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Polymers and Its Application in Light Emitting Diodes: A Review Article

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Abstract
Polymers are widely used in electrical and electronic applications and also play a very important role in human life. Our body is made of lot of polymers, like Proteins, enzymes, etc. They are substances whose molecules have high molar masses and are composed of a large number of repeating units. Other naturally occurring polymers like wood, rubber, leather and silk are serving the humankind for many centuries now. Today's development of polymeric electroluminescent diodes for flat panel displays offers many advantages, including their versatility for fabrication, flexibility, low operating voltage, and the ease with which color tuning of light emission can be achieved. It has different applications such as antistatic coating of polymers and glass, high conductive shell, organic light emitting diode displays, nano-fiber electrodes for unit stimulation, solar cells, cathode material in electrolytic capacitors, printing wiring panels, textile fibers with colour varying properties, transparent electrodes for thick-film electroluminescence, source gate and drain in the quickly developing organic semi-conductors field. One of the applications of polymer is to use in the fabrication of light emitting diodes and the one which is produced from the organic polymer is more advantageous over the inorganic one.
Keywords: light emitting diode, polymers, organic light emitting diodes

INTRODUCTION

They are also substances whose molecules have high molar masses and are composed of a large number of repeating units and are formed by chemical reactions in which a large number of molecules called monomers are joined sequentially, forming a chain. They are classified by the characteristics of the reactions by which they are formed. If all atoms in the monomers are incorporated into the polymer, the polymer is called an addition polymer (Shakhashiri, 2012) and they are widely used in electrical and electronic applications. In early works, polymers have been used as insulators because of their high resistivity and dielectric properties. Polymer-based insulators are used in electrical equipment to separate electrical conductors without passing current through themselves. The insulator applications of polymers include printed circuit boards, wire encapsulants, corrosion protective electronic devices, and cable sheathing materials (Chilton, 1995; Goosey, 1995). They didn't use widely in electrical and electronic applications only, but also they play a very important role in human life. In fact, our body is made of lot of polymers, like Proteins, enzymes, etc. Other naturally occurring polymers like wood, rubber, leather and silk are serving the humankind for many centuries now (William, 2004; Callister, 2004). They have several advantages, such as easy processing, low cost, flexibility, high strength, and good mechanical properties. In the microelectronic fabrication industry, polymers are used in the photolithography process. Polymers can become suitable materials for optoelectronic and photonic applications. Optical characterizations of polymer such as optical absorption, luminescence spectra, infrared dichroism, and Raman polarization are the most vital tools used to examine the electronic properties of polymers (Alias *et al*., 2013).

The synthetic polymers used are also quite vast ranging from organic polymers based on alpha olefins to inorganic materials based on silicones. Commonly used synthetic polymers are acrylic acid based polymers, polyacrylamides, and alkylene oxide based homopolymers and copolymers (Patil, 2013; Ferritto, 2013). In 1977, however, the conductivity of polyacetylene increases significantly upon doping with various electron acceptors or electron donors (Shirakawa *et al*., 1977). The conjugated structure with alternating single and double bonds or conjugated segments coupled with atoms providing p-orbitals for a continuous orbital overlap (e.g., N, S) seems to be necessary for polymers to become electrically conducting (Nalwa, 1997; Chien, 1984). The recent development of polymeric electroluminescent diodes for flat panel displays offers many advantages, including their versatility for fabrication (especially over a large area), flexibility, low operating voltage, and the ease with which color tuning of light emission can be achieved. In practice, transparent indium tin oxide (ITO) coated glass is often used as the anode and a layer of low work-function metal (e.g., aluminum, calcium) is used as the cathode. Upon application of an electrical voltage to the LED device, electrons from the low work-function cathode (i.e., Al) are injected into the lowest unoccupied molecular orbital (LUMO) of the PPV layer, whereas holes from the high work-function anode (ITO) are injected into the highest occupied molecular orbital (HOMO). These injected charges migrate under the influence of the applied electric field and combine in the Band gap of the PPV layer, leading to emission of light. The wavelength (and hence the color) of the photons thus produced depends on the energy gap of the organic light-emitting material. Since conjugated polymers can have energy gaps over the range between 1 and 4eV (1240-310 nm), polymer-based LEDs should, in principle, emit light

across the whole spectrum from ultraviolet to near infrared (Williams, 1987; Hall, 1987).

