

Short Lifetimes of Light Emitting Polymers

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Introduction

The following manuscript was submitted as part of the MPhil program in *Microelectronic Engineering and Semiconductor Physics* at the Microelectronics Research Centre (MRC) of the Cavendish Laboratory at the University of Cambridge. The manuscript is a literature survey undertaken by the author as part of the MESP program during Lent term 1997 and is the basis of a talk of the same title given at the MRC on January 20, 1997.

1 Basic Layout of Presentation

Before introducing the main topic of this paper—short lifetimes of light emitting polymers—a few introductory sections are provided for background considerations. Background materials include short introductions to polymers and electroluminescence

in polymers, before mechanisms responsible for the short lifetimes of light emitting polymers and related issues are discussed.

This survey is intended to be comprehensive but by no means exhaustive. In the following sections, there are instances in which two or more sections share related information; to eliminate redundancy, an issue will be addressed in full in the section where it has most relevance and will only be briefly mentioned in any other relevant sections.

2 History of Light Emitting Polymers

2.1 Polymers

Much of the terminology we will encounter for polymers, also affectionately known as macromolecules, rose out of the combined *efforts* of organic chemists, who created them, and the physical chemists, who characterized their physical properties.

Polymers are chains of smaller molecular components, called monomers. As a simple example, the polymer polyethylene (PE) is constructed (or polymerized) from the precursor ethylene by breaking the double bond in the ethylene molecule, as shown successively in Figures 1 and 2 below.

Polymers exist in many varieties ranging from the very simple repeating patterns of chains of monomers, to the somewhat more sophisticated molecular patterns as found in copolymers—polymers composed of two or more chemically distinguishable monomers. Copolymers, in turn, can exist in many configurations, owing to the many ways the individual monomers can be ordered. There are block polymers, in which large sections are repeated along the polymer chain; graft polymers where another polymer is attached as a

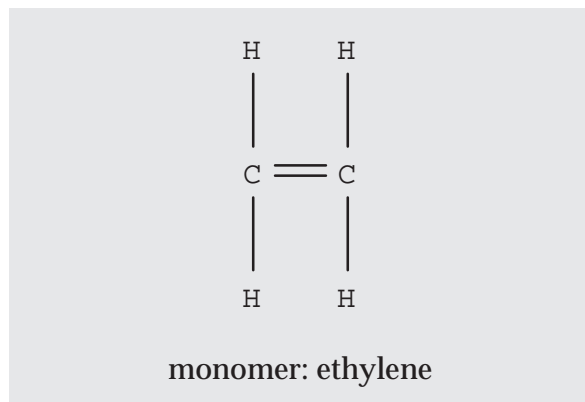


Figure 1: The *double-bonded* precursor to polyethylene: ethylene.

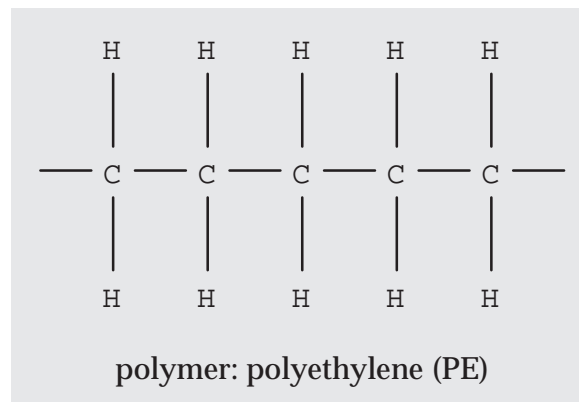


Figure 2: The single-bonded polymer polyethylene (PE).

side chain; random polymers where the different monomer units take on, as the name suggests, a random ordering to form the polymer chain; and so on.

Another important class of polymers is conjugated polymers. Conjugated polymers consist of carbon backbones with alternating single and double bonds and have shown great potential as light-emitting materials.

2.2 Light Emitting Polymers

The first organic electroluminescent devices [1][2] were discovered around the time the first light-emitting diodes (LEDs) were introduced into the commercial market in 1962. Like today, early devices were hampered by fabrication and packaging problems and short lifetimes [3].

Electroluminescence (EL) was first observed in conjugated polymers in 1990 by Burroughes *et al.* [4], which reveals the relative youth of this field. Evidence for electroluminescence from the seminal paper by Burroughes *et al.* is shown in Figure 3.

Prior to this, electroluminescence had been wit-

nessed in organic molecules by Tang and Van Slyke in 1987 [5], who revived interest in organic EL. All of these were originally preceded by the work of Partridge in 1983 [6], whose work largely went unnoticed.

Since the advent of electroluminescent polymers, conjugated polymeric materials with emissions spanning the broad spectrum of visible [4][8][9][10][11][12][13] and non-visible radiation (near infrared [14]) have been fabricated, as shown in Figure 4. A voltage-tunable-luminescent device has been fabricated using poly(thiophene) blends [14][15]. One group [16] has created white-light devices by using appropriate combinations of these EL materials.

Many polymers are now known to display electroluminescence. Among the favorites are poly(phenylene vinylene) [PPV] (Figure 5), and variations on a theme, poly(2-methoxy-5(2'-ethyl)hexoxy-phenylene vinylene) [MEH-PPV] (Figure 6), [DP-PPV] (Figure 7), poly(2,5-bis(5,6-dihydrocholestan-oxy)-1,4-phenylene vinylene) [BCHA-PPV], and [CN-PPV], and a plethora of others including aluminum tris(8-oxyquinolate) [Alq₃], poly(2-dodecoxy-p-phenylene) [C12OPPP],

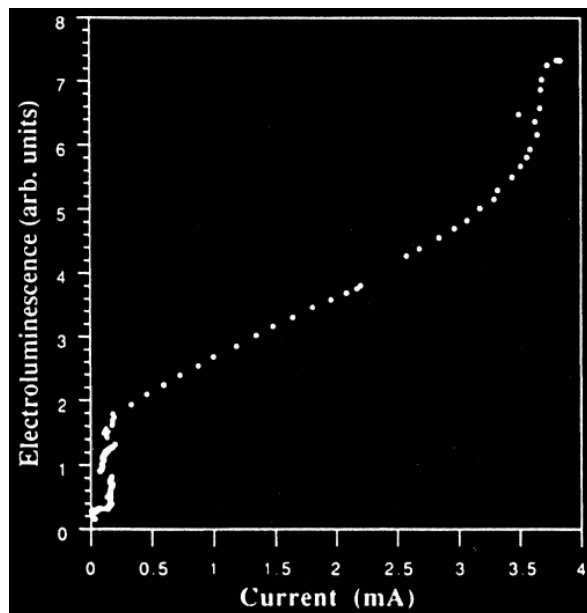


Figure 3: Electroluminescence in PPV. From Burroughes *et al.* [4].

and poly(3-octylthiophene) [P3OT]. The chemical structures of many other EL polymers not already mentioned along with their full-width, half-maximum EL emission range can be found in Figure 4.

