M}_w$ 108GE: 157,000 g/mol</td>
<td>2.00% DCH18Cr6:LiTr in cyclohexanone</td>
<td>5.4:4.9:1</td>
<td>1.06%</td>
</tr>
<tr>
<td>T</td>
<td>1.00% MEH-PPV In cyclohexanone Low $\text{M}_w$ MEH-PPV</td>
<td>2.00% DCH18Cr6:LiTr in cyclohexanone</td>
<td>5.1:4.9:1</td>
<td>0.67%</td>
</tr>
<tr>
<td>G</td>
<td>2.13 % ADS108GE In cyclohexanone $\text{M}_w$ 108GE: 157,000 g/mol</td>
<td>2.00% DCH18Cr6:CsClO$_4$ in cyclohexanone</td>
<td>5.4:5.1:1.5</td>
<td>1.06%</td>
</tr>
<tr>
<td>M</td>
<td>2.30% MEH-PPV In cyclohexanone High $\text{M}_w$ MEH-PPV</td>
<td>2.00% DCH18Cr6:CsClO$_4$ in cyclohexanone</td>
<td>5.1:5.1:1.5</td>
<td>1.00%</td>
</tr>
</tbody>
</table>

Table 2.1 LEC Solution Compositions

### 2.2.3 Device Fabrication

The entire device fabrication procedure was completed in a nitrogen filled M-Braun Glove box with a built in evaporator (Figure 2.4).
41

Figure 2.4 Glove Boxes. All device fabrication was completed in the above glove box system. The left hand box was used for solution preparation and spin coating while the right box was used for thermal evaporation and device storage. The two boxes are connected via a small antechamber allowing sensitive material to be transferred from on box to another without exposure to the environment.

2.2.3.1 Planar Devices

The following procedure was used in the preparation of the planar devices:

1. An LEC test solution was chosen and allowed to stir for a minimum of 3 hours prior to use, to ensure the thorough mixing of the blend;

2. Spin Coating: 80 μL of LEC solution was pipetted carefully onto a sapphire substrate and allowed a few seconds to spread. The substrate was rotated on a Chemat Technology
KW-4A spin coater at 1500 RPM for 1 minute to form a thin uniform polymer film. This was immediately followed by additional rotation at 2500 RPM for two minutes to facilitate drying. Substrates were then left on a hot plate at 50 °C overnight to complete the drying process;

3. Annealing (PEO-based LEC films only): Films were annealed on a hot plate at 400 K for 10 minutes and then quenched by quickly transferring to a room temperature copper heat sink; and

4. Evaporation:

   - Symmetric Electrodes: Electrode material was deposited on top of the dry polymer film by thermal evaporation through a shadow mask. The electrode thickness depends on the metal, 200-150 nm for Ca, 100 nm for both Ag and Al and 30-40 nm for Au. A tungsten basket or filament was used to heat the metals.

   - Asymmetric electrodes: Electrode thicknesses are as for symmetric devices. The evaporation was done in a two step process (Figure 2.5). In step 1, the first metal was evaporated while selectively blocking either the center or outer two electrodes with strips of metal. Substrates and masks were then removed from the evaporator, and the masks were switched between substrates to expose new regions film and protect the existing electrodes. In step 2, everything was placed back in the evaporator, and the second metal was evaporated. This process has now been retired as we have recently procured new asymmetric shadow masks.
Figure 2.5 Asymmetrical Evaporation. An illustration depicting the asymmetrical electrode evaporation process. In step one the first metal was deposited by evaporation through a shadow mask while selectively blocking either the center or two outer electrodes. The masks are then switched between substrates and the second metal is deposited in step 2.

2.2.3.2 Sandwich Devices

The following procedure was used in the preparation of the sandwich devices:

1. An LEC test solution was chosen and allowed to stir using a magnetic stir bar and stir plate for a minimum of 3 hours prior to use. This ensured the thorough mixing of the blend;

2. Substrates: either a 1.5 cm by 1.5 cm glass or ITO coated glass substrate was chosen;
3. Bottom electrode: For ITO coated glass substrates, the ITO served as the bottom electrode. For plain glass, a semi-transparent electrode was created by thermally evaporating a thin layer of chromium (3 nm), followed by 10 nm of gold through a shadow mask;

4. Spin Coating: 80 μL of LEC test solution was pipetted carefully onto the electrode coated substrate and the solution was given a few seconds to spread. It was then rotated on a spin coater at 1500 RPM for 1 min followed by an additional rotation at 2500 RPM for 2 min. Substrates were left on a hot plate at 50 ºC overnight to dry; and

5. Evaporation of top electrode: Aluminum (100 nm) or Calcium (150 nm) electrodes were deposited on top of the dry polymer film by thermal evaporation through a shadow mask.

2.3 Device Characterization

Prior to testing, the outside edges of the film were scraped off the substrate, to ensure the film and devices were electrically isolated from the test equipment.

Planar devices were tested in a Cryo-Industries microscopy cryostat with a 1.5 mm thick/24 mm diameter quartz window with a custom built sample holder (Figure 2.6). The small size of the cryostat allows it to be transferred directly into the glove box through the antechamber. In this way, the sample may be loaded into the cryostat inside the glove box ensuring that there is no possibility of oxygen or water contamination of the sensitive luminescent polymers. The cryostat with sample was sealed and removed from the glove box and the entire apparatus was transferred to the testing station and promptly evacuated to a pressure of approximately 5.0 X10⁻⁵ torr by a BMH 70 Dry oil-free turbo pump. The cryostat has rigid front and rear supports, and it was
secured to the optical table during operation to eliminate drift or vibrations. The cryostat has a wide range of operational temperatures from 4 to 500 K, by using liquid nitrogen or helium as coolant, which is delivered through a vacuum insulated transfer line. Temperature control is automated and precision of ±0.01 K is easily achieved through the use of small heaters attached to the sample holder and cold finger. Given that LEC frozen junctions can be realized at temperatures above 100 K the cryogen of choice in our lab was liquid nitrogen.

Figure 2.6 Microscopy Cryostat
A Nikon D200 digital camera was used to image PEO-based devices and a Q-imaging camera for crown ether based devices. Both cameras were attached to a Nikon fluorescence microscope and used to record time lapse photographs of the devices during operation. A mercury lamp fitted with a UV2A-DM400 330-380 nm UVA filter supplied illumination. A Keithly 237 High Voltage Source Measurement Unit was used to drive the devices while simultaneously measuring the current. For devices that were not imaged, an amplified Hamamatsu photodiode (SC2281-01) connected to a Keithley 2010 Multimeter was used to measure the relative EL intensity. All the above instrumentation was interfaced to a computer and the data was recorded using Labview (Figure 2.7).
Figure 2.7 Planar Device Testing
Sandwich devices were tested in the glove box at room temperature. They were attached to a specialized device holder enclosed in a small test box. The box effectively blocked out any ambient light during operation. Implanted in the box was a Hamamatsu photodiode (SC2281-01) used to measure the relative EL. A Keithly 238 Source Measurement Unit was used to drive the devices while simultaneously measuring the current.
Chapter 3 The Effects of Electrode Materials in PEO based LECs

3.1 Introduction

Electrochemical doping, which is a combination of an electrochemically induced redox reaction, followed by compensation by a nearby ion of opposite sign, is central to LEC operation [30-33, 35, 38, 39, 51, 74-77]. P-doping involves the injection of holes from the anode into the polymer’s HOMO, oxidizing the macromolecule while anions compensate the charge; conversely, n-doping involves the injection of electrons from the cathode into the polymer’s LUMO, reducing the macromolecule while cations compensate the charge. The p- and n-doped regions grow in size eventually meeting to form a p-n junction from which light is emitted. It is well documented that upon doping, the conductivity of conjugated polymers rises dramatically. As the doping level continues to increase, they undergo a gradual semi-conductor to metal transition [19-22, 41]. High levels of doping are easily achieved in LECs as the electrolyte typically has a high degree of ion mobility and the salt concentration is approximately 10 % by weight of the total film composition [32, 77]. In the heavily doped regime, the “metallic”-polymer/electrode interface behaves as a metal/metal interface and charge injection is essentially ohmic, as the Schottky barrier becomes thin enough for charge to tunnel through. Consequently, unlike PLEDs the performance of LECs is not critically dependent on the energy gap between the electrode work functions and polymer HOMO/LUMO. Therefore, these devices work at low operating voltages, in a single layer configuration, with stable metals as electrodes and in symmetric configurations [91].
It is therefore not surprising that there had been few investigations into the effects of electrode composition on LEC performance [90-96]. Research has been limited to comparisons between two different materials [91, 92], or systems where ionic concentration or doping is low [93]. Comparison studies have generally focused on the role of the cathode, as PPV and its derivatives are largely p-type materials, namely, hole mobility greatly exceeds electron mobility in the polymer matrix [97]. These works suggest optimization of the cathode will help improve the less favored electron induced n-doping [74]. In 2003, Sun et al. [91] demonstrated that a low work function cathode, such as barium, improved device performance [91]. Other studies have focused on cathode induced device degradation [94, 95] and the electrochemical reduction of cathodic materials [96]. Work by Shin et al demonstrated the choice of anode material was shown to influence the onset of p-doping [92]. In general however, anode investigations have largely focused on performance gains reached by the careful surface preparation of ITO through solvent cleaning, hydrochloric acid or oxygen plasma treatment. These methods effectively increase the ITO work function by making a smoother surface for more intimate polymer/electrode contact with lower sheet resistance, higher polarity and higher total surface energy [90, 91].

