



The role of the polymer solid electrolyte molecular weight in light-emitting electrochemical cells



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ABSTRACT

Different molecular weights (M_w) of poly (methyl methacrylate) (PMMA) were used as the base for the polymer solid electrolyte (PSE) in light-emitting electrochemical cells (LECs). The rheological properties of the LECs formulations are influenced by the M_w of PMMA. The M_w of PMMA also influences the PSE ionic conductivity and therefore affects the threshold voltage of the devices. Furthermore, partial segregation of the two polymers is observed, which correlates directly to the PMMA M_w . The device with the best performance was prepared with a PMMA M_w of 350,000 and exhibited an effective maximum luminance $\sim 3000 \text{ cd m}^{-2}$.

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1. Introduction

The almost unlimited spectrum of organic compounds, which properties range from insulators, semiconductors to conductors, has made the fabrication of a large variety of optoelectronic devices possible establishing the field of organic electronics. The advancements in this field of research have been motivated by the feasibility of fabricating devices from solution allowing for the use of roll-to-roll compatible techniques at low cost and high throughput [1–3]. Among the different organic electronic devices, light-emitting electrochemical cells (LECs) represent an alternative technology for the roll-to-roll fabrication of lighting appliances [4]. The potential of LECs resides in the nature of their working principle and lower fabrication complexity compared to OLEDs, since only one active layer

composed of a blend of an organic semiconductor and an electrolyte is needed for their operation. In addition, no low work function metal is necessary for their operation, since the included ionic species dynamically form carrier injection layers upon applied bias [5,6]. Recently, ionic metal complex based LECs have achieved operation lifetimes over 4000 h above 600 cd m^{-2} [7]. Furthermore, Sandström et al. have reported polymer LECs with brightness of up to 150 cd m^{-2} fabricated by a roll-to-roll compatible technique, demonstrating the scale-up potential of this technology [4].

The performance of LECs not only depends on the choice of the semiconductor material, which would ultimately define the emission spectrum of the device. In addition, the choice of electrolyte and its ratio to the semiconductor directly impact the turn-on voltage, turn-on time, and lifetime of the devices [8,9]. A higher ionic conductivity has been observed to reduce the threshold voltage (V_{th}) and turn-on time [10]. On the other hand, lower ionic conductivity has a beneficial effect on the device lifetime [11]. Another important point is the use of an electrolyte with a large electrochemical window

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which would hinder detrimental side reactions between the electrolyte and the semiconductor or contacts [12]. Finally, analogous to the bulk heterojunction OPVs, not only the electrical properties of the components are important, but also an optimized microscopic morphology. Phase separation has been observed in LECs based on Poly (styrene oxide) (PEO) and semiconducting polymers. The phase separation promoted PEO domains with low ionic conductivity adversely affecting the performance of the device [13–16]. Any approach meant to optimize the formulation of the solutions towards the fabrication of devices via a printing or coating roll-to-roll process will have an impact on the morphology and performance of the devices [17,18]. Therefore, it is important to explore ways to equilibrate the processability of the functional inks and the performance of organic electronic devices towards the use of large scale printing techniques.

In the present work, we investigate the effect of the average molecular weight (M_w) of the poly (methyl methacrylate) (PMMA) on the microstructure and performance of polymer based LECs. A mixture of PMMA with different M_w ranging from 3500 to 996,000 and tetrabutylammonium tetrafluoroborate (TBABF₄) was used as a polymer solid electrolyte (PSE) within the devices. A poly (phenylvinylene) derivative, colloquially named super yellow (SY), was used as the emitting material. Atomic force microscopy (AFM) measurements revealed two distinct morphologies arising from phase separation. The presence of a PMMA rich phase was confirmed by fluorescence microscopy measurements and was found to increase in direct correlation to the M_w . Electroluminescence microscopy images confirmed that the dynamic p–i–n junction only form in the SY rich area resulting in a smaller effective emitting area. It was found that V_{th} correlates directly with the ionic conductivity of the PSE which was in turn dependent on the M_w of PMMA. The device prepared with a PMMA M_w of 350,000 exhibited the best performance with a maximum luminance (L_{max}) of ~ 2200 cd m⁻². The effective luminance (L_{eff}) of the devices increased up to $\sim 40\%$ when taking into account the actual emitting area of the device.