Polymer Types

Polymers are classified in several ways-by how the molecules are synthesized, by their molecular structure, or by their chemical family. For example, linear polymers consist of long molecular chains, while the branched polymers consist of primary long chains and secondary chains that stem from these main chains. The better way to classify polymers is according to their mechanical and thermal behavior. Industrially polymers are classified into two main classes-plastics and elastomers.

Plastics

Plastics are moldable organic resins. These are either natural or synthetic, and are processed by forming or molding into shapes. They have the properties of; light weight, wide range of colors, low thermal and electrical conductivity, less brittle, good toughness, good resistance to acids, bases and moisture, high dielectric strength (use in electrical insulation), etc. They are classified in to two groups depending on their mechanical and thermal behavior. These are; thermoplasts (thermoplastic polymers) and Thermosets (thermosetting polymers).

Thermoplasts

These plastics soften when heated and harden when cooled-processes that are totally reversible and may be repeated. These materials are normally fabricated by the simultaneous application of heat and pressure. They are linear polymers without any cross-linking in structure where long molecular chains are bonded to each other by secondary bonds and/or inter-wined. They have the property of increasing plasticity with increasing temperature which breaks the secondary bonds between individual chains. Common thermoplasts are: acrylics, PVC, nylons, polypropylene, polystyrene, polymethyl methacrylate (plastic lenses or perspex), etc.

Thermosets

These plastics require heat and pressure to mold them into shape. They are formed into a permanent shape and cured or 'set' by chemical reactions such as extensive cross-linking. They cannot be re-melted or reformed into another shape but decompose upon being heated to too high a temperature. Thus thermosets cannot be recycled, whereas thermoplasts can be recycled. The term thermoset implies that heat is required to permanently set the plastic. Most thermosets composed of long chains that are strongly cross-linked (and/or covalently bonded) to one another to form 3-D network structures to form a rigid solid. Thermosets are generally stronger, but more brittle than thermoplasts. Advantages of thermosets for engineering design applications include one or more of the following: high thermal stability, high dimensional stability, high rigidity, light weight, high electrical and thermal insulating properties and resistance to creep and deformation under load. There are two methods whereby cross-linking reaction can be initiated-cross-linking can be accomplished by heating the resin in a suitable mold (e.g. bakelite), or resins such as epoxies (araldite) are cured at low temperature by the addition of a suitable cross-linking agent, an amine. Epoxies, vulcanized rubbers, phenolic, unsaturated polyester resins, and amino resins (ureas and melamines) are examples of thermosets.

Elastomers

Also known as rubbers, these are polymers which can undergo large elongations under load, at room temperature, and return to their original shape when the load is released. There are number of man-made elastomers in addition to natural rubber. These consist of coil-like polymer chains those can reversibly stretch by applying a force (William, 2004; Callister, 2004; Harper, 1996).

Conducting Polymers

Conducting polymers (CPs) have drawn significant interest of researchers for more than 30 years because of their economical importance, superior stability, lighter weight, better workability, resistance to corrosion and satisfactory electrical conductivity. Some of the applications of CPs include: rechargeable batteries, electrochromic display devices, light reflecting or light transmitting appliances for optical information, sensors and storage for glare reduction systems and smart windows in automobiles and buildings, polymeric light emitting diodes (PLEDs), photovoltaic devices, transistors, electromagnetic shielding against electro-magnetic interferences (EMI) and printed electronic circuits (Ravindra *et al*, 2015). There are four major classes of semiconducting polymers that have been developed so far which include conjugated conducting polymers, charge transfer polymers, ionically conducting polymers and conductively filled polymers. The conductively filled polymers were first made in 1930 for the prevention of corona discharge.

Polyacetylene

In the mid-1970s, polyacetylene (PA) was accidentally fabricated by Shirakawa, the first polymer capable of conducting electricity. It is an organic polymer with the repeating unit $(C_2H_2)_n$ (Heeger, 2001).

Poly (3, 4-ethylenedioxythiophene)

Poly (3, 4-ethylenedioxythiophene) (PEDOT) is a CP based on 3, 4-ethylene dioxyl thiophene monomer. Advantages of PEDOT are optical transparence in thin, oxidized films, very high stability and reasonable band gap and low redox potential (Kirchmeyer, 2005; Reuter, 2005). It can be used in lots of different applications such as antistatic coating of polymers and glass, high conductive shell, organic light emitting diode displays, nano-fiber electrodes for unit stimulation, solar cells, cathode material in electrolytic capacitors, printing wiring

panels, textile fibers with colour varying properties, transparent electrodes for thick-film electroluminescence, source gate and drain in the quickly developing organic semi-conductors field (Groenendaal *et al*., 2000).