In the literature, there is a distinct lack of a systematic study on the influence of electrode composition on the performance of LECs, yet there is the often ubiquitous assumption these effects can be neglected [30-33, 35, 38, 39, 51, 74-77]. In this work, we investigated the validity of this assumption. A series of sandwich and planar configuration LECs with various combinations of gold, calcium, silver and aluminum electrodes on identical MEH-PPV (poly[5-(2-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene]):PEO (poly ethylene oxide):LiTr (Lithium trifluoromethanesulfonate)-based films were constructed. In striking contrast to what was previously believed, we demonstrated that the doping profile, doping propagation speed, emission
zone shape, emission zone location, EL turn-on, and EL efficiency are all strongly affected by the choice of electrode materials. Just as in PLEDs, LECs with asymmetrical electrodes optimized for both electron and hole injection resulted in the best overall performance. We explain the observed effects in terms of the electrode work function difference, which affects doping initiation and all subsequent device behaviors.

3.2 Experimental Details

For this study planar LECs with electrode length of 8 mm and an interelectrode spacing of 1 mm were fabricated using test solution Ø (Table 2.1) a MEH-PPV:PEO:LiTr blend. These devices featured annealed LEC films 310 ± 7 nm thick, as determined by profilometry, with the following symmetric and asymmetric electrode configurations Al-Al, Au-Au, Ca-Ca, Ag-Ag and Ca-Au. The extremely large planar LECs offer unprecedented spatial and temporal resolution for the imaging study of dynamic LEC processes [32, 33, 77, 87, 98-100]. Planar devices were operated at 315 K and 250 V applied bias.

To confirm observed results were not exclusive to LEC of planar configuration, sandwich devices were fabricated on 1.5 cm by 1.5 cm glass substrates coated with semi transparent chromium (3 nm) and gold (10 nm) bilayer electrodes. An LEC film was deposited on top via spin casting, using the same method and solution as described for planar devices, followed by an identical drying and annealing procedure. Calcium electrodes 200 nm thick were deposited on top of the film creating a device with an active area of approximately 0.05 cm². Devices were tested in the glove box at room temperature.
3.3 Planar Cells-Results and Analysis

Figure 3.1 displays the doping profiles of these devices under UV illumination 18 seconds after the application of a 250 V bias. Note the devices shown in Figure 3.1.5 and Figure 3.1.6 are identical Au/polymer blend/Ca devices that differ only in the polarity of voltage bias. In each device, the undoped film appears as a red expanse located between the two electrodes. The color results from the photoluminescence (PL) of MEH-PPV under UV illumination. The dark profiles radiating from the various electrodes correspond to p- or n-doped regions whose PL is partially quenched. P-doping, which originates from the positively biased top electrodes in all six devices, causes heavier PL quenching than n-doping [33].

Figure 3.1 clearly shows that in devices with symmetric electrodes, p-doping from Au anode (Figure 3.1.1) is both faster and more uniform than from Ca anode (Figure 3.1.2). In the Ca-Ca device p-doing is fan-shaped and sporadic. Although the most prominent “fan” reached nearly the same distance as the p-doping in the Au-Au device, the average p-doping propagation speed in the Ca-Ca device is much lower than in the Au-Au device. The p-doping from the Al-Al (Figure 3.1.3) device and the Ag-Ag (Figure 3.1.4) device are similar. They are less uniform than that of the Au-Au device but are much faster and cover a larger area than in the Ca-Ca device.

N-doping profiles, on the other hand, appear to differ very little in the four devices with symmetric electrodes. This is in large part due to the generally much slower and more uniform n-doping propagation in extremely large MEH-PPV:PEO:LiTf devices [32, 33, 87, 98, 99, 101]. Closer inspection, however, shows that n-doping in the Ca-Ca device (Figure 3.1.2) is approximately 20-30 % faster than in the Au-Au device (Figure 3.1.1). The most significant difference in the doping profile is observed in the Au-Ca devices. The asymmetric high-low work function electrodes of these devices resemble that of a PLED [102]. Under forward bias
(Au positive, Ca negative), both p- and n-doping are the fastest and most uniform among all devices (Figure 3.1.5). Under reverse bias, both p- and n-doping are the slowest and most uneven.

Figure 3.1 The Doping Profile of Six 1 mm Planar LECs Imaged Under UV Illumination. Electrode configurations are as follows: (1) Au-Au, (2) Ca-Ca, (3) Al-Al, (4) Ag-Ag, (5) Au-Ca under forward bias (Au wired positive), and (6) Au-Ca under reverse bias (Ca wired positive). Images are shown 18 seconds after the application of a 250V bias with the exception of device (6), which is shown after 48 seconds, due to its exceptionally slow doping-propagation speed.
Figure 3.2 shows the same devices when they reach a current of 0.1 mA, with the exception of the Au-Ca reverse-biased device (Figure 3.2.6), which is at its maximum current of 0.06 mA. At this current level, p- and n-doping have already made full contact, and EL can be easily observed in all devices. The onset of EL is accompanied by a sharp increase in the level of doping, as indicated by the much darker shading of the doped regions. In all these devices, the emission zone is off-centred and closer to the cathode, which is again characteristic of many MEH-PPV:PEO:LiTf planar LECs of millimeter-sized gap. The Au-Au device (Figure 3.2.1) was imaged under UV illumination with room light on, which reveals the gold electrodes and the color of the doped regions. The rest of the devices were imaged under UV illumination only. In the Ca-Ca (Figure 3.2.2) device and the Au-Ca reverse-biased (Figure 3.2.6) device, a continuous emission zone was not formed due to the chaotic p-doping propagation. Instead, the emission zone would form in discrete sections that could temporarily “burn out” as the current increased. This is accompanied by a sharp drop in current and the initiation of EL in other regions of the p-n junction. The emission zones of Al-Al and Ag-Ag devices are largely continuous, except in regions of the Ag-Ag device where the p-n junction is almost perpendicular to the direction of applied potential. In these vertical regions of the p-n junction, EL is not observed because there is no current flow across the junction.
Figure 3.2 The Electroluminescence of the Six 1 mm Planar LECs Imaged Under UV Illumination. These are the same devices as shown in Figure 1 and in the same order. The devices are at an operational current of 0.1 mA except for device (6), which is shown at its maximum current of 0.06 mA. Note that device (1) was imaged under UV and room light. The shutter speed for Au-Au device was 4s, while the shutter speed of other devices was 1s. The electrodes of the rest of the devices have been presented in false color for clarity.

Not surprisingly, the most uniform emission zone is observed in the forward-biased Au-Ca device where both the p- and n-doping propagation is the smoothest. The dramatic difference in doping and EL profiles between forward- and reverse-biased Au-Ca devices has also been
observed by device current and EL intensity measurements. Figure 3.3 shows the time evolution of device current and EL intensity of two identical 1 mm Au-Ca devices, one under forward bias and the other under reverse bias. The difference between the two devices is again significant as the forward-biased device attained current and EL intensity nearly 5 times that of the reverse-biased device. Note that the significant fluctuations in the current and EL of the reverse-biased device is caused not by measurement noise, but by the emission zone “burn-out” behavior mentioned above.

Figure 3.3 Time Evolution of Device Current and EL Intensity of Au-Ca Planar LECs Under Forward and Reverse Bias. Both devices are at 315 K. The applied voltage bias is 250 V.
Device current and EL intensity measurements were also been carried out on planar LECs with symmetric electrodes. Figure 3.4 shows the time evolution of current and Figure 3.5 the time evolution of EL intensity in the 4 symmetric devices. The performance of the symmetric devices is quite similar apart from Ca-Ca, which demonstrated, low current, burn out behavior and a discontinuous emission zone similar to Ca-Au reverse bias.

