

Advances in Plexcore™: Technology for Printed Electronic Devices

Troy Hammond* and Shawn Williams

Plextronics, Inc., 2180 William Pitt Way, Pittsburgh, PA, 15238, USA

Phone: +1-412-423-2030, x 118 Email: thammond@plextronics.com

Abstract

Plextronics develops conductive polymer technology (trademarked Plexcore™) that will enable the broad market commercialization of printed electronic devices. This talk will emphasize advances to our Plexcore™ HIL technology – a soluble non-acidic hole injection layer (HIL) technology for OLEDs – which is designed to dramatically improve device efficiency and lifetime of flat panel displays and solid state white-lighting.

Plexcore™ HIL

The rapid growth of OLED markets will occur when device performance, particularly lifetime, and production costs are optimized. Plextronics Inc. is using a versatile technology platform to develop HIL technology that will address critical degradation factors of solution processed OLEDs. In particular, significant effort has been applied to understanding the impact of inputs including the inherently conductive polymer, dopant system, solvent system, and additional functional additives, on resulting HIL film properties, which are presented here.

The Hole Injection Layer (HIL) serves several functions in an OLED:

- a. Allow for the efficient injection and transport of holes from the anode to the light-emitting layer by bridging the energy gap between these two layers.ⁱ
- b. Block electrons from flowing out of the emitting layer and into the anode without recombination.ⁱⁱ
- c. Block oxygen diffusion from the ITO anode into the electroluminescent (EL) polymer and prevent degradative oxidation.ⁱⁱⁱ
- d. Planarize the anode surface to prevent shorts between layers that reduce device lifetime and efficiency.^{iv}

An effective HIL enables holes and electrons to be more evenly concentrated in

the emitting layer, maximizes recombination in the EL layer at low power input levels, and enhances device performance in all of the categories listed above. The dense film structure and morphology of a well-applied film provides a uniform conducting path for hole migration to the EL/HIL interface, which could lead to decreased turn-on voltages and to superior luminescent performance.^v However PEDOT:PSS, an HIL material that has been used extensively for this function, has issues including its acidic and aqueous nature that have been identified to cause device degradation and have been discussed extensively in the literature.^{vi} The opportunity presents itself for a robust HIL technology platform that meets the required functionality, addresses clearly identified issues that lead to device degradation, and is flexible enough to be tailored to many device structures.

Technology platform

A non-acidic and organic solvent based technology platform is being developed for HIL. Relative to current technologies, its non-corrosive nature will improve display lifetime and the use of easily removable organic solvents instead of water will improve manufacturing and lifetime. The objective is to impact critical display parameters through control over HIL inputs, including tunable energy levels to better match the anode and emitting layers, planarization of anodes to sub-nanometer

RMS roughness, and multiple solvent choices for manufacturing ease and reduced TAC times.

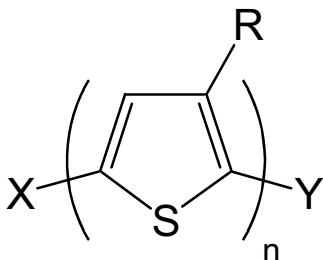


Figure 1: A general structure of a Regioregular Poly(3-substituted thiophene) where R = a general alkyl or aryl group which may contain a chemical functional group; X & Y = terminal groups on the polymer chain such as a hydrogen atom, a halide (e.g., Br or Cl), or an alkyl or aryl group which may contain other chemical functional groups; and n = is the polydispersity index or the number of repeat units on the polymer chain.

In developing this technology platform, a quantitative method is used to map control of HIL inputs to their effect on display performance. Inputs include the structure of the conductive polymer, solvent system, dopant system, planarization agent, and other functional additives. The expected output of current activities is a general HIL technology that can be easily modified and adapted to specific device architectures. Further developments will advance this model to build a variety of HIL systems tailored for specific device architectures, emitters, and application methods.

Design and control over critical HIL inputs

The most critical input is clearly the inherently conductive polymer (ICP) design. The ICP technology is based on regioregular poly(3-substituted)thiophenes (RRPT). This is a platform technology that allows fundamental polymer properties to be tailored including structure, molecular weight, polydispersity, HOMO energy level,

absorption band-gap, and end-group functionality.

