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Polymer Light-Emitting Electrochemical Cells: organic semiconductor devices augmented by ions

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Polymer light-emitting electrochemical cells (LEC) was invented in 1994 to facilitate the injections of charge carriers into luminescent conjugated polymers in light emitting diodes. Initially, the benefits of adding a solid electrolyte into the organic semiconductor devices was eminent: electrons could be effectively injected from a stable metal like aluminum into the lowest unoccupied molecular orbitals which are 1 eV higher than aluminum's work function; and the driving voltage was substantially reduced. Also, the emissive layer could be much thicker than that allowable for tunneling charge injection interfaces. Michael Rubner at MIT obtained similar results with conjugated small molecules such as a soluble derivative of $[\text{Ru}(\text{bpy})_3]^{2+}(\text{PF}_6^-)_2$, a compound that had been studied for eletrogenerated chemiluminescence long before LEC was first reported. The presence of mobile ions in the LECs and consequently overpotential could induce degradation which has been partially addressed over the years. Karl Leo and Junji Kido, et al. introduced immobile ions or "doped" the organic semiconductor via organic donor-acceptor complex, which have leap frogged the operational stability of OLEDs.

Works by Richard Friend, Ian Parker and others in the early 1990's showed that the conjugated polymer/electrode interfaces could be modeled as tunnelling barriers. The work function difference between ITO, a commonly used transparent anode, and calcium is around 1.8 eV. Low electron and hole injection barriers are feasible when using a small band gap polymer such as MEH-PPV to produce orange light emission. For blue light emitting polymers, large barriers are inevitable. The emissive layer has to be made as thin as processing can produce a defect-free layer, typically around 100 nm for spin coating. Even so, the driving voltage was often tens of volts, and the blue polymer OLEDs fabricated at the time were very short lived, even though the quantum efficiency was decent. In finding a solution to this challenge, the doping propagation model that Olle Inganäs and me used to simulate the polypyrrole/polyethylene bilayer bending beams inspired me to introduce electrochemical doping into the polymer OLEDs. Thus, a commonly used ionically conductive polymer, polyethylene oxide plus lithium triflate, was selected to supply the mobile dopants. The Wessling precursor of PPV was selected thanks to its compatibility with the PEO-lithium salt. The resulting blend of an ionically conductive and an electronically conductive polymers showed remarkably improved electroluminescent performance compared to control OLEDs based on ITO/PPV/Al. The driving voltage was lower, the quantum efficiency was higher, and the operational stability was also enhanced.

Alan Heeger, Jun Gao, Ludvig Edman, and others separately confirmed the formation of p-i-n junction in the polymer LECs by optical beam induced current measurements, direct imaging under microscope, and measurement of electrostatic potential distribution by scanning Kelvin probe microscopy. Light emission and major potential drop were observed to occur at the junction. This p-i-n junction model may not rule out other mechanisms, particularly when the junction is not formed to exhibit the ideal doping profiles at the electrode interfaces. Electrical

double layers could dominate at driving voltage well below the band gap of the conjugated polymer, i.e. the onset of simultaneous p- and n-doping.

The junction model essentially guides the material selection to fabricate high performance LECs. Three electronic/ionic polymer blend systems were examined in the early years include (MEH-PPV + PEO-lithium salt) and (polyfluorene with ethylene oxide side chains + lithium salt), in addition to the (PPV + PEO-LiTf) system used in the very first LEC device. Morphological control was a critical factor in the device performance: one had to consider the tradeoffs among carrier transport, ionic mobility, luminescence quenching, and accessibility of doping ions into the low-polarity conjugated polymer domain. Furthermore, mobile ions could lead to electrochemical over-reaction or degradation at high driving voltages. Freezing the ions after the formation of the p-i-n junction appears to be effective to slow down such degradation.

The added freedom in electrode selection for LECs allows the fabrication of devices without the use of high vacuum: Sue Carter printed silver paste as the cathode; carbon nanotube coating could also be used as the cathode, as well as the anode. LECs formed by sandwiching the emissive polymer layer between a pair of carbon nanotube electrodes were flexible, even stretchable if the nanotubes were coated on elastomeric substrate.

The LEC is now intertwined with many other fields. It is exciting to witness the latest progress in LEC performance and exploration of unique applications. Here I merely state my personal view on what occurred in the past that helped shape the field as it is today. More history and exciting developments are covered by the authors who wrote the chapters of this book. My hat's off to these active researchers who have made critical contributions to the field. I am indebted to Dr. Chi Zhang, Dr. Yang Yang, Dr. Yong Cao for helping fabricate the first generation of polymer LECs, Prof. Alan Heeger for polishing the junction model, and Dr. Gang Yu for suggesting the planar LEC structure to image the junction.