

Polymeric anodes for improved polymer light-emitting diode performance

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We have studied polyaniline and polyethylenedioxythiophene transparent electrodes for use as hole-injecting anodes in polymer light emitting diodes. The anodes were doped with a variety of polymer and monomer-based acids and cast from either water or organic solvents to determine the effect of the dopant and solvent on the hole-injection properties. We find that the anodes with polymeric dopants have improved device quantum efficiency and brightness relative to those with small molecule dopants, independent of conductivity, solvent, or type of conducting polymer. For the most conducting polymer anodes [$\sigma > 2(\Omega \text{ cm})^{-1}$], diodes could be made without an indium tin oxide underlayer. These diodes show substantially slower degradation. © 1997 American Institute of Physics. [S0003-6951(97)00316-1]

Since the discovery of electroluminescence in polymers,¹ substantial research has gone into improving the light output, power efficiency, and lifetime of electroluminescent polymers in a diode device structure. Typically, the polymer light emitting diode (PLED) consists of a transparent hole-injecting anode, for example $\text{In}_2\text{O}_3:\text{Sn}$ (ITO), and electroluminescent conjugated polymer, and an electron injecting cathode such as Ca or Al. The device quantum efficiency and driving voltage depend on the charge-injection properties at the interfaces between the electroluminescent polymer and electrodes.²⁻⁴ Recent research has shown that this interface also plays an important role in device lifetime; chain scission of the electroluminescent polymer is aided by the chemical reaction of the vinyl carbon with oxygen contributed by the ITO anode.⁵ These effects can be partially mitigated by using polyaniline which is doped with conducting polystyrenesulfonic acid [(PSS)-polyaniline (PAni)] as the transparent anode.⁶ This material acts as a barrier to oxygen reaction and as a planarizing layer to inhibit electrical shorts and improve device lifetime; in addition, increases in device brightness and efficiencies are observed. These results suggest a thorough study is needed to understand how changes in the polymeric anode and ITO underlayer affect PLED device performance.

In this letter, we determine the effect that the dopant, solvent, and type of conducting polymer have on the device performance and lifetime with and without ITO in the device structure. We show that device performance is improved more markedly with polymer-based dopants independent of conductivity, solvent, or type of conducting polymer. Moreover, we show that device lifetime is substantially improved when ITO is eliminated from the device structure.

The diodes were prepared using electroluminescent polymer poly(2-methoxy-5(2'-ethyl)hexoxyphenylenevinylene (MEH-PPV) and Al-coated Ca cathodes as described elsewhere.^{5,6} All measurements were done in a dry nitrogen glove box. In Table I, we list the conducting

polymer anodes, dopant type, solvent, conductivity, and external quantum efficiency (QE) at 7 V, radiance at 7 V before aging, and radiance at 7 V after 200 h of aging. The two types of conducting polymers studied were polyaniline (PAni) and polyethylenedioxythiophene (PEDT).⁷ The PAni materials were doped with two different polymer dopants, polystyrenesulfonic acid and polyacrylamidopropanesulfonic acid, and two monomer dopants, amidopropanesulfonic acid and camphor sulfonic acid, for comparison. The solvents used were H_2O , *n*-methyl pyrrolidinone (NMP), and fluorinated alcohols, the latter allowing the advantage of coating inside the glove box.⁸

In Fig. 1, we show the radiance and current as a function of applied voltage for the different PAni anodes. The behavior below 1.5 V is due to extrinsic effects associated with the leakage current and in general increases with increasing conductivity of the polymer anode depending on the accuracy of the patterning. The behavior above 1.5 V is intrinsic with variances on the order of $\pm 20\%$ depending on small changes in diode area and thickness. The low-field behavior and the

TABLE I. Performance of PLEDs with various polymer anodes (100 nm MEH-PPV).^a

Dopant-polymer/ solvent ^b	$\sigma(\Omega \text{ cm})^{-1}$	%QE at 7 V	L (cd/m ²) at 7 V fresh	L (cd/m ²) 200 h at 7 V
PSS-PAni/H ₂ O	0.1	1.4	4000	30 w/ITO ^c
PSS-PAni/NMP	0.1	1.0	1500	
PAPS-PAni/H ₂ O	discontinuous	1.1	1200	
APS-PAni/FA	100	0.4	3000	
			1000 w/Au	50 w/Au
CSA-PAni/FA	200	0.3	1800	
PSS-PEDT/H ₂ O	2	1.3	4000 w/ITO	30 w/ITO
			300 w/Au	35 w/Au
			180 none	60 none

^aAll error bars are $\pm 20\%$ of value. With ITO underlayer unless otherwise noted.

