

High operating temperature stable OLEDs with reduced reflectivity cathodes

Zoran D. Popovic, Hany Aziz, George Vamvounis, Nan-Xing Hu and Tony Paine
Xerox Research Centre of Canada, Mississauga, Ontario L5K 2L1, Canada
 Phone : +1-905-823-7091 ext. 421 , E-mail : Zoran.Popovic@crt.xerox.com

Abstract

The understanding of the mechanism of device degradation has been accomplished recently, for devices using AlQ₃ electron transport and emitter molecule. In this presentation the experimental evidence for the degradation mechanism of AlQ₃ based devices will be reviewed, showing that the hypothesis of an unstable AlQ₃⁺ cation explains a large amount of experimental data. This hypothesis, however, explains not only the room temperature device degradation in time but also sheds light on temperature stability of OLEDs. Dependence of half-life of a series of devices with an emitter layer composed of a mixture of AlQ₃ and different hole transport molecules (mixed emitter layer) will be discussed when they are operated at elevated temperatures. These results can also be explained in the framework of an unstable AlQ₃⁺ species. An OLED structure containing a doped mixed emitter layer will be described, which shows extraordinary stability, half-life of 1200 hours at operating temperature of 70 C and initial luminance of 1650 cd/m². We will also discuss a novel Black Cathode™ OLED with reduced optical reflectivity, which is also stable at elevated temperatures. The new cathode utilizes a conductive light-absorbing layer made of a mixture of metals and organic materials.

1. Introduction

We will first review the mechanism proposed for the long-term degradation of Organic Light Emitting Diodes (OLEDs) based on tris(8-hydroxyquinoline) aluminum (AlQ₃). [1] The injection of holes into AlQ₃ was found to be the main factor responsible for device degradation. Using photoluminescence spectroscopy, it was discovered that photoluminescence quantum efficiency of AlQ₃ layers, where predominantly holes were transported, decreased upon prolonged current flow. The discovery that device degradation is driven by the instability of AlQ₃ cations naturally explains why different OLED stabilizing strategies, such as, doping the hole transport layer (HTL), [2] introducing a thin buffer layer of copper phthalocyanine (CuPc) at

the hole-injecting contact, [3] or using a mixed emitting layer of hole and electron transporting molecules, [4] are effective.

Devices with mixed emitter layers, based on the hole transport molecule (N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine (NPB) and electron transport and emitter molecule AlQ₃ show remarkable high temperature stability. [5] In order to clarify why this is the case we investigated a number of devices with different hole transport materials (HTMs) in the mixed emitter layer. [6] The results show that the dependence of device stability on temperature and HTM used can also be understood in the framework on unstable AlQ₃ cations, whose degradation products lead to fluorescence quenching and non-radiative electron-hole recombination. [7,8]

In order to increase contrast of OLED devices and eliminate mirror-like finish of metallic cathodes polarizing filters are usually used. These filters contain polymeric materials, which may not be able to withstand elevated temperatures and they also add significant cost to device manufacturing. We developed novel cathodes, based on mixed organic metal layers (MOMLs), which are intrinsically dark and therefore substantially reduce OLED device reflectivity. In addition, these new Black Cathode™ OLEDs operate without any problems at elevated device temperatures.

2. Experimental

The mixed layer device structure is shown schematically in Figure 1. In addition to NPB we also used two other hole transport molecules (HTMs) in the mixed layer, N,N'-diphenyl-N,N'-bis(3-methylphenyl)(1,1'-biphenyl)-4,4'-diamine (TPD), and 1,1'-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC). The OLEDs studied had the following structure: indium-tin-oxide (ITO) anode/ NPB hole transport layer (~200Å thick) / HTM(~50%)+AlQ₃(~50%)+(optional dopant, ~0.4%) mixed emitting layer (~800Å thick) / AlQ₃ electron transport layer (~200Å thick)/ Mg:Ag cathode. The devices were fabricated by the deposition of the organic materials and the cathode metals using

2.1 / Plenary

thermal evaporation at vacuum base pressure of about 5×10^{-6} torr on UV ozone cleaned ITO-coated glass substrates. The mixed emitting layer was formed by co-deposition of HTM, AlQ₃ and optional dopant at a rate of $\sim 4 \text{ \AA/s}$, 4 \AA/s , and 0.03 \AA/s , respectively. Mg:Ag cathode ($\sim 1200 \text{ \AA}$ thick) was formed by co-deposition of Mg and Ag at a rate of 4 \AA/s and 0.4 \AA/s , respectively. Deposition rates were individually controlled using quartz crystal monitors.

