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Electrical properties of polymer/metal interface in polymer light-emitting devices: electron injection barrier suppression

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The electrical characterization of a high efficient multilayer polymer light emitting diode using poly[(2-methoxy-5-hexyloxy)-*p*-phenylenevinylene] as the emissive layer and an anionic fluorinated surfactant as the electron transport layer was performed. For the sake of comparison, a conventional single layer device was fabricated. The density current vs. voltage measurements revealed that the conventional device has a higher threshold voltage and lower current compared to the surfactant modified device. The effective barrier height for electron injection was "suppressed". The influence of the interfaces and bulk contributions to the dc and high frequencies conductivities of the devices was also discussed.

The electroluminescence in poly(*p*-phenylene-vinylene) (PPV) reported in 1990 [1] has attracted attention on the use of conjugated polymers in light-emitting diodes. In such device, the density of injected carriers into the polymer is mainly controlled by the energy barriers between the work function of the metallic electrodes and the electronic affinity (ionization potential) of the polymer. The manipulation of these factors can improve the both, the quantum efficiency as well as the operating voltage of the devices [2, 3]. In order to improve the devices characteristics by enhancing the carrier injection, an additional hole/electron transport layers has been used [4, 5]. Among the materials used recently as transport layer, ion containing organic polymers [6–9] where the ionic groups are fixed to the molecule backbone have demonstrated an high performance. The reasons why these ion-containing materials, which are fixed at the cathode/emissive layer interface, can improve PLEDs performance are not yet completely understood. However two main reasons for this behavior are considered [9]: (i) The improvement of the interfacial adhesion between the polymer and the metal; (ii) polarization effects due to the strong dipole from the ion pair at the interface interfering with the electrical field, which makes the electron injection from the Al cathode easier [7]. The second reason seems to be the most important considering the performance of PLEDs. Tight packing of monolayers of ionic groups at the interface polymer/metal could be a more efficient way to improve electron injection phenomena. Fluorinated surfactants are known to be very effective to self-organize into supramolecular assemblies and can be an interesting candidate as electron-injecting material [10]. Hydrocarbon surfactants based on lithium salts of anionic ether sulfates have been applied successfully for increase the performance of PLEDs [11] that was attributed to the alignment of the surfactant dipoles induced by the ethyleneoxide groups of the surfactant molecule at the interface with the aluminum cathode. Recently neutral surfactants also have been applied in PLEDs structures, obtaining an improvement of approximately one order of magnitude in the current density of the devices [12].

In this work we report on a series of current vs. voltage (J vs. V) and impedance spectroscopy measurements of multilayer PLED using ITO as the anode, poly[(2-methoxy-5-hexyloxy)-*p*-phenylene-vinylene]

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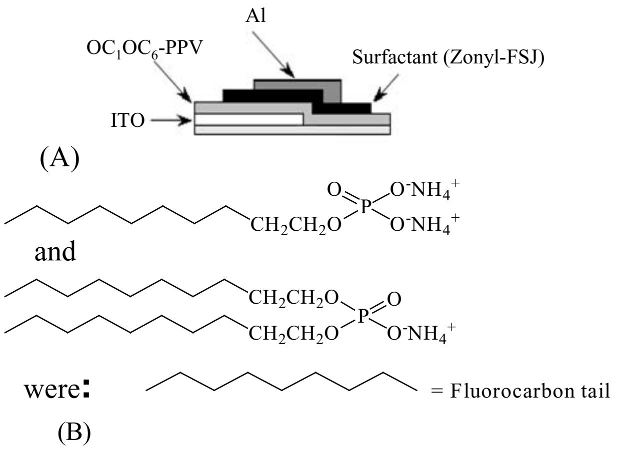

Figure 1 Schematic illustration of (A) multilayer polymer light-emitting diode and (B) the surfactant structure.

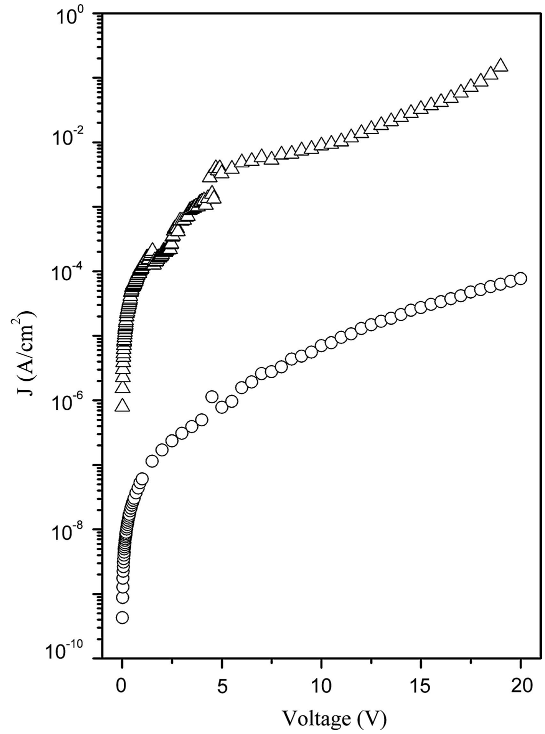

Figure 2 *J* vs. *V* curves obtained from single (o) and multilayer (Δ) devices.