The similar electroluminescent (EL) and photoluminescent (PL) spectra of these materials [17][18][19][20][21] suggest that the same mechanisms are responsible for both phenomena, justifying, in many cases, why these terms are used interchangeably in the literature. In support of this assertion, an experiment by Tang and Van Slyke [5] has shown an increase in both EL and PL by fluorescent-dye doping of Alq₃-based devices.

2.3 Synthesis of Polymers

The synthesis of polymers is an important consideration in the fabrication of light emitting de-

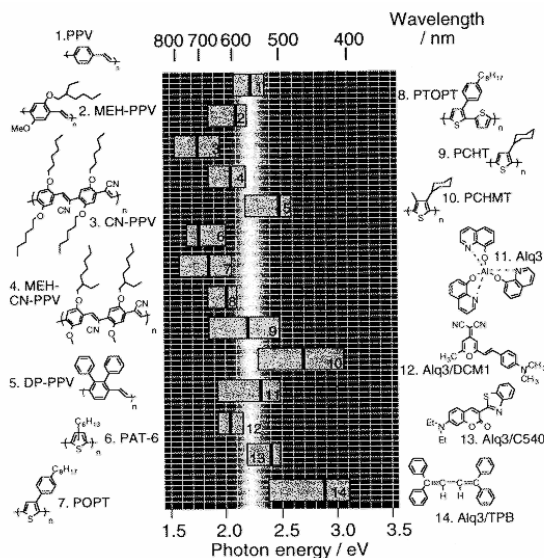


Figure 4: Polymeric materials with emissions spanning the broad spectrum of visible and non-visible radiation have been synthesized. From Gymer [7].

vices. The various properties of polymers, particularly solubility, limit the methods by which devices can be constructed. There are different routes to PPV from different precursors, as shown in Figures 8 and 9. For example, one synthesis of the insoluble conjugated polymer PPV is a two-step process: a precursor monomer is polymerized and forms a soluble precursor polymer, after which the precursor is spin-coated onto a substrate and thermally converted to PPV at a temperature ranging between 200°C to 300°C in a vacuum or inert (argon) atmosphere [22]. This can lead to the formation of hydroxyl groups [23] and carbonyl groups [24]—residues left over from the conversion process. The effects of carbonyl on the luminescence of devices is discussed in a later section.

Alkoxy-substituted derivatives of PPV, such as BCHA-PPV, are soluble in organic solvents which allows for casting of solid films [26].

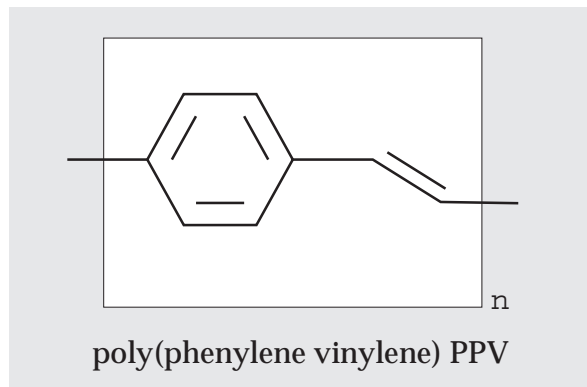


Figure 5: Monomer of the electroluminescent polymer poly(phenylene vinylene) [PPV].

Purity in polymeric materials, although not as significant as in inorganic materials like crystalline semiconductors, is becoming more of a concern; Sheats *et al.* [3] have reported that the lifetime of a TPD/Alq₃ device (where Alq₃ was co-evaporated with 0.5 wt% quinacridone of 98% nominal purity) exhibited a lifetime factor 10^{-4} less than a similar device where the quinacridone was purified by a sublimation technique.

2.4 Utilizing Light Emitting Polymers

Organic light emitting diodes (OLEDs) may be utilized for many purposes ranging from replacing standard light emitting diodes (LEDs), to flat panel displays, and flexible displays [18] for niche applications. Devices have exhibited high resolution, fast switching, and fast emission [7]. They also tend to activate at voltages as low as 3 Volts and tend to operate below 10 Volts [27]. They are also light-weight relative to the existing technology.

However, even with these laudable attributes, the following factors are preventing this new technology from dominating the competing technologies at this

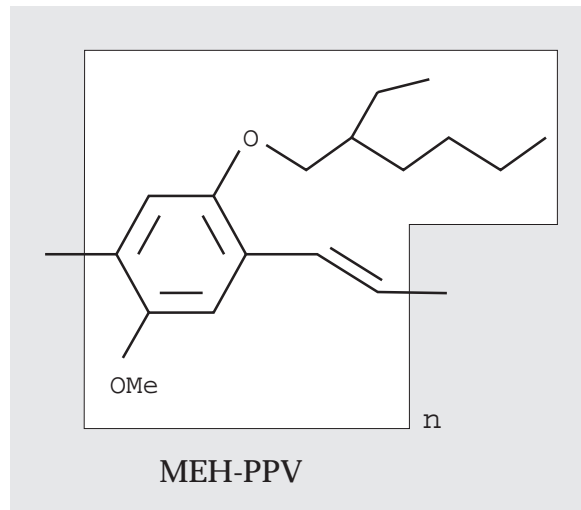


Figure 6: Monomer of the electroluminescent polymer poly(2-methoxy-5-(2'-ethyl)hexoxy-phenylene vinylene) [MEH-PPV].

time: the processes by which polymers are synthesized and processed, as discussed earlier, and device degradation once the device has been fabricated. Among other problems cited is the need to improve luminous efficiency and color gamut [27] (see Figure 10). In this paper, we will concentrate mainly on the problems of device lifetimes and degradation, and some related peripheral issues.

3 The Physics of Light Emitting Polymers

3.1 Electroluminescence

In the seminal paper by Burroughes *et al.* [4], electroluminescence—in this case emission of yellow-green light—was induced by applying a voltage across a layer of poly(phenylene vinylene) [PPV]. Since that time, electroluminescence has been observed in many other polymers [28][29].

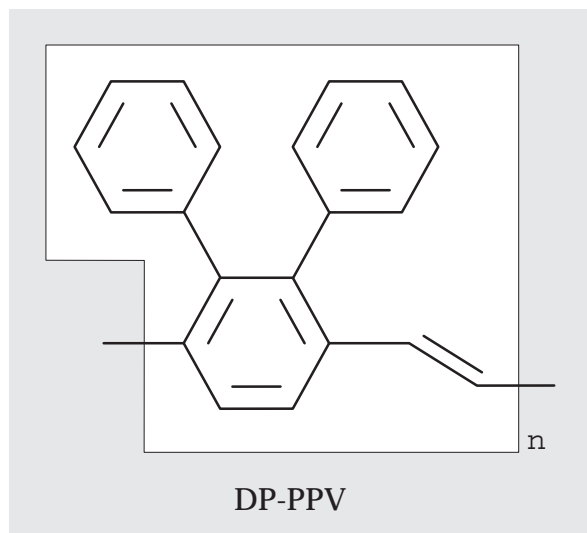


Figure 7: Monomer of the electroluminescent polymer DP-PPV.