Figure 3.4 Time Evolution of Current in Symmetric Devices
EL turn-on time and relative EL efficiency have been extracted for both symmetric and asymmetric devices, see Table 3.1. Time lapse images were analyzed using a custom MATLAB® script (Appendix A), where the average n- and p-doping front locations and emission zone positions/standard deviations were determined. Doping velocities were calculated by plotting the p- or n-doping front location versus time. Data for Ca-Au forward biased is shown in Figure 3.6. Similar graphs were created for other devices but not shown. We see the doping speed for both p- and n-doping is a constant function of time, slowing just prior to the two fronts.
meeting (at 29 s) which supports observations reported previously [34]. Note that doping speeds and emission zone position for Ca-Ca and Au-Ca reverse bias could not be accurately calculated due to extremely uneven doping/emission zone profiles.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Work Function&lt;sup&gt;1&lt;/sup&gt; (eV)</th>
<th>Maximum Current&lt;sup&gt;2&lt;/sup&gt; (mA)</th>
<th>P-Doping Speed&lt;sup&gt;3&lt;/sup&gt; (μm/s)</th>
<th>N-Doping Speed&lt;sup&gt;3&lt;/sup&gt; (μm/s)</th>
<th>Emission Zone Position&lt;sup&gt;3,4&lt;/sup&gt;</th>
<th>Time to first EL&lt;sup&gt;5&lt;/sup&gt; (s)</th>
<th>Relative EL Efficiency&lt;sup&gt;6&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Au</td>
<td>5.31-5.47</td>
<td>0.423</td>
<td>0.427</td>
<td>22 ± 2</td>
<td>5.4 ± 0.8</td>
<td>0.84 ± 0.03</td>
<td>91</td>
</tr>
<tr>
<td>Al-Al</td>
<td>4.06-4.26</td>
<td>0.616</td>
<td>0.640</td>
<td>18.7 ± 0.7</td>
<td>5.9 ± 0.2</td>
<td>0.82 ± 0.04</td>
<td>47</td>
</tr>
<tr>
<td>Ag-Ag</td>
<td>4.52-4.74</td>
<td>0.367</td>
<td>0.462</td>
<td>21 ± 1</td>
<td>2.5 ± 0.4</td>
<td>0.79 ± 0.05</td>
<td>74</td>
</tr>
<tr>
<td>Ca-Ca</td>
<td>2.87</td>
<td>0.137</td>
<td>0.163</td>
<td>Na</td>
<td>4.8 ± 0.1</td>
<td>Na</td>
<td>30 ± 1</td>
</tr>
<tr>
<td>Ca-Au</td>
<td>0.645</td>
<td>0.489</td>
<td>29.7 ± 0.1</td>
<td>15.3 ± 0.2</td>
<td>0.77 ± 0.02</td>
<td>16.6 ± 0.7</td>
<td>100</td>
</tr>
<tr>
<td>Forward</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Ca-Au</td>
<td>0.071</td>
<td>0.145</td>
<td>Na</td>
<td>6.2 ± 0.2</td>
<td>Na</td>
<td>57 ± 1</td>
<td>33</td>
</tr>
<tr>
<td>Reverse</td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

Table 3.1 Comparison of LEC performance<sup>1</sup> Work function data from CRC Handbook of Chemistry and Physics, 86<sup>th</sup> Edition, 2005-06, pp.12-114. <sup>2</sup> Device currents in the first column were obtained from devices that underwent imaging. Device currents in the second column were obtained from a separate set of six devices. <sup>3,5</sup> P-doping speed and emission zone position could not be calculated for Ca-Au reverse and Ca-Ca devices due to exceptionally irregular profiles. <sup>4</sup> Fractional location of emission zone relative to anode. <sup>6</sup> Relative EL efficiency refers to the EL intensity measured at a fixed current of 0.1 mA and normalized such that the efficiency of the Au-Ca forward bias device is equal to 1.
Figure 3.6 N- and P- Doping Front Locations vs. Time for Ca-Au Forward Bias. Using the data presented in the graph the doping speed was calculated for this device; similar graphs were created for other devices but not shown.

Forward biased Au-Ca showed first measurable light output at 17 s, which is only 28% of the 59 s required for the same device under reverse bias. Symmetric devices all had intermediate turn-on times of around 30 s. This is at first surprising considering the great difference in the doping profiles of the Au-Au (Figure 3.1.1) and Ca-Ca (Figure 3.1.2) devices prior to EL turn-on. However, the time required for junction formation will depend on both n- and p-doping speeds. Average speeds calculated for the symmetric devices are very similar,
supporting the EL turn on data. Calculated doping speeds support the qualitative analysis presented in the discussion of Figure 3.1.

The maximum current attained is a direct measure of the device’s maximum doping level and conductivity. Al-Al and Au-Ca forward-biased devices have the highest current, while the Ca-Ca and Au-Ca reverse-biased devices have the lowest current. On the other hand, the EL intensity of the devices at the same operational current of 0.1 mA (with the exception of the Au-Ca reverse-biased device, which was at its maximum current of 0.09 mA) is a measure of the devices’ relative quantum efficiency at this current. The relative EL efficiency data shown in Table 3.1 were normalized such that the Au-Ca forward-biased device had an efficiency of 1. We see the most efficient device is again the Au-Ca device under forward bias, while the most inefficient device is the Au-Ca device under reverse bias.

3.4 Discussion

The above results lead us to the rather striking conclusion that, at least in extremely large planar LECs, electrode material and/or the polarity of voltage bias can strongly affect nearly every aspect of the device operation. In addition, the trend displayed by the various devices, especially the dramatic difference observed in asymmetric Au-Ca devices under forward and reverse bias, suggest almost PLED-like behavior [102].

We believe work function difference is responsible for all electrode effects observed in the above LECs. It is true that charge carrier injection in an LEC becomes ohmic and less sensitive to electrode work function when the doping level is sufficiently high. However, we should also realize that in order for electrochemical doping to occur, electronic charges must be injected first [103]. Unlike chemical doping, the extra electronic charge carriers responsible for
electrochemical doping and associated conductivity increase must be injected externally across the electrode/polymer interface. Hole injection (p-doping) will therefore depend on the difference between the anode work function and MEH-PPV’s HOMO (5.1 eV [104, 105]) while electron injection (n-doping) will depend on the difference between the work function of the cathode and MEH-PPV’s LUMO (2.7 -2.9 [104, 105] eV). Therefore, p-doping from Au is faster than from Ca simply because Au is a much more efficient hole injector than Ca, and holes are needed for the p-doping of MEH-PPV. The opposite holds true for n-doping. Thus, we can understand why electrode work function affects the initiation and speed of electrochemical doping.

We expect doping initiation from a poor hole-injector such as Ca to be sensitive to the fluctuation of a local electrical field. This behavior is clearly seen in Figure 3.1, where p-doping in the Ca-Ca device and the reverse-biased Au-Ca device is highly localized. P-doping in these devices appears to originate from discrete spots along the electrode/polymer interface. These doping-initiation spots are where the local curvature of the electrode edge, and therefore the local electrical field, are the highest. Cone like features which demonstrated self-reinforcing behavior were observed, p-doping in these areas propagated very rapidly. On the contrary, p-doping initiation in the Au-Au device and the forward-biased Au-Ca device is continuous along the electrode edge, indicating that hole injection from Au is sufficient to induce doping due to its high work function, even in regions of small curvature. The doping profiles of Al-Al (Figure 3.1.3) and Ag-Ag (Figure 3.1.4) demonstrate a high degree of similarity. This is expected as the work functions of Ag and Al differ by only 0.3-0.7 eV.

It should be stressed here that the planar LECs described here were all fabricated from two identically machined shadow masks. We therefore expect similar roughness at the electrode edges of all devices. At an atomically smooth interface, charge injection would occur uniformly
along the entire electrode edge. In reality, the interface is rough, and for electrode materials where there is a high barrier for charge injection, the doping will preferentially initiate at local imperfections in the electrode edge where the electric field is higher. Additionally, the polymer films were cast from the same solution under identical conditions, so the difference in doping speed and doping uniformity among the devices are not caused by a difference in phase morphology or ion mobility of the films, which are two other factors greatly influencing doping.

The uniform n-doping in the Au-Au device (Figure 3.1.1) is quite unexpected as Au has the highest barrier for electron injection. The appearance of uniform p-doping appears to enhance the uniformity of the corresponding n-doping. It is well known that n- and p-doping are intimately linked processes [78, 81]. However this trend was not seen in Ca-Ca here p-doping was very poor, suggesting that hole injection is a dominant process in MEH-PPV based films which may lie in the fact that MEH-PPV and all PPV based polymers are primarily hole transporting materials [97]. We expect the effect of the electrode work function is most significant when charge injection in LEC is analogous to that of a PLED, as is the case in devices were the doping mechanism is hindered or unfavorable. This is due to such factors as the polymer having intrinsically low carrier mobility, using an electrolyte with low ion mobility or concentration [93, 106], or for device operation at low temperatures [51]. The Au-Ca forward bias (Figure 3.1.5) with the lowest barriers for charge injection, had the most uniform n- and p-doping profiles, and the Au-Ca reverse bias with the highest barriers (Figure 3.1.6), were the most non uniform.