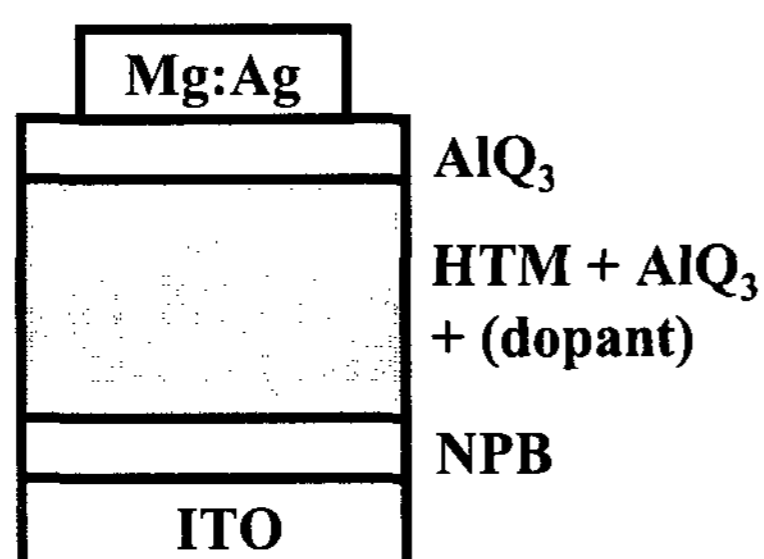


Figure 1. Schematic diagram of OLED structures described in this work. Dopant in the mixed emitter layer is optional.

The structure of Black Cathode™ LED is as follows. On top of organic layers an optional thin injection layer (Ca or other) is deposited first followed by a co-evaporated mixture of metals, one of which in these particular examples is silver, and AlQ₃. The whole cathode is topped by Ag or Mg:Ag.

OLED operational stability measurements were carried out using 1 KHz, 50% duty cycle AC driving conditions at an average constant current density of 31.25 mA/cm^2 in the forward bias direction and -15 V reverse bias. AC as opposed to DC driving was used as it is known to reduce the possibility of device shorting.[3] For testing at elevated temperatures, flexible electric heating tape was wound around the OLED test box, and controlled using Omega CN9000 temperature controller. The OLED temperature was monitored using a thermocouple in contact with the OLED substrate. The OLEDs were kept in a dry nitrogen atmosphere throughout the experiment.

3. Results and discussion

Figure 2 shows results from device operational stability tests for mixed emitter layer OLED structures doped with quinacridone (DMQ). Experimental conditions are given in the figure caption. Curves A and B were measured on devices having a structure shown in Figure 1. We were also successful to

achieve stable OLED operation for temperatures exceeding 70°C by introducing further device modifications, without changing the mixed emitting layer. Curve C on Figure 2 shows results from the modified device when operated at 100°C . Assuming coulombic degradation [3] for operation at L_0 of 100 cd/m^2 , $t_{1/2}$ is projected to be 78,500 hours, 18,700 hours and 8,600 hours, for operation at 22°C , 70°C , and 100°C , respectively. Compared to results reported for single-layer "organic alloy" OLEDs when operated at 65°C ($t_{1/2} \sim 320$ hours for L_0 of 1486 cd/m^2 , which can be projected to $t_{1/2} \sim 4800$ hours for L_0 of 100 cd/m^2),[9] $t_{1/2}$ of our devices is about 4 times longer at a somewhat higher temperature (70°C).