Poly (phenylene vinylene)

PPV is the most studied conjugated polymer for electroluminescence (EL) emission. It is a diamagnetic substance, capable of electroluminescence and has extremely low electrical conductivity of the order of 10^{-13} S/cm having structure which is intermediate between that of PA and PP. The electrical conductivity enhances upon doping with iodine, ferric chloride, alkali metals or acids but with less stability. Generally, unsubstituted unaligned PPV shows reasonable conductivity with doping ranging from 10^{-3}-100 S/cm synthesized via the popular Gilch route. The emissive layer of first PLED is prepared using PPV in 1990 (Burroughes, 1990).

Polyphenylene and Polyparaphenylene

PPP is the precursor to a CP of the rigid-rod polymer host family made of repeating p-phenylene units and converted to its conducting form using an oxidant or a dopant. In 1980, PPP was doped to attain the conductivity comparable to PA (Ballard, 1998).

Polypyrrole

Polypyrrole (PPy) is a type of organic polymer formed by polymerization of pyrrole. It was shown to be a CP in 1968.

Some Structures of Conducting Polymers

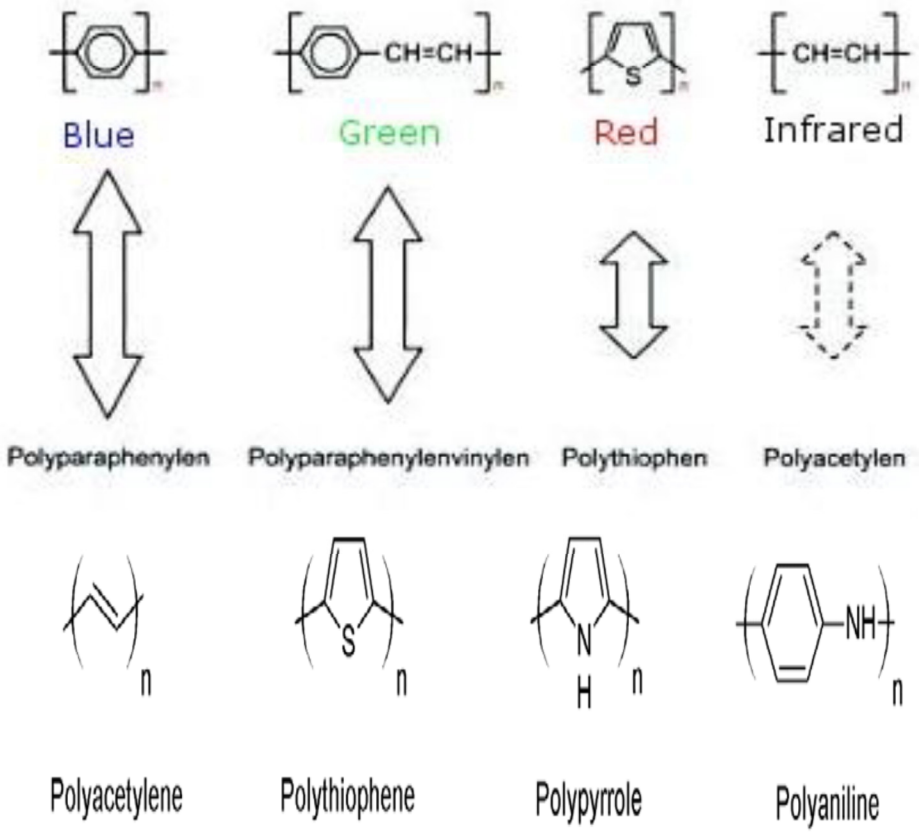

Figure 1: First generation of conjugated polymers

Table 1: Structures, Energy band gap and Conductivities of Conducting Polymers

Polymer	Discovery	Structure	Energy band gap (eV)	Conductivity (S/cm)
Polythiophene	1981		2.1	$10 - 10^3$
Polyacetylene	1977		1.5	$10^3 - 1.7x10^5$
Polyaniline	1980		3.2	30 - 200
Polypyrrole	1979		3.1	$10^2 - 7.5x10^3$
Poly(3,4-ethylene-dioxythiophene)	1980		1.1	300
Poly(p-phenylene vinylene)	1979		2.5	$3 - 5x10^3$
Polyphenylene and(polyparaphenylene)	1979		3.0	$10^2 - 10^3$