Figure 3.6 shows that both p- and n-doping speeds are constant prior to the junction formation. In addition, p-doping propagation is faster than n-doping propagation. These results are consistent with past observations in planar LECs based on symmetric electrodes. We used to believe doping propagation speed was solely determined by the mobility of counterions in the
electrolyte, and the difference in cation and anion mobility is the cause of the asymmetric doping propagation speed. However, our results here clearly suggest that the injection of electronic charges also plays an important role in determining the doping propagation speed.

In all our planar devices, the emitting p-n junction is found to be closer to the cathode, which is a typical behavior for MEH-PPV/PEO/LiTr based LECs [32, 33, 87, 98, 99, 101]. The off-center location is clearly the product of the asymmetry in n- and p-doping propagation speed. Previous work in our group has shown that the emission zone position can be strongly affected by the type of the cations in the electrolyte [77]. Here our results show that a more centered and straight emission zone can also be obtained by using asymmetric electrodes to optimize the injection of both electrons and holes. A more centered emission zone reduces the probability of exciton quenching by the metal electrodes [77], and is of particular importance in sandwich LECs where the interelectrode spacing is only a few hundred nanometers.

### 3.5 Sandwich LECs

Now that we have demonstrated the importance of electrode work function in extremely large planar LECs, the question remains: does electrode work function have the same effect in ultra-thin sandwich LECs? Figure 3.7 shows the I-V-EL curves of forward and reverse-biased Ca-Au sandwich devices operated at 3.5 volts. After 100 s, the current of forward-biased device is approximately 3 times, while the EL intensity is nearly 1,000 times that of the reverse-bias device. Notice also the much more unstable current profile, which is consistent with the observations of Au-Ca reverse bias in planar configuration. Similar asymmetric current and EL have also been observed in sandwich devices operated at 3 volts and in devices with ITO and Ca electrodes.
3.6 Conclusions

In summary, we have demonstrated that electrode work function strongly affects nearly every aspects of LEC operation. The implications of the above results and analysis are quite obvious in terms of LEC performance optimization. To obtain LECs with a fast response, a smooth and centered emission zone, and high efficiency, it is desirable to use asymmetric
electrodes with work functions that are well matched to the HOMO and LUMO of the luminescent polymer. With a PLED-like electrode configuration, a significant amount of electronic current is injected even at a low doping level, leading to faster and more uniform doping propagation. This in turn affects the subsequent EL emission process. In elucidating the LEC operating mechanism, we tend to stress how electrochemical doping benefits electronic charge injection. The results shown here suggest that the reverse is at least equally important.
Chapter 4 Extremely Large Crown Ether Planar LECs

4.1 Introduction

Within the LEC blend, both the speed of electrochemical doping and the local density of electrochemically generated charge carriers are influenced by the diffusion of counterions from the electrolyte into the luminescent semiconducting polymer. The more compatible the electrolyte material with polymer, the more efficient this process will be [56]; consequently, the response time and performance of LECs will depend strongly on both the ionic conductivity of the solid electrolyte and the morphology of the electro-active blend. The ideal LEC blend therefore consists of a homogenous interpenetrating network of ionic and electronic conducting components [69]. However, in reality, LEC films are prone to phase separation as polymer-polymer mixtures have low entropy gains upon mixing as luminescent polymers are generally non-polar and solid electrolytes tend to be polar [56, 57, 86]. Phase separation slows electrochemical doping [69], increases surface roughness and causes variations in film thickness, which leads to device degradation in sandwich cells through the presence of high electric fields in thin regions [68].

The first LECs based on the conducting yet highly polar PEO macromolecule demonstrated phase separation [31, 58-60]. PEO has the added disadvantages of possessing a crystalline phase at room temperature that is not ion-conductive, and it is insoluble in most solvents commonly used for dissolving conjugated polymers, limiting the choice of luminescent polymers [51]. To circumvent the detrimental effects of phase separation, Cao et al. introduced a
bi-functional (molecules with a polar-nonpolar structure) liquid component with high dielectric constants into LEC blends [58]. This additive ensured maximum interfacial contact between PEO and luminescent polymer phases, and their plasticizing effects have been shown to enhance ion mobility and charge carrier concentration [58]. This new blend composition allowed the construction of LECs with faster turn on times, lower turn on voltages and higher brightness [58], demonstrating that intimate contact between polymer and electrolyte can lead to better overall device performance. However, the drawback to the additive method is it reduces the fraction of the conjugated luminescent polymer in the active layer [60]. Other attempts to reduce phase separation have included the introduction of ethylene oxide oligomer side groups, as functional moieties grafted onto the electroluminescent polymer chain [60], thus eliminating the need for a separate ion-solvating species. However, these “hybrid” materials, tend to have insufficient ion conductivity. In 1997, Cao introduced a particularly elegant solution to the problem by replacing the ion transporting PEO with small molecule crown ethers [56], which due to their non-polar nature and small size exhibit minimal phase separation from the luminescent polymer.

Crown ethers have large planar ether rings with oxygen atoms pointing inward. They form exceptionally stable complexes with alkali metals, which is caused by the close-fitting of the alkali metal ion into the hole in the middle of the ligand. These complexes are readily soluble in many organic solvents as a result of the large hydrophobic groups present on the outside of the ring [63, 65-67]. The small size of the crown ether molecule allows the complex to be easily incorporated in the luminescent polymer matrix [51, 56]. These blends still exhibit some phase separation, but on a much smaller scale as compared to PEO-based LEC blends [69]. For example, Edman et al. observed 25 nm-sized crown ether/salt domains in films of DCH18Cr6:LiTr:super-yellow (phenyl-substituted PPV copolymer) compared to 150 nm-diameter PEO rich domains in PEO:LiTr:super-yellow blends [86].
The charge transport mechanism in crown ether based electrolytes is fundamentally different than in PEO electrolytes. In the former, cations “hop” from ring to ring, while anions diffuse through the polymer matrix [68]. To permit charge transport in such an electrolyte, the cation cannot be too strongly bound in the ring, therefore a combination cation and ether is chosen with a purposeful ring mismatch. It was shown that a combination of the Li$^+$ cation and DCH18Cr6 demonstrated the best ionic conductivity in MEH-PPV based LEC blends [56]. Despite this optimization, the ionic conductivity of crown ether blends is still much lower than that of identical PEO blends. As a result, the largest planar crown ether LEC to date featured an inter-electrode gap of only 50 μm [86].

In the previous chapter, we demonstrated that asymmetrical electrodes optimized for charge injection greatly enhance device performance in PEO based LECs. We show here the universal applicability of this discovery to demonstrate extremely large planar crown ether LECs. The largest device constructed featured an inter-electrode spacing of 1 mm. Through the use of time-lapse fluorescence imaging, we present the first ever images of the doping profiles and emission zones of crown ether based LECs. We explore the crown-ether based frozen junction concept and observe that, in contrast to what was previously reported [40, 78, 86], the ionic motion is not truly frozen at room temperature. In addition, these devices give us the first opportunity to study the doping and emission processes of the LEC minus the effects of phase separation.

4.2 Experimental Details

LEC films featuring crown ether-based electrolytes were spin cast onto 1.5 cm by 1.5 cm sapphire substrates from 80 μL of solution N (108GE:DHC18Cr6:LiTr), T (MEH-
PPV:DHC18Cr6:LiTr), G (108GE:DHC18Cr6:CsClO₄) or M (MEH-PPV:DHC18Cr6:CsClO₄), as per Table 2.1. Here DCH18Cr6 refers to a 50/50 mixture of cis-syn and cis-anti - cis-dicyclohexano-18-crown-6, MEH-PPV is the familiar poly[5-(2-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] and 108GE is the fluorene copolymer poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-co-(2-methoxy-5-(ethylhexyloxy)-1,4-phenylene)]. Symmetric or asymmetric electrodes with nominal 0.5 mm or 1 mm spacing were thermally evaporated on the dry films in the following configurations; Au-Ca, Au-Al and Al-Al on 108GE films and Au-Ca or Au-Al on MEH-PPV films. Due to manufacturing difficulties, the actual inter-electrode spacing demonstrated a variation of approximately ±0.1 mm. All fabrication procedures were completed in a glove box filled with dry nitrogen.