^bPSS=polystyrenesulfonic acid, PAPS=polyacrylamidopropanesulfonic acid, APS=acrylamidopropanesulfonic acid, CSA=camphor sulfonic acid, NMP=*n*-methyl pyrrolidinone, FA=fluorinated alcohol.

^cw/ITO=with ITO, w/Au=with thin Au stripes, non=polymer anode only.

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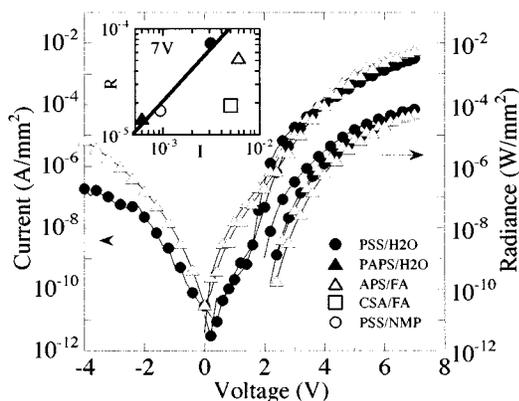


FIG. 1. Main figure shows current-radiance-voltage curves for ITO/PANI/MEH-PPV/Ca/Al, with different PANi dopants, polystyrenesulfonic acid (PSS-circle) and acrylamido-propanesulfonic acid (APS-up triangle) dopants. Insert shows radiance (W/mm^2) vs current density (A/mm^2) at 7 V for two polymer dopants, polyacrylamidopropane-sulfonic acid (PAPS-solid up triangle) and polystyrenesulfonic acid (PSS-circles), and two monomer dopants, acrylamidopropanesulfonic acid (APS-open up triangle) and camphor sulfonic acid (CSA-square). The solvents are water (H_2O -closed symbols), *n*-methylpyrrolidinone (NMP-open) or fluorinated alcohols (FA-open). Solid line=1% external quantum efficiency.

steep exponential rise at 1.8 V in the IV curves is independent of the anode material (ITO, PANi, PEDT), suggesting that this regime is cathode limited.⁷ For the high-field behavior, we observe similar currents for all sample studies; however, the polymeric-based anodes have greater light output than the monomer-doped anodes, resulting in larger quantum efficiencies (Table I). This effect is displayed graphically in the insert to Fig. 1 where radiance versus current at 7 V is plotted for each sample. Points above and left of the solid line represents external quantum efficiencies greater than one percent.

The device performance does not depend on the solvent; we observe similar behavior for the monomer-doped acrylamidopropanesulfonic acid (APS)-PANi in fluorinated alcohols and NMP, organic solvents with different boiling temperatures (59 and 82 °C, respectively). In addition, we observe only a slight reduction in performance for the PSS-PANi in NMP compared to H_2O which may be accounted for by additional quenching introduced by residual LiCl which is added to the NMP solution for stabilization. The solvent does affect surface roughness; high resolution optical microscopy shows that the PSS-PANi films dissolved in NMP have a surface roughness comparable to the thickness of the film (i.e., the film was noncontinuous) while the films from H_2O appear smooth and continuous over the entire substrate. Similar measurements on the camphorsulfonic acid films revealed spots where the polymer coagulated. Nonetheless, the initial performance of the device did not appear to depend substantially on the morphology of the polyaniline film, suggesting that planarization is not the main mechanism by which the polymeric anodes improve the device performance. This may account for similarities in the continuous and network PANi films observed by previous workers^{6,9} and implies that the increase in the surface area from networklike electrodes may not substantially aid hole injection.