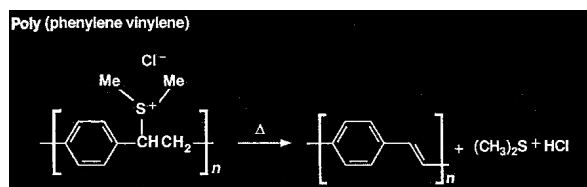


Figure 8: Soluble precursor synthetic route for poly(phenylene vinylene) [PPV]. From Reynolds [25].

Electroluminescence is brought about by injecting electrons and holes from opposite sides of the conjugated polymer which then recombine in the polymer to form self-localized excited states that decay radiatively [4] (see Figure 11).

It is preferable to asymmetrically inject electrons via a low work-function cathode (approximately 3–4 eV [3]) and holes via a transparent, high work-function anode [27][21] (approximately 5 eV [3]). The conjugated polymer layer sandwiched between the two electrodes acts as a recombination cen-

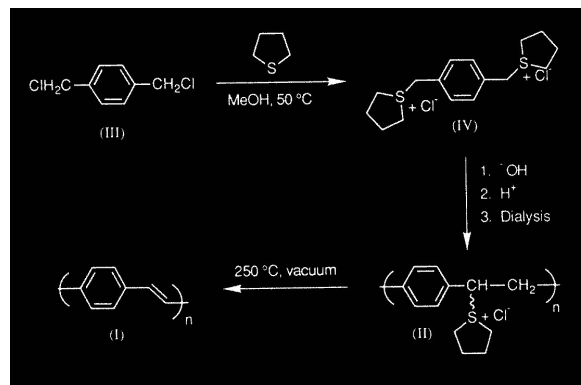


Figure 9: Synthetic route to PPV. From Burroughes *et al.* [4].

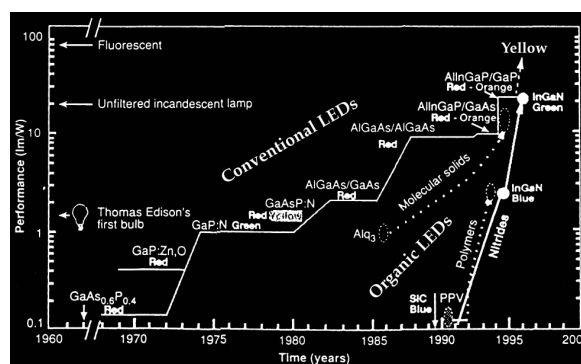


Figure 10: Progress in LED efficiency. Adapted from Sheats *et al.* [3].

ter and must exhibit efficient luminescence, charge transport, and efficient charge transfers with both electrodes [3] (see Figure 12). Indium-tin-oxide (ITO) has become the *de facto* anode material.

The inherent asymmetry built into these devices leads to some current rectification, and hence these devices are usually referred to as light emitting diodes (LEDs), although Jeglinski *et al.* reported electrical and electroluminescent symmetric behavior in a light emitting diode utilizing poly(phenylene acetylene) [PPA] as the electrolumines-

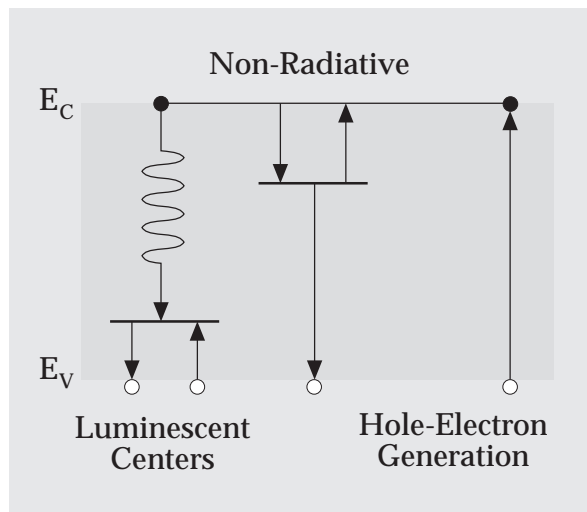


Figure 11: Electroluminescence is brought about by recombining electrons and holes in the bulk polymer. Not all electrons and holes will *recombine*, due to various non-radiative traps or quenching sites inside the polymer, like carbonyl groups formed by photo-oxidation. Adapted from Ivey [30].

cent polymer [31].

Excitation is achieved mainly along conjugation lengths consisting of 10 to 15 monomers [3]. In PPV, for example, the excitation moves directly to a non-radiative interchain exciton, although reversions to the radiative intrachain excitations are possible [32]. Charges move along the polymer by electron transfer reactions [33] (hopping) between polymer molecules. In polymers which exhibit the structural symmetry of PPV, these excitations exist in three varieties: (uncharged) polarons (polaron excitons), singly charged polarons, and doubly charged polarons (bipolarons) [4][34][35] (see Figure 13). Interchain transport is thought to be far less efficient than tunneling through σ bonds [36][37]. Mobilities of holes in polymers tend to be in the range of $10^{-4} \text{ cm}^2/Vs$ and $10^{-8} \text{ cm}^2/Vs$;

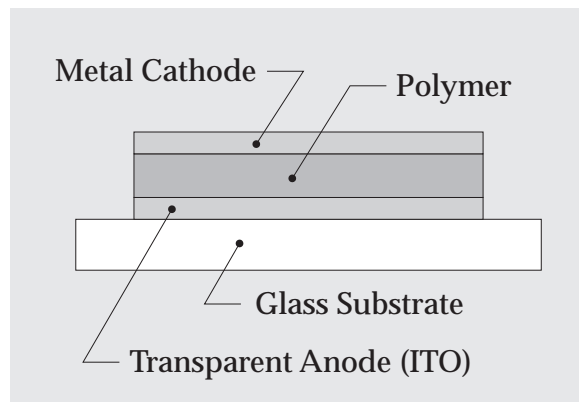


Figure 12: In a typical single-layer device, the electrons are injected into the polymer from a low work-function metal cathode and holes are injected into the polymer from a high work-function transparent anode. In the applied electric field, the electrons and holes recombine in the bulk polymer and form excited states which decay radiatively.

electron mobilities are even lower, thought to be due, in part, to trapping sites containing oxygen [38].