(Source: Ravindra *et al*., 2015)

Application of polymer for lighting devices

Solid state lighting devices including white light emitting diodes (LEDs), organic LEDs (OLEDs), quantum-dot LEDs (QLEDs) and carbon-dot LEDs (CLEDs) are promising energy efficient lighting sources for displays and general lighting. LEDs are replacing traditional lamps for both general lighting and display applications, whereas OLEDs are finding their own special applications in various areas. QLEDs and CLEDs have advantages such as high quantum yields, narrow emission spectra, tunable emission spectra and good stability over OLEDs, so applications for these devices are being extended to new types of lighting sources. One fifth of global power consumption is used for lighting; therefore, it is very important to develop energy-saving lighting devices as part of an energy sustainability strategy. Lighting devices emit photons of different wavelength ranges, depending on the luminescent material used and the mechanism for light generation. Large display devices such as TVs are becoming bigger and hence they need brighter and more efficient backlighting devices; whereas small display devices such as mobile phones and notebook computers require more energy efficient backlights for better battery life (Tak *et al.*, 2012).

Figure 2: Fabrication of smart TVs and smart phone from polymers **(**Source: Xiaodi, 2006).

When sufficient energy is applied to a semiconducting polymer, electrons from the HOMO level (valence band) are excited to the LUMO level (conduction band). This excitation process leaves holes in the valence band, and thus creates "electron-hole-pairs (EHPs)". When these EHPs are in intimate contact (i.e., the electrons and holes have not dissociated) they are termed "excitons". In presence of an external electric field, the electron and the hole will migrate (in opposite directions) in the conduction and valence bands, respectively. By adding a hole transport layer (HTL) and an electron transport layer (ETL) to the three-layer device one can expect the equalization of injection rates of holes and electrons, consequently leading to a higher electroluminescent efficiency of the OLEDs. This is because of the better balance of a high work function between the indium tin oxide (ITO) and the HTL, and a low work function between the cathode and the ETL in OLEDs (Nguyen *et al.*, 2013).

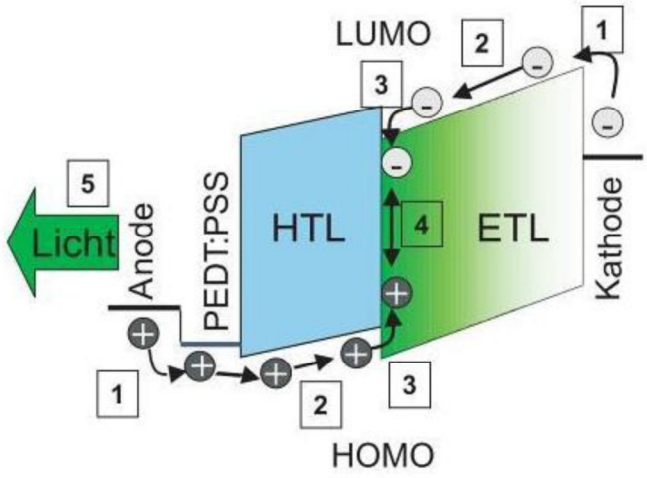

Figure 3: Advanced polymer light emitting diode setup (Source: Huang *et al.*, 2006).

However, the surface of ITO is chemically and physically well defined, and may degrade the performance of the hole injecting electrode in OLEDs and other applications with time. PEDOT:PSS is another widely used hole injection layer in polymer light-emitting diodes (PLEDs), although the aqueous PEDOT:PSS dispersion can cause degradation due to its acidic nature and the presence of moisture, leading to reduced device lifetime. The introduction of PEDOT: PSS also decreases the transmittance of the ITO substrate, which is not helpful in light management. The hole transporting polymer is usually a polystyrenesulphonic acid doped poly (dioxyethylene thienylene) (PEDOT: PSS). It has two major roles, one of which is the formation of a thin film by spin-coating that can smooth the surface of ITO, and the other more important role is that this film has a higher work-function than an ITO film, which is good for hole injection due to the lower height of the injection barrier. The PEDOT: PSS as the hole transporting layer, efficient luminance can be achieved in PLEDs that employ many different kinds of polymer materials, especially for red and green-emitting polymers (Xian-Yu D., 2011).

