

Polymeric anodes for organic light-emitting diodes

J.C. Scott,⁽¹⁾ S.A. Carter^(1,2), S. Karg⁽¹⁾ and M. Angelopoulos⁽³⁾

⁽¹⁾IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, USA

⁽²⁾Physics Department, University of California, Santa Cruz, CA 95064, USA

⁽³⁾IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY 10598, USA

Abstract

Polymer light-emitting diodes based on PPV, for example MEH-PPV, are known to be susceptible to photo-oxidative degradation. The formation of the carbonyl species in the polymer results in quenching of the luminescence. In addition the oxidation process reduces the conjugation of the polymer, leading to lower charge carrier mobilities and consequently higher operating voltages. Previous *in situ* FTIR studies revealed that even in a dry inert atmosphere polymer oxidation occurs, and that ITO can act as the source of oxygen. In order to explore further the nature of the oxidation mechanism and to provide guidance for its elimination, we have studied the behavior of MEH-PPV LEDs prepared with conducting polymer anodes. When a layer of polyaniline is present between the ITO and the MEH-PPV the device characteristics improve dramatically: the injection voltage drops, the luminous efficiency increases and, most significantly, the rate of decay of the luminance decreases by up to two orders of magnitude. These data not only confirm that ITO is a source of oxygen, but also imply that the oxidation mechanism is due to direct interfacial reaction. We compare several different forms of polyaniline, with different dopants, as well as a derivative of a polythiophene.

Keywords: Electroluminescence, polyaniline and derivatives, polythiophene and derivatives, poly(phenylene vinylene) and derivatives, metal/insulator interfaces, light sources, photo-oxidation, organic light-emitting diodes, polymeric anodes

Polymer light emitting diodes[1] (PLEDs) are being actively examined as materials for technological application. Their external power efficiency, color versatility, brightness, angular emission profile and weight are all attractive for use in flat-panel, portable displays. The property which has so far prevented extensive commercialization of PLEDs is their lifetime, but here too significant progress has been made and there are reports[2] of operating lifetimes in the range of several thousand hours.

In a previous publication[3] we identified two of the mechanisms which contribute to the degradation and eventual failure of PLEDs based on a single layer of MEH-PPV with indium-tin oxide (ITO) anode and calcium cathode. It was found using infrared (IR) spectroscopy that even in the absence of atmospheric oxygen and moisture, oxidation of MEH-PPV occurs, revealed as aromatic aldehyde formation and loss of conjugation. The formation of carbonyl species is consistent with loss of emissive efficiency due to its known fluorescence quenching effect.[4] The loss of conjugation affects device operation by reducing charge carrier mobility and hence increasing the operating voltage. Changes in the ITO IR spectrum suggested that the ITO anode can serve as the source of oxygen for carbonyl formation. Subsequently[5] we described experiments in which a layer of polyaniline (PAni) was coated between the ITO and the MEH-PPV layers. This was shown to

reduce the rate of oxidative degradation, as well as to reduce the formation of shorts. Thus the lifetime of MEH-PPV diodes was greatly extended. The use of PAni anodes has also been reported by Yang *et al.* [6] [7] and by Roitman and coworkers.[8] In this paper, we present data on several different modifications of PAni as well as on a derivative of polythiophene.

We examine the behavior of diodes, all having an MEH-PPV active layer and a calcium cathode, prepared on different anode materials and structures. In order to determine the effect of dopant, and in particular its molecular mobility, we used several different dopants for PAni; two of these are polymeric anions, namely sulfonated polystyrene (pss) and polyacrylamidopropane sulfonate (pas); while two are small molecule dopants - camphor sulfonate (csa) and acrylamidopropane sulfonate (as). The possible role of the solvent was studied by casting the conducting polymer from a variety of solvents, namely water, N-methylpyrrolidinone (NMP), hexafluoro-*iso*-propanol (HFIP) and tetrafluoropropanol (TFP). Our previous work was done exclusively with PAni-pss/H₂O while that of the UniAx and HP groups focussed on PAni-csa/*m*-creosol. In addition we prepared anodes of polyethylenedioxythiophene (PEDT) doped with pss and cast from aqueous solution.[9] These materials have conductivities ranging from 0.1 S/cm (PAni-pss/H₂O) to 100 S/cm (PAni-as/HFIP). The PAni samples have a maximum