The device performance also does not depend on the anode conductivity. The monomer-doped APS-PANi/

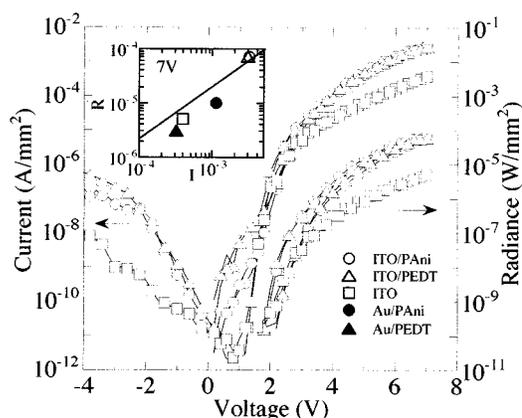


FIG. 2. Main figure shows current-radiance-voltage curves for PLEDs with different conducting anodes: PANi (circles), polyethylenedioxythiophene (PEDT-triangles) and ITO (square). Insert shows radiance (W/mm^2) vs current density (A/mm^2) at 7 V for different polymer anode underlayers, ITO (open) or Au stripe (closed). Device structures are underlayer/conducting polymer/MEH-PPV/Ca/Al. Solid line=1% external quantum efficiency.

fluorinated alcohol (FA), the most conducting material with $\sigma \sim 200 (\Omega\text{cm})^{-1}$, performs similarly to materials with over two orders of magnitude lower conductivity (Table I). We note that this material is significantly less transparent which accounts for some of the reduced efficiency. These results suggest that the variance in performance is due to differences in how the polymer and monomer-dopants affect charge injection into the MEH-PPV. A possible explanation is that the free monomer acids which remain in the material after doping are significantly more mobile under an applied electric field than the polymer acids and therefore can diffuse into the MEH-PPV to act as traps and/or luminescence quenchers.

To test the dependence on the type of conducting polymer, we also studied polyethyldioxythiophene (PEDT) doped with polystyrenesulfonic (PSS) acid and dissolved in water.⁷ Comparisons between PSS-PANi/ H_2O and PSS-PEDT/ H_2O are shown in Fig. 2. Current, radiance, and quantum efficiency are the same within the $\pm 20\%$ error bars. The PEDT anode has an order of magnitude higher conductivity than the PANi anode, resulting in large leakage currents which are strongly dependent on the patterning of the PEDT. All the polymer-based anodes perform consistently better and more repeatably than our best ITO samples in which we observe order of magnitude changes based on differences in the ITO surface preparation; ITO is known to have problems with water absorption and oxidation at the surface. Differences in the work function of the polymer anode materials could account for the improved charge injection.¹⁰ However, device structures consisting of inorganic transparent anodes that have different (lower) work functions, such as ZnO:Al and InN, reveal very similar performance to ITO indicating that work function of the anode cannot be the critical factor in determining the low-voltage performance.^{10,11} Since the improved results do not depend strongly on film conductivity, morphology, or dopant, our results suggest that the main function of the polymer anode is to create a clean repeatable surface, devoid of oxidation or water, to which the MEH-

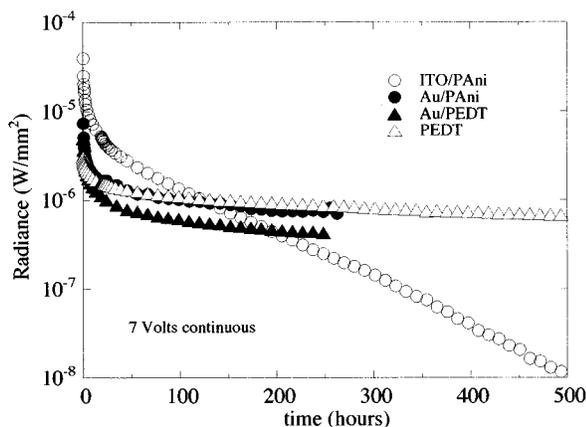


FIG. 3. Radiance lifetime studies for different PLED device structures. Devices without ITO in the device structure have improved long lifetime behavior. $1 \text{ W/mm}^2 = 7.3 \times 10^7 \text{ cd/m}^2$.