4 Device Degradation and Lifetimes

Lifetimes for OLEDs have been reported near 5,000 hours for the best light-emitting polymers [40], but most devices don't operate near this figure (see Figure 14). Light emitting polymer devices exhibit short lifetimes for various reasons; among the various direct and indirect issues cited in the literature are: photo-oxidation, singlet oxygen, *dark spots*, reactive metal contacts, problems in injection of electrons and holes, quantum efficiency, recombination efficiency, barrier height between hole transport layer (HTL) and ITO [41], recrystalliza-

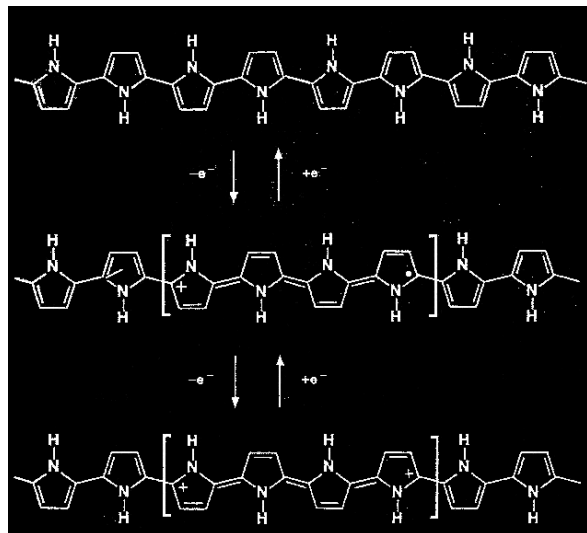


Figure 13: Oxidation and reduction (doping): charge carrier formation, polaron ($-e^-$) and bipolaron ($-2e^-$), in polypyrrole. Adapted from Reynolds [25].

tion of HTL [42], interdiffusion across organic layers [43], device configuration [41], deterioration of electrode layers [44], luminance decay rate directly proportional to injection current density [45], cumulative and irreversible coulombic degradation [45], and many others. Few of the cited issues above will not be addressed further as they are not the dominant degradation mechanisms in light emitting polymers.

In order to systematically address the synergistic issues, we will deal with each issue on an individual basis. Since device degradation can take place in any of the three layers of the usual single-layer devices; i.e., the metal cathode, the transparent anode, and also within the polymer itself, the following sections will be organized as follows:

5 Polymer-Related

5.1 Photo-Oxidation

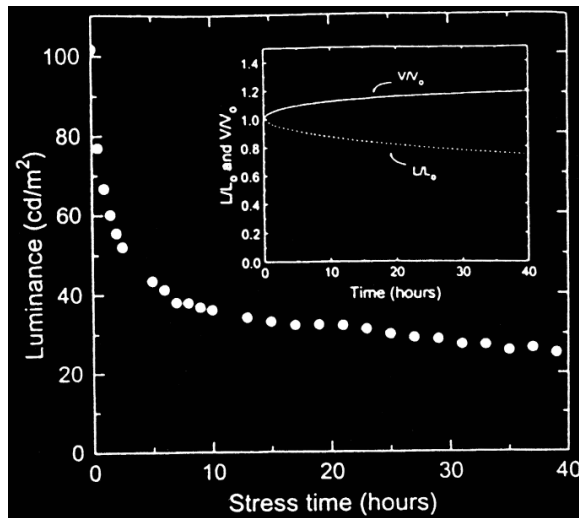


Figure 14: Degradation of luminance vs. time for biased device. Inset shows evolution of luminance and applied voltage for constant-current stressed device. From McElvain *et al.* [39].

5.2 Singlet Oxygen and Chain Scissions

5.3 Carbonyl Groups and Other Destructive Species

5.4 Oxygen Migration from ITO Anode and Micro-shorts

5.5 Recrystallization and Other Structural Changes

5.6 Quantum Efficiency

6 Cathode-Related

6.1 Dark Spots

6.2 Reactive Metal Contacts

6.3 Electromigration-Induced Diffusion

6.4 Electron Injection

7 Anode-Related

7.1 Oxygen Migration from ITO

7.2 Indium-Tin-Oxide Damage

7.3 Indium Migration out of ITO and Indium Contamination of EL Polymer

8 Charge Transport Layer-Related

5 Polymer-Related

5.1 Photo-Oxidation

The lifetimes of devices is severely compromised if they are operated in an oxygen atmosphere. This instability in air was originally witnessed in early electron conduction experiments with aromatic hydrocarbon polymers [25].

Welch *et al.* [46] concluded that photo-oxidation, also referred to as photodegradation, is related to the functionalities present on the polymer, catalytic effects of the substrate, itself a function of the electronic configuration, and UV exposure conditions.

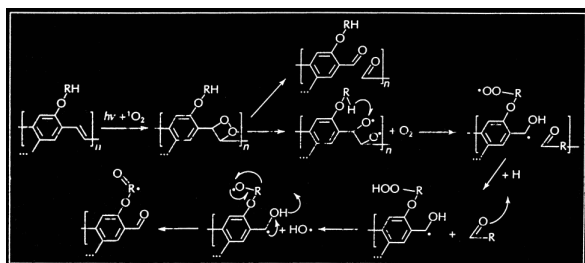


Figure 15: Oxidation mechanism for alkoxy-substituted PPV derivatives showing formation of esters, aromatic aldehydes, and alcohols. From Cumpston and Jensen [47].

Yan *et al.* [48] have shown that the intensity of PPV emission is greatly reduced if luminescence experiments are carried out in an oxygen atmosphere rather than a nitrogen atmosphere. There is much evidence suggesting that device lifetimes are longer in nitrogen atmospheres [49][50]. This suggests

that reactions involving oxygen are one facet of device degradation. Inhibitors of photo-degradation can come in many varieties, ranging from chain-breaking acceptors, chain-breaking donors, UV absorbers, metal deactivators, stoichiometric and catalytic peroxide decomposers, and excited state-quenchers. UV absorbers, for example, work by absorbing radiation and converting it to thermal energy [51]. Chromophores, the absorbers of light in the polymers, redirect the excitation energy to quenchers that help convert the absorbed energy to vibrational energy. Peroxide decomposers help decompose peroxides to alcohols.

According to Faucitano *et al.* [51], photo-oxidation and photothermal oxidation are complex free-radical processes strongly dependent on the chemical nature of the polymer. Chemical stabilizers against various photo-oxidative mechanisms have been developed, but must be tailored for each specific polymer. The photo-oxidative mechanisms create a plethora of functional groups such as carbonyls, acids, esters, and alcohols (see Figures 15 and 16), along with unsaturation, chain scissions, and crosslinks. The complete loss of mechanical properties of polypropylene (PP) can be triggered by one oxidized carbon atom per 200 atoms. The oxidation leads to polar functional groups which further deteriorate other properties of the polymers including dielectric properties, transparency, and hydro-repellence. Residual catalysts, used in the fabrication of polymers, have also been shown to be contributors to photo-oxidation.