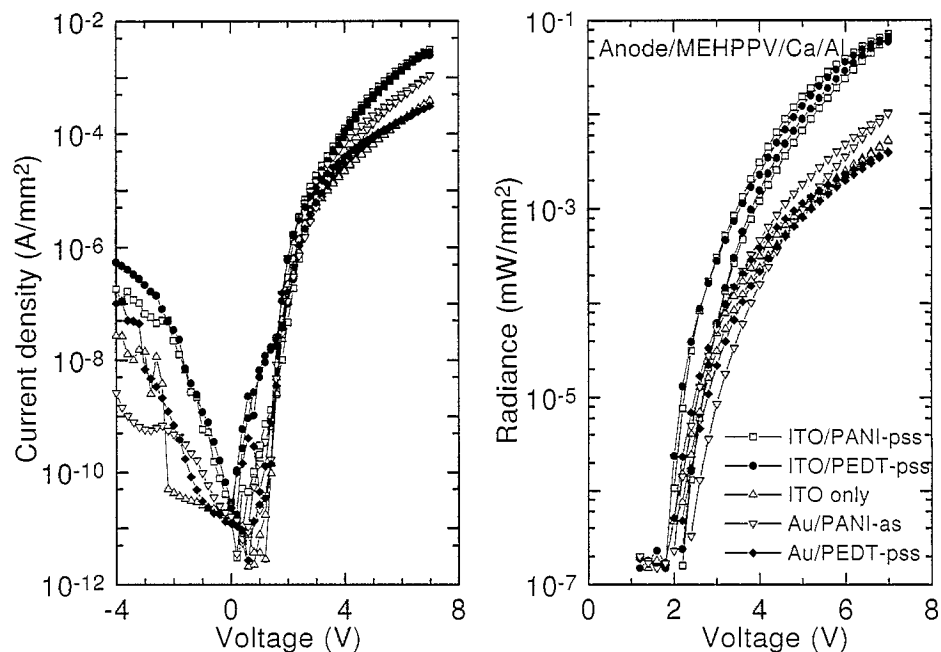


Fig. 1 Current-voltage and radiance-voltage of five LEDs based on MEH-PPV with various anode structures as indicated.

transmission in the green, while PEDT is transparent in the blue. Complete details of the conducting polymers used will be given in a longer article.[10]

The transparency and conductivity of none of these materials is sufficient to act as a satisfactory anode contact without an additional, more highly conductive contact to prevent significant voltage drop and (possibly) resistive heating. Therefore we coated most sample on an ITO underlayer. Several samples were prepared instead with narrow gold stripes on each side of the conducting polymer anode, and we also examined diodes with only conducting polymer on the anode side. The last have considerable series resistance (approximately 300 kOhm) which limits the current as the diodes turn on.

The conducting polymer was spin-coated on top of ITO, Au or bare glass (Corning 7059) to a thickness of 100 nm and dried in a vacuum oven at 120°C for two hours to remove residual solvent. The MEH-PPV film was deposited by spinning from xylene solution in a dry nitrogen atmosphere. The samples were then transferred directly to a vacuum chamber for the deposition of 25 nm Ca followed by 25 nm Al, both by thermal evaporation. The current-voltage behavior was measured with a

Keithley model 238 source-measure unit and the radiated power simultaneously determined with an integrating sphere and Optical Laboratories model 730C radiometer. Aging behavior (current and radiance as a function of running time) was monitored under constant voltage drive conditions using HP 34401A multimeters to measure the current and the output of UDT Si photodetectors. In all cases several sets of devices were aged side-by-side to permit direct comparison of materials exposed to the same ambient conditions.

