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A method to determine the presence of oxygen in organic light-emitting diodes (OLEDs)

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A method to determine the presence of oxygen in organic light-emitting diodes (OLEDs)

by

Alexander Joseph Smith

A thesis submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Electrical Engineering

Program of Study Committee:

Joseph Shinar, Major Professor

Ruth Shinar

Mani Mina

Iowa State University

Ames, Iowa

2010

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ABSTRACT

Organic light emitting diodes (OLEDs) have great potential to replace current commercial display offerings. However, most of the materials comprising the OLEDs suffer degradation effects from the presence of environmental oxygen and water, as both compounds can penetrate into the device. Much research and effort have been put into fabrication methods and proper device encapsulation to help mitigate these environmental effects.

A new approach for assessing the level of molecular oxygen (O_2) in OLEDs is presented. As a first step, organic films that serve as the emitting layers in OLEDs were fabricated and exposed to known levels of gas-phase O_2 . By doping such layers with a photoluminescent, oxygen sensitive dye molecule, measurements of the oxygen level under different gas-phase O_2 concentrations were made using a voltage pulsed LED as an excitation source and a photomultiplier tube that monitored the decaying photoluminescence (PL). The PL decay time is related to the O_2 level in the organic layer.

Next, devices were made by similarly doping the emitting layers with the aforementioned oxygen sensitive molecule and the devices' electroluminescence (EL) decay following a voltage pulse was observed; the EL decay times were compared with those obtained from the PL experiments of the same emitting layers. By comparing these two sets of data, the oxygen contained within a specific layer of the device can be measured by simply applying a brief voltage pulse to the device, collecting and then analyzing the resultant EL decay curve. This method is inexpensive and easy to introduce to the fabrication process and could have

repercussions as the quest for longer device lifetimes continues since the oxygen level in the emitting layer of the device can then be related to its long-term stability.

CHAPTER 1 . INTRODUCTION

Organic Light Emitting Diodes (OLEDs) have attracted much interest in research for their potential in display and lighting applications. The advantages of OLEDs over current market technologies are numerous. Some of these characteristics include low power consumption, high contrast ratio, wide field of view, compatibility with substrates such as glass and plastic, flexibility in size and design, as well as the potential for inexpensive, large scale device fabrication.

OLED penetration into the marketplace faces several factors that must be overcome before wide scale market share is achieved, at least among large scale displays. As with any new technology, startup costs are high, which affect the price. In 2008, Sony debuted an 11 inch OLED television for \$2,500. Considering that televisions with different technologies (plasma, LCD) at that time were readily available in much larger sizes with a significantly smaller price tag, it is not surprising that in early 2010 Sony scuttled production of the TV, citing lack of demand (1). Small dimension (1-5 inches) OLEDs appeared initially as displays in car stereos, digital cameras and cell phones and recently enjoyed an increase in market share. With the recent success of Apple's iPad there now exists a significant potential market for mid-size (up to 10-11 inches) OLED displays in the growing tablet PC market. OLEDs are also promising for niche lighting applications.

The symptom of slow market emergence of OLEDs is based primarily on the costs associated with the production of a large display. There are many considerations, both fabrication and material related, that inhibit the production of a large size display. The

requirements for OLED fabrication parallel many aspects of crystalline semiconductor fabrication; clean substrates, proper etching, and uniform depositions are all required. However, expensive clean rooms found in inorganic processing are not necessary. Due to the materials involved in organic electronics there is an extra consideration that is of utmost importance. The influence of oxygen and water cannot be ignored as these compounds, in particular water, have deleterious effects on device performance. Much research on the causes behind the degradation of devices due to oxygen and water has been performed, (2). Exposure to water is a major culprit leading to the degradation of devices, though molecular oxygen (O_2) cannot be discounted. It is the goal of current researchers and engineers to mitigate the contamination and resulting performance deterioration of OLEDs due to these naturally occurring elemental factors.

1.1 General Background

1.1.1 OLED Structure & Operation

A basic OLED structure consists of organic layers set between an indium tin oxide (ITO) anode and a metal cathode. ITO is a conductive, transparent layer, allowing the electroluminescence (EL) to pass through (3). The structure is seen in Figure 1.1.

The organic layers are comprised of an electron transport layer (ETL), an emitting layer, and a hole transport layer (HTL). Application of a forward bias results in injection of electrons and holes from the cathode and anode, respectively, to a recombination zone. This zone is often within the area of the ETL that borders the HTL. Other layers of organic and

inorganic materials can be added to aid hole or electron injection by lowering the potential barriers they face, as well as carrier transport.

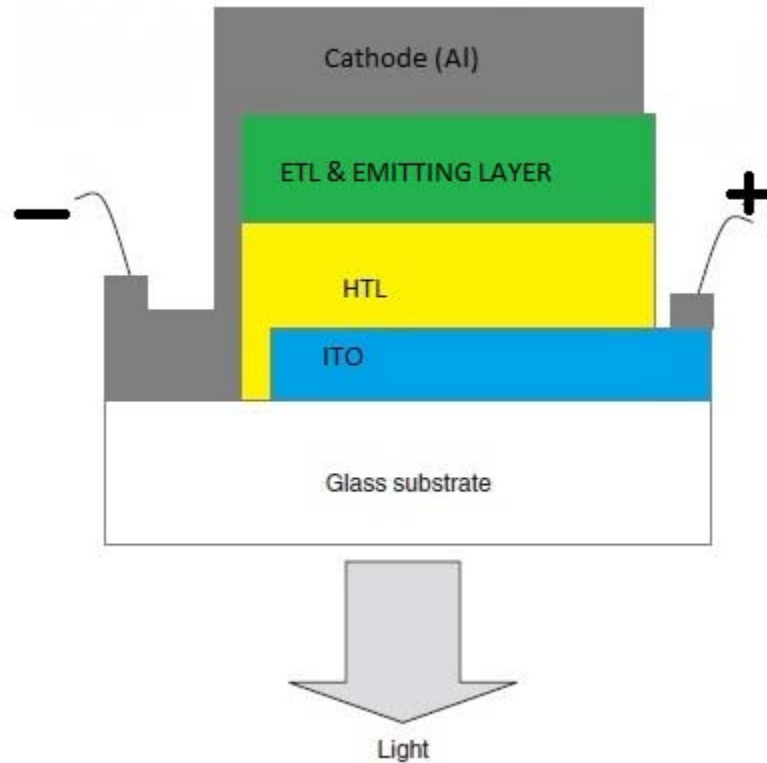


Figure 1.1 Structure of a basic two layer OLED

The operation of the device is similar to that of any diode. This process is seen in Figure 1.2 and described as follows. As a positive voltage is applied at the anode (ITO) and a negative voltage at the cathode (Al), carriers are injected and move across the ETL and HTL. From an energy level standpoint, the lowest unoccupied molecular orbital (LUMO) of the organics is analogous to the conduction band in inorganic semiconductors. An incoming electron from the cathode will occupy the LUMO of the ETL. Similarly, the highest occupied molecular orbital (HOMO) of the organic semiconductors is analogous to the valence band; under the

applied bias, holes from the anode move to the HOMO of the HTL. As holes and electrons approach the recombination zone, near the middle of the device, a Coulombic attraction develops between the oppositely charged particles, forming excitons (3). When these excitons decay radiatively, photons are emitted (4).

