

Fapei Zhang,
Andreas Petr,
Uwe Kirbach,
Lothar Dunsch

Electropolymerized buffer layers in OLED

Charge injection is the most important step in the operation of OLED as displays. The phase boundary of the organic materials with the inorganic optical transparent electrode is determining the charge injection in OLEDs. We have shown that by introduction of an electropolymerized buffer layer in a small molecular OLED charge injection can be influenced and the operating voltage can be significantly decreased. Furthermore luminous efficiency is considerably enhanced.

It is expected that in the next years most of the commercial displays like monitors or liquid crystal displays will be replaced by displays based on organic light emitting diodes (OLEDs).

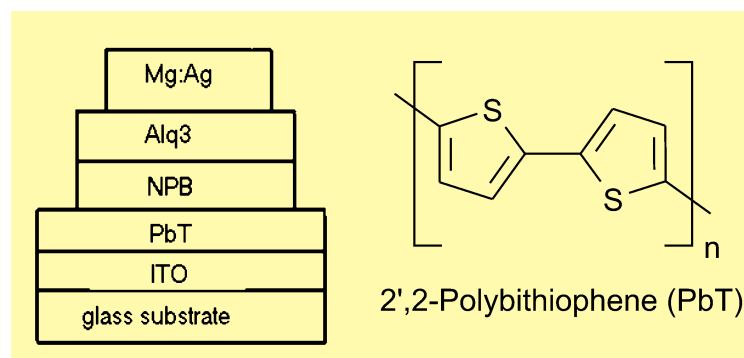
This new generation of displays has important advantages. They are flat and emissive. Moreover the viewing angle and temperature range of operation is not limited like in the case of LCD displays. Full colour displays are possible and the first displays are already commercially available. The currently limiting factor for a broad application of OLED displays is the lifetime. The aim of our main work is to increase the lifetime. In an OLED light is produced in an emissive layer by recombining holes and electrons. For that purpose at the cathode electrons and at the anode holes were injected. For metals with low work function electron injection is facile. The difficult thing is hole injection. Here we have to use an optical transparent electrode like ITO coated glass. Even plasma treatment of the ITO can not increase the work function up to the value of the highest occupied molecular orbital of

improved. Electropolymerization will provide layers with enhanced morphological and electrochemical stability.

We found that electrochemically prepared polybithiophene (PbT, Figure 1) offers some advantages compared to other conjugated polymers^[1,2]. First, PbT is highly morphological stable (up to 350 C), and the glass transition temperature is high. Second, PbT is chemically and electrochemically stable in air, and can be kept electroactive in electrolytes during long redox cycles, which should benefit the operating stability of OLED devices. Electropolymerization is a convenient and common method for the growth of PbT layer [1]. We have shown that this electrochemically formed polymeric semiconductor can be utilized as effective hole-injection contact and improve dramatically the performance of small molecular NPB/Alq₃ bilayer system.

Polybithiophene films were prepared by the electropolymerization of 2,2-bithiophene. Preparation of the films were achieved by potential cycling between 0 V and 1.2 V, using 0.1 M tetrabutylammonium hexafluorophosphate (N(Bu)₄PF₆, in acetonitrile as supporting electrolyte. The layers are semitransparent and in the neutral state that means undoped after electropolymerization. They are amorphous and smooth up to a thickness of 60 nm determined by Scanning Electron Microscopic (SEM) measurements. Cyclic voltammograms in Figure 2 show good reversibility of charging and discharging the layer, indicating high electrochemical stability. The ionization potential (IP), equivalent to HOMO level^[3], was estimated from onset of oxidation peak V_{onset} . Using the relation $IP = V_{\text{onset}} + 4.45$ (eV), the value is about 5.0 eV. We also measured the IP value of NPB (inset of FIG.2), which is 5.25 eV. This indicates that the PbT layer can improve hole-injection because

Fig. 1
Device configuration
and molecular
structure.



the used organic material. That means it remains a remarkable high barrier for hole injection. Our aim is to introduce an additional electropolymerized buffer layer which makes hole injection much more efficient. It was shown by use of spin coated layers of chemically produced polymers that hole injection can be