(OC$_1$OC$_6$-PPV) as the emissive layer, an anionic fluorinated surfactant (ammonium salt of perfluoroalkylethylphosphate, Zonyl FSJ) as the electron transport layer, and aluminum as the cathode. The results aimed to determine the influence of electron transport layer on the electrical characteristics of the devices by fitting the results using models of equivalent circuits.

The PPV derivative OC$_1$OC$_6$-PPV was chemically synthesized using methods described elsewhere [13], while the surfactant material was obtained from DuPont (Zonyl-FSJ®) and has the general formula $CF_3(CF_2)_nCH_2CH_2OP(O)(O^-NH_4^+)_2$ and/or $[CF_3(CF_2)_nCH_2CH_2O]_2P(O)(O^-NH_4^+)$). OC$_1OC_6$-PPV films (200 nm thick) was cast from chloroform (1% wt) solution onto the ITO layer. The surfactant layer was prepared by spin-coating an aqueous solution (0.1% wt.) onto the deposited emissive layer. The aluminum electrode was vacuum evaporated ($A = 0.17$ cm^2). Fig. 1 shows the scheme for the multilayer device fabricated. For comparison, a conventional single layer device, without the surfactant layer, was also fabricated. Impedance measurements were carried out using a 1260 Solartron Frequency Response Analyzer in the 1 to 10^5 Hz frequency range with amplitude voltage (V_a) kept equal to 100 mV. Density current vs. voltage (J vs. V) curve was carried out in a Keithley 238 unity. All measurements were performed at room temperature, under vacuum and in the dark.

In order to figure out the role of the surfactant layer, current density *vs.* voltage characteristics of the devices were carried out and shown in Fig. 2. The curves were obtained in forward bias where ITO is positively biased and Al electrode grounded. The current density of the multilayer device is three orders of magnitude higher at 10 V than the conventional single layer device. The electron transport layer (surfactant) plays an important role on improving the injection negative carriers, respectively.

It is important to note that the threshold voltages for light emission are high compared to other multilayer devices reported in the literature [12, 14]. In this case, were not used hole transport layers or lower work function metals cathode or special film forming techniques in order to improve the device performance. The device was constructed in the simplest way in order to turn the conclusion about the effect of the surfactant layer clearer to be taken. Thus, the 10 V decrease in the threshold voltages for light emission can be considered as highly significant.

The hypothesis of enhanced electron injection was confirmed by impedance spectroscopy measurements, which allow one to distinguish between bulk and interface processes. At high frequencies the process is governed by the bulk of the polymer and at low frequencies by the interface [15, 16]. Fig. 3A shows the real impedance curve for the device without any electron injection material where two plateaus can be observed, one at low frequencies and one at high frequencies. The low frequency plateau (~ 1–8 Hz) is correlated to the impedance of the OC$_1$OC$_6$-PPV/Al interface, presenting a slightly variation with the bias voltage due to the decreasing in the potential barrier (from $\sim 8 \times 10^7\ \Omega$ at 0 V to $\sim 1 \times 10^7\ \Omega$ at 3 V) and the high frequencies plateau ($\sim 4 \times 10^4 - 10^5$ Hz), which remains unchanged for all bias voltage, is related to the ITO resistance. Fig. 3B shows the real impedance curve for the device with the surfactant layer displaying only one plateau. The real impedance at low frequencies, in such device is approximately one order of magnitude lower than for the device without the surfactant layer evidencing the enhancement in the electron injection. The real impedance at low frequencies (<30 Hz) decreases from

