Characteristics of a conducting polymer anode for flexible OLED using screen printing method

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Abstract

We report on the fabrication and characterization of an OLED with an anode completed using screenprintable conducting polymer containing PEDOT: PSS. The demonstration of this organic transparent anode for OLEDs shows a good possibility for flexible displays using this polymeric electrode.

1. Introduction

There has been a rapid progress in the area of flexible electronic devices including organic electronic devices and displays because of their numerous applications. In order to realize such devices, it is required to achieve high mechanical flexibility and low fabrication cost, especially for commercialization.^[1,2]

Flexible electronics and displays require flexible electrodes materials which are electrically conducting and optically transparent. Those materials should be comparable to Indium Tin Oxide (ITO) which has been widely used as powerful transparent electrodes in many electronic applications. However, Indium tin oxide is not suitable for flexible applications because Indium migration from the surface causes device failure,^[3,4] the film has high sheet resistance and surface roughness when deposited at a low temperature compatible with plastic substrates, and it cracks when bended repeatedly. As an alternative to ITO, a promising candidate for flexible electrode materials is a conducting polymer such as poly(3,4-

ethylenedioxythiophene) (PEDOT) or poly(3,4ethylenedioxythiophene): poly(styrenesulfonic) (PEDOT:PSS). These conducting polymers have been employed in device development mainly because of their excellent electro-optical properties.^[5]

We used a new form of PEDOT:PSS which was modified by designing and adding unique nanoparticle binders considering water resistance, chemical stability, and mechanical tolerance as an anode material. The anode was fabricated using screen printing, which is an efficient fabrication method with a low cost and high scalability. However, there have been no reports on the employment of screen printing process for these applications.

In this work, we show that characteristics of an OLED device completed successfully using a printable conducting polymer anode, which implies that this conducting polymer could be employed for many flexible device applications.

2. Experimental

Anode used in this work is a screen-printable organic transparent electrode (OTE) materials with high stability based on PEDOT:PSS (PriMet-P, DPI Solutions, Inc). While the conventional OTE printed by PEDOT:PSS itself or modified PEDOT:PSS formulation shows low durability due to its deficient water and chemical resistance, the environmental stability of OTE printed by PriMet-P is improved by unique binder design. The usual roles of binder polymer in the paste are to enhance the cohesion and adhesion of OTE on the transparent substrate, to provide mechanical strength and to raise the viscosity adaptable to screen-printing method. However, binder polymers simultaneously lower the conductivity of OTE. PriMet-P was composed of PEDOT:PSS and nanoparticle binders, which provide high durability without any loss of conductivity.

PriMet-P was screen-printed on a transparent glass substrate as an anode. ITO film anode was fabricated using a commercial ITO-coated glass substrate for comparison.

The structure of the OLED device employed for this work is shown in Fig. 1. Organic structures consisted of a 200 nm N,N'-bis-(1-naphthyl)-N,N'diphenyl-1,1-biphenyl-4,4'-diamine (NPB) hole transport layer (HTL), а 50 nm tris-(8hydroxyquinoline) aluminum (Alq₃) electron transport and emission layers (ETL & EML) deposited 1-2 Å/s in a thermal evaporator with a base pressure of low 10^{-6} torr. The cathode is an Al:Li layer with a thickness of 100 nm, which was formed by an evaporation process. After all depositions, the devices were hermetically sealed with adhesives and cover plates of glass. The active area for both of the OLED fabricated with conducting paste (hereafter referred to as CP-OLED) and the OLED with ITO (hereafter referred to as ITO-OLED) was 5 mm \times 5 mm.



Fig. 1. Structure of the OLED device.

Glass substrates were cleaned by sequentially sonicating in a de-ionized water, acetone, and isopropyl alcohol and UV cleaning at 254 nm prior to use. After that, the conducting paste was patterned by the screen-printing method. In case of ITO glass substrates, ITO thin film anodes were patterned using photolithography.

The screen mask used in the experiment was made of nylon fabric with 325 mesh count/inch, which means that a thread diameter is $28 \mu m$ and opening

size is about 28 μ m. After being printed, the polymer films were annealed at 120 °C for 30 min to remove excess H₂O and free solvent after 30 min of drying process employed to suppress any unexpected effect from the bubble formation.

The film thickness was measured using a stylus profilometer (Tencor Alpha-Step). The sheet resistance was obtained by four-point probe method normally used to characterize thin film. The work function of the film was determined by UPS (UV Photoelectron Spectroscopy). Optical spectra such as transmittance and absorbance were measured using a UV-visible spectrophotometer (UV-3101PC, Shimadzu Co.). The refractive index of the anode films were analyzed by Spectroscopic Ellipsometer (VUV-VASE[™] VU-302, J. A. Woollam Co., Inc).

The J-V-L characteristics of the OLED devices were measured using a Keithley 2400 sourcemeasurement unit. The luminance was measured using a PR-650 Specrascan photometer.

3. Results and discussion

The surface sheet resistance of the conducting polymeric layer was ~2000 Ω /sq when the thickness of the film is ~180 nm. The refractive index of this film is ~1.6 in the range of 400–700nm which is lower than that of ITO (1.8–2.1).^[6] Its optical properties of the conducting film, the transparency and absorbance properties are shown in Fig. 2.