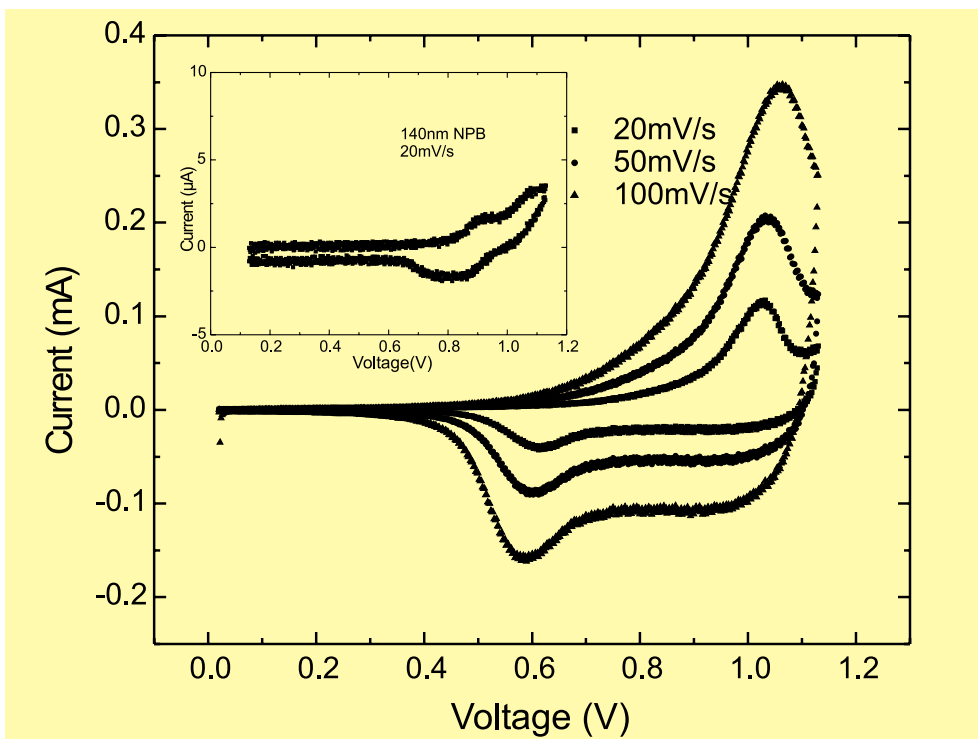


Fig. 2
Cyclic voltammogram (CV) of PbT films deposited on ITO. The measurement was performed in 0.1 M $N(Bu)_4PF_6$ /acetonitrile solution. Inset: CV of 140 nm NPB on ITO.

se the HOMO level of the PbT is in between the work function of ITO and the HOMO of NPB.

Hole-only devices were made to investigate the influence of PbT on I-V characteristics. In these devices, the organic layer is sandwiched between ITO anode and Ag cathode. In the ITO/55-nm PbT/Ag structure, high current at relatively low field (inset of Fig. 3) indicates high hole injection and transpor-

ting ability. In the second configuration, the organic layer is the hole-transport layer N,N'-Di(naphthalen-1-yl)-N,N'-diphenyl-benzidine (NPB) with or without PbT layer (Fig. 3). The current of the PbT-sandwiched device exceeds that in the NPB at voltages above 4 V and is more than one order of magnitude larger at higher voltages. Since the NPB layers have the same thickness in both cases, higher current can be correlated to a

