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Transient and d.c. analysis of the operation mechanism of light-emitting electrochemical cells

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Abstract – Light-emitting electrochemical cells (LECs) made of electroluminescent polymers were studied by d.c. and transient current-voltage and luminance-voltage measurements to elucidate the operation mechanisms of this kind of device. The time and external voltage necessary to form electrical double layers (EDLs) at the electrode interfaces could be determined from the results. In the low- and intermediate-voltage ranges (below 1.1 V), the ionic transport and the electronic diffusion dominate the current, being the device operation better described by an electrodynamic model. For higher voltages, electrochemical doping occurs, giving rise to the formation of a p-i-n junction, according to an electrochemical doping model.

Introduction. – Organic light-emitting devices constitute an important branch in organic optoelectronics due to their great potential to be used in a wide range of applications, from dot-pixels for color displays to large-area panels for ambient illumination [1–6]. Differently from organic/polymeric light-emitting diodes (OLEDs/PLEDs), whose technology is already quite well developed, polymeric light-emitting electrochemical cells, LECs [7], are devices whose performance is still not satisfactory for commercial applications, but had presented a growing interest in recent years [8–12]. The main feature of a LEC is that the active layer comprises a blend of a conjugated electroluminescent polymer (EP) and a polymer electrolyte, which confers to them advantageous characteristics like bipolar operation (in forward or in reverse bias) and low operating voltages, regardless of the work function of the electrodes and of the thickness of the active layer [7]. On the other hand, LECs have some drawbacks as slow response time, imposed by the low ionic mobility, lower voltage stability and shorter lifetime [13], which limit their technological applications. Moreover, there is still a lot of discussion about the fundamental operation mechanism of LECs, which is not completely understood until now. In this sense, studies which can provide accurate information about the injection and transport phenomena in LECs are very important for overcoming most of the technological limitations that still persist.

The operation behavior of LECs is usually explained by two antagonist models: i) an electrodynamic model (ED) [14,15], which considers that the ionic charge separation due to the external bias is enough to lower the energy barriers for electronic charge injection from the electrodes and that the subsequent electronic transport in the bulk is a diffusion-limited process; ii) an electrochemical doping model (ECD) [7,16], which states that the ionic charge separation intermediates the electrochemical doping of the conjugated polymer, giving rise to Ohmic contacts at the electrode interfaces and to the formation of a p-i-n junction in the active layer. The fundamental difference between these two models is that, in the ED model, practically the whole the electric field is confined close to the electrode interfaces, where the

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uncompensated ionic charges cause the formation of electric double layers (EDLs), and the electronic transport in the bulk is carried out by diffusion in an almost null electric-field region, whereas, in the ECD model, the formation of two doped regions (of n-type close to the cathode and of p-type close to the anode) increases the conductivity of the bulk, provoking the drift of the opposite electronic charges which recombine in the insulating region that separates the doped regions.

We report here results from d.c. and transient current measurements in LECs that indicate that both ED and ECD models are partially valid to explain the operation of the devices, each one being more appropriate to describe the electrical behavior according to the amplitude of the applied external bias.

Materials and methods. – Polymer light-emitting electrochemical cells were built by spin-coating a blend comprising a conjugated electroluminescent polymer and a polymer electrolyte onto ITO-covered glass substrates and, then, thermally evaporating, through appropriate shadow masks, Al electrodes (10 mm² in area), in high-vacuum conditions. Spin-coating parameters were adjusted to give rise to polymeric films of 300 nm in thickness. Three different polymers (all provided by American Dye Source, Inc.) were used as the active-layer organic semiconductor: a green-emitter (GE), poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-vinylenevinylene)]; a blue-emitter (BE), poly[(9,9-dioctylfluorene-2,7-diyl)]; and a red-emitter (RE), poly[(9,9-dioctyl-2,7-divinylene fluorenylene)-alt-co-(9,10-anthracene)]. The electronic band-gap values for the RE, GE and BE polymers were 2.3 eV, 2.5 eV and 2.7 eV, respectively, determined by cyclic voltammetry, confirming the material datasheet from the supplier. The polymer electrolyte comprised a mixture of poly(ethylene oxide), PEO, and lithium trifluoromethanesulfonate, CF₃SO₃Li, and was added to the electroluminescent polymer (EP) solutions to result in blends with a 1:1 (EP:PEO) weight ratio. Even though different lithium salt concentrations in the polymer blend had been tested, all the results presented here were obtained using a 10:1 (PEO:CF₃SO₃Li) weight ratio.

Electrical measurements were carried out using a Keithley 2400 source-measure unit to measure the d.c. current-voltage (I-V) characteristics and a Keithley 617 electrometer to read the photocurrent from a calibrated photodiode to obtain the luminance-voltage (L-V) curves. For transient current measurements, a HP3325B function synthesizer was used to drive the devices, whereas the current was measure using a Keithley 610C electrometer with the analog output connected to an Agilent HP54610B oscilloscope.

Results and discussion. – Figure 1(a) shows the I-V and L-V curves obtained from a ITO/GE:PEO:CF₃SO₃Li/Al device with a lithium salt concentration of 10%, at room temperature. The device operates almost symmetrically in both polarities, showing two apparently linear regions: one less conductive between 0 V and 4 V, and another region, with higher slope, between 4 V and 7 V. The turn-on voltage (Vₜ) determined from the onset of the electroluminescence (EL) was found to be about 3.5 V. However, the observation of the monolog graph of the conductivity (obtained from the derivative of the I-V curve) vs. the applied voltage (fig. 1(b)) reveals that the electrical behavior of this device is even more intricate. One can observe that there is a low-voltage region where the conductivity increases slowly with the voltage, followed by a steeper increase around the onset of the device and then saturating to an almost constant value for higher voltages.