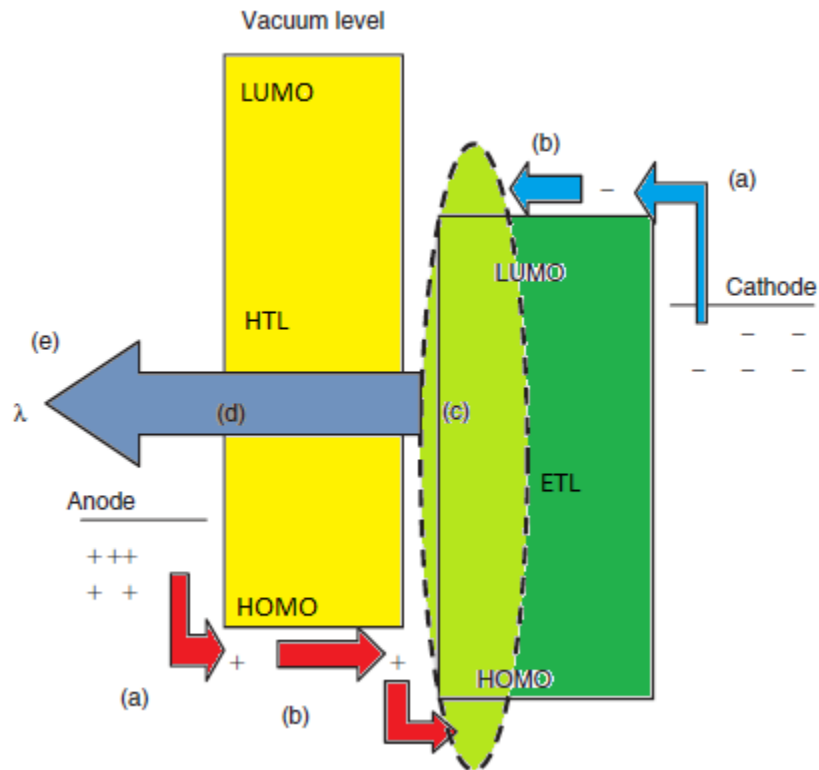


Figure 1.2 An energy diagram representation of light emission in a two layer OLED. The five key processes are: (a) injection of holes and electrons at the anode and cathode, (b) charge transport through the device, (c) exciton formation, (d) exciton decay and finally (e) light emission (5).

It is worth mentioning that fluorescent or phosphorescent emission can occur depending on the organic materials used. In fluorescent materials the radiative decay is limited to singlet

excitons and the lifetime of such excited states is of the order of 10 nanoseconds. For phosphorescent materials, emission occurs from triplet excitons (6). In these materials excited states can last hundreds of nanoseconds to microseconds.

1.1.2 OLED Fabrication Methods & Materials

There are two classes of OLEDs: small molecule OLEDs (SMOLEDs) and polymer light emitting diodes (PLEDs) (7). Though the operation of both devices is the same, methods of their fabrication are different. SMOLEDs are fabricated by thermal evaporation in a vacuum chamber. A diagram of a typical thermal evaporator setup is seen in Figure 1.3.

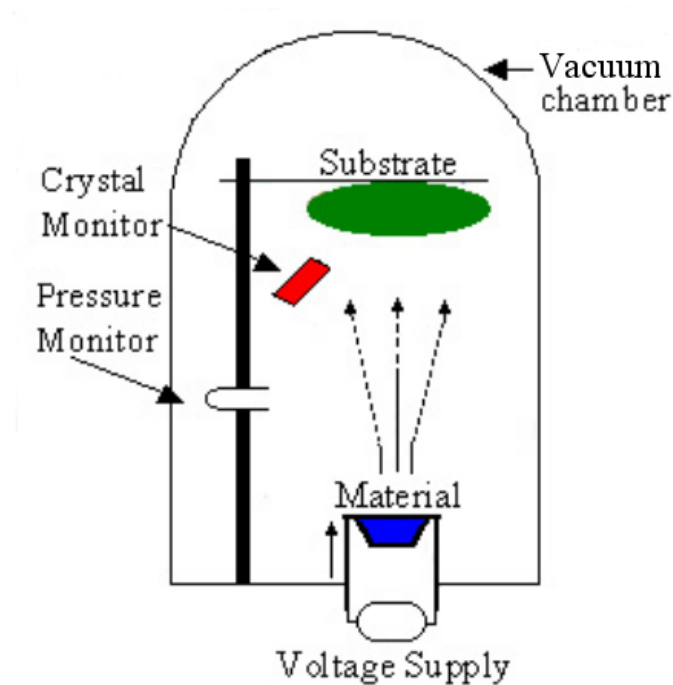


Figure 1.3 Setup of a thermal evaporation system.

A voltage or current supply increases current in a metal coil that holds a crucible with the material to be deposited in it. As the coil heats the crucible, the material vaporizes under this heat. A thickness monitor determines the thickness of the material as it is deposited on the substrate. The pressure monitor determines the pressure inside the chamber.

Doping of small organic materials is done by co-deposition, where two (or more) materials are heated and vaporized simultaneously. The deposition rate of each material is carefully controlled to ensure that the proper host to guest weight ratio is met.

PLED fabrication is done with the polymers or their mixtures dissolved in solvents that are spin coated, screen printed, or inkjet printed. Cathode deposition is done in a thermal evaporation system.

Doping of polymers is done by mixing host and guest materials at the proper ratio in common solvent(s).

Some common OLED materials and their peak emission wavelength are listed in Table 1.1.

Table 1.1 Common light emitting organic materials

Abb. Name	Type	Peak Emission (nm)
Alq ₃	Small molecule	530
NPD	Small molecule	429
MEH-PPV	Polymer	607
PFO	Polymer	428
PVK	Polymer	420

1.1.3 Sensing with Platinum/Palladium Octaethylporphyrin (Pt/PdOEP)

Porphyrins are a class of organic compounds that are essential to life. Both hemoglobin in animals and chlorophylls of plants are porphyrins (8). An important characteristic of a porphyrin is that it binds metals. It is the metal that determines the properties of a porphyrin. For example, in hemoglobin's case, iron binds to an oxygen molecule and later delivers it to the cell where it's needed (9).