5.2 Singlet Oxygen and Chain Scissions

Singlet oxygen has been cited as a major contributor to photo-oxidation [52]. These reactions, characterized by very low activation energies, are a re-

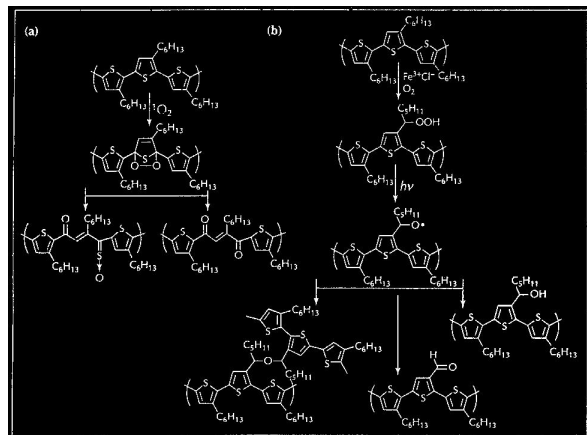


Figure 16: Singlet oxygen (a) and free-radical degradation (b) of P3HT. From Cumpston and Jensen [47].

sult of the interaction between radicals on the polymer's oxygen's unpaired electrons when oxygen is in the ground state.

Singlet molecular oxygen ($a^1\Delta_g$) gives rise to chain scissions in BCHA-PPV [26]. The same group reports that singlet oxygen does not appreciably react with stilbene, the monomer analogue for the BCHA-PPV system. Photochemical absorption may also induce cis-trans isomerization of vinylene moieties and, as is the case in stilbenes—cyclization [53]. Gibson and Pochan suggested in 1982 that singlet oxygen led to the degradation of polyacetylene [54]. Holdcroft *et al.* [55][56] reported that singlet oxygen reacts with the poly(3-alkylthiophenes).

It has been shown that the free electrons of oxygen in polymers containing oxygen reduce the amount of conjugation. According to Scott *et al.*, the reduction in conjugation does not manifest itself in a spectral change; the expected blueshift is mitigated by the creation of quenching centers.

5.3 Carbonyl Groups and Other Destructive Species

A significant residual of the thermal conversion of a precursor into the polymer PPV is the aromatic aldehyde carbonyl moiety. It has been shown [22] that the carbonyl content (not present in the precursor) reduces luminescence of such devices, as shown in the Figure 17. Carbonyl formation and subsequent decrease of fluorescence has been witnessed in the UV irradiation of a PPV precursor [57]. Papadimitrakopoulos [22] also report that trace amounts of oxygen and prolonged exposure of the polymer to elevated temperatures creates carbonyl moieties and reduces luminescence.

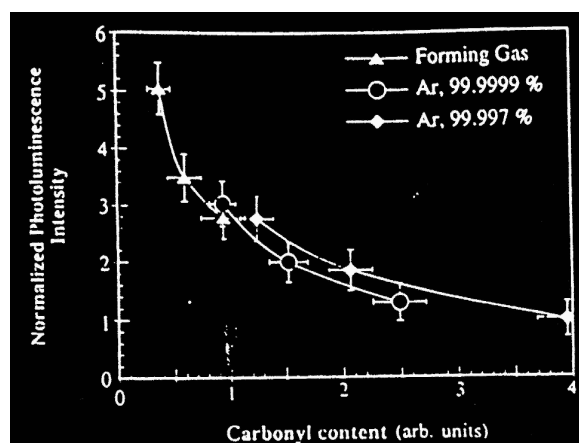


Figure 17: Effect of carbonyl content on the photoluminescence of PPV films. From Papadimitrakopoulos *et al.* [22].

Welch *et al.* [46] concluded that the formation of carbonyl groups during photodegradation was dominant in the presence of the metals Al and Au as electrodes. In non-oxidative conditions, there occurred no formation of carbonyl groups, however, in the case of Cu, the photodegradation of the polymers in oxidative and non-oxidative conditions was

still substantial, although the latter was 4.5 times as slow. To combat this problem of carbonyl formation, Papadimitrakopoulos *et al.* [22] has reported that the thermal conversion of the PPV precursor in a reducing atmosphere consisting of 15% hydrogen in nitrogen substantially reduced the amount of carbonyl moieties.

5.4 Oxygen Migration from ITO Anode and Micro-shorts

Scott *et al.* [27] report the oxidation of MEH-PPV using a Ca cathode and ITO anode, suspecting the migration of oxygen out from the ITO anode, which ultimately led to the quenching of luminescence and increase in device impedance. They also report the existence of microscopic shorts (in the end stages of operation) through the polymer which eventually reduce the active area of the LED and lead to thermal runaway. It has been recommended that a less conductive and less transparent layer between the polymer and the anode be used to prevent oxygen migration; those who have used a polyaniline layer have demonstrated improved behavior [18][58]. It is conjectured that the microshorts are due to electrode surface roughness, particulate contamination, and inhomogeneities within the polymer.

Devices that are encapsulated exhibit much longer lifetimes than unencapsulated devices, as shown in Figure 18. Encapsulated devices eliminate any external sources of oxygen, but not necessarily any internal oxygen sources like an ITO anode.

5.5 Recrystallization and Other Structural Changes

Operating temperatures have an effect on the spectral output of devices, as shown in Figure 19. Excessive heating of the polymer can cause problems

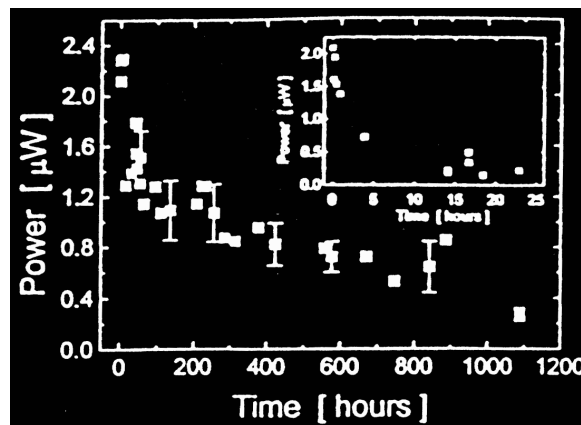


Figure 18: Luminance statistics of encapsulated OLEDs. Inset is statistics for unencapsulated devices. From Burrows *et al.* [44].

as well; although some light emitting polymers that are sublimated exhibit very good efficiencies, and have been tuned for specific emissive wavelengths, these devices have exhibited problems in device performance stability due to recrystallization and other structural changes [4].

5.6 Quantum Efficiency

The internal quantum efficiencies, defined as the number of photons emitted for the number of electrons injected, have increased in the last few years. Early device efficiencies ranged at about 0.1%, but have recently been brought into the 1% range. Quantum efficiencies as high as 4% have also been reported [21]. A 4% quantum efficiency means that the radiant (or luminous) efficiency, a function of driving voltage, refractive index, and other factors [59], is only around 0.25% [27].