Regioselective polymerization techniques are used to finely control the absolute structure of the polymeric materials and will support a variety of 3-substituent functionalities. The choice of a pendant “R” group or end-group functionality (including copolymers) allows further tuning of the structural, electronic, optical, and morphological properties of these soluble conductive polymers.

The conductivity of the HIL system is a determining factor for device voltage and current. Conductivity is selectively controlled by the oxidation state of the RRPT. Control of conductivity is derived from the polymer backbone structure as well as through the use of a proprietary set of doping materials that has been developed for use with these RRPT polymers.

Our ability to manipulate the backbone structure of these materials allows us to tune the solubility of polymer and, therefore, the characteristics of our HIL system. This, in turn, allows us to design and manipulate film properties such as hydrophobicity, morphology, doped stability, and surface energy and to control the interaction of our HIL with other layers in the device

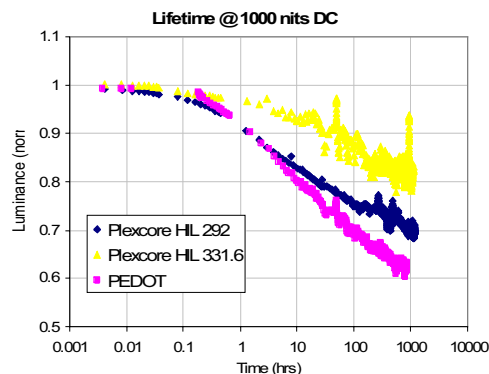


Figure 2. Lifetime in DC drive for devices with a PEDOT HIL and for two Plexcore HIL formulations. Starting luminance is 1000 nits.

architectures. Given the wide variance in the solubility characteristics of doped and undoped ICPs this flexibility in design can be used to overcome difficult processing problems. For instance, the backbone of the ICP can be tailored to develop HIL systems that resist solvents that are used to deposit the LEP in OLEDs such as toluene and xylene.

The planarizing agent serves several key functions in this HIL system. First, it is the matrix in which the RRPT and other additives are dispersed. It helps to planarize the ITO of the transparent anode, decreasing device “hot spots” or electric field inhomogeneities caused by peaks in the film morphology. It contributes to the transparency of the HIL film as well as to the transport of holes to the emitter. It also increases device efficiency by blocking electrons.

Recent results

Feedback from partners and customers clearly indicates that the most significant performance metric to target is the improvement in lifetime performance with Plexcore HIL vs. that obtained with other solution processed HIL technology. Shown in the figure 2 below is the lifetime performance of two versions of Plexcore HIL with a commercial polymeric emitter. It is apparent that the lifetime of HIL 292 and HIL 331.6 outclass the control devices using PEDOT. These performance benefits with Plexcore HIL are due to its tunability and excellent compatibility with this emitter. In this case, these systems were less efficient than the PEDOT-based devices and hence were driven at higher current densities to achieve the same starting luminance of 1000 nits. Nevertheless the superior lifetime was still achieved.

New Plexcore HIL formulations have been developed with comparable efficiencies as shown with Plexcore HIL 381.2 in figure 3 below in the I-V performance relative to PEDOT. Lifetime testing for these systems is now underway.

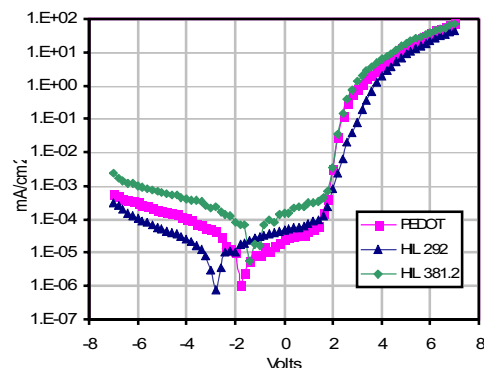


Figure 3. Current density versus voltage for two Plexcore HIL systems versus PEDOT. HIL 292, for which lifetime data is provided in figure 2, has lower efficiency relative to PEDOT. Recent HIL systems match or exceed PEDOT in efficiency.