A more accurate analysis of the electrical operation of the device could be obtained from the transient current responses (I-t) due to the application of constant voltage steps to the device.

The results are shown in fig. 2, where they are divided into three different voltage ranges, for better visualization: i) a low-voltage region, up to 600 mV (fig. 2(a)); ii) an intermediate voltage region (fig. 2(b)), from 0.6 V to 1.1 V; and iii) a high-voltage region (fig. 2(c)), from 1.1 V to 7 V. The current response to the voltage step application presents a slow initial increase, achieving its maximum...
value only after about 100 ms to 200 ms. This time can be associated to the time needed to promote the kinetic dissociation of ions in the solid electrolyte.

For voltages below 700 mV (region i), the $I-t$ curves present a peak, which is followed by a monotonic decay tending to a stationary value. This can be explained by the saturation of the ionic transport (the electrodes are blocking for ions) and the establishment of the steady-state electronic conductivity, which is still low for such low voltages. In region ii), the current peak is replaced by a plateau (fig. 2(b)), which can be interpreted as an increase in the electronic/ionic contribution ratio to the total current. In region iii) (fig. 2(c)), the stationary value of the current increases by about 4 orders of magnitude, evidencing the higher contribution of the electronic carriers to the conduction, due to the electrochemical doping of the conjugated polymer.

From these $I-t$ curves, a log-log $I-V$ plot was built (fig. 3) by computing the stationary (or peak, for region i)) current values. From fig. 3, one observes that the PLEC exhibits an Ohmic behavior for voltages below 600 mV (region i)), and then, after an inflexion point, it presents a steeper response that extends up to 1.1 V (region ii)). A third region (iii)), starting at 1.1 V up to 7 V, can be also distinguished from the region ii). This region also has a superlinear behavior (but less steep than in region ii)) and is where the onset of the electroluminescence occurs ($V_t \sim 3.5$ V, for the GE polymer).

Similar LECs, using the same device structure and geometry, were made by replacing the GE polymer by the RE and BE polymers, which yielded $V_t$ values of 3.2 V and 3.9 V, respectively. By plotting the obtained values of $V_t$ vs. $E_G$ (band-gap energy of the polymers) for these three PLEC (fig. 4), a linear behavior is observed, whose extrapolation from the linear fitting intercepts the $V_t$-coordinate ($E_G \rightarrow 0$) at 1.1 V. This voltage coincides quite well with the value at the second inflexion point in fig. 3.

These results can be interpreted as evidence that the maximum voltage drop in the EDLs formed by the ionic motion in the polymeric electrolyte is about 1.1 V. For external applied voltages below this value, the electrical field in the bulk is negligible, and the current is mainly due to the ionic migration towards the electrodes. However, for external voltages above 600 mV, injected electronic charge carriers also start to contribute to the current, in a diffusion-dominated process, according to the ED model. Although the EDL formed by the Li$^+$ ions can be considered as a Helmholtz-like layer and the almost immobile CF$_3$SO$_3^-$ ions form a layer that is better described by the Gouy-Chapman model [17], we will consider here, for simplicity, that both EDLs are similar and can be represented by a simple plane capacitor equation: $C = \varepsilon_0 \varepsilon / d$, where $\varepsilon$ is the dielectric constant, $\varepsilon_0$ is the free space permittivity, $d$ is the width of the EDL. In this picture, if we consider $d$ equal to 10 nm [15], a voltage drop of 0.1 V will result in an electric field of $10^5$ V/cm, which is sufficient to start electronic charge injection into the conjugated polymer [18]. Considering a dielectric constant of 3, the calculated amount of ionic charge in each EDL is about $1.6 \times 10^{-8}$ C, for a voltage of 600 mV. By integrating the $I-t$ curve for this voltage in fig. 3, this charge is achieved for an integration time of 240 ms, which can be considered the time necessary to build up the EDLs and to initiate the electronic injection from the electrodes.

Above 1.1 V, the voltage drop extends beyond the borders of the EDLs, increasing the electric field in the bulk. As the electric field increases in the bulk, it drives the injected electrons (holes) towards the anode (cathode), promoting the electrochemical $n(p)$-doping of the conjugated polymer. During the electrochemical doping process, the n- and p-doped regions increase, making the whole device more conductive (as can be confirmed by the superlinear behavior in fig. 3) until the p-i-n junction is completely established and the electroluminescence of the device starts. After the onset of the device, the device conductivity still shows some initial increase due to the enhancement of the current caused by the bimolecular recombination of electrons and holes [19], but becomes practically constant with further increase on the applied voltage (as can be seen in fig. 1(b)).
Conclusions. – From the presented results, we conclude that, for LECs in a sandwich-type structure and with high lithium salt concentration, a time higher than 200 ms is necessary to establish the EDLs at the interfaces and to start the electronic injection from the electrodes. In the low-voltage regime (< 0.6 V), the device current is mainly dominated by ionic transport, becoming dominated by electronic transport after the maximum voltage drop (1.1 V) in the EDLs is achieved. Until the maximum voltage drop is applied, the LECs operation can be better described by the ED model; however, for higher voltages, the evidence of formation of an electrochemical p-i-n junction suggests that the ECD model is more suitable to explain the device operation mechanism.

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