A class of photoluminescent (PL) porphyrins of interest in molecular oxygen (O_2) sensing includes octaethylporphyrins with platinum or palladium in their center. Platinum octaethylporphyrin (PtOEP) and palladium octaethylporphyrin (PdOEP) are advantageous materials to use; they exhibit excellent sensitivity to oxygen over a significant range of O_2 concentrations, they dissolve in common solvents and can be used as dopants in both SMOLEDs and PLEDs. Their absorption bands are in the near UV and visible range, allowing use of inexpensive and readily available LEDs as excitation sources (10). The absorption and emission are strong enough that high power light sources are not necessary for excitation. The Stokes shift of these materials when exciting at ~ 535 nm is ~ 100 nm (The PL band peaks at ~ 635 nm) (11), which eliminates the need of narrow full width half maximum light sources and filters.

The absorption (inset) and emission spectra of PdOEP are seen in Figure 1.4. The peak wavelength for absorption is the Soret band at 390 nm, which corresponds to the second excited singlet (S_2) state of the molecule (12). There are two weaker bands around 512 nm and 545 nm corresponding to the S_1 state. From this, it is observed that the optimal light source for excitation should be in the near UV. A deep blue or purple LED will satisfy this

requirement. However, an adequately bright green LED can also serve the purpose of excitation of this indicator molecule if absorption of the host (or matrix) by UV wavelengths is a concern.

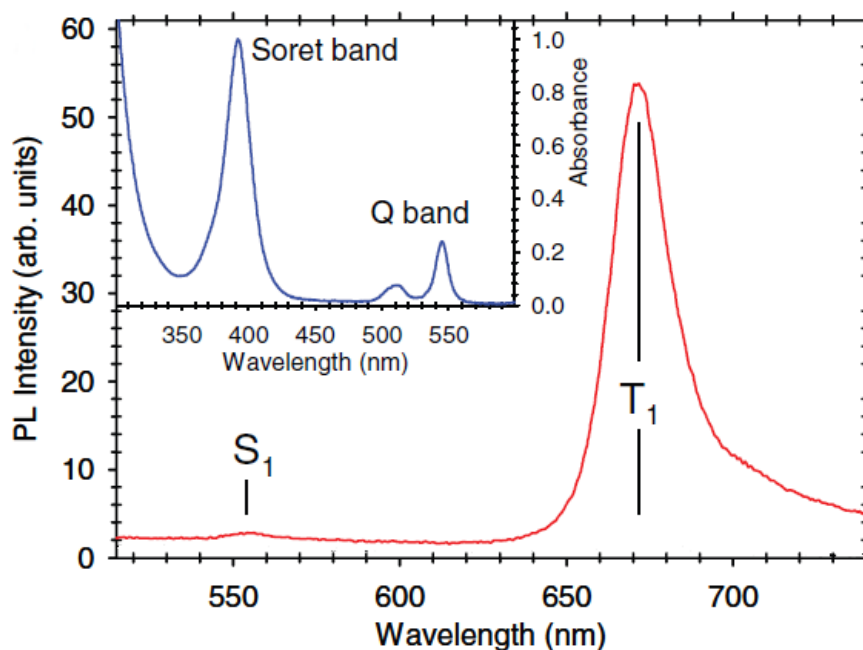


Figure 1.4 Absorption (inset) and emission spectra of PdOEP immobilized in a polymeric film. The respective spectra of PtOEP are similar but blue shifted by ~ 15 nm. (13)

To sense oxygen with PtOEP or PdOEP in a solid state, these indicator molecules are typically immobilized in a polymer matrix. This matrix should allow adequate oxygen penetration to the point where collisions with the indicator molecules are likely with a fast response time. The appropriate film can be used for monitoring oxygen in the gas-phase or in solution (usually water based). An external light source, such as a LED or OLED, is shone on the film. The light excites states within the indicator molecule. The emission is from triplet

states. If no oxygen is present the PL decay time is ~100 microseconds (μs) for PtOEP and ~1 millisecond (ms) for PdOEP. The emission is red, around 650 nm for PtOEP, 665 nm for PdOEP.

If oxygen molecules diffuse through the matrix and collide with indicator molecules, the PL of the oxygen-sensitive dye is quenched. This means that the decay time of the excited state is shortened and the PL intensity reduced (14). This leads to two methods that can be employed to detect O_2 , PL intensity or lifetime. Both follow ideally the Stern-Volmer (SV) linear relationship:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[\text{O}_2]$$

Where I_0 and τ_0 are the unquenched intensity and decay time values, respectively, and K_{SV} is a temperature- and sensor-dependent constant. I and τ are the intensity and decay time for a particular O_2 concentration.

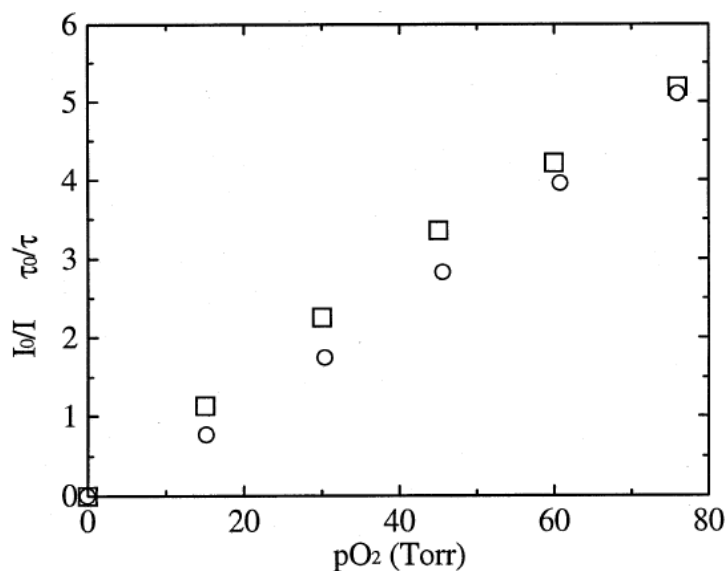


Figure 1.5 Stern-Volmer plot of PtOEP in intensity (○) and lifetime (□) immobilized in pPEGMA9. (15)

The results from intensity and decay time measurements are similar as seen in Figure 1.5. Despite this similarity, lifetime measurements are generally more reliable as they depend on an intrinsic property of the Pt/PdOEP molecule. The intensity method depends on a constant intensity of light incident on the film or, in other words, a similar number of excited molecules for each measurement taken, a requirement that is not always practical due to environmental factors, i.e., background light, or minor changes in the excitation source and sensing film.