A 1000 V bias and temperature of 330 K were established as optimal operational parameters for these extremely large planar LECs. Devices were tested in a custom built Cryo-Industries microscopy cryostat evacuated to a pressure of approximately 5.0 X10⁻⁵ torr by an oil free turbo pump. A Q-imaging camera was attached to a Nikon microscope and used to record time-lapse fluorescence images of the devices during operation. UV Illumination was supplied by a mercury lamp fitted with a UV2A-DM400 330-380 nm UVA filter. For devices that were not imaged, an amplified Hamamatsu photodiode (SC2281-01) was used to measure the relative EL intensity. All the above instrumentation was connected to a computer and data was recorded using Labview. Depending on the nature of the experiment, asymmetric devices were run in either forward or reverse bias. Forward bias requires that Au be wired as positive and Ca or Al be wired as negative.
4.3 Results

4.3.1 Doping and Emission in Extremely Large Planar Crown Ether LECs

PEO-based LECs have readily been demonstrated in extremely large planar configuration with symmetric electrodes, the largest to date having an inter-electrode spacing of 11 mm [32]. Due to the lower ionic conductivity of crown ether LEC blends, the largest planar device to date featured Au-Au electrodes and a spacing of only 50 μm. Our attempt to turn on millimetre scale crown ether-based planar LECs was unsuccessful. Figure 4.1 shows the active area and time evolution of device current and photoluminescence of a symmetric Al/108GE:DHC18Cr6:LiTr/Al planar LEC with an inter-electrode spacing of 0.53 mm (d55 3.5). Figure 4.1.1 shows the LEC film prior to the application of voltage bias. The bright green color results from the UV induced PL of the luminescent polymer. In Figure 4.1.2 through Figure 4.1.5 we see dark regions emanating from both top and bottom electrodes. The dark regions are caused by PL quenching associated with the electrochemical doping process. The p-doping originates from the anode (top) and n-doping from the cathode (bottom). With time, the n- and p-doped regions grow in size approaching the center of the device. In contrast to PEO-based Al-Al devices where p-doping is always darker, here the n-doping seems to cause heavier PL quenching. The p-doping profile is erratic and jagged, with the largest “features” appearing at local imperfections at the electrode edge, while n-doping is more uniform. Despite the formation of the p-n junction (Figure 4.1.5), the current continues to drop suggesting no charge recombination (light emission) is occurring. Figure 4.1.7 and Figure 4.1.8 shows the n-doping gradually encroaching on the anode side and growing darker. When the n-doping makes contact with the anode, the current gradually begins to increase but remains less than 100 nA. Finally as
in Figure 4.1.9, the device is completely enveloped with n-doping. Light emission through radiative recombination was not observed in this device, and the current did not climb above its initial value of 120 nA
Figure 4.1 Time Evolution and Current of AI/108GE:DCH18Cr6:LiTr/Al LEC D55 (3.5). This device featured a 0.53 mm inter-electrode spacing operated at 1000 V bias and 330 K, it was imaged under UV illumination. Images were recorded using time-lapse photography 1) Device prior to application of bias 2) Device at 12 seconds after the application of bias 3) 30 seconds 4) 48 seconds 5) 72 seconds 6) 120 seconds 7) 252 seconds 8) 582 seconds 9) 1842 seconds
Dramatically different device behaviours are observed when the symmetric Al-Al are replaced with asymmetric electrodes for optimized charge injection. Figure 4.2 shows the time evolution of current and PL of a device (d54 3.5) featuring a gold cathode (wired positive), calcium anode (wired negative), 0.52 mm inter-electrode spacing and a 108GE:DHC18Cr6:LiTr active layer blend. Panels 1 through 4 show the device under UV illumination while the final two photographs, Figure 4.2.5 and Figure 4.2.6, were imaged under room light in order to reveal the electrodes. Figure 4.2.1 shows the device prior to the application of a voltage bias. The PL quenching caused by p-and n-doping are clearly visible 12 s after the application of a 1000 V bias (Figure 4.2.2). Unlike the symmetric device, the doping fronts are very uniform and the p-doping which originates from the upper electrode is both faster and darker than the n-doping. The p-and n-doped regions meet (Figure 4.2.3) to form a junction near the cathode. The device current continues to increase, as does the doping concentration, indicated by the increasing level of PL quenching observable in both the p- and n- regions (Figure 4.2.4). From the junction, light emission is observed from the radiative recombination of injected holes and electrons. The emission zone is very smooth, a product of the uniform doping profiles and it lacks the sharp finger like shapes seen in PEO-based LECs (Figure 4.2.5 and Figure 4.2.6).
Figure 4.2 Time Evolution and Current of Au/108GE:DCH18Cr6:LiTr/Ca D54 (3.5). This device was operated at a 1000 V bias at 330 K with a 0.52 mm inter-electrode spacing, images 1-4 were imaged under UV illumination while images 5 and 6 were imaged under room light to reveal the electrodes.  
1) Prior to the application of voltage bias.  
2) The device 12 seconds after the application of bias  
3) 30 seconds  
4) 108 seconds  
5) 198 seconds  
6) 498 seconds
In addition, to Au/108GE:DHC18Cr6:Litr/Ca cell, asymmetric Au-Al devices were created. Figure 4.3 shows the time evolution and current of such a device (d29 1.3) featuring a 0.49 mm inter-electrode spacing, with Au wired as the anode (positive) and Al as the cathode (negative). Note that in this figure the current is plotted versus a logarithmic time axis. In Figure 4.3.1, we see the pristine unbiased film. Shortly after the application of a voltage bias (Figure 4.3.2 at 6 sec and Figure 4.3.3 at 12 sec) both p- and n-doping are clearly visible. The p-doping appears diffuse and propagates rapidly while the n-doping front moves more slowly with a well defined edge. The doping fronts meet to form a p-n junction (Figure 4.3.4) located in close proximity to the cathode. As in the previous device, the current, doping concentration, and therefore PL quenching, increases (Figure 4.3.5). Meanwhile faint light emission at the junction is also observed. The uniform doping profiles again lead to the formation of a smooth emission zone, but unlike the Au-Ca cell, the light-emitting p-n junction gradually drifts towards the anode during operation (Figure 4.3.6 through Figure 4.3.9), with its final location being relatively centered (Figure 4.3.9). During this propagation, the emission zone gradually becomes more jagged.
Figure 4.3 Time Evolution and Current of an Au/108GE:DCH18Cr6:LiTr/Al LEC D29 (1.3). This device was operated at 1000 V and 330 K; it was imaged under UV illumination and featured an inter-electrode spacing of 0.49 mm. 1) The device prior to the application of a voltage bias 2) 6 seconds after the application of bias 3) 12 seconds 4) 42 seconds 5) 84 seconds 6) 654 seconds 7) 1044 seconds 8) 1464 seconds 9) 2874 seconds
In order to ensure that the observed phenomena were not unique to the luminescent polymer used, large planar Au/MEH-PPV:DHC18Cr6:Litr/Ca were created. The time evolution and current of one such device (d44 1.3) is shown in Figure 4.4 featuring an inter-electrode spacing of 0.56 mm. All photographs were obtained under UV illumination except Figure 4.4.6 which was imaged under room light to reveal the electrodes. Figure 4.4.1 shows the pristine film prior to the application of the voltage bias. Here the red color results from the PL of MEH-PPV under UV illumination. Twenty-four seconds after the application of the voltage bias (Figure 4.4.2) uniform p- and n-doping fronts are clearly visible. MEH-PPV based crown ether devices demonstrated the greatest asymmetry in p- and n- doping velocities, which is evident from the much greater volume occupied by p-doping in Figure 4.4.2. Due to the slow n-doping velocity the junction is formed close to the cathode (Figure 4.4.3). PL quenching and current continue to increase indicating an ever increasing level of doping after the junction is initially formed, as seen in Figure 4.4.4 and Figure 4.4.5. Unlike 108GE devices where the current showed an initial exponential increase followed by a slow gradual plateau, the current rises sharply in MEH-PPV devices throughout the entire operation and then suddenly collapses. Like 108GE devices with Au-Al electrodes, the emission zone gradual drifts towards the anode, which contradicts previous observations for MEH-PPV:PEO:Litr devices [87]. However, unlike the 108GE devices, the junction only moves so far and then remains stationary while light emission continues to increase (Figure 4.4.5). Under continued operation, the junction begins to widen and become less uniform (Figure 4.4.6).
Figure 4.4 Time Evolution and Current of Au-Ca MEH-PPV/DCH18Cr6/LiTr D44 (1.3). This device featured an inter-electrode spacing of 0.56mm it was operated at 330K with a 1000V applied bias. Images 1-5 were taken under UV illumination, while 6 was taken under room light in order to reveal the electrodes. 1) The device prior to the application of a voltage bias 2) 24 seconds after bias application 3) 36 seconds 4) 480 seconds 5) 1080 seconds
The p-/n-doping front and emission zone locations were extracted from time-lapse fluorescent images using a custom MATLAB® script (Appendix B). P-/n-doping/emission zone velocities were calculated and presented in Table 4.1. EL profiles were analyzed and used to calculate the turn on time (time to first EL) and efficiency (EL/Current). These results are presented in Table 4.2.

