Blue and Green Light-Emitting Electrochemical Cells with Microsecond Response Times

S. Tasch, a,1 J. Gao, b F. P. Wenzl, a L. Holzer, a G. Leising, a, * A. J. Heeger, b U. Scherf, c and K. Müllen c

*Institut für Festkörperphysik, Technische Universität Graz, A-8010 Graz, Austria
b Institute for Polymers and Organic Solids, University of California, Santa Barbara, Santa Barbara, California 93106-5090, USA
Max-Planck-Institut für Polymerforschung, D-55128 Mainz, Germany

Light-emitting diodes based on conjugated polymers (PLEDs) can be realized with promising efficiencies over the entire visible spectral range. The most attractive potential application of PLEDs is their use in emissive flat panel displays. In order to realize PLEDs with operating lifetimes which fulfill the values required for industrial applications, efficient devices with low operating voltages are necessary. Low operating voltages are more easily realized with small bandgap conjugated polymers, because the mismatch between the energy bands of the polymers and the work functions of the electrodes is smaller than for wide bandgap polymers. Thus, it has proved to be easier to realize red-orange and green PLEDs with low operating voltages and high efficiencies.

However, the fabrication of blue PLEDs with low turn-on voltages and sufficient lifetimes is absolutely necessary to realize multicolor flat panel displays. Moreover, one of the most promising ways to produce multicolor displays is based upon blue PLEDs, and the realization of red and green light emission through down-conversion.

Recently, a new type of polymer light-emitting device, the polymer light-emitting electrochemical cell (LEC) has been described and analyzed. LECs have the advantage that the electroluminescence (EL) onset occurs for all emission colors at bias voltages which are approximately equal to the single-particle energy gap $E_g$ divided by the electron charge $e$. In LECs, electrochemical doping of the conjugated polymer takes place near both electrodes thereby creating a p-type doped region near the anode and an n-type doped region near the cathode. In between these p- and n-doped zones a region with low, intrinsic conductivity remains. Thus, a p-i-n junction is created in situ.

The formation of the p-i-n junction is not an instantaneous process but depends on the mobility of the ions in the three-component blend consisting of a conjugated polymer (which has to be both electrochemically active and luminescent), an ion transport polymer, and a molecular salt. We demonstrate the realization of efficient blue and green LECs based on blends of the conjugated polymer $m$-LPPP [methyl substituted ladder-type poly(paraphenylene) (LPPP), prepared according to Ref. 14] and poly(ethylene oxide) (PEO) complexed with LiCF$_3$SO$_3$ (lithium trifluoromethanesulfonate) or LiClO$_4$ (lithium perchlorate, latter components were purchased from Aldrich), which are characterized by very low response times below 30 μs. Similar low response times have been observed only in frozen junction LECs so far. This fast response makes LECs based on $m$-LPPP attractive for applications in passively addressed pixelated displays.

Experimental

The active layers of the LEC devices were fabricated by spin-casting the blend of $m$-LPPP:PEO:LiCF$_3$SO$_3$ (or LiClO$_4$) from cyclohexanone (which dissolves all three components) solutions (similar to Ref. 13) onto glass substrates covered with indium-tin oxide (ITO), Al, Ag, or Au. For the other electrode Al, Ag, or Au was evaporated (in high vacuum) on top of the blend film.

The EL spectra were recorded with a charge-coupled device (CCD) spectrometer (Oriel 77400 and Princeton Instruments CCD-576). For the pulsed measurements, the LECs were driven by a 1 kHz square wave from a low frequency pulse generator, and the response was measured by a photodiode with the output displayed on an oscilloscope. The absorption of the LEC during operation was recorded with a Perkin Elmer A9 spectrometer.

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In reverse bias [bottom electrode (e.g., ITO) as the cathode] light emission was clearly observable with the naked eye above -2.7 V (where also the onset of the current occurs), with Al as the top electrode. For LECs with ITO as the bottom and Au as the top electrode even lower onset voltages were obtained. In these LECs, the blue light emission from m-LPPP was already visible and detected at -2.2 V. This value is surprisingly low, when one considers that the energy gap of m-LPPP is about 2.7 eV and represents one of the lowest reported onset voltages for blue light emission in EL devices up to now. The occurrence of EL emission below voltage values of \(E_c/e\) has also been reported and discussed for other LECs (Ref. 13 and 17).

However, in the forward direction the onset of emission was usually between 4 and 10 V depending on the operation conditions (Ref. 19). We emphasize that this effect (i.e., that the onset in reverse bias for the m-LPPP LECs occurs before that in forward bias) is independent on the electrode material, and hence, on the calculated barrier heights for charge carrier injection at the interface’s active layer and/or electrodes and, therefore, the behavior of the LECs based on m-LPPP is completely different from the characteristics of PLEDs.