The detection sensitivity, $S = \tau_0/\tau_{100}$ or I_0/I_{100} , is the ratio of the PL lifetime (or intensity) of the indicator molecule in the absence of oxygen when these values are the largest, to the value of the lifetime (or intensity) under 100% oxygen. For PtOEP in a gas environment, sensitivities of 30 are common. For PdOEP, also under a gas environment, with $\tau_0=1$ ms and $\tau_{100}= 10$ μ s or less, sensitivities over 100 are possible. One drawback to this method of

sensing is that as O₂ concentrations increase it becomes more difficult to discriminate accurately between close τ values, as the PL signals and therefore the signal-to-noise ratio decrease. Because of its high sensitivity, PdOEP is very useful in detecting very low oxygen concentrations in the 0-2 ppm range that could be common in OLED layers.

1.1.4 Device Degradation Mechanisms

There are several factors that contribute to shortened device lifetime, but the dominant degradation mechanism is the exposure of the device to atmospheric water and to a significant but lesser extent, oxygen. In un-encapsulated devices this exposure rapidly leads to oxidation and de-lamination of the metal cathode (16). In the organics, singlet oxygen can often effectively sever the polymer chains as well as react with carbon, creating quenching centers that decrease the EL. The effects of this can be mitigated by encapsulating the device (17) in an inert atmosphere, as found in a glovebox, where the oxygen and water are kept at low levels (<1ppm). In one approach, a glass slide is affixed to the exposed device by an epoxy and a desiccant can be used in the device package to absorb any residual water that the device may encounter.

There are several other internal degradation mechanisms that include recrystallization of amorphous organic layers, indium migration from the anode into the device, unstable organic molecules and trapped charges at sharp interfaces (18), but these are minor by comparison.

1.2 Background of Phosphorescent PtOEP and PdOEP Doped OLEDs

A drawback of OLEDs with fluorescent emitters is that due to the requirements of spin conservation, these materials emit radiatively only from singlet ($S=0$) states. Singlet states

obeying this conservation account for only 25% of the excitons, the rest (75%) are triplet excitons and undergo nonradiative transitions (19). This low internal quantum efficiency affects device performance. A solution is to introduce a phosphorescent dopant that radiatively emits from triplet states thus utilizing both singlet and triplet states following singlet to triplet energy transfer. If doped with a phosphorescent analyte sensitive molecule, such devices can also be used directly in sensing applications without the need for a sensing film in addition to the excitation source.

1.2.1 Efficient Phosphorescent Emission

Devices have been made with the emitting layer, Tris(8-hydroxyquinolato)aluminium (Alq_3) doped with the phosphorescent dye PtOEP (20). Such devices emit phosphorescence from triplet excitons of the PtOEP molecule. Also, singlet excitons can be converted into triplet excitons. The quantum efficiency is much greater than undoped Alq_3 , which can only emit from singlet excitons. External quantum efficiencies were 4% compared to 1% from a basic Alq_3 device. Maximum external quantum efficiencies of 19% have been realized with this method (21). For this energy transfer to occur, the absorption spectrum of the dye molecule (dopant) must overlap the emission spectrum of the donor (host), thus the emission of the device will be predominantly that of the dye molecule. The EL of the PtOEP doped device was compared to the PL of a 500Å thick film of the same composition that was excited by a laser. The results obtained by optical pumping were performed with a nitrogen laser at 337nm that excited a ($\text{Alq}_3 + 6 \text{ wt. \% PtOEP}$) film. At this wavelength, the laser output is absorbed principally by Alq_3 , ensuring the same transfer mechanisms should occur between the host and the dye as those by EL. The results are seen in Figure 1.6.

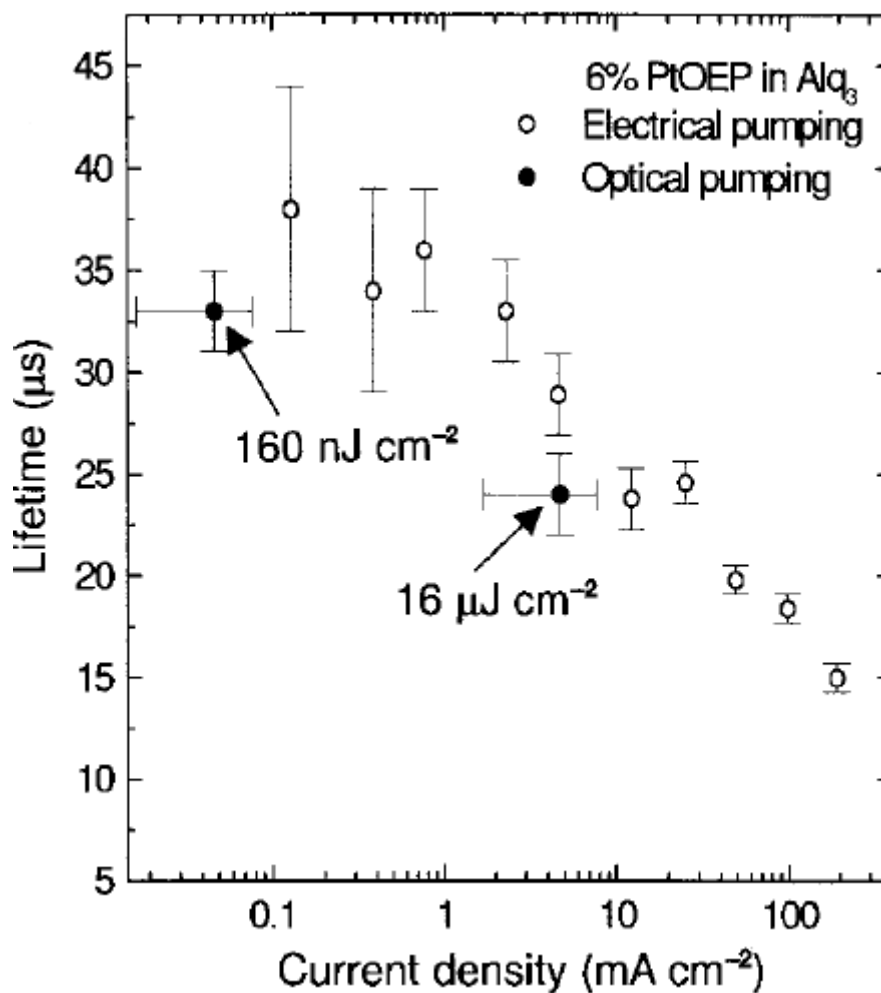


Figure 1.6 Lifetime of PtOEP in Alq₃ host by electrical and optical pumping. The changes in lifetime correlate with an increase/decrease in electrical or optical pumping (20).