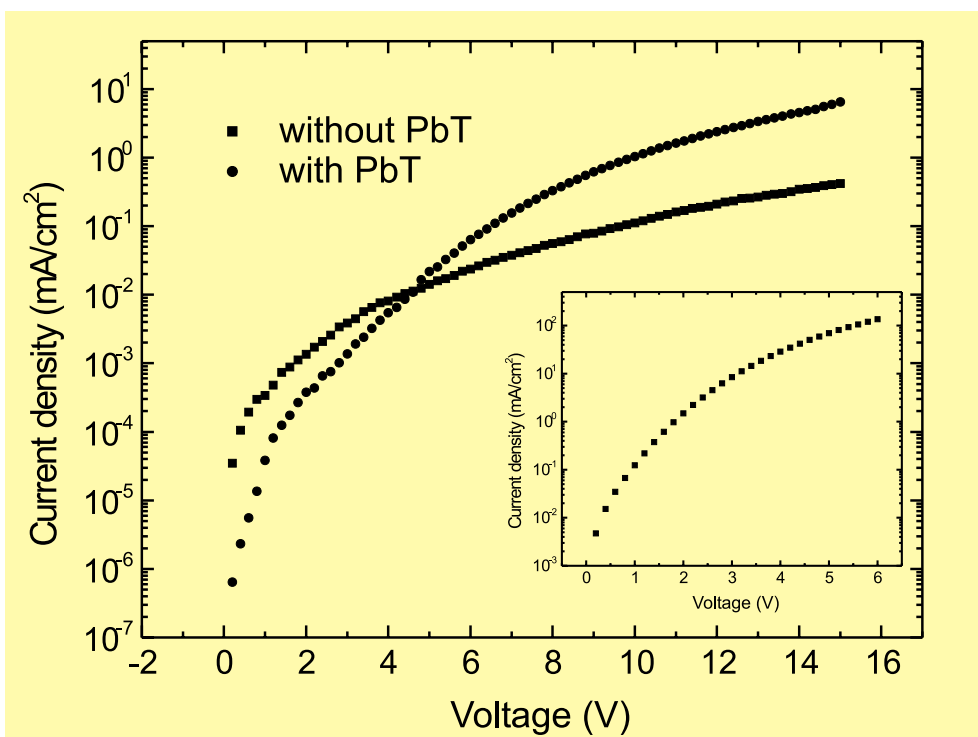
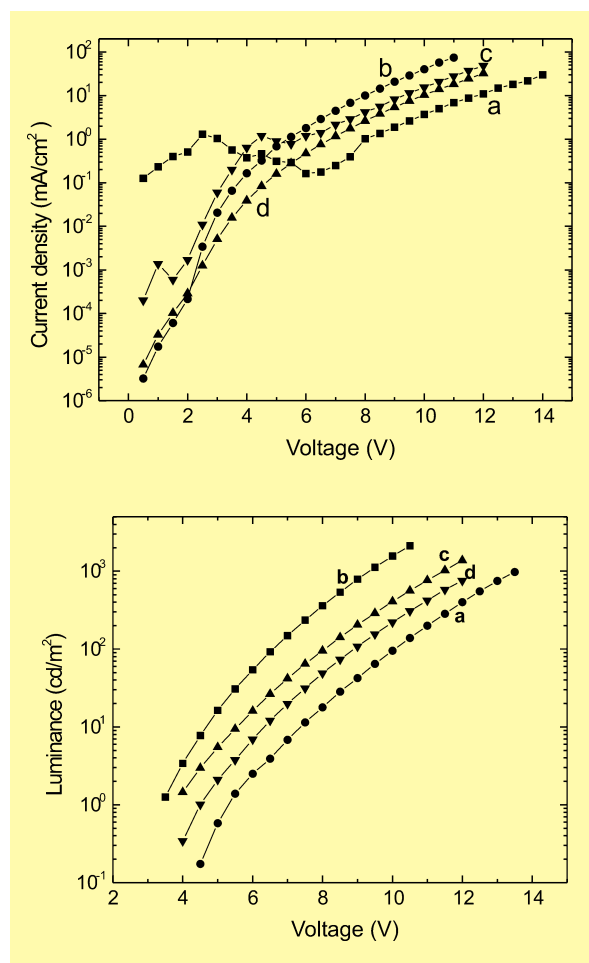


Fig. 3
I-V characteristics of hole-only devices with and without PbT layer. The thickness of NPB and PbT layer is 200 nm and 35 nm, respectively. Inset: I-V curve of ITO/PbT/Ag devices.