One benefit of the Plexcore platform, which begins by solvating the inherently conductive polymer, is the stability of the resulting HIL. Currently available solution processed HILs create challenges for the display manufacturer in terms of storage and handling, often requiring refrigerated temperatures and leading to process control variability. We have investigated the HIL system shelf life as determined by solution-phase dynamic light scattering and performance in devices for systems stored at high temperature (40C), room temperature (~22C) and low temperature (~5C). Figure 4 shows efficiency results with a commercial polymeric emitter for each of these systems after storage for one, two, and six weeks. Each system was stable over this time period.

Figure 5 shows the initial, one week, and six week efficiencies for the high temperature system. The high temperature system began to show deterioration in device performance at 10 weeks. The room temperature and low temperature systems have shown no deterioration, most recently, at 21 weeks storage. This performance is dramatically superior to that observed from dispersions such as PEDOT and will be critical for the manufacturability of OLED displays.

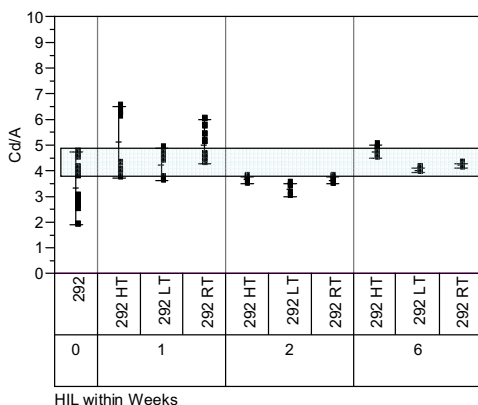


Figure 4. Candelas per amp for devices made with Plexcore HIL 292 initially and stored for one, two, and six weeks at high (HT), low (LT), and room (RT) temperatures. No appreciable change was observed for any of these systems.

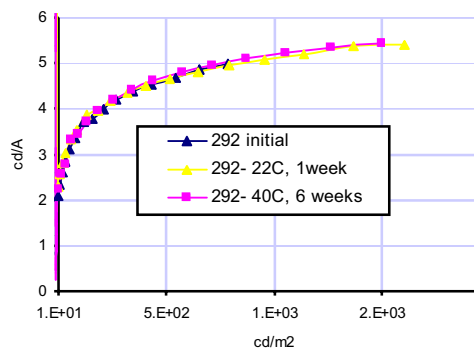


Figure 5. Candelas per amp versus nits for devices where the HIL formulation was stored at high temperature (40C) for one, two, and six weeks before fabrication of the device. No appreciable change in device performance was observed.

Outlook

A robust “mapping engine” is being developed that translates variations in HIL film specifications into OLED display parameters. Plextronics collaborates with display manufacturers and technology development partners to accelerate development of this model and get early insights into its application across a spectrum of device architectures. Initial results are encouraging that the model is functional in leading to improved display performance and lifetime.

ⁱ Shinar, J. *Organic Light Emitting Devices*, Springer-Verlag New York, Inc. **2004**.

ⁱⁱ Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem. Int. Ed.* **1998**, *37*, 402.

ⁱⁱⁱ Kim, J.-S., Ho, P.K.H.; Greenham, N.C.; Friend, R.H. *J. Appl. Phys.* **2000**, *88*, 1073.

^{iv} de Kok, M. M.; Buechel, M.; Vulto, S. I. E. ; van de Weijer, P. ; Meulenkamp, E. A. ; de Winter, S. H. P. M.; Mank, A. J. G.; Vorstenbosch, H. J. M.; Weijtens, C. H. L.; van Elsbergen, V. *Phys. Stat. Sol.* **2004**, *201*, 1342.

^v Chen, S.; Wang, C. *Appl. Phys. Lett.* **2004**, *85*, 765

^{vi} de Jong, M.P.; van Ijzendoorn, L.J.; de Voigt, M.J.A.; *Appl. Phys. Lett*, **2000**, *77*, 14.; Crispin, X. *et.al.*; *J. Poly. Sci Part B*, **2003**, *41*, 2561.