The results of Figure 1.6 confirm that the EL of the device and the PL of the film result in similar lifetimes. In fact, a decrease in optical density correlates with the same result as a decrease in current density; lifetime increases for both cases. It is therefore safe to make direct comparisons of the results obtained from both PL and EL methods.

1.2.2 OLED as a Sensor

Assuming that the same energy transfer mechanism is at work under EL as in PL, the oxygen sensing capabilities of PtOEP can be utilized within a device, excited by the EL of the host. A device with poly(N-vinylcarbazole) (PVK) as an emitting host was doped with PtOEP and sensed dry O_2 in lifetime and intensity modes (22). Great care was taken to ensure oxygen permeation into the PtOEP/PVK emitting layer, by excluding transport and blocking layers that could impede the oxygen from reaching the PVK/PtOEP layer and by depositing an aluminum cathode with very narrow dimensions.

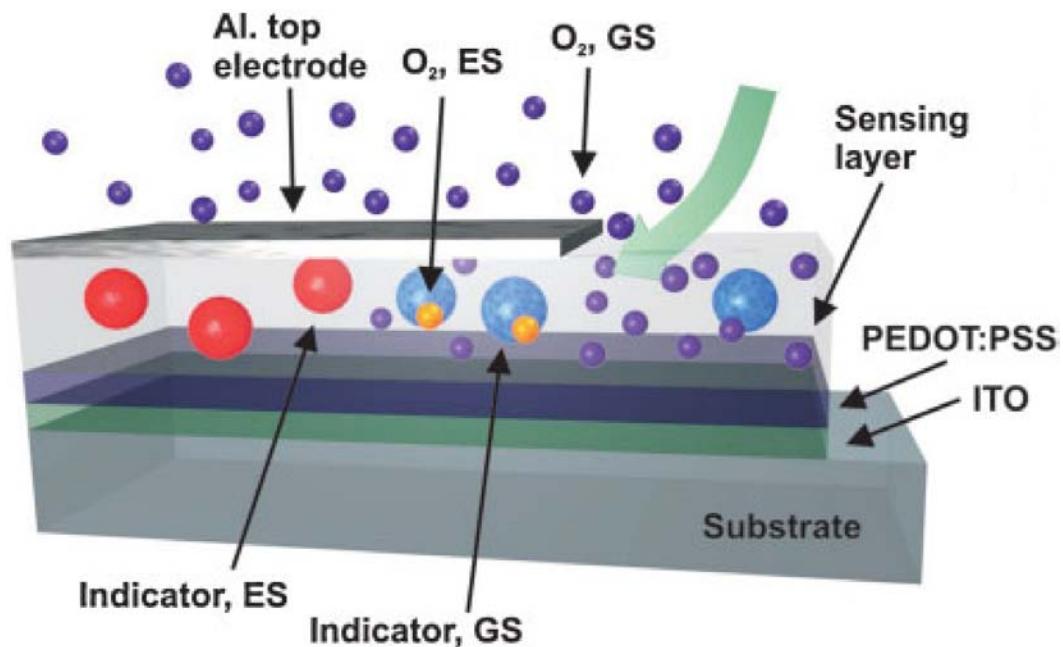


Figure 1.7 Working principle of oxygen probe. O_2 in the ground state (GS) enters the area under the cathode and quenches an indicator (PtOEP) molecule in the excited state (ES)

(22).

The structure as seen in Figure 1.7, shows how O₂ molecules can enter beneath the cathode where they quench the excited states of the PtOEP, and thereby decrease its lifetime. Repeatable results were obtained for a narrow oxygen range (0%-20%) but the concept of device sensing was confirmed.

CHAPTER 2 . ORGANIC LAYERS AS OXYGEN SENSORS

As discussed, PtOEP and PdOEP can be co-deposited with other organics to enhance the quantum efficiency of light emission from such layers in OLEDs. The application of such devices can be extended beyond lighting to sense O₂. The concept has been proven; oxygen can penetrate into organic layers in the OLED at levels sufficient to have an effect on the PL/EL lifetime of excited states.

Since O₂ has detrimental effects on organic layers, it makes sense to utilize these facts to try to determine with what ease or difficulty oxygen will permeate into these layers and then correlate such results with long term device stability.

2.1 Organic Layers & Device Fabrication

2.1.1 Preparation

Devices and layers were fabricated from the same batch to eliminate the possibility of any material differences. First, two glass substrates, each 1" x 2", coated with ITO from Colorado Concept Coatings LLC, were etched in a 50:50 solution of HCl : water to generate a pattern of two strips of ITO per substrate, 2mm wide with at least 2 mm separation. To confirm the desired structure of ITO, the conductivity of the strips was measured after the etch using a multimeter. Next, using a diamond scribe the substrates were cut in half, leaving four, 1"x 1" substrates. The substrates were then cleaned according to the following procedure.

1. Ultrasonicated for 15 minutes in surfactant (40ml Neutrad +1200ml de-ionized water +800ml isopropanol)
2. Rinsed in running tap water for 15 minutes
3. Ultrasonicated in isopropanol for 3 minutes
4. Ultrasonicated in acetone for 5 minutes
5. Ultrasonicated in isopropanol for 2 minutes

Substrates were then blown dry with compressed argon gas after which they were treated with UV ozone for 5 minutes to increase the ITO's work function.

2.1.2 Fabrication

The fabrication procedure differs if the devices and films used small molecular materials or polymer materials, both methods are described.

Small molecule OLED and film fabrication

The substrates were loaded into a glovebox with an inert argon atmosphere with O₂ concentrations of ~1-10ppm. These were then placed inside a thermal evaporation chamber which was pumped down to at least a base pressure of $1-2 \times 10^{-6}$ Torr.

Devices with doped Alq₃ or *N,N'*-diphenyl-*N,N'*-bis(1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine (NPD) (both obtained from H.W. Sands) emitting layers were fabricated; in each case the dopant level was 2 wt.% PdOEP (obtained from H.W. Sands). The complete device structure was ITO/MoO₃-5nm/NPD-45nm/Alq₃+2% PdOEP-50nm/Al-70nm for the Alq₃ emitting device and ITO/MoO₃-5nm/NPD+2% PdOEP-45nm/Al-80nm for the NPD

emitting device. One of the substrates was removed before final aluminum deposition for both the Alq₃ and NPD structures. This serves as the film used to test O₂ permeability and develop SV calibration curves under different O₂ concentrations.