Device efficiencies of 0.05% [4] and quantum efficiencies of 0.01% photons/electron [60] for ITO/PPV/Ca and ITO/PPV/Al devices have been reported [22]. The introduction of an electron

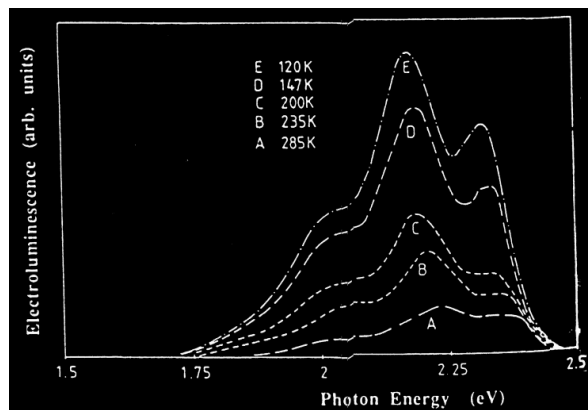


Figure 19: Thermal effects on the electroluminescent spectrum of PPV. Adapted from Burroughes *et al.* [4].

transport layer (see Figure 27) to ITO/PPV/Ca single layer devices has brought the efficiency up to 0.8% [19].

6 Cathode-Related

6.1 “Dark Spots”

Some early fabricated devices exhibited *dark spots* which were thought to be due to nonuniformities of the layers, in particular, the metal electron-injecting electrode. These *dark spots* would invariably be non-emissive areas of the device and usually increased the impedance [27] of the devices. Others attributed the *dark spots* to chemical reactions taking place at the polymer/metal interface. Recently, the use of less reactive metals for the electron-injecting layer [61] with the introduction of a charge transporting layer [62], specifically an electron transport layer, has mitigated these problems. Electrochemical cells, which facilitate operation at lower voltages, used in conjunction with less reactive metals for charge-injecting electrodes,

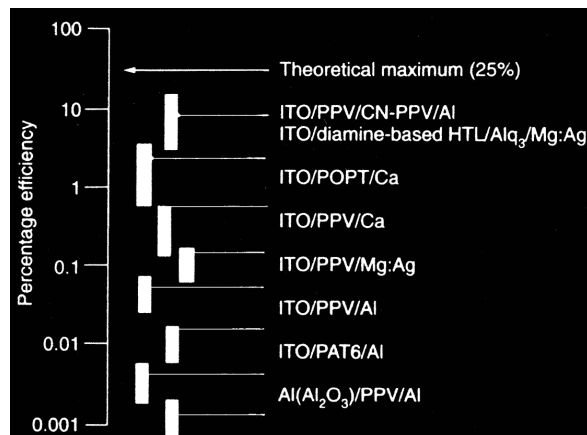


Figure 20: Quantum efficiencies of various electroluminescent anode/polymer/cathode configurations. Adapted from Gymer [7].

seem to have eliminated this particular problem [13]. Device failure of early electroluminescent devices was originally attributed to Joule heating at the metal/polymer interface [4].

Recent experiments have shown that *dark spots* may be due to water-induced delamination [39].

6.2 Reactive Metal Contacts

Device performance may also be hampered by the migration of impurities [63] and dopants [64]. Welch *et al.* have studied the effect of metal substrates on the photodegradation of polymers [46]; they conclude that aluminum causes more photodegradation on the polymers polyvinyl flouride [PVF] and polyacrylonitrile [PAN] than do the other metals they studied, namely copper (Cu), silver (Ag), and gold (Au). They concluded that for PAN, the hierarchy of degradation under oxidative conditions was the following: $\text{Cu/PAN} \gg \text{PAN} \gg \text{Al/PAN} > \text{Au/PAN} > \text{Ag/PAN}$.

The formation of carbonyl groups during photodegradation was dominant in the presence of the

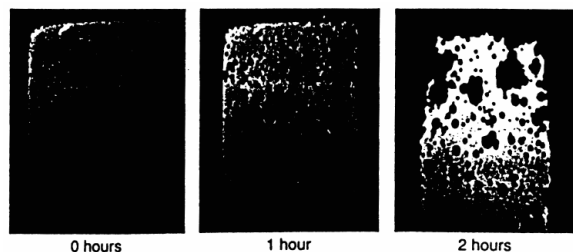


Figure 21: Degradation of device: EL in an ITO/TPD/Alq₃ plus quinacridone/Mg device operated in N₂. Note formation of circular *dark spots*. These *dark spots* grow only in the presence of H₂O but not in N₂, negligibly in O₂, and independent of operation. Experiments show that *dark spots* are regions of water-induced delamination. From Sheats *et al.* [3].

metals Al and Au. In non-oxidative conditions, there occurred no formation of carbonyl groups, however, in the case of Cu, the photodegradation of the polymers in oxidative and non-oxidative conditions was still substantial, as mentioned earlier. The high heat capacities of the metals has been ruled out as a contributing factor responsible for the photodegradation of the EL polymer.

Scott *et al.* [27] report the degradation of Ca/Al cathodes, as shown in Figure 22.

6.3 Electromigration-Induced Diffusion

Cumpston and Jensen [65] report that the degradation of Al cathodes (see Figures 23 and 24) is due to the electromigration-induced diffusion of aluminum, which creates the non-emissive *dark spots*. According to their observations, the cathode defects occurred only in the active regions of the device and not in regions where there was no opposing ITO, which suggest that high current density-based

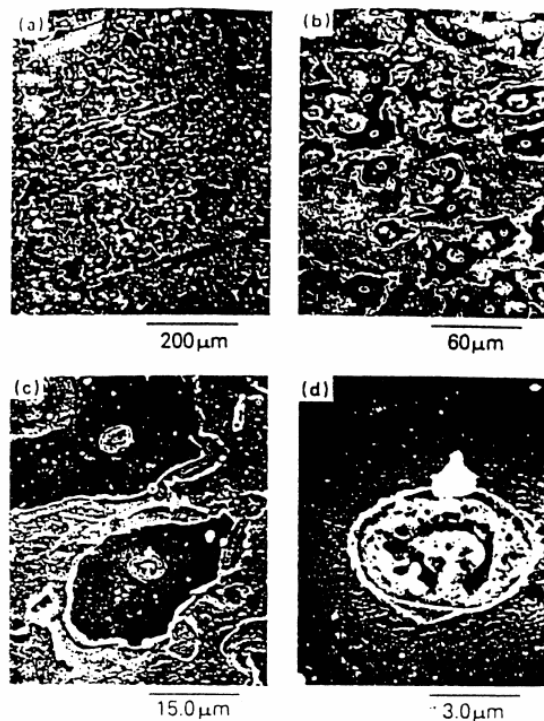


Figure 22: SEM images of degradation of Ca/Al cathode after complete device failure. From Scott *et al.* [27].

mechanisms are at work here. These effects may be due, in part, to the original morphology between the conjugated polymer film and Al cathode and are exacerbated by high currents and high temperatures. Fou and Rubner [66] report that polymers derived by chemical self-assembly do not exhibit *dark spots*. To reduce the electromigration-induced diffusion, it has been suggested that an overlying layer of metal can prevent the creation of island-morphology *dark spots*. Such Ag or Al [67] layers have been used to protect low work-function metals such as Mg or Ca [27][44].