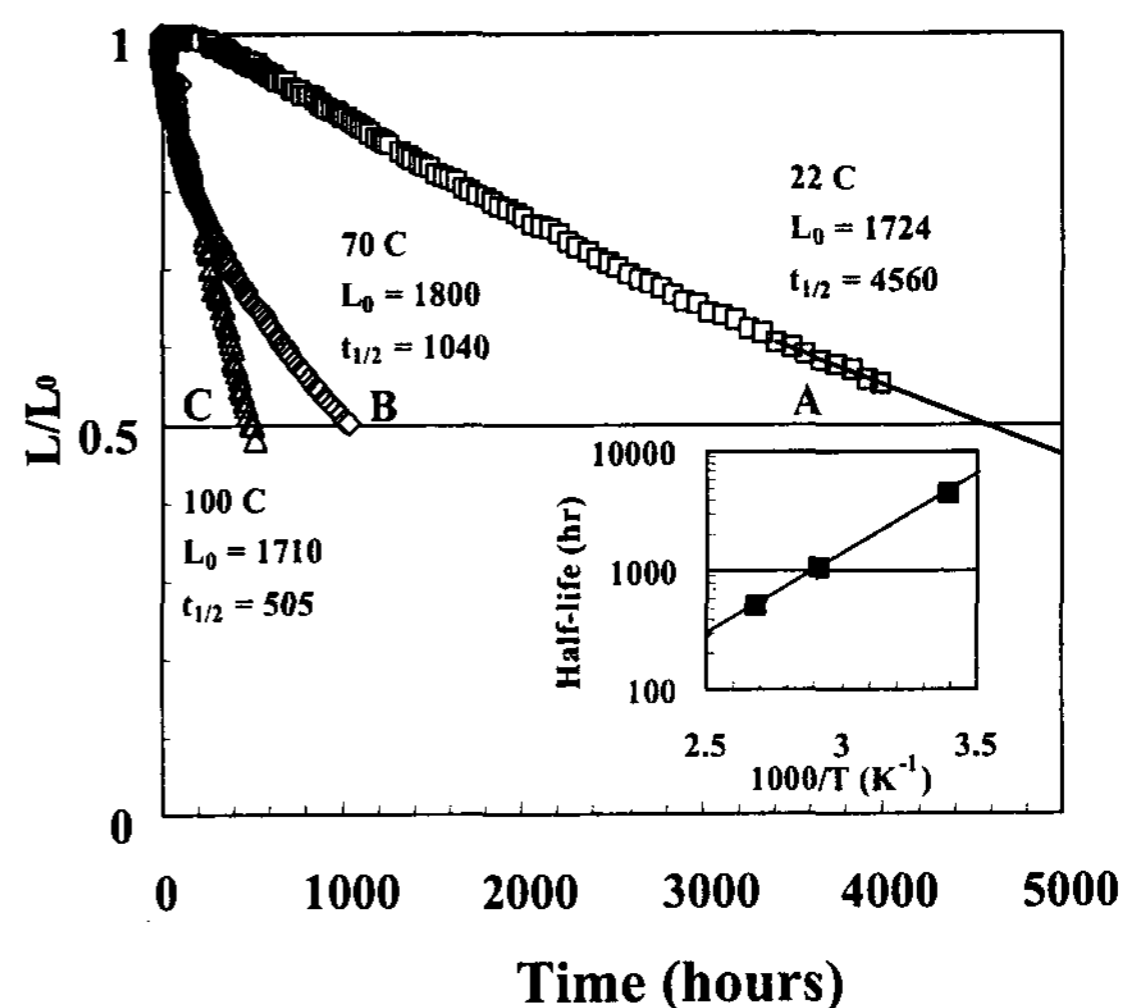


Figure 2. Normalized luminance versus time for NPB containing mixed layer OLED doped with DMQ operated at different temperatures, using AC driving at an average constant current density of 31.25 mA/cm^2 . L_0 values are in cd/m^2 , and the half-life values, $t_{1/2}$, are in hours. The insert shows OLED half-life versus reciprocal temperature in semi-logarithmic plot. Best straight line fit to the data gives activation energy of 0.27 eV.

When NPB in the mixed layer is substituted with other hole transport molecules, TPD and TAPC, the device half-life is reduced as well as the temperature dependence and the activation energy, as shown in Figure 3. These results can be understood in the framework of the unstable AlQ₃ cations whose degradation products lead to device performance degradation. In the mixed emitter layer holes are moving by hopping between NPB molecules and

electrons by hopping between AlQ₃ molecules. The excited state is generated by direct recombination of NPB⁺ and AlQ₃⁻ to generate the excited state AlQ₃*. The only AlQ₃⁺ species are generated by thermal excitation from NPB⁺. The activation energy therefore will reflect the difference of HOMO energy levels of the HTM and AlQ₃, with higher activation energy leading to longer device life and stronger temperature dependence.[5,6]