An explanation for this unexpected behavior can be found by analyzing the distribution of the ions within the active layer of the LEC by secondary ion mass spectroscopy (SIMS) (a detailed analysis of the SIMS results is published elsewhere). For an active layer spin cast onto ITO, the overall concentration of the Li ions and triflate ions is significantly higher near the ITO electrode than near the surface of the active layer (by a factor of 15 and 2.5, respectively). After evaporating Al as the top electrode on the active layer, the negative triflate ions drift toward the top electrode (which acts as the anode) due to the internal electric built-in field. A detailed theoretical description of this scenario can be found in Ref. 20.

In case the polarity of the internal built-in field is reversed (by using, e.g., ITO as the bottom and Au as the top electrode) a shift of the negative triflate ions toward the anode is observed. In contrast, the position of the positive (Li\(^+\)) ions is not significantly altered by changing the polarity of the internal built-in field but it is preferentially near the (ITO) bottom electrode. This suggests, that the motion of the Li\(^+\) ions is restricted within the active layer and that the Li\(^+\) ions seem to be anchored near the bottom electrode. The reason for that interesting behavior of the positive ions in the active layer is currently being further investigated.

Due to the presence of the Li\(^+\) ions near the bottom electrode the n-doping process of m-LPPP will be possible only from that electrode, which in this case must be wired as the cathode (reverse direction). This observation is in agreement with the recorded characteristics of the m-LPPP LECs (see above).

Overall, one must consider that the performance of LECs is strongly influenced by the preparation conditions and the purity of the applied materials. Therefore, it is difficult at the present stage to rule out whether the observed phenomena of m-LPPP LECs are more related to intrinsic properties of m-LPPP or (which seems more probable) to extrinsic effects. This will be the challenge for further investigations.

This unexpected behavior of the ions is the main reason for the observed low response times of the LECs based on m-LPPP under pulsed operation, where turn-on response times (which we define as the time required to get from 10 to 90% of the maximum EL brightness) below 30 \(\mu\)s are obtained (comparable to the time resolution of the electronic equipment used for the measurements) (Fig. 2). This value is significantly below the reported value for the turn-on response of other LECs, which range from 30 \(\mu\)s (achieved by optimizing the phase morphology of the active layer of the LEC by additives) to several minutes. Similarly fast response times have been reported for “frozen junction” LECs. Such a frozen junction is generated by cooling the LEC, after the formation of the p-i-n junction, down below the glass transition temperature of the ionic conductive polymer. In that temperature regime the ions are not mobile in the active layer. Since no ionic motion takes place at these low temperatures, fast response times in the microsecond regime can be achieved.
The turn on response of fresh and discharged LECs based on m-LPPP is significantly slower (approximately 20 s when operated at a bias voltage of 6 V) (Fig. 2) than that of LECs, which have already been operated at room temperature. This gives evidence that trflate ions, which can move to the anode under operation (see above), do not return immediately to their initial positions if there is no potential applied but will stay near the anode (the Li+ ions seem to be anchored near the bottom electrode anyway). The emission color of a fresh LEC based on m-LPPP changes from blue to green within the first minutes of operation. This effect is only partly reversible. In the EL spectrum, this color change is visible as a decrease of the two dominant peaks at 460 and 490 with respect to the peaks at 530 and 560 nm (Fig. 4). This change of the emission color is generated by the interaction of m-LPPP with the polar environment, as we have observed for m-LPPP in other polar matrices. Similar effects have also been observed in LECs based on other conjugated polymers. An increase of the long wavelength component in the EL emission spectrum under operation is less obvious when the interaction between m-LPPP and PEO is restricted. This is the case for LECs based on m-LPPP with very low PEO or very high PEO concentrations. In the latter case, the interaction is limited by the larger scale phase separation which is observed in blends with high PEO concentrations.

The EL spectra of fresh and discharged LECs (ITO/m-LPPP:PEO: LiCF3SO3/Al (concentration is 20:10:3) in dependence of operation time, when operated continuously at -4 V. The thickness of the active layer is 200 nm. The EL spectrum recorded after 30 s represents the final EL spectrum.

Figure 4. EL spectra of fresh and discharged LECs.

Conclusion

We have demonstrated, that blue and green light-emitting LECs can be fabricated with m-LPPP as the light-emitting polymer. These LECs exhibit extremely low onset voltages between 2.2 and 2.7 V in reverse direction for blue emission. In addition to the low onset voltages, their intrinsically low response time under pulsed operation in the microsecond regime, which is attributed to the restricted motion of the ions in the LEC, makes these LECs based on m-LPPP interesting for display applications.

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