Polymer OLED and film fabrication

1ml of PEDOT:PSS (from H. C. Starck) was spin coated on the ITO/glass substrate at 2000rpm for 120 seconds and baked for 30 minutes at 100°C on a hotplate before being transferred into a glove box, where baking continued for another 30 minutes at 100°C. A solution of 6 mg/ml PVK with 2 wt.% PdOEP in chloroform was prepared and ultrasonicated for 1 hour before being loaded into the glovebox. 500 µl were spin coated on substrates for 60 seconds at 1000 rpm and then baked for 1 hour in the dark at 70°C. The substrates were loaded into a thermal evaporator and pumped down overnight to ensure any residual moisture or solvent was removed. An aluminum layer 70 nm thick was deposited. The device structure was ITO/PEDOT:PSS/PdOEP-doped PVK/Al-70nm. One structure was without the Al layer as it served for testing the film's response to oxygen for SV calibration purposes.

2.2 Organic Layer and Device Testing

2.2.1 O₂ Permeability of Organic Layers

To test the permeability of oxygen into the organic layers (Alq₃, NPD and PVK), SV calibration curves were made by testing each respective film's response under varying O₂ concentrations. The doped films of Alq₃, NPD and PVK were enclosed in clear 1" x 1" polystyrene cases with a hole just large enough for a tube to be inserted to deliver a mixture of oxygen and argon gases. A near UV LED (UniqueLEDs Product# 0805VUV0C) with peak emission at 405nm was used as the excitation source of these films. Back detection mode was used as seen in Figure 2.1. This mitigates the amount of EL from the LED that can enter the light detector, a photo multiplying tube (PMT), thus eliminating the need for an optical filter.

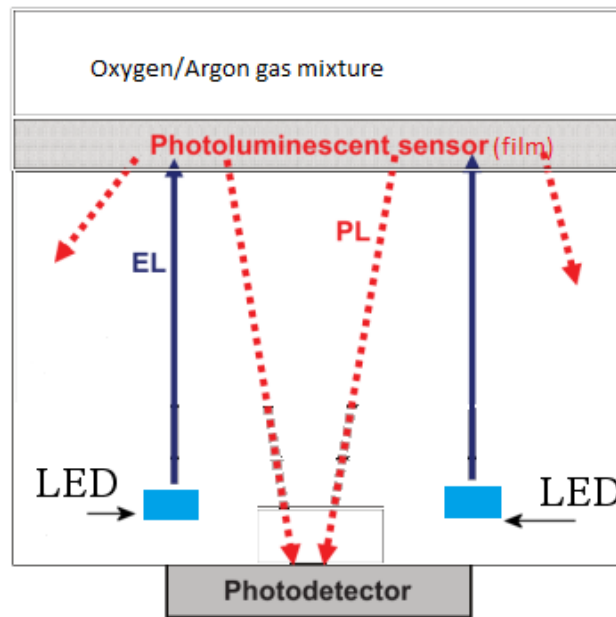


Figure 2.1 “Back detection” geometry used in PL measurements.

The LED was pulsed with an Avtech AV-1011B pulse generator for 1ms at 4V. The PL was monitored with a Hamamatsu R6060 PMT at ~970V, which was connected to a Tektronix TDS 2024 Oscilloscope. Oxygen concentrations were adjusted between argon and dry oxygen using mass flow controllers. While the rates were varied between the concentrations of oxygen and argon, total flow rate remained constant at 100 sccm.

2.2.2 O₂ Presence in OLEDs

The devices' emission spectra were all measured using an Ocean Optics 2000 Spectrometer. This was done to confirm that the EL of these devices originates from the PdOEP molecules in the host (~665 nm). The peak emission wavelength for the devices is seen in Table 2.1.

Table 2.1 Peak wavelength of devices' EL

PdOEP-doped emitting layer	Peak wavelength (nm)
Alq ₃	669.5
NPD	665.9
PVK	665.9

The EL lifetimes of devices doped with PdOEP in the emitting layers of Alq₃, NPD and PVK were measured by pulsing the devices for 1ms at their turn on voltages, ~4-7V. The EL was collected by the PMT and sent to the oscilloscope where a computer accessed the data.

CHAPTER 3 . RESULTS AND DISCUSSION

3.1 Oxygen Permeability of Organic Layers

Decay curves were analyzed for best fit at gas-phase O_2 concentrations of 0%, 5%, 10%, 20%, 40%, 80%, and 100%. Shown in Figures 3.1-3.3 are examples of the exponential PL decay curves of organic films doped with PdOEP. Oxygen concentrations of 0%, 20% and 100% are displayed to show the trend of shorter lifetimes with increasing oxygen in all cases, regardless of the host material.

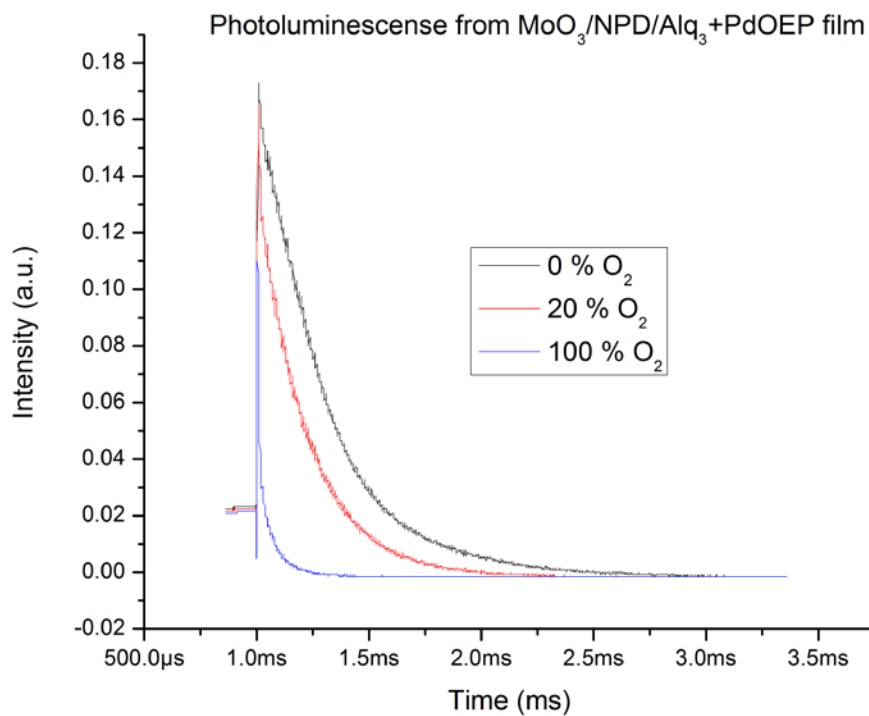


Figure 3.1 PL decay curves from an Alq_3 doped with PdOEP film.