2. Materials and methods

SY (PDY-132 LIVILUX, Merck), PMMA (Sigma Aldrich, $M_w = 3500; 120,000; 350,000; 996,000$, Polydispersity Index = 2.5, 6.5, 4.5, 6.5, respectively) and TBABF₄ (Sigma Aldrich) were dissolved separately in anisole for several hours. Subsequently, the solutions were mixed at a 1:1.25:0.25 weight ratio of SY, PMMA and TBABF₄, respectively and stirred overnight. The solutions were then spin coated onto pre-structured ITO covered glass for 60 s at 1700 rpm yielding a layer thickness of ~ 100 nm. Ag top contacts (100 nm) were thermally evaporated through a shadow mask to define the active area of the device (0.24 cm²). The electrical and optical characterization of the devices were performed using a calibrated BOTEST system at a measuring speed of 0.1 V s⁻¹. The samples utilized for the determination of the PSE ionic conductivity were also prepared by spin coating using PMMA and TBABF₄ solutions in a 1.25:0.25 ratio. The viscosity of the solutions

was measured at 23 °C using a fluid volume of 1 ml on the cone-plate geometry by a HAAKE MARS rheometer.

Morphology measurements were performed using a Nanosurf AFM in dynamic mode configuration with a Si cantilever. Thickness measurements were performed using a Veeco profilometer. The fluorescence and electroluminescence microscope images were recorded using a Nikon eclipse 80i fluorescence microscope through the ITO electrode. For the fluorescence images, a halogen lamp with a band pass blue filter (465–495 nm) was used as an excitation source. The emitted light was recorded through a green band pass filter with a bandwidth from 515 nm to 555 nm. The images of the devices under operation were captured without any filter.

3. Results and discussion

A schematic representation of the working principle of the LECs prepared in this work is presented in Fig. 1 as described by the electrochemical doping model [4,19]. The active layer comprising a blend of SY and the PSE (PMMA: TBABF₄) was sandwiched between an ITO and Ag contacts. Upon applied bias, the mobile ionic species contained in the film migrate to the corresponding electrode to electrostatically compensate injected carriers giving rise to electrochemically doped regions of SY. The highly conductive p-doped and n-doped regions at the interface of Ag and ITO grow until a light emitting p–n junction is formed.

The surface morphology of the prepared devices is presented in Fig. 2. For the samples with M_w higher than 3500, round-shaped domains (*P*) and networking paths (*S*) were observed, suggesting phase separation between the components. The area of domain *P* was observed to increase in direct correlation to the M_w of PMMA. Such phase separation occurred by a spinodal decomposition mechanism originated by the entropy gain in polymer/polymer blends [20–22]. Roughness (rms) within each of the domains was found to be below 0.8 nm and 1.4 nm for the *P* and *S* respectively. Cross sectional analysis of the step height between the domains was observed to range between 5 and 10 nm, much lower than the average sample thickness of (~ 100 nm).

Fig. 3 presents the optical microscopy images of the different LECs in operation at a current density of ~ 15 mA cm⁻². The samples exhibited the distinctive yellow emission of SY which is observed not to be homogeneous throughout the sample. The sample with M_w 3500 also showed an inhomogeneous emission as a result of phase separation which was not evident by AFM. By comparing the features with the AFM measurements presented in Fig. 2, we concluded that only the *S* domains are electroac-

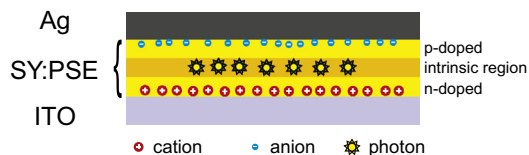


Fig. 1. Schematic of a polymer based light-emitting electrochemical cell.

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