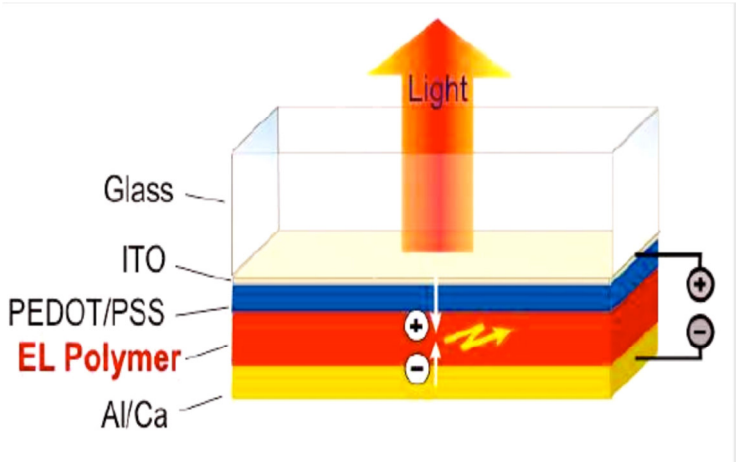

Figure 4: Two electrodes of different work functions such as Ca, and Indium- tin- oxide, (ITO), separated by an electroluminescent (EL) polymer, which emits light when electrons and holes are injected from the electrodes (Morgado *et al*., 2004).

Organic semi conductive thin films have caused extensive interest among scientists worldwide over the past two decades because of their versatility and ease of preparation, leading to various potential applications in electrical and electronic devices such as transistors, photodiodes and light-emitting diodes (LEDs). In 1987, by using two-layer organic light-emitting diodes (OLEDs), a team in Kodak demonstrated devices with appropriately low operation voltages and attractive EL efficiencies by exploiting suitable small-molecule materials and structures (Xian, 2011).

Light-emitting diodes

Polymer light-emitting diodes PLEDs are promising candidates for the next-generation displays, particularly for portable electronic devices such as cellular phones. Recently, phosphorescent dopants have been successfully used in organic light-emitting diodes OLEDs to improve the device performance by breaking the spin conservation rule (Fang-Chung Chen *et al.*, 2002). LEDs are solid-state semiconductor devices which contain a single p-n junction, that is, the junction of a p-type layer where the carriers are positively charged holes and an n-type layer in which current is carried by mobile electrons. LEDs pass an electrical current in the direction where electrons move from the n-region to the p-region. The electrons then recombine with holes to generate photons of light. The light emitted by a LED is usually in a narrow band of wavelength corresponding to the energy associated with electron-hole pair recombination (Hayer, *et al*., 2004).

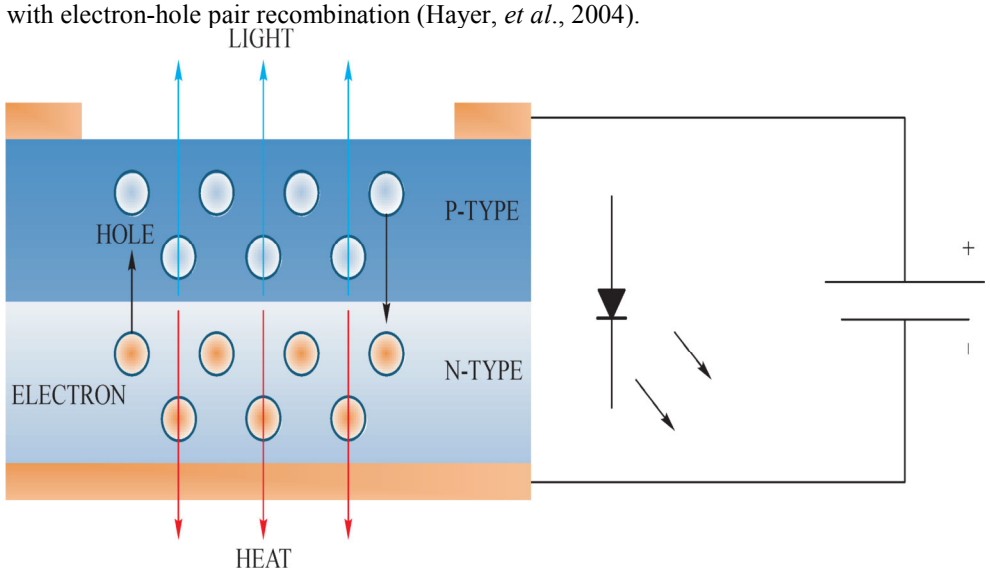

Figure 5: Structure which shows light formation from N-type and P-type layers (Tak *et al*., 2012).