Some examples of current-voltage and radiance-voltage behavior is shown in Figure 1. In almost all cases the current is higher, at the same voltage, for conducting polymer anodes than for ITO. The exceptions are those cases where there is no ITO underlayer and therefore there is a significant voltage drop in the anode lead. The increased current results in increased radiance, with the exception again of the cases where the Au stripe on the substrate partially blocks the emitted light. When the data are plotted as quantum efficiency or power efficiency (Figure 2) it can be seen that both PANi and PEDT doped with pss yield higher efficiencies than ITO anodes. Moreover, extremely high brightness can be achieved - a radiance of 7×10^{-2} mW/cm² (reached at 7 V) corresponds to a luminance

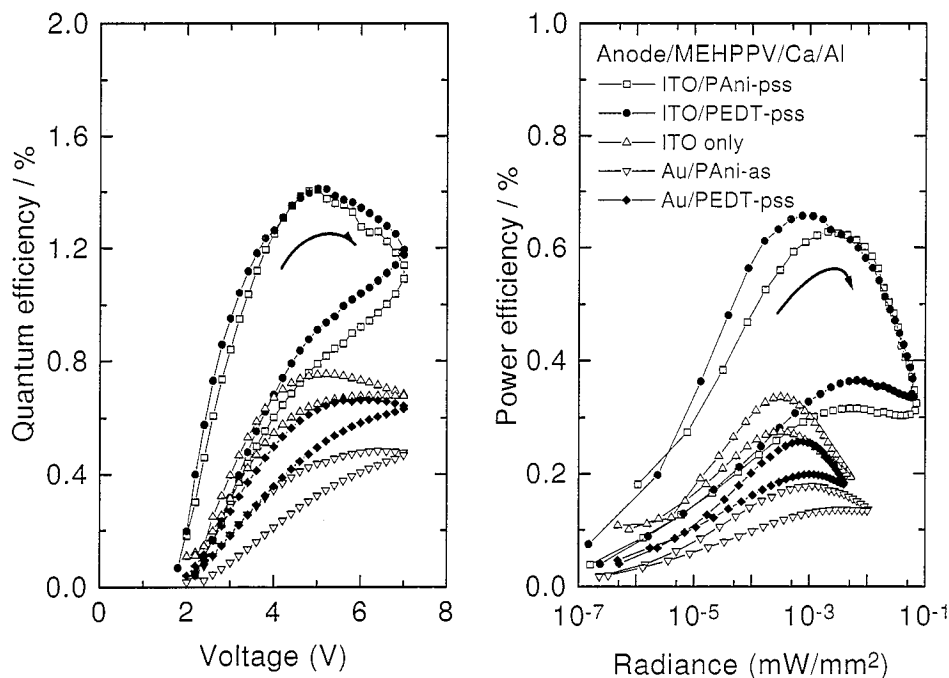


Fig. 2 Quantum efficiency vs. voltage and power efficiency vs. radiance for the same five devices as in Fig. 1.

of 5000 cd/m^2 . These high drive levels, up to 200 mA/cm^2 , cause considerable hysteresis in the response, as can be observed particularly in the efficiency curves.

Conducting polymer anodes result in more reproducible response than ITO anodes for reasons that probably relate to some unidentified changes in the ITO surface during preparation or storage. Higher currents and greater efficiencies are obtained with polymer dopants than with small molecule dopants. We have found no systematic trend in behavior due to the solvent from which the conducting polymer is coated. In particular, water as a solvent for both PAni and PEDT results in devices which are just as bright and efficient as organic solvents.