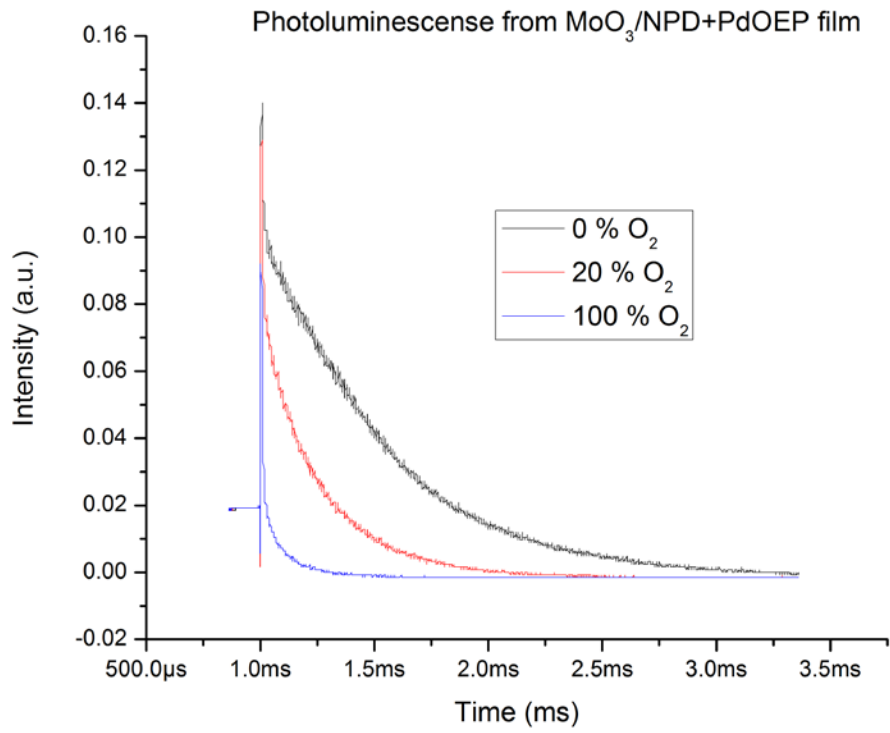


Figure 3.2 PL decay curves from an NPD doped with PdOEP film.

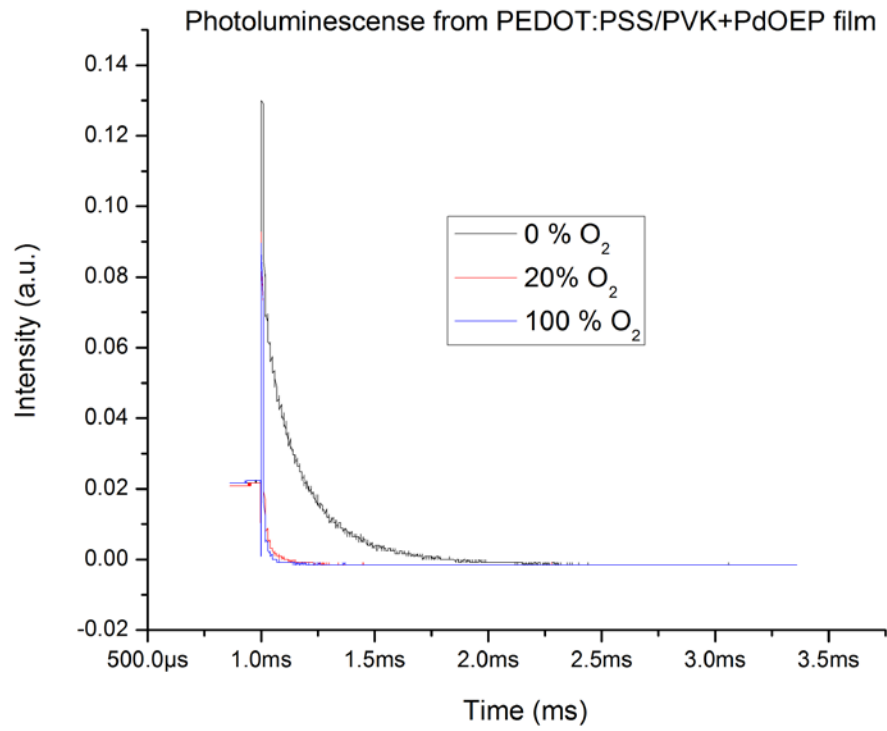


Figure 3.3 PL decay curves from a PVK doped with PdOEP film

The SV calibration plots for Alq₃, NPD and PVK are seen in Figure 3.4

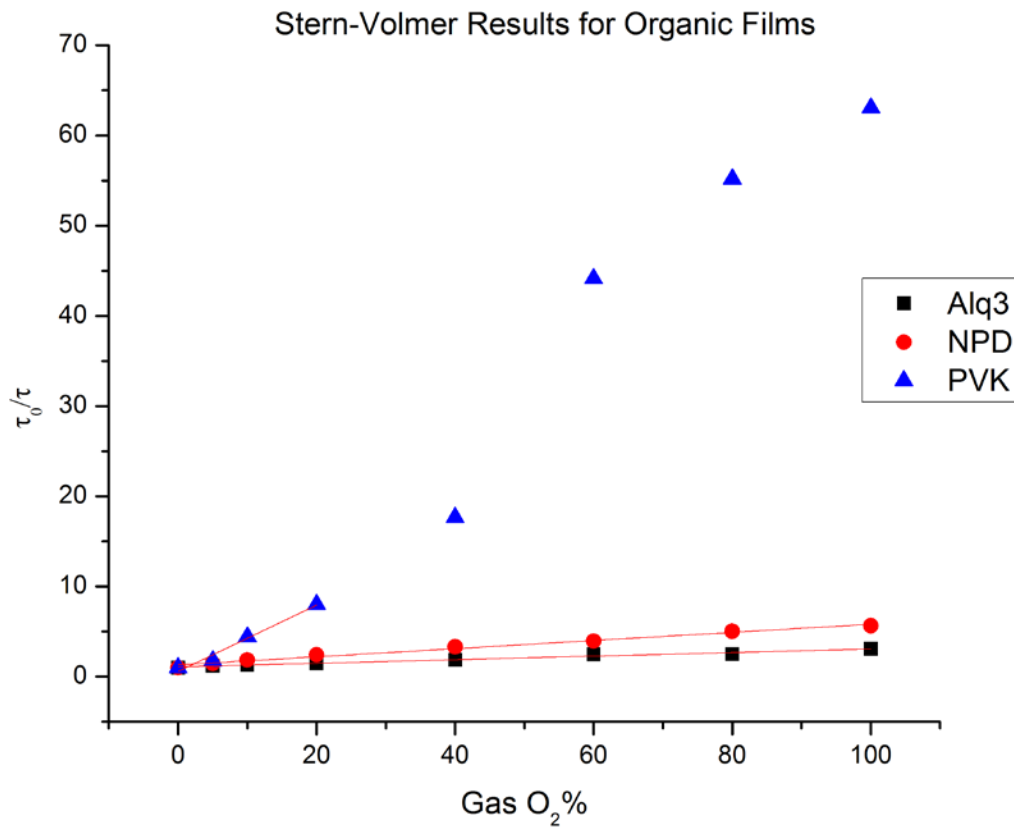


Figure 3.4 Stern-Volmer plots and best fit for Alq₃, NPD and PVK films.