Aziz and Xu [68] report that the formation of microscopic spots which create high current paths because of high electric fields which owe their exist-

tence to defects and edges in the cathode/polymer interface.

Do *et al.* [69] report the degradation of Al cathodes in an ITO/TPD/Alq₃/-Al device. Aluminum was used because of its higher stability than MgAg. The size of the *dark spots* was in direct relation to the applied voltage. Material movement from the edges was particularly noticeable. Significant evidence for cathode degradation suggests that *dark spots* were almost entirely composed of the transparent aluminum oxide Al₂O₃, same as the expected top layer ($< 100\text{\AA}$) of the Al electrode. The *dark spots* were also thought to occur in regions overlying heat and/or gas evolution and crevasse formation in the underlying EL organic layers.

Also, it was noticed that the longer the devices were placed in storage, the lower the EL intensity was found to be; this is attributed to crystallization of the TPD layer and slow oxidation of organic layers and Al cathode layers.

In a later paper by Do *et al.* [70], experiments further support the idea that the morphology of the Al cathode surface is related to deformations of the organic EL layer underneath, specifically gaseous evolution of oxygen and hydrogen thought to be a result of electrolysis of H₂O in the device.

6.4 Electron Injection

Electron injection takes place at the metal cathode/polymer interface. The metal should be a low work function metal, i.e., calcium and magnesium; however, these metals are very reactive and can contribute to device breakdown. Recent advances have added a charge transporting layer [62] (see Figure 27) between the electrodes and the polymer (see Reactive Metal Contacts). Introduction of these transport layers has led to an optimization of light output for selected wavelengths of emitted

light [71].

More efficient injection contacts have been used to improve device performance [72][73]. Cathode materials being used are Al ($\Phi_w = 4.3eV$), Ag ($\Phi_w = 4.3eV$), In ($\Phi_w = 4.1eV$), Mg ($\Phi_w = 3.7eV$), Ca ($\Phi_w = 2.9eV$), ZrC ($\Phi_w = 3.6eV$) [74], and others. Anode materials are usually ITO ($\Phi_w \approx 4.7eV$) or Au ($\Phi_w = 5.1eV$). It has been noted that Al forms covalent bonds with the polymer and Ca forms ionic Ca and bipolarons [3]. Mg is thought to interact weakly and ZrC is stable in air. Electrodes of aluminum and silver/magnesium alloys are also being employed [7].

Van Slyke *et al.* [45] report that the luminance decay rate is directly proportional to injection current density, meaning that this coulombic degradation is cumulative and may be irreversible; however, it has been proposed that an AC bias current would prevent the formation of trapped space charges in the organic layers. This is interesting in light of the result advanced by Jeglinski *et al.* [31] regarding the symmetrically electric and luminescent behavior of PPA.

7 Anode-Related

Anode materials are usually a transparent, high work-function metal such ITO ($\Phi_w \approx 4.7eV$) or Au ($\Phi_w = 5.1eV$). There are problems associated with migration of oxygen and indium from the anode, as explained in the following sections.

7.1 Oxygen Migration from ITO

Scott *et al.* [27] report the oxidation of poly(2-methoxy-5(2'-ethyl)hexoxy-phenylenevinylene [MEH-PPV] using a Ca cathode and ITO anode, suspecting the migration of oxygen out from the ITO anode, which ultimately led to the quenching

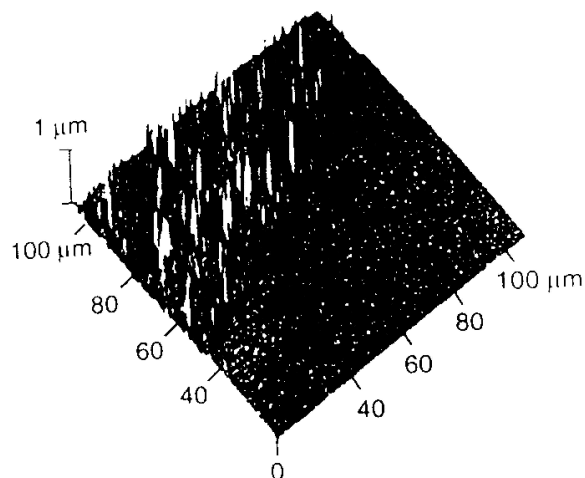


Figure 23: Atomic force micrograph of dark spot and neighboring pristine aluminum. From Cumpston and Jensen [65].

of luminescence and increase in device impedance. This effect obviously degrades both the polymer and the anode.

7.2 Indium-Tin-Oxide Damage

Chao *et al.* [75] report damage of ITO anodes, especially at high electric field strengths (see Figures 25 and 26). This damage manifests itself in volcano-like structures similar to those caused by electromigration-induced Al diffusion in Al cathodes, as described by Cumpston and Jensen [65]. Chao *et al.* suspect the high electric fields and Joule heating as the cause of these morphologies, whose depth ranges between 40 nm and 60 nm. The electrical resistance of the same ITO increases by 3 or 4 orders of magnitude from the original ITO samples.

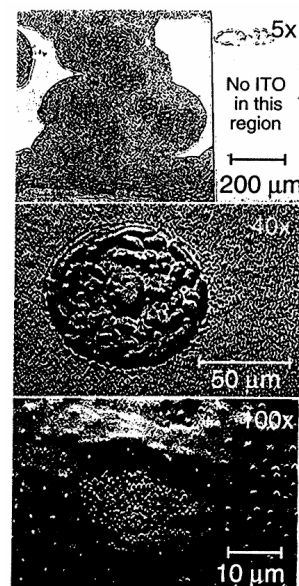


Figure 24: Optical micrograph showing dark spot formation. From Cumpston and Jensen [65].

7.3 Indium Migration from ITO and Indium Contamination of EL Polymer

Esselink and Hadziioannou [76] and others [69] cite that the mechanical and thermal stability of polymer/electrode interfaces plays an important part in determining the lifetime of a device. They report that indium forms small granules of 30 nm width which form larger clusters. Because of an annealing procedure, it was found that indium had diffused through the anode/polymer interface into the polymer poly(3-octylthiophene) (P3OT); in a similar experiment, no diffusion of Al into the P3OT layer from the Al cathode was evidenced. Similarly, Schlatmann *et al.* [77] report indium contamination of the polymer, but, unlike Esselink and Hadziioannou, also report the contamination of the sequenced conjugated block

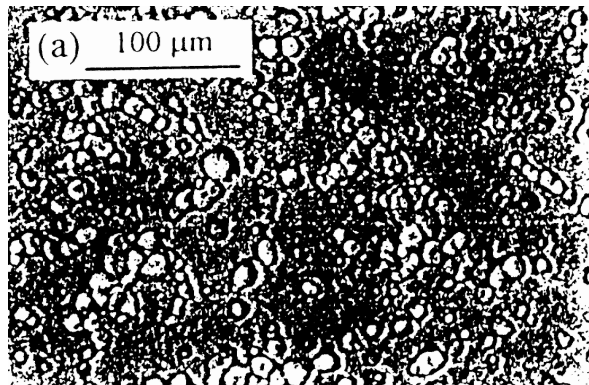


Figure 25: Morphology of ITO surface of damaged ITO/C12OPPP/Ca/Ag device as viewed from ITO side. From Chao *et al.* [75].

copolymer poly[dimethylsilylene-p-phenylene-vinylene-(2,5,5,2'',5''-tetrabutoxy-p-terph-enyl-4,4'-ylene)-vinylene-p-phenylene] [Si-*p*PPV1] by aluminum from the cathode.