Light-emitting diodes (LEDs) are narrow-band light sources based on semiconductor components, with wavelengths ranging from the infrared to the ultraviolet. The first LEDs were studied and constructed during the 1950s and 1960s in several laboratories (Akasaki, 2014; Nakamura, 2014). LEDs are mostly used as lighting sources. The first LED has been demonstrated in 1936 by George Destriau. When they applied a potential on ZnS:P powder placed between two electrodes, they observed the emission of a low intensity red light. That discovery led to the development of a large variety of red, orange, yellow or green inorganic light-emitting

diodes. In 1962, General Electric commercialized the first inorganic LED which was based on phosphorous doped gallium arsenide (GaAs: P). Light-emission from an organic material has only been reported for the first time in 1963 by M. Pope and collaborators. Today, some electronic devices made of OLEDs such as flat screen televisions, MP3 player, digital cameras and smart phones are commercially available. Electroluminescence is defined by the emission of light induced by charge recombination. So, in order to have working LEDs, charges must be injected in the material. At the anode, an electron is removed from the HOMO of the light-emitting material, creating a positive charge carrier. At the cathode, an electron is inserted in the LUMO of the light-emitting material creating a negative charge carrier. The hole and the electron travel to their opposite electrodes under the influence of the applied electric field.

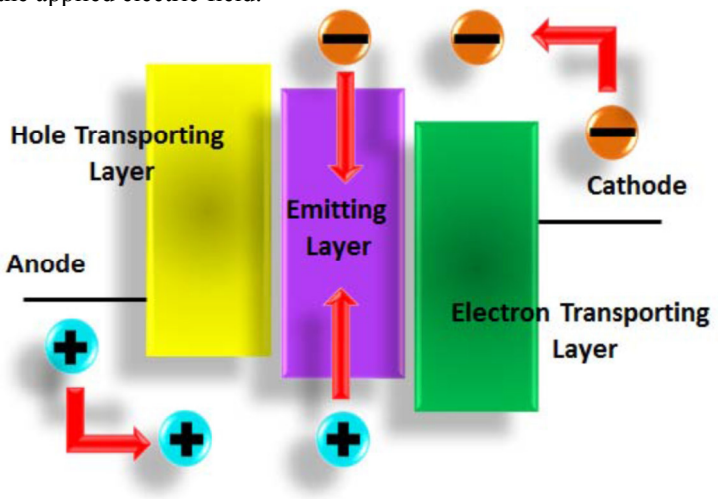

Figure 6: Schematic working mechanism for LEDs (Source: Huang *et al*., 2006).

Application of polymer in organic light emitting diode

An OLED is a device which emits light under application of an external voltage. It is a new technology which has the potential to replace the existing lighting technologies. The attraction to organic semiconductors for lighting and display application has started during 1950-1960 because of the high fluorescence quantum efficiency exhibited by some organic molecules and their ability to generate a wide variety of colors (Tae-W, 2004). There are two main classes of OLED devices: those made with small organic molecules and those made with organic polymers. OLEDs have unique properties like, lightweight, flexible, transparent and color tune ability, which makes them an ideal modern light source. It is a solid-state semiconductor device that is 100 to 500 nanometers thick and consists of a conducting layer and an emissive layer, all together sandwiched between two electrodes and deposited on a substrate. The conduction in organic layer is driven by delocalization of p electrons caused by conjugation over all or part of the organic molecule. Thus, OLEDs are double charge injection devices, requiring the simultaneous supply of both electrons and holes to the electroluminescent material sandwiched between two electrodes (Tae-W, 2004). They reached the point where their efficiency and stability are now suitable for commercial display applications (Tessler *et al*., 1998). There are two primary considerations for the OLEDs efficiency; how much light emission is generated and how much of the generated light is extracted out. The extraction of light from the OLED devices using surface plasmons is made by incorporated in the polymer emitting layer of the gold or silver nanoparticles (Aziz *et al*., 2016).