As can be seen in Figure 3.4, Alq₃ and NPD both exhibit relatively low sensitivities to oxygen, demonstrating that oxygen cannot permeate the layers as easily as into PVK. The SV plots for Alq₃ and NPD are linear along the whole range of oxygen concentrations unlike the situation for PVK.

As previously mentioned, the ideal Stern-Volmer relationship used as the basis for analysis is:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[O_2]$$

This was used in the lifetime (τ) mode for the experiments described. Finding the best fit of the nearly linear curves found in Figure 3.1 follow this equation closely. The best fit data are as follows.

$$\text{Alq}_3: \frac{\tau_0}{\tau} = 1.085 + 0.020[O_2]$$

$$\text{NPD}: \frac{\tau_0}{\tau} = 1.310 + 0.045[O_2]$$

$$\text{PVK}: \frac{\tau_0}{\tau} = 0.584 + 0.368[O_2]$$

These can be rearranged to solve for the ambient O_2 for a particular known lifetime (τ). Measuring the oxygen content within the film with a technique such as SIMS (secondary ion mass spectrometry) should enable calibration of the oxygen within the film vs. the ambient oxygen. τ_0 was found experimentally.

For PVK the range of the PdOEP lifetime values is the greatest, from nearly $900\mu\text{s}$ in a pure argon environment down to $14\mu\text{s}$ under pure oxygen, exhibiting the greatest permeability to oxygen out of all the layers studied. Additionally, PVK's SV plot is linear only in the low oxygen regime. The decay time values for PdOEP in Alq_3 and NPD at 100% oxygen are $214\mu\text{s}$ and $200\mu\text{s}$ respectively, indicating a low permeability of oxygen. Table 3.1 shows the lifetime range of the films as well as their sensitivity.

Table 3.1 PdOEP-doped film PL decay lifetimes, sensitivities

PdOEP-doped emitting layer	Observed lifetime under 0% oxygen (μs)	Observed lifetime under 100% oxygen (μs)	Overall Sensitivity (τ_0/τ_{100})
Alq ₃	660	214	3.1
NPD	1130	200	5.7
PVK	883	14	63.1

Using the SV calibration plots obtained for each PdOEP-doped layer, it is possible to qualitatively assess the oxygen level in such emitting layers in OLEDs. Since the EL decay time of each of the devices is determined by that of the PdOEP (Table 2.1), the EL following a voltage pulse yields a level of oxygen proportional to that in the OLED. The decay times and the corresponding estimated O₂ levels are seen in Table 3.2. As seen, the PVK layer shows the highest oxygen (shortest decay time). As all the devices were fabricated under comparable conditions with the actual oxygen exposure comparable, the calculated higher oxygen level indicates a higher level within the layer.

Table 3.2 EL decay lifetime and corresponding O₂ exposure level

PdOEP-doped emitting layer	EL decay time (μs)
Alq ₃	454
NPD	676
PVK	407

The value of τ (407 μs) is shortest for PdOEP:PVK, indicating the highest oxygen level within that device layer, as expected from the calibration lines of Figure 3.1. The oxygen level in the PdOEP:NPD emitting layer is the lowest of the three (based on the highest τ

value of 676 μs). This low value is expected from the SV plot of the respective film, however, the oxygen level in the PdOEP:Alq₃-based device is higher than expected. It is possible that unintentional variations in the oxygen level during fabrication are responsible for this behavior. Differences in the aging and post-fabrication oxygen permeability may also play a role. Future studies should address those issues systematically.

3.2 Conclusion and Recommendations for Future Work

A method to determine the presence of oxygen in OLEDs was explored. Such a method might also be relevant to determination of water levels in OLEDs, if the oxygen and water levels are related. Organic layers and devices with emitting layers of PdOEP-doped Alq₃, NPD and PVK were fabricated. Calibration curves based on the PL decay time were created to establish a relationship for oxygen permeability into the organic layers. OLED electroluminescence decay times following a voltage pulse were compared to PL lifetimes as a direct way to assess the oxygen level within the OLED.

The results indicate the highest oxygen level within the PdOEP:PVK-based device, as expected from the SV calibration plots. However, the results deviate from the expectation for the PdOEP:Alq₃-based device. This situation may be due to the experimental conditions with higher than optimal levels of oxygen in the glovebox during fabrication. This should be further investigated. Devices should be fabricated in a very low O₂ glove box and the vacuum of the evaporation chamber should be broken only under those conditions. These devices should be compared to those made under higher O₂ conditions. Ideally, devices could be made where a break in the vacuum is not required. This method may lead to optimized fabrication processes where there is little to no exposure to oxygen of the devices.

Long term monitoring of the oxygen level in the devices should also be performed for both encapsulated and un-encapsulated devices. Testing the stability of un-encapsulated devices can allow for a relatively quick method (only a few days) to determine which organic materials/device structures are more susceptible to the presence of oxygen. Testing the long term stability of encapsulated devices should be done to aid in evaluating the quality of encapsulation methods.

It may also be of interest after determining oxygen concentrations of a film to see if the oxygen permeation process is reversible. This would be done by placing a device that has been exposed to oxygen for a period of time into a vacuum chamber and pumping the chamber to low pressures. After this is done, the device's EL can be measured. The results would answer whether or not oxygen can effectively be removed from OLEDs after fabrication and perhaps prolong their life.

Photoluminescence measurements of Pt/PdOEP-doped devices should also be performed as a method to determine oxygen presence in OLEDs. This can be done without turning the device on, so it can work with "dead" devices. Instead, to measure a pixel's O₂ concentration, the emission side of the glass (non-cathode) should be sealed off with opaque tape everywhere but the pixel of interest. Then an excitation source (LED, laser) can excite the Pt/PdOEP contained within the pixel and emitted photoluminescence can be measured by a PMT or photodiode. These results can also be compared with electroluminescent results to further confirm that the same decay processes are at work between EL and PL excitation as well as offering an alternate way to detect oxygen in OLEDs.

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