Fig. 2. Optical transmittance and absorbance of conducting polymer.

As the film transmittance is 80–85% without any absorption of the light in the visible spectrum region, we can conclude that the requirement for the

transparent electrodes through which light is extracted was satisfied.

The work function of this conducting paste is about 4 eV which is a little bit lower than that of ITO (4.4–4.9 eV).^[7] In addition, it is a result different from the fact that the conducting polymer film based PEDOT:PSS is > 5 eV.^[8] The low work function of anode electrode is disadvantageous for hole injection and this leads to an increase of the driving voltage of the OLED. Although this value gives the demerit as an anode, it shows the potential application to bottom cathode.^[9]

Fig. 3 shows turn-on voltages of both devices. Despite a large difference in high sheet resistances between ~2000 Ω /sq for the conducting polymer and 9 Ω /sq for ITO, the measured turn-on voltage for the CP-OLED is 27 V which is not much higher than that for the ITO-OLED, 22 V. Higher voltage was needed for the CP-OLED than for the ITO-OLED in order to achieve the same luminance. This is attributed to the relatively poor conductivity and large energy band barrier induced from low work function between anode and organic material. A considerably high sheet resistance of the conducting polymer limits the current flow through the OLED device. The higher shifted driving voltage in both cases is due to their thick hole transport layer.



Fig. 3. Current density vs voltage of CP-OLED and ITO-OLED. (Inset: Photograph of CP-OLED with an emissive area of 5 mm \times 5 mm at 100 cd/m²)

Figs. 4a and b are plots of luminance and external electroluminescence quantum efficiency (η_{EL}) with respect to the current density. Although CP-OLED has drawbacks such as relatively poor electrical property

and low work function, extracted light at the same applied current per unit area is little more for CP-OLED (see Fig. 4a). This result is consistent with that the external electroluminescence quantum efficiency (η_{EL}) obtained in CP-OLED is up to ~2.0% while that of OLED using ITO anode is ~1.0%.



Fig. 4. (a) Luminance vs current density and (b) external electroluminescence quantum efficiency as a function of current density measured for CP-OLED and ITO-OLED.

This result could be due to the different refractive index of the conducting polymer. According to Snell's law, we can calculate a critical angle (θ_{12}). The ratio of the optical energy transmitted into from material 1 (anode) into material 2 (substrate) to the total emitted energy is given as $2B = \{1-[1-(n_2/n_1)^2]^{1/2}\}$.^[6] In case of ITO-OLED, $n_1 = 1.8$ (ITO), $n_2 = 1.46$ (glass),^[6] $\theta_{12} = 54^\circ$, 2B = 0.41; i.e., 41% of the optical energy is coupled into the glass substrate in the angle region below 54°. On the other hand, in case of CP-OLED,

 $n_1=1.6$ (CP), $n_2=1.46$ (glass), $\theta_{12}=66^\circ$, 2B=0.59 i.e., 59% of the optical energy is transmitted into the substrate in the angle region below 66°, which means that more light with less guided modes is extracted in the CP-OLED. This indicates that the conducting polymer film is more beneficial to outcoupling of light than ITO film.

4. Summary

We prepared conducting polymer films by a screen printing method and implemented it in small molecule OLED devices. The parameters of the conducting polymer films were determined and we found that the transmittance, the refractive index, and the work function are above 80%, 1.6, and ~4.0 eV, respectively. A higher external electroluminescence quantum efficiency was obtained in CP-OLED using these films and the performance of CP-OLED is comparable to ITO-OLED despite their relatively poor conductivity. These results indicate that the screenprintable transparent conducting polymer used in this study is a potential candidate for an anode of flexible OLED and is also expected to be widely used in the areas of touch panels and illumination sources such as back light units as well as flexible displays.

5. References

- J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holms, *Nature*, **347**, 539 (1990).
- N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, *Science*, 258, 1474 (1992).
- H. Aziz and Z. D. Popovic, *Chem. Mater.*, 16, 4522 (2004).
- P. Melpignano, A. Baron-Toaldo, V. Biondo, S. Priante, R. Zamboni, M. Murgia, S. Caria, L. Gregoratti, A. Barinov, and M. Kiskinova, *Appl. Phys. Lett.*, 86, 041105 (2005).
- 5. L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. R. Reynolds, *Adv. Mater.*, **12**, 481 (2000).
- G. Gu, D. Z. Garbuzov, P. E. Burrows, and S. Venkatesh, *Opt. Lett.*, **22**, 6, 396 (1997).
- C. C. Wu, C. Z. Wu, J. C. Sturm, and A. Kahn, *Appl. Phys. Lett.*, **70**, 1348 (1997).
- X. Crispin, F. L. E. Jakobsson, A. Crispin, P. C. M. Grim, P. Andersson, A. Volodin, C. Van Haesendonck, M. Vander Auweraer, W. R. Salaneck, and M. Berggren, *Chem. Mater.*, 18, 4354 (2006).

 T. Y. Chu, J. F. Chen, S. Y. Chen, C. J. Chen, and C. H. Chen, *Appl. Phys. Lett.*, **89**, 053503 (2006).