<table>
<thead>
<tr>
<th>Device</th>
<th>N-doping Velocity (μm/s)</th>
<th>P-doping Velocity (μm/s)</th>
<th>Max Current (nA)</th>
<th>Junction Velocity (μm/s)</th>
<th>Initial Emission Zone Location</th>
<th>Final Emission Zone Location</th>
<th>Emission Zone Smoothness</th>
<th>Inter-Electrode Spacing (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D29</td>
<td>4.6±0.8</td>
<td>22.1±0.3</td>
<td>7547</td>
<td>0.053</td>
<td>0.72</td>
<td>0.38</td>
<td>11.7</td>
<td>0.49</td>
</tr>
<tr>
<td>D38</td>
<td>6±n/a</td>
<td>37.4±0.7</td>
<td>1465</td>
<td>0.035</td>
<td>0.85</td>
<td>0.67</td>
<td>0.552</td>
<td>0.57</td>
</tr>
<tr>
<td>D43</td>
<td>11.7±0.3</td>
<td>19.8±0.2</td>
<td>5738</td>
<td>0.055</td>
<td>0.71</td>
<td>0.63</td>
<td>0.458</td>
<td>0.44</td>
</tr>
<tr>
<td>D54</td>
<td>1.2±0.2</td>
<td>16±1</td>
<td>3589</td>
<td>0.192</td>
<td>0.72</td>
<td>0.69</td>
<td>11.9</td>
<td>0.52</td>
</tr>
<tr>
<td>D44</td>
<td>1.88±0.08</td>
<td>63.4±n/a</td>
<td>17985</td>
<td>0.428</td>
<td>0.83</td>
<td>0.66</td>
<td>76.4</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Table 4.1 Crown Ether LEC Characteristics. 1,2 Fractional emission zone location relative to anode. 3 Standard deviation of emission zone location averaged over time

<table>
<thead>
<tr>
<th>Device</th>
<th>Time to first EL (s)</th>
<th>Efficiency at 0.5μA</th>
<th>Spacing (mm)</th>
<th>Max Current (nA)</th>
<th>Initial Current (nA)</th>
<th>Max EL (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D23</td>
<td>11.7±0.6</td>
<td>0.79</td>
<td>0.52</td>
<td>1271</td>
<td>51</td>
<td>0.66</td>
</tr>
<tr>
<td>D62</td>
<td>9.2±0.9</td>
<td>0.44</td>
<td>0.71</td>
<td>844</td>
<td>139</td>
<td>0.43</td>
</tr>
<tr>
<td>D60</td>
<td>7.1±0.4</td>
<td>0.15</td>
<td>0.51</td>
<td>20470</td>
<td>13</td>
<td>0.12</td>
</tr>
<tr>
<td>D66</td>
<td>14.8±0.9</td>
<td>0.30</td>
<td>0.62</td>
<td>17068</td>
<td>32</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Table 4.2 Crown Ether Photodiode Results

80
108GE has been shown to have efficient and balanced charge injection characteristics [107]. This property is most likely responsible for the higher efficiencies and similar doping speeds of Au/108GE:DCH18Cr6:LiTr/Ca and Au/108GE:DCH18Cr6:LiTr/Al devices. The efficiency of the Au-Ca device is lower than that of the Au-Al device as there may be a higher degree of PL quenching from heavier doping concentrations in the former device. On average the Au-Ca 108GE devices demonstrated slightly faster doping speeds resulting in faster turn on times. In all asymmetric DCH18Cr6/LiTr devices, p-doping was faster than n-doping which is identical to behavior seen in PEO-based devices. MEH-PPV devices demonstrated the highest asymmetry between p- and n-doping speeds, which support the qualitative observations presented in the figures above. Despite the much slower n-doping, the very rapid p-doping resulted in MEH-PPV devices having very similar turn on times as compared to 108GE devices. MEH-PPV devices reached higher peak currents than 108GE devices. This may be a result of the wider band gap of 108GE which makes charge injection more problematic.

Due to the lower degree of phase separation, emission zones in crown ether blend films were very smooth as compared to similar PEO-based devices. For comparison, work by Alem and Gao [108] and Chapter 3 may be consulted. This is also demonstrated by the small standard deviations presented in the table above. All devices exhibited some degree of emission zone drift towards the anode during operation. In Au/108GE:DCH18Cr6:LiTr/Ca devices, the junction initially drifts towards the cathode, however after a short time the movement reverses and it commences propagation towards the anode. Conversely in Au/108GE:DCH18Cr6:LiTr/Al, drift is almost solely in the direction of the anode. In Au/MEH-PPV:DCH18Cr6:LiTr/Ca, the junction initially drifts towards the anode, however, eventually a stable location is reached and it begins to widen and degrade. In all cases, the drift velocity is a function that varies little with time, as seen in Figure 4.5 Overall Au/108GE:DCH18Cr6:LiTr/Al emission zones were the most centered,
followed closely by Au/MEH-PPV:DCH18Cr6:LiTr/Ca. Crown ether MEH-PPV devices had more centered emission zones than equivalent MEH-PPV PEO devices.

Figure 4.5 Crown Ether LEC Emission Zone Drift During Constant Voltage Operation
4.3.2 Au/MEH-PPV:DCH18Cr6:LiTr/Al Devices

A series of Au/MEH-PPV:DCH18Cr6:LiTr/Al devices were constructed with 0.5 mm inter-electrode spacing. Under forward bias doping and junction formation were observed. However, the device current never surpassed 150 nA and EL was not detected, suggesting that crown ether cells based on MEH-PPV require the optimization of both the cathode as well as anode.

4.3.3 Reverse Bias

To further investigate the importance of electrode work function in LECs with low ion mobility, Au/108GE:DCH18Cr6:LiTr/Ca and Au/MEH-PPV:DCH18Cr6:LiTr/Ca devices were operated in reverse bias configuration, that is with Au wired as the cathode (negative) and Ca as the anode (positive). Figure 4.6 shows two such devices (d56 3.5 Figure 4.6.1 and d58 3.5 Figure 4.6.2) with their associated current profiles under a bias of -1000 V. Surprisingly, doping was observed in both cases, preferential originating from local imperfections in the electrode edge. As in the MEH-PPV:PEO:LiTr devices described in the past chapter, the doping profiles were erratic and discontinuous. The sharply increasing current seen in the MEH-PPV device is caused by the formation of intermittent junctions allowing a path for current flow formed at the intersections of p-doping cones and n-doping. No light emission was observed in any reverse bias devices.
Figure 4.6 Reverse Bias 0.5 mm Crown Ether LECs with Current Plots. 1) Device 56 (3.5) Au/108GE:DCH18Cr6:LiTr/Ca at 330 K, 1000 V reverse bias 2) Device 58 (3.5) Au/MEH-PPV:DCH18Cr6:LiTr/Ca at 330 K, 1000 V reverse bias

4.4 Cesium Perchlorate Devices

In addition to the DCH18Cr6:LiTr electrolyte solutions, solutions featuring cesium perchlorate (CsClO₄) were prepared. Cesium perchlorate is shown to enhance device performance in PEO based LECs by slowing the p-doping velocity allowing the formation of more centered emission zones [77]. P-doping is slowed by the increased difficulty faced by the
cesium ion as it diffuses through the LEC blend due to its much larger size. The diameter of the cesium ion (1.67 Å) makes it too large to fit in the hole of the DCH18Cr6 ring (1.3-1.5 Å) [63], suggesting the binding energy of the resulting complexes should be low, hopefully allowing efficient ion motion and conductivity.

A 1100 V bias, the maximum allowed by our test equipment, was applied to a Au/108GE:DCH18Cr6:CsClO₄/Ca cell and a Au/MEH-PPV:DCH18Cr6:CsClO₄/Ca at 350 K. However, none of the cesium devices exhibited doping as current profiles support these observations, as seen in Figure 4.7. The current would peak from the initial ionic contribution then quickly decrease. It is possible the large cesium cation size or its tendency to form double complexes with two adjacent DCH18Cr6 rings [63] interfere with the “hopping” mechanism of ion transport. Without adequate cation mobility, these cells do not function due to lack of electrochemical doping.
4.5 Junction Relaxation and De-Doping

PEO-based LECs at room temperature operate in what is known as dynamic junction mode, meaning upon removal of the voltage bias, the junction relaxes as the counter ions diffuse back into the electrolyte [33, 35, 87]. This behavior was observed in both MEH-PPV:DCH18Cr6:LiTr and 108GE:DCH18Cr6:LiTr devices at 330 K regardless of the electrode configuration. Figure 4.8 shows a Au/108GE:DCH18Cr6:LiTr/Al cell initially operated at 1000
V. Upon the removal of the bias, n-doping retreated rapidly while the withdrawal of p-doping was slower (Figure 4.8.2 and Figure 4.8.3). Upon relaxation, the formerly n-doped region exhibits two distinct areas: (Figure 4.8.3) one lighter in color adjacent to the cathode which, upon comparison with the initial device junction, represents the initial volume of n-doping at the time of junction formation; the other and darker region is the area into which the n-doping expanded as a result of junction drift. This darker region may be remnants of partial p-doping, which relaxes more slowly, overrun by the advancing n-doping front during device operation.