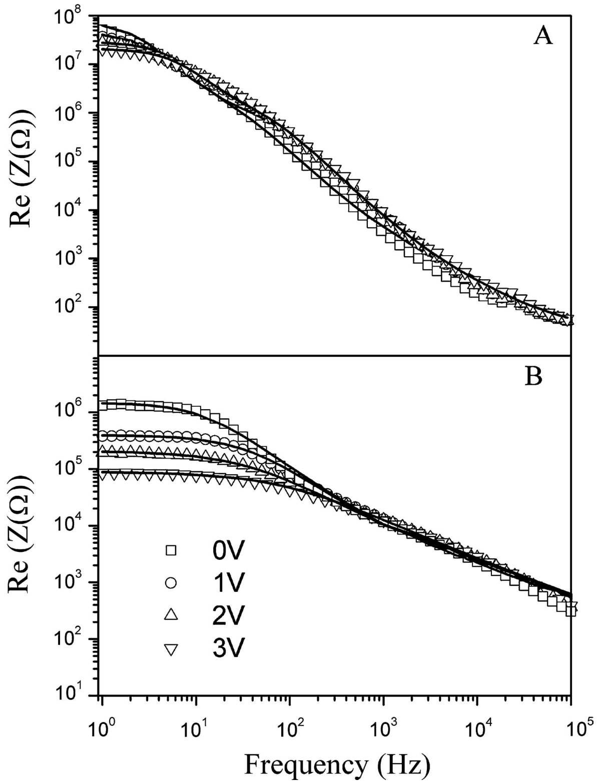

Figure 3 Real part of the impedance versus frequency for different bias voltages for (A) ITO/OC_1OC_6-PPV/Al and (B) ITO/OC_1OC_6-PPV/Surfactant/Al devices. The full lines are fits to the data for an equivalent circuit described by Equation 1.

1.5×10^6 Ω to 1×10^5 Ω at 0 V and 3 V bias voltages, respectively.

The real impedance data can be modeled using equivalent electric circuits, as described elsewhere [14]. For the single device two parallel resistor-capacitor networks are connected in series, one representing the OC_1OC_6-PPV layer (R_p, C_p) and another the OC_1OC_6-PPV/Al interface (R_{int}, C_{int}). Also included in the equivalent circuit is a small series resistance $R_S(\sim 50\ \Omega)$ that is probably due to an ohmic contact at the hole injecting ITO/OC_1OC_6-PPV interface. Equation 1 gives the real part of the impedance, where α has been incorporated to account for a distribution of relaxation times expected for polymer samples [17].

$$Z^* = \frac{R_{int}}{1 + (i\omega R_{int} C_{int})^{1-\alpha_{int}}} + \frac{R_p}{1 + \left(i\omega R_p C_p\right)^{1-\alpha_p}} + R_S \quad (1)$$

Table I exhibits the parameters employed in the fitting. When the bias voltage is varied, the parameters in Equation 1 used for fitting the data remain practically the same, with the exception of the network representing the interface (R_{int} and C_{int}). One could expect that the insertion of a surfactant layer would bring additional interface effects. On the contrary, a visual inspection of the data in Fig. 3B for the multilayer device indicates that interface effects (at low frequencies) appear to be suppressed. The data can then be modeled with just one parallel arrangement of resistor and capacitor (R_p, C_p) with a small resistance R_S in series. As for the fitting parameters, given in Table I, it is now observed that R_p decreases with bias voltage. In conclusion, these results indicate that the insertion of the surfactant layer affects the Al interface of the device, thus improving electron injection.

The surfactant dipoles could assume at least two orientation in the deposited layer; (i) oriented by the electrical field, thus forming a positive layer due to the $NH4^+$ ionic species and (ii) in an orientation dictated by the bond angles and molecular structure imposed by the specific interaction between ethyleneoxide group and aluminum [11]. The dipoles oriented at the interface leads to a decrease in the barrier for electron injection. Campbell *et al.* studied the use of self-assembled monolayer (SAM) of polar compounds in electroluminescent devices (EL) with the architecture: glass-Ag/ polar compounds/EL polymer/Ca [18]. These authors showed that dipoles with negative charge placed at the Ag anode of organic electronic devices, decreases the Schottky energy barriers at the interface.

In our surfactant EL-polymer/Al interface modified devices the dipoles formed by ion pairs ($O^-NH_4{}^+$) are not linked to Al or to the EL-polymer, thus they orient themselves with an applied electrical field [9]. The electrostatic interaction between $NH_4{}^+$ of the surfactant and the electrons of the cathode (Al) cause an increase of the injection of these carriers from the interface. This is called switching effect [19]. The mechanisms through which the electrons reach the EL polymer layer are difficult to establish though. One possibility would be these electrons moving toward the anode until reaching the EL layer, overcoming the repulsion from the negative charges in the surfactant due to the electrical field strength.