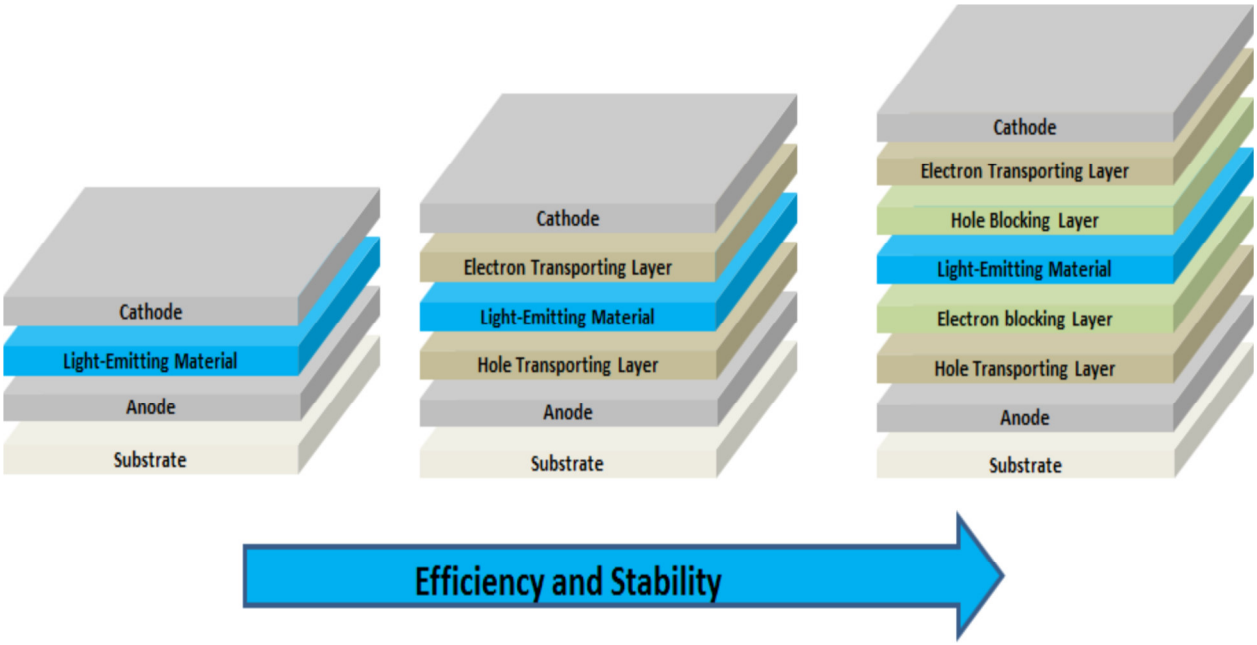

Figure 7: Examples of structures for OLEDs and PLEDs (Source: Huang *et al*., 2006).

There are many differences between optically and electrically pumped devices, the most obvious one is the existence of current and the unavoidable voltage drop associated with it. It consisted of bottom contact of indium-tin-oxide ~ITO~on glass on top of which Al stripes were deposited to reduce voltage drop associated with the ITO. The top electrode was made thick, so as to absorb heat efficiently from the polymer, and served as a first-stage heat sinking for the device (Tessler *et al*., 1998).

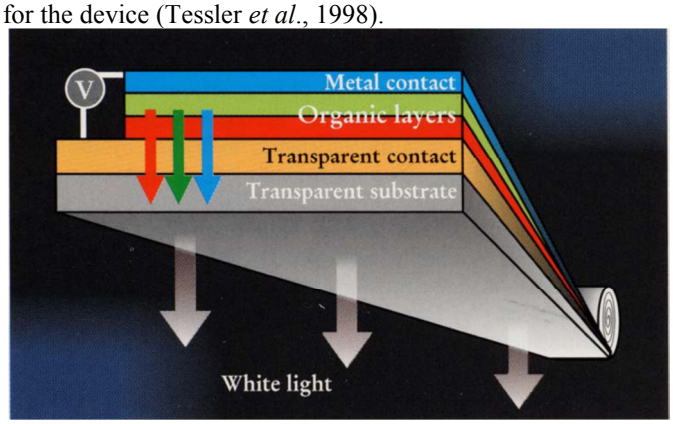

Figure 8: Structure of OLED which shows how white light is generated from the metal contact and organic layers (Source:http://www.OIDA.org).