Figure 4.8 Junction Relaxation in D43 (1.3) Au/108GE:DCH18Cr6:LiTr/Ca at 330 K. 1) Shows the device prior to the removal of bias 2) The device 10 seconds after the removal of bias 3) After 60 seconds no bias

The Au/108GE:DCH18Cr6:LiTr/Ca device in Figure 4.9 was recharged at 500 V and 340 K and the bias was reversed to observe doping relaxation under a voltage bias. Figure 4.9.1 through Figure 4.9.4, which were taken at 10 sec intervals, show the rapid retreat of p doping. After extended application of reverse bias, the remnants of doping did not completely disappear and reverse doping could not be initiated (Figure 4.9.5). The absence of reverse bias doping is very likely the result of poor charge injection under reverse bias.
Figure 4.9 De-Doping of D29 (3.5) Au-Al 108GE/DCH18Cr6/LiTr at 330 K. 1) The junction at 500 V applied bias 2) Junction 10 seconds after the application of a -500 V bias 3) After 20 seconds 4) After 30 seconds 5) After 120 seconds

4.6 Room Temperature Frozen Junctions

In 1998 Yu et al. reported room temperature frozen junction LECs based on DCH18Cr6/LiTr blends [40], this was further investigated by Edman et al. in 2004 [40, 79, 87]. In all cases, the devices were turned on at elevated temperatures (60 °-80 °C), then cooled to room temperature. In the former work, the existence of a frozen junction was supported by the observation of 1) no hysteresis on fast I-V scans 2) rectifying I-V scans and 3) negligible discharge current at zero bias. Edman’s device was charged at 80 °C and then quickly cooled to room temperature. After cooling, the bias was removed and the device was allowed to sit at room
temperature for 1 hour. After this resting period the bias was reapplied and light emission was observed immediately [86].

An Au/108GE:DCH18Cr6:LiTr/Ca asymmetric device was turned on using a 1000 V bias at 340 K. Once the current began to plateau (approximately 1000 nA), the device was cooled rapidly to 300 K. The bias was removed and the device was allowed to sit at room temperature for approximately 18 hours. The next day when the same voltage bias was reapplied, no light emission was observed and negligible current was recorded. The device was imaged under UV light, and it was immediately obvious the junction had relaxed as there was the distinct appearance of an undoped intrinsic region lacking PL quenching in place of the former junction.

Our results show crown ether 108GE devices do not form stable room temperature frozen junctions. In the previous studies, devices were only allowed to sit unbiased for one hour, or measurements were made immediately upon cooling [40, 86, 109]. Crown ether LECs have intrinsically much lower ion mobility than corresponding PEO-based devices and it may be the junction at least initially appears frozen. Edman argued that at 23 °C the LEC blend should consist of a mixture of luminescent polymer glass and a crystalline phase of DCH18Cr6:LiTR with melting temperature of 56 °C, therefore there should be no ionic motion at room temperature. However, in our initial exploratory work extremely large crown ether LECs were easily turned on at temperatures as low as 320K (47 °C). There is also research that suggests that in cases where the ether ring and cation have significant mismatch, the formation of amorphous phases is more likely. Therefore, there should still be ion mobility at room temperature [62].
4.7 Conclusions

The above results clearly demonstrate the important role of charge injection in the operation of LECs. For LECs based on crown ether as described in this chapter, the relative low ion conductivity of CE:LiTf electrolyte is compensated by the use of asymmetric electrodes for efficient electron and hole injection. For the first time, we have demonstrated crown-ether based planar LECs with millimetre scale inter electrode spacing. The superior morphology of the LEC film leads to highly uniform doping propagation, and as a result, a very smooth emission zone. The less chaotic doping propagation process makes it easier to extract important device parameters such as doping propagation speeds and emission zone position. By direct imaging of these extremely large planar LECs, we also show that crown ether electrolyte does not lead to stable frozen-junction LEC that can be operated at room temperature.
Chapter 5 Conclusions

5.1 Conclusions

We have shown that electrode composition strongly affects nearly every aspect of LEC operation. The difference between the electrode work function and polymer LUMO/HOMO levels determines the ease of charge injection into the initially undoped semiconducting LEC film. Doping profile and velocity, turn on time, efficiency emission zone shape and location are all affected. Using a PLED like asymmetric electrode configuration, we obtain LECs with a faster response, a smooth and centered emission zone, and high efficiency. In this configuration a significant amount of electronic current is injected even at low doping levels, leading to faster and more uniform doping propagation. This in turn affects the subsequent EL emission process. In the past, many have stressed how electrochemical doping benefits electronic charge injection, the results shown here suggest that the reverse is at least equally important.

For crown ether-based LECs, the relatively low ionic conductivity of CE:LiTf electrolyte is compensated by the use of efficient electron and hole injecting asymmetric electrodes. We have demonstrated and imaged the first ever crown ether-based planar LECs with millimetre scale inter-electrode spacing. The homogenous morphology of crown ether-based LEC films leads to highly uniform doping propagation, and as a result, a very smooth emission zone. These improvements in the device operation make it easier to extract important parameters, such as doping propagation speeds and emission zone position. By direct imaging of these extremely large planar LECs, we demonstrate that crown ether-based LECs do not exhibit stable frozen-junction behaviour at room temperature.
5.2 Future Work

For a more complete understanding of the influence of the electrode material and the roll of charge injection on LEC performance, some critical items still require investigation.

The remarkable uniformity seen in the emission zones and doping profiles presented in this work are astounding; however, could these be improved? Currently the doping and emission zone uniformity in our crown ether-based LECs are not limited by the film morphology but by the smoothness of the electrode edge. A new method of electrode production is required to obtain better quality data. Electrodes produced via lithography and chemical etching would demonstrate a much higher degree of surface uniformity, hopefully leading to ultra uniform doping profiles and emission zones.

Despite the vastly different morphologies of PEO- and crown ether-based LECs, both systems demonstrated constant doping propagation speeds up to the moment of junction formation. This suggests that they are fundamentally driven by the same process; however this must be more fully investigated. The more uniform doping contours produced by smoother electrodes, would allow the more accurate determination of their positions and velocities. Additionally, EL data could be used to conduct a detailed study of response time (time to first EL) and lifetime as a function of electrode material. A theoretical model of the electrochemical doping process should be constructed. A good model could provide excellent insight into questions such as: why is the doping velocity is constant? Or, why does the emission zone drift?

Currently, it is difficult to disentangle which process, charge injection or ionic mobility limits LEC response. It was shown improving the charge injection in a system with limited ionic mobility, such as crown ether LECs, led to dramatic performance improvements. In contrast, a
system with excellent ionic mobility and a polymer into which it is difficult to inject charges should be investigated such as a PEO:LiTr system combined with a high band gap blue polymer such as poly-[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene]. The comparison of the performance of such a device with symmetrical versus asymmetrical electrodes could potentially help to clarify the role of charge injection versus mobility.
References


MATLAB® script used to analyze results from chapter 3.