As stated above, the primary motivation for exploring the use of conducting polymer anodes was to attempt to eliminate the oxidation process caused by the migration of oxygen out of the ITO into the emissive polymer layer. Indeed, as reported previously for PAni-pss/ H_2O [5], we observe greatly reduced degradation rates of devices with the other conducting polymer anodes tested relative to those with ITO in contact with the MEH-PPV layer. For example, a PEDT-pss/ H_2O device run at a constant 7 V started with a brightness of 2500 cd/m^2 and was still quite visible (20 cd/m^2) after 200 hours. Similarly the decay in emission for conducting polymers doped with small molecules

is about two orders of magnitude. Under these conditions, the light output with ITO anodes decreases by more than four orders of magnitude and falls below the limit of our photo-detector. We also examined devices without the ITO underlayer to assist in lateral conduction. These are much less intense at the same voltage because of the additional series resistance so a direct comparison is difficult. Nevertheless it is clear that the decay rate is reduced, and may even be lower than when the ITO underlayer is present. Hence it is clear that by eliminating the direct contact between ITO and MEH-PPV, significant increases in lifetime can be achieved.

The issue of the mechanism for oxidation by ITO can be addressed by the above observations. Since the conducting polymer layer is 100 nm or less it is unlikely to provide a significant diffusion barrier to molecular oxygen which is well known to permeate amorphous polymers.[11] Therefore we suggest that the oxidation is driven by a direct interfacial reaction, perhaps electrochemical in nature. For example, after a hole has crossed the anode/polymer interface it is motion into the bulk is relatively slow because of its low mobility and the image charge potential which tends to localize it in the interfacial region. The resulting cationic form of the polymer is more reactive than the neutral state and may attract an oxygen anion

from the ITO bulk. Such a process can be minimized by choice of anode material.

We have presented data on the electrical and optical properties of MEH-PPV LEDs prepared on a variety of PANi and PEDT anodes and have compared their aging behavior relative to devices on ITO. In agreement with the concept of oxidation by the transfer of oxygen atoms from ITO to the conjugated polymer, the degradation rate is reduced by many orders of magnitude. The injection characteristics and efficiency of the polymeric anodes is also improved over that of ITO, leading to higher brightness at the same operating voltages. Poly-anion dopants show better behavior in general than small molecule dopants, especially in short term stability (the "burn-in" regime). None of the conducting polymers reported here had high enough conductivity/transparency to be useful as a complete substitute for ITO.

Acknowledgements: S.A. Carter acknowledges support by the NSF/MRSEC program through CPIMA. We are grateful to P.J. Brock and R. DiPietro for synthesis of the MEH-PPV used in this work.

References

- [1] J. H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackey, R.H. Friend, P.L. Burns and A.B. Holmes, *Nature*, **347**, 539 (1990).
- [2] F. Cacialli, R.H. Friend, S.C. Moratti and A.B. Holmes, *Synth. Metals* **67**, 157 (1994).
- [3] J.C. Scott, J.H. Kaufman, P.J. Brock, R. DiPietro, J. Salem and J.A. Goitia, *J. Appl. Phys.* **79**, 2745 (1996).
- [4] M. Yan, L.J. Rothberg, F. Papadimitrakopoulos, M.E. Galvin and T.M. Miller, *Phys. Rev. Lett.* **73**, 744 (1994).
- [5] S. Karg, J.C. Scott, J.R. Salem and M. Angelopoulos, *Synth. Metals* (in press, Sept. 1996).
- [6] Y. Yang and A.J. Heeger, *J. Appl. Phys.* **64**, 1245 (1994).
- [7] Y. Yang, E. Westerweele, C. Zhang, P. Smith and A.J. Heeger, *J. Appl. Phys.* **77**, 694 (1995).
- [8] D.B. Roitman, J. Sheats, H. Antoniadis, M. Hueschen and Y. Yang, *Proc. 27th Internat. SAMPE Tech. Conf.* Vol. 27, p681 (1995).
- [9] Provided by Bayer Corp.
- [10] S.A. Carter, J.C. Scott, S. Karg and M. Angelopoulos (to be published).
- [11] W.R. Vieth, *Diffusion in and Through Polymers* (Hanser Verlag, Munich, 1991).