Organic electroluminescent materials have been the subject of intense research for use in light emitting diodes (LEDs). When compared with liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) require lower energy input, have a wider viewing angle with improved color contrast, and can be made much thinner (Robert, 2004; Lambeth, 2004). Polymer-based OLEDs are usually fabricated by spin-coating techniques whereas small dye molecules are preferably vapor-deposited under ultra-high vacuum conditions (Dirk *et al*., 1995). An organic light-emitting diode (OLED) consists of several semiconducting organic layers sandwiched between two electrodes, at least one of them being transparent. Thin OLEDs are already being used in many mobile devices and TVs, and the next generation of these panels will be flexible and bendable. Among all high-efficiency/eco-friendly light, OLEDs have the closest spectral distributions to natural light, even in its most natural state (Askari, 2014).

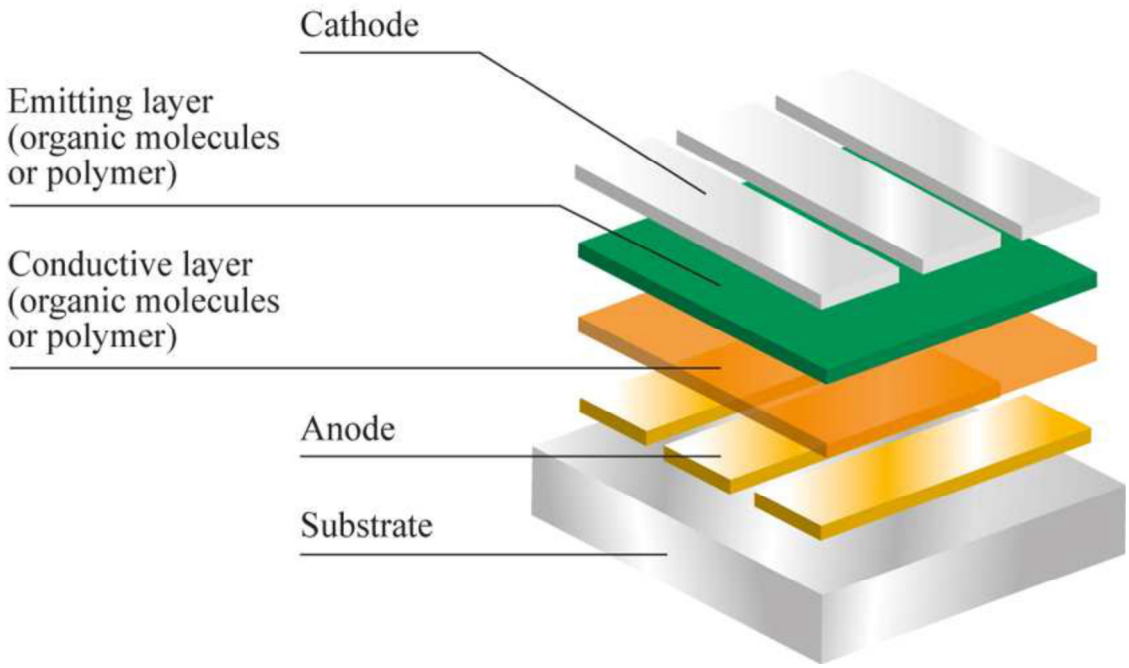

Figure 9: Structure of OLED which has emitting layer and conducting layer (Source: Tae-W, 2004).
They are attracting much attention due to their potential applications for solid state lighting and flat-panel displays. Although much effort has been devoted to the optimization of OLED performance, carrier injection barriers between the organic materials and the electrodes remain a limiting factor (Deang *et al*., 2009).

CONCLUSION

The application and acceptance of using Conducting Polymers was increased from time to time in different companies. It is used in sensor technologies as an electrode modification in order to enhance sensitivity, to impart selectivity, to suppress interference and to give a support matrix for sensing materials. The conductivity of polymers depends upon the doping percentage, arrangement of polymer chains, conjugation length and the purity of the samples. In today's development, OLEDS are prepared using vacuum processed small organic molecules whereas polymers have the advantage of being solution processable, providing better opportunities to make large-area devices. The use of white PLEDs has different performance; requirements very different from other single-color PLEDs used in polymer flat panel displays. The performance of PLED is still poor when we compare with the development of OLED in some aspects, especially the efficiency and stability of the phosphorescence and white emitting devices. OLEDs are unconventional, large area thin film, nearly two-dimensional devices. In general they are disseminated light sources, distinctly different from point sources such as light bulbs and also they will operate at very low voltages of the order of 3-5V.

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