By: Donna Hohertz and Jay Weymouth

These two programs take a series of sequentially numbered grey scale .jpg images and through the use of two user defined and one preset threshold determines the electrode (preset), n-doping (user defined) and p-doping (user defined) edges. The program then fits these thresholds with a straight line (y=mx+b). The images and associated fits are displayed during the fitting process to allow the user to adjust parameters if necessary. Finally all edge locations in pixels and fit coefficients are output into an ascii .txt file.

function RunAlltest(path, start, last, t1, t2, fname)
%RunAll(path, start, last, t1, t2, fname)
%Input the path of the images
%The start and the last image numbers
%The thresholds of the start and last junctions
%The filename of the output matrix

pre = '.Img';
post = 'grey.jpg';

outarr = zeros(last-start+1, 11);
outarr1 = zeros(3872,(last-start+1)*4);

for cnt = start:last
    imname = strcat(path, pre, int2str(cnt), post);
    [c1, c2, c3, d1, d2, d3] = EdgeFind2(imname, t1, t2);
    outarr(cnt-start+1, 1) = start;
    outarr(cnt-start+1, 2) = c1.p1;
    outarr(cnt-start+1, 3) = c1.p2;
    outarr(cnt-start+1, 4) = c2.p1;
end
outarr(cnt-start+1, 5) = c2.p2;
outarr(cnt-start+1, 6) = c3.p1;
outarr(cnt-start+1, 7) = c3.p2;

outarr1(:,(1+((cnt-start)*4))) = d1;
outarr1(:,(2+((cnt-start)*4))) = d2;
outarr1(:,(3+((cnt-start)*4))) = d3;

end

save(fname,'outarr', 'outarr1', '-ASCII');

function [coeff1, coeff2, coeff3, edgearr, ndoparr, pdoparr] = EdgeFind2(filename, thresh1, thresh2)

%thresh1 = 150;
%thresh2 = 150;
thresh3 = 10;

%Variable name ===== FILE INPUT STUFF ==
Picture = imread(filename, 'jpeg');
Picture = flipdim(Picture, 1);

%How many rows to loop through
rows = size(Picture, 2);
cols = size(Picture, 1);

%Initializing the edge array
edgearr = zeros(rows, 1);
ndoparr = zeros(rows, 1);
pdoparr = zeros(rows, 1);

%Number of 'real' edges we find
cnt2 = 0;

for cnt = 1:rows
  %Find the electrode edge
  tmp = find(Picture(:,cnt) ~= 0, 1);
  if (isempty(tmp) == 0)
    edgearr(cnt) = tmp;
  end
  %Find the n doping edge
  tmp = find(Picture(:,cnt) >= thresh1, 1);
  if (isempty(tmp) == 0)
ndoparr(cnt) = tmp;
else if (cnt > 1)
    ndoparr(cnt) = ndoparr(cnt-1);
else ndoparr(cnt) = edgearr(cnt);
end
end

%Find the next minimum point past the n doped region
tmpy = find(Picture(ndoparr(cnt):cols, cnt) <= thresh3, 1) + ndoparr(cnt) - 1;
%PREVIOUS LINE IS THE PROBLEM == SOMEHOW IT'S TOO BIG BY 1
%Solution -- subtract one
if (isempty(tmpy) ~= 0)
    tmpy = cols;
end

%Find the p doping edge that is only as far as the next low zone
tmp = find(Picture(ndoparr(cnt):tmpy,cnt) >= thresh2, 1, 'last') + ndoparr(cnt);
if (isempty(tmp) == 0)
    pdoparr(cnt) = tmp;
else if (cnt > 1)
    pdoparr(cnt) = ndoparr(cnt-1);
else pdoparr(cnt) = edgearr(cnt);
end
end

end

%Calculate the fit to our line
coeff1 = fit((1:3872)', edgearr, 'poly1');
coeff2 = fit((1:3872)', ndoparr, 'poly1');
coeff3 = fit((1:3872)', pdoparr, 'poly1');

%Display the picture and keep it up
figure;
imagesc(Picture);
hold;
%Overlay the picture with the fitted electrode edge
plot(1:3872, coeff1(1:3872), 'red');
%Overlay the picture with the n doped
plot(1:3872, ndoparr(1:3872), 'black');
plot(1:3872, coeff2(1:3872), 'blue');

%Overlay the picture with the p doped
plot(1:3872, pdoparr(1:3872), 'red');
plot(1:3872, coeff3(1:3872), 'red');
Appendix B MATLAB® Code 2

MATLAB® script used to analyze results in Chapter 4.

By: Donna Hohertz and Jay Weymouth

These two programs take all grey scale .tif images in a single folder and through the use of two user defined and one preset threshold determines the electrode (preset), n-doping (user defined) and p-doping (user defined) edges. The program then fits these thresholds with a straight line \( y = mx + b \). The images and associated fits are displayed during the fitting process to allow the user to adjust parameters if necessary. Finally all edge locations in pixels and fit coefficients are output into an excel .xls file.

```matlab
function RunAlltiff(path, t1, t2, fname)
  %RunAll(path, start, last, t1, t2, fname)
  %Input the path of the images
  %The start and the last image numbers
  %The thresholds of the start and last junctions
  %The filename of the output matrix

  %%%PROBABLY USELESS
  %pre = '^Img0';
  %post = 'grey.jpg';
  %outarr = zeros(last-start+1, 11);
  %outarr1 = zeros(3872,(last-start+1)*4);
  %%%

  %run through the path directory and gets all .tif files
  flist = dir(strcat(path, '*.tif'));
  last = size(flist,1);
  % added by Donna
  %outarr = zeros(last, 11);
  %outarr1 = zeros(3872,3*last);

  for cnt = 1:last
    %%%PROBABLY USELESS
  end
```

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% First make the name of the image with the path, pre, number and post
% imname = strcat(path, pre, int2str(cnt), post);
%%%

tempfile = flist(cnt);
imname = tempfile.name;
imdate = tempfile.date;

% Then run the FUNCTION
[c1, c2, c3, d1, d2, d3] = EdgeFindtiff(imname, t1, t2);
% Now output to the output array
outarr(cnt, 1) = cellstr(imname);
outarr(cnt, 2) = cellstr(imdate);
outarr(cnt, 3) = cellstr(num2str(c1.p1));
outarr(cnt, 4) = cellstr(num2str(c1.p2));
outarr(cnt, 5) = cellstr(num2str(c2.p1));
outarr(cnt, 6) = cellstr(num2str(c2.p2));
outarr(cnt, 7) = cellstr(num2str(c3.p1));
outarr(cnt, 8) = cellstr(num2str(c3.p2));

outarr1(:,(1+((cnt-1)*3))) = d1;
outarr1(:,(2+((cnt-1)*3))) = d2;
outarr1(:,(3+((cnt-1)*3))) = d3;

tit01(1 + ((cnt-1) * 3)) = cellstr(imname);

end

xlswrite(fname, outarr, 1);
xlswrite(fname, tit01, 2, 'a1');
xlswrite(fname, outarr1, 2, 'a3');
% save(fname,'outarr', 'outarr1', '-ASCII');

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function [coeff1, coeff2, coeff3, edgearr, ndoparr, pdoparr] = EdgeFindtiff(filename, thresh1, thresh2)

%thresh1 = 150;
%thresh2 = 150;
thresh3 = 10;

%Variable name ===== FILE INPUT STUFF ==
Picture = imread(filename, 'tiff');
Picture = flipdim(Picture, 1);

%How many rows to loop through
rows = size(Picture, 2);
cols = size(Picture, 1);

%Initializing the edge array
edgearr = zeros(rows, 1);
ndoparr = zeros(rows, 1);
pdoparr = zeros(rows, 1);

%Number of 'real' edges we find
cnt2 = 0;

for cnt = 1:rows
    %Find the electrode edge
tmp = find(Picture(:,cnt) ~= 0, 1);
    if (isempty(tmp) == 0)
        edgearr(cnt) = tmp;
    end

    %Find the n doping edge
    tmp = find(Picture(:,cnt) >= thresh1, 1);
    if (isempty(tmp) == 0)
        ndoparr(cnt) = tmp;
    else if (cnt > 1)
        ndoparr(cnt) = ndoparr(cnt-1);
    else ndoparr(cnt) = edgearr(cnt);
    end
end

%Find the next minimum point past the n doped region
tmpy = find(Picture(ndoparr(cnt):cols, cnt) <= thresh3, 1) + ndoparr(cnt) - 1;

%PREVIOUS LINE IS THE PROBLEM == SOMEHOW IT'S TOO BIG BY 1
%Solution -- subtract one
if (isempty(tmpy) ~= 0)
    tmpy = cols;
end

%Find the p doping edge that is only as far as the next low zone

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tmp = find(Picture(ndoparr(cnt):tmpy,cnt) >= thresh2, 1, 'last') + ndoparr(cnt);
if (isempty(tmp) == 0)
    pdoparr(cnt) = tmp;
else if (cnt > 1)
    pdoparr(cnt) = ndoparr(cnt-1);
else pdoparr(cnt) = edgearr(cnt);
end
end

%Calculate the fit to our line
coeff1 = fit((1:rows)', edgearr, 'poly1');
coeff2 = fit((1:rows)', ndoparr, 'poly1');
coeff3 = fit((1:rows)', pdoparr, 'poly1');

%Display the picture and keep it up
figure;
imagesc(Picture);
hold;
%Overlay the picture with the fitted electrode edge
plot(1:rows, coeff1(1:rows), 'red');
%Overlay the picture with the n doped
plot(1:rows, ndoparr(1:rows), 'black');
plot(1:rows, coeff2(1:rows), 'blue');

%Overlay the picture with the p doped
plot(1:rows, pdoparr(1:rows), 'red');
plot(1:rows, coeff3(1:rows), 'red');
%hold off;