PPV polymer can more effectively adhere to. In addition, the ions in the polymeric anodes can partially dope the interface providing more Ohmic contacts and better injection.

The conductivities are sufficiently high in both APS-PAni/FA and in PPS-PEDT/H₂O that light emission can be achieved without using an ITO underlayer (Fig. 2). Similar results using camphore sulfonic acid (CSA)-PAni dissolved in *m* cresol have been observed previously.¹² The (APS)-acrylamidopropanesulfonic acid PAni/hyperfine-structure (HFS) sample, with $\sigma \sim 200 \text{ } (\Omega \text{ cm})^{-1}$, has an initial device performance that is weakly dependent on the presence of an ITO underlayer. The PEDT-based device has two orders of magnitude lower conductivity, and as such we observe significant IR loss across the device, resulting in greatly reduced light output at higher voltages, but the same quantum efficiency. This effect can be mitigated by incorporating very thin (0.2 mm) Au stripes into the device structure to minimize the current drop across the sample, yielding a device with the same efficiency and only slightly reduced light output than for the ITO-based samples. This method gives us the ability to eliminate ITO as a source of oxygen from the device.

The decay in the current and radiance as a function of time was measured on 12 diodes per substrate. The diodes were driven at large constant dc voltages (7 V)¹³ and large initial light output ($\sim 1000 \text{ cd/m}^2$) to induce more rapid aging in order that comparisons could be made between different diodes on month time scales. Average lifetime behavior on samples with and without ITO are shown in Fig. 3. We note that devices made with an ITO layer only, typically fail in a few days and are not shown on this graph for clarity.⁷ There are two regimes of aging: a “short-term” aging where the current drops an order of magnitude within the first few hours and “long-term” aging where the current drops much more slowly over hundreds of hours. By 200 h of continuous aging, all diodes, independent of the underlayer, have decayed to luminances on the order of 40 cd/m^2 at current densities $I \sim 10^{-3} \text{ A/cm}^2$. In general, the brightest diodes with the higher current densities decayed the most rapidly; however, the diodes with the ITO in the device struc-

ture continued to decay more rapidly even when the current densities were below that of the devices without ITO in the structure. In the next 200 h, the light output in non-ITO devices decayed less than 20% while the ITO-based diodes lost nearly another order of magnitude. This effect is also observed if the diodes are aged at a much lower dc voltage (4 V) and current density.¹⁰ These results indicate that the long-term device failure is accelerated by the presence of ITO, caused by photo-oxidation of the light-emitting polymer via oxygen evolved from the ITO. The mechanism for the short-term aging is currently under further investigation.

We have shown that devices made with transparent organic polymer anodes yield improved performance over inorganic anodes independent of type of polymer, solvent, or conductivity. These results imply that the improvement is due to the ability of the polymer anode to make a repeatable clean interface with good adhesion and hole injection into the electroluminescent polymer. Both polyaniline and polythiophene-based polymers can be made sufficiently conducting and transparent so that device structures without ITO can be assembled. Devices made without ITO have greatly reduced long-term decay suggesting a possible path to making long-lasting MEH-PPV polymer light-emitting diodes (LEDs).

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¹⁰ Work functions for the conducting polymers are currently under further investigation. For ITO, work functions can vary as much as $4.6 \pm 0.5 \text{ eV}$ depending on the method of preparation and state of oxidation; however, the “turn-on” voltage remains near 1.8 V for most of MEH-PPV diodes studied independent of the anode. S. A. Carter, M. Angelopoulos, P. J. Brock, J. Salem, and J. C. Scott, unpublished results. See also Ref. 13.

¹¹ We note that different cathode materials (and cathode work functions) result in several order of magnitude changes in the low-voltage performance providing further evidence that the low-voltage behavior is mainly limited by the electron injection. Similar results have been found previously by H. Suzuki, *Appl. Phys. Lett.* **69**, 1611 (1996), and references therein.

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