In conclusion, polymer light emitting diodes (PLEDs) using ITO as the anode, poly[(2-methoxy-5-hexyloxy)-*p*-phenylene-vinylene] (OC_1OC_6-PPV) as the emissive layer, a fluorinated anionic surfactant as the electron transport layer, and aluminum as the cathode (ITO/OC_1OC_6-PPV/Surfactant/Al) were constructed and characterized with respect to its electrical performance. The effect of the surfactant in decreasing the resistance and increasing the current is notable, supporting its use as an electron injection layer. The energy barrier for electron injection

TABLE I Parameters used in fitting the experimental data of Fig. 3 to Equation 1. ($R_S = 50$ (Ω))

Device	$^*R_{int}$ (Ω)	$^*C_{int}$ (*F*)	α_{int}	$^*R_p$ (Ω)	C_p (F)	α_p
Single layer	$<7.5 \times 10^7$ (0 V)	$>6 \times 10^{-9}$ (0 V)	0.01	1×10^6	3×10^{-8}	0.008
Multi-layer	–	–	–	1.5×10^6 (0 V)	4.6×10^{-8}	0.2

$^*R_{int}$ decreases from 7.5×10^7 at 0 V to 2×10^7 Ω at 3 V. C_{int} increases from 5×10^{-8} Ω at 0 V to 8×10^{-7} at 3 V. R_p decreases from 1.5×10^6 at 0 V to 9×10^4 Ω at 3 V.

was suppressed and the best adjustment was achieved considering a zero resistance barrier at the interface. The improvement in the device with the anionic surfactant was also observed visually by the intense and more constant light emission. The device with surfactant showed less dark spots and a lower tendency to fail during operation, even at higher voltages. The mechanisms which are involved in the decrease of electron injection need further experimentation; however it is clear the effect of dipoles, including non metallic counterions, such as the ammonium ion used in our experiments.

Acknowledgments

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References

1. J. H. BURROUGHES, D. D. C. BRADLEY, A. R. BROWN, R. N. MARKS, K. MACKAY, R. H. FRIEND, P. L. BURNS and A. B. HOLMES, *Nature* **347** (1990) 539.
2. W. BRÜTTING, S. BERLEB and A. G. MÜCKL, *Organic Elec.* **2** (2001) 1.
3. V. I. ARKHIPOV, E. V. ENNELLANOVA, Y. H. TAK and H. BÄSSLER, *J. Appl. Phys.* **84** (1998) 848.
4. C. J. BRABEC and N. S. SARICIFTCI, in "Semiconducting Polymers: Chemistry, Physics and Engineering," 1st edn. (Willey,VCH, 2000).
5. A. MARLETTA, E. PIOVESAN, N. C. SOUZA, C. A. OLIVATI, D. T. BALOGH, N. O. DANTAS, R. M. FARIA and O. N. OLIVEIRA JR, *J. Appl. Phys.* **94** (2003) 5592.
6. G. E. JABBOUR, Y. KAWABE, S. E. SHAHEEN, J. F. WANG, M. M. MORRELL, B. KIPPELEN and N. PEYGHAMBARIAN, *Appl. Phys. Lett.* **71** (1997) 1762.
7. S. H. KIM, K. H. CHOI, H. M. LEE, D. H. HWANG, L. M. DO, H. Y. CHU and T. ZYUNG, *J. Appl. Phys.* **87** (2000) 882.
8. A. EISENBERG, *Macromolecules* **23** (1990) 4098.
9. T. W. LEE, O. O. PARK, L. M. DO, T. Y. ZYUNG, T. AHN and H. K. SHIM, *J. Appl. Phys.* **90** (2001) 2128.
10. G. MARTINI, S. RISTORI and M. VISCA, "Ionomers: Characterization, Theory and Application," edited by Shulamith Schlick, (CRC Press, New York, 1996).
11. Y. CAO, G. YU and A. J. HEEGER, *Adv. Mater.* **10** (1998) 917.
12. Y. H. NIU, H. MA, Q. XU and A. K. Y. JEN, *Appl. Phys. Lett.* **86** (2005) 083504.
13. F. M. MARCONI, R. F. BIANCHI, R. M. FARIA and D. T. BALOGH, *Mol. Cryst. Liq. Cryst.* **374** (2002) 475.
14. C. A. OLIVATI, M. FERREIRA, A. J. F. CARVALHO, D. T. BALOGH, O. N. OLIVEIRA JR., H. VON SEGGERN and R. M. FARIA, *Chem. Phys. Lett.* **408** (2005) 31.
15. I. H. CAMPBELL, D. L. SMITH and J. P. FERRARIS, *Appl. Phys. Lett.* **66** (1995) 3030.
16. A. J. CAMPBELL, D. D. C. BRADLEY and D. G. LIDZEY, *J. Appl. Phys.* **82** (1997) 6326.
17. C. J. F. BÖTTCHER and P. BORDEWIJK, in "Theory of electric polarization," (Elsevier Scient. Pub. Comp., Netherlands, 1978).
18. I. H. CAMPBELL, S. RUBIN, T. A. ZAWODZINSKI, J. D. KRESS, R. L. MARTIN, D. L. SMITH, N. N. BARASHKOV and J. P. FERRARIS, *Phys. Rev.* **B 54** (1996) 14321.
19. R. C. HUGHES, *J. Appl. Phys.* **51** (1980) 5933.

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