Fig. 4
Performance of Multilayer OLED under vacuum. Top: I-V characteristics, bottom: luminance-voltage characteristics. Device b-d have 20-25 nm injection inter-layer and 70 nm Alq₃ layer, as well as the NPB layer with the thickness of 70 nm (b), 87 nm (c), 100 nm (d), respectively. Device a: no PbT layer, thickness of NPB is 70 nm.



decreased barrier as result of incorporating the PbT layer. It demonstrates that PbT is effective to enhance hole injection in the contact of ITO and NPB. Multilayer OLED devices consist of NPB with varied thickness (70-100 nm) and 70 nm of Alq₃ on PbT-coated ITO anode. The same structure with no PbT was also fabricated as control device. Mixture of Mg and Ag (10:1) was used as cathode. The current-voltage (I-V) and luminance-voltage characteristics of these OLEDs are plotted in Fig. 4. The device without hole-injection layer shows poorly-behaved I-V feature. Up to now it is not clear what the reason for that negative slope of the current is. Leakage, shorts or inhomogeneities were discussed in the literature. However, for the device with incorporated PbT, well-behaved I-V feature is shown. The leakage current is suppressed by 4 to 5 orders of magnitude at lower field, meanwhile onset of light emission (turn-on voltage) decreases as expected. The current and luminance is drastically enhanced even at larger thickness of organic layers for a given voltage, and

are more than one order of magnitude larger compared to that in devices without PbT at the same layer thickness of NPB and Alq₃. The operating voltage is reduced by 3 V at the same luminance. Table 1 summarizes the performance of both devices. Luminous efficiency reaches 1.7 lm/W for the device with injection layer, in contrast to 1.1 lm/W for the control devices. So higher performance is reached, which should be originated from a remarkably increased hole injection between ITO and NPB by insertion of the PbT layer. However, since quantum efficiency is slightly reduced for this device, we suppose that the hole is the main charge carrier in this kind of device and the electron injection from the cathode is now the main limiting factor for EL processes. With further optimization by cathode engineering, for example by introduction of LiF/Al as cathode^[4], from which the electron injection will be

enhanced remarkably, more balanced injection and transport of holes and electrons can be achieved, and higher quantum efficiency and luminance is expected.

Table 1 Performance of a 70-nm NPB/70-nm Alq₃ structure with- and without- PbT layer

	OLED with PbT	OLED without PbT
Luminance (cd/m ²) at 10V	1560	100
Current density (mA/cm ²) at 10V	42	3
Operating voltage (V) for 100cd/m ²	6.5	10
Max. Luminous efficiency (lm/W)	1.7	1.1
Quantum efficiency (cd/A)	3.8	4.5

Fig. 5 shows EL spectra of the control device and the device with PbT. They are almost identical, with a peak at about 530 nm, although the color of the PbT thin layer is orange. We found out, that there is no significant dependence of the PbT thickness on the I-V-L feature of the device in the thickness range of 15-35 nm (experiments are not discus-

sed here). At lower thickness, the leakage current increases for the OLEDs. However, the further increase of the thickness will lead to much larger absorption loss of EL emission through the PbT layer causing lower luminous efficiency. The polybithiophene layer used here was undoped. The doped (oxidized) PbT should be more favorable due to the higher conductivity and transmission factor^[5]. This work is currently under investigation.

In conclusion, stable electropolymerized polybithiophene layers can serve well as an efficient hole-injection contact in OLED devices, which leads to a reduction of operating voltage, as well as the enhanced luminous efficiency. It was demonstrated that the incorporation of a polymerization process into vapor-deposited small molecular OLED is an alternative approach to improve the performance of OLEDs. This result will be very encouraging for the extension into other anode structures based on polymer (semiconducting and conducting)/small molecule interface.

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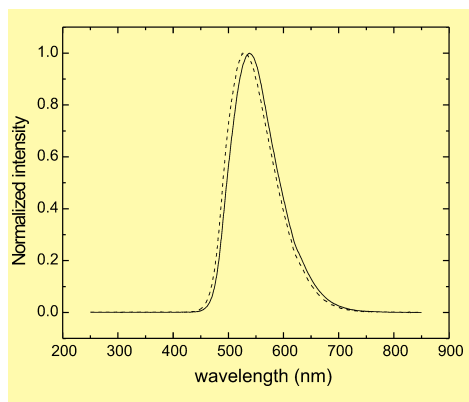


Fig. 5
EL spectra of
ITO/NPB/Alq₃/Mg:Ag
with (—) and without
(---) PbT layer.