Aziz and Xu [68] report infinite resistance of the ITO in failed devices and that indium (In) concentrations in the ITO had decreased. In their experiments, both aluminum and indium concentrations in the electrodes were reduced when compared to the background matrix of the cathode and anode, respectively. Aziz and Xu further report experiments suggesting that this outflux of electrode material is not due to local heating at temperatures which exceeded the degradation temperature of the polymer PPV. This anodic and cathodic corrosion is synergistic and was reported to also hold true for other anode/cathode materials including Mg and Au, respectively. Thus, Aziz and Xu propose an electrochemical mechanism for electrode degradation. It is suggested that the ionic conductivity of the PPV layer is enhanced by moisture and other impurities.

Gautier *et al.* [78] report a modification to the

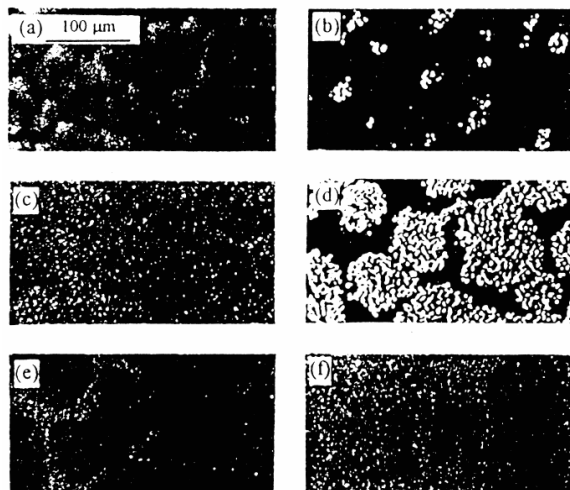


Figure 26: Morphology of poly(isobutylene) [PB] film coated on ITO surfaces for various voltages. From Chao *et al.* [75].

polymer/ITO interface consisting of a 35 Å layer, whose density is intermediate of the interfacing layers. This further supports the transport of oxygen into the polymer from the ITO.

8 Charge Transport Layer-Related

Single layer devices have been modified by the introduction of electron and hole transport layers (see Figure 27). Single layer devices create unbalanced charge injection which have the effect of reducing the recombination efficiency [3], thus charge transport (or injection) layers may be used for the anode or cathode or both. A new electroluminescent configuration utilizing a doped-hole transport layer as the emitter demonstrated an improved stability and a half-life of 3600 hours [79].

Van Slyke *et al.* [45] report highly stable electroluminescent Alq-based devices which includes

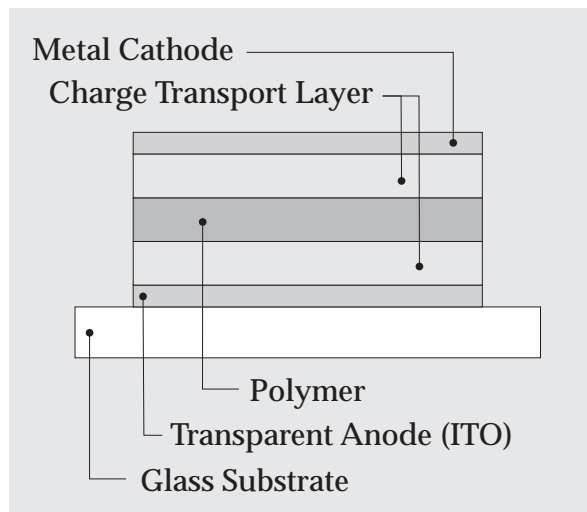


Figure 27: Modified devices utilize charge transport layers between the cathode/polymer and anode/polymer interfaces to increase electron and hole injection, respectively.

a CuPc stabilized hole-injecting contact and a hole-transport diamine layer using a naphthyl-substituted benzidine derivative; they also incorporated an alternating current which drives the device, as opposed to a direct current activation. The i-Si/ITO/CuPc/NPB/Alq/Mg:Ag device was reported to have a half-life of 4000 hours and an initial luminance of 510 cd/m^2 . However, the hole-transporting layer was reported to have a low thermal tolerance. Hole transport layers include polymers such as N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine [TPD] and poly(9-vinylcarbazole) [PVK]. Adachi *et al.* [41] noted that device stability relates inversely with the barrier energy of the hole-injecting contact.

Although charge transport layers have been introduced to increase electron and hole injection, it seems that these novel approaches and variations to

single layer devices are not without problems. Interdiffusion of charge transport layers has been reported by Fujihira *et al.* [43]. In their observations, TPD and Alq₃ diffused into each respective layer during heating. The poor thermal stability of TPD is also thought to cause crystallization [42][80].

Conclusion

This literature survey explored the many facets of device degradation and the mechanisms responsible for the short lifetimes of light emitting polymers. Among the mechanisms cited for the degradation of polymers was singlet oxygen, photo-oxidation, formation of carbonyl groups and other optically quenching chemical species, chemical artifacts of polymer synthesis, chain scissions, and indium contamination; among the mechanisms discussed for cathode degradation were *dark spots* thought to be a result of delamination due to water vapor, electromigration-induced diffusion of cathode metals, morphology of polymer/cathode interface, Joule heating, metal reactivity, and/or metal heat capacities; among the mechanisms cited for anode degradation were oxygen and indium migration out of ITO and into EL polymer; and the crystallization and diffusion of charge transport layers.

Disclaimer

Although the nature of this review focuses on the negative aspects of this nascent field, it is the author's sincere wish that they are not viewed as such. These aspects of device degradation merely demonstrate the exciting challenges that lie ahead for those who labor in this field and the knowledge of material properties, and the physical processes that govern them, that is to be derived from their

work.

Acknowledgements

I am indebted to the professors of the Microelectronics Research Centre for extending me the opportunity to study at the University of Cambridge.

In relation to this survey, I would especially like to thank Dr. Richard Gymer of the Optoelectronics group at Cambridge for supervising my project. I would also like to extend my gratitude to Dr. Haroon Ahmed for allowing this literature survey project to be undertaken. I also would like to thank Dr. H. F. Wittmann for providing many valuable bibliographic resources and reading an early version of the manuscript (all errors still reside with the author). Finally, I would especially like to extend my gratitude to Martin Liess, working in Dr. Zeev Vardeny's group at the University of Utah, for introducing me to this particularly interesting problem in solid state physics.

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