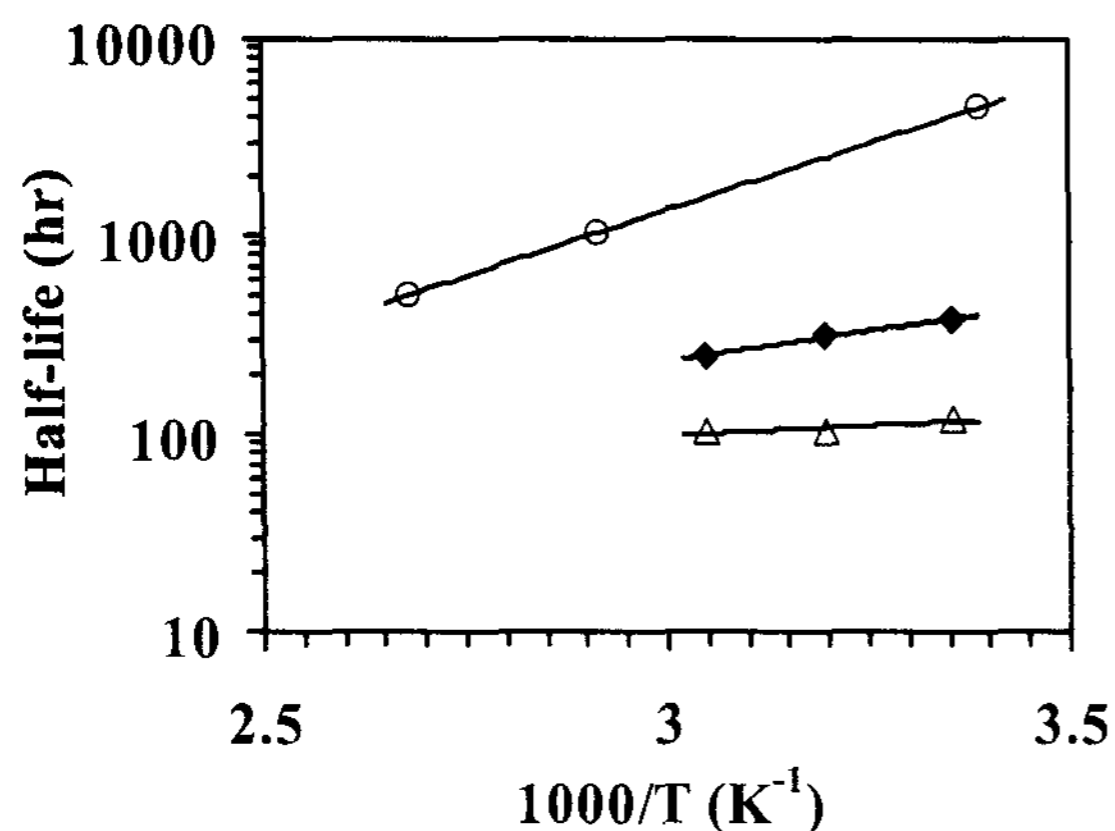


Figure 3. OLED half-life versus reciprocal temperature in semi-logarithmic plot. Best straight line fit to the data gives activation energy of 0.27, 0.12 and 0.04eV for devices containing NPB doped with DMQ (○), TPD (◆) and TAPC (△), respectively.

The reflection spectra of OLED devices with and without the Black CathodeTM are given in Figure 4. The composition of cathodes for different devices is given in Table 1. We introduce sun/eye integrated reflection (SEIR) as a figure of merit for the OLED reflectivity properties. This quantity is simply average reflectivity under sunlight illumination conditions, weighted with the eye spectral response. Table 1 gives SEIR for different cathode configurations, with 4% glass substrate front surface reflection subtracted. The introduction of a Black CathodeTM leads to a substantial reflectivity reduction. As expected the Black CathodeTM leads also to brightness reduction by about a factor of two, except in case of cell B, which has poor electron injection and reduced efficiency.

Device degradation at 90°C for the reference device and device A are given in Figure 5. The reduction of light output and increase of operating voltage in time are essentially identical for both devices. We can therefore conclude that our low reflectivity cathodes

have excellent thermal properties and do not accelerate device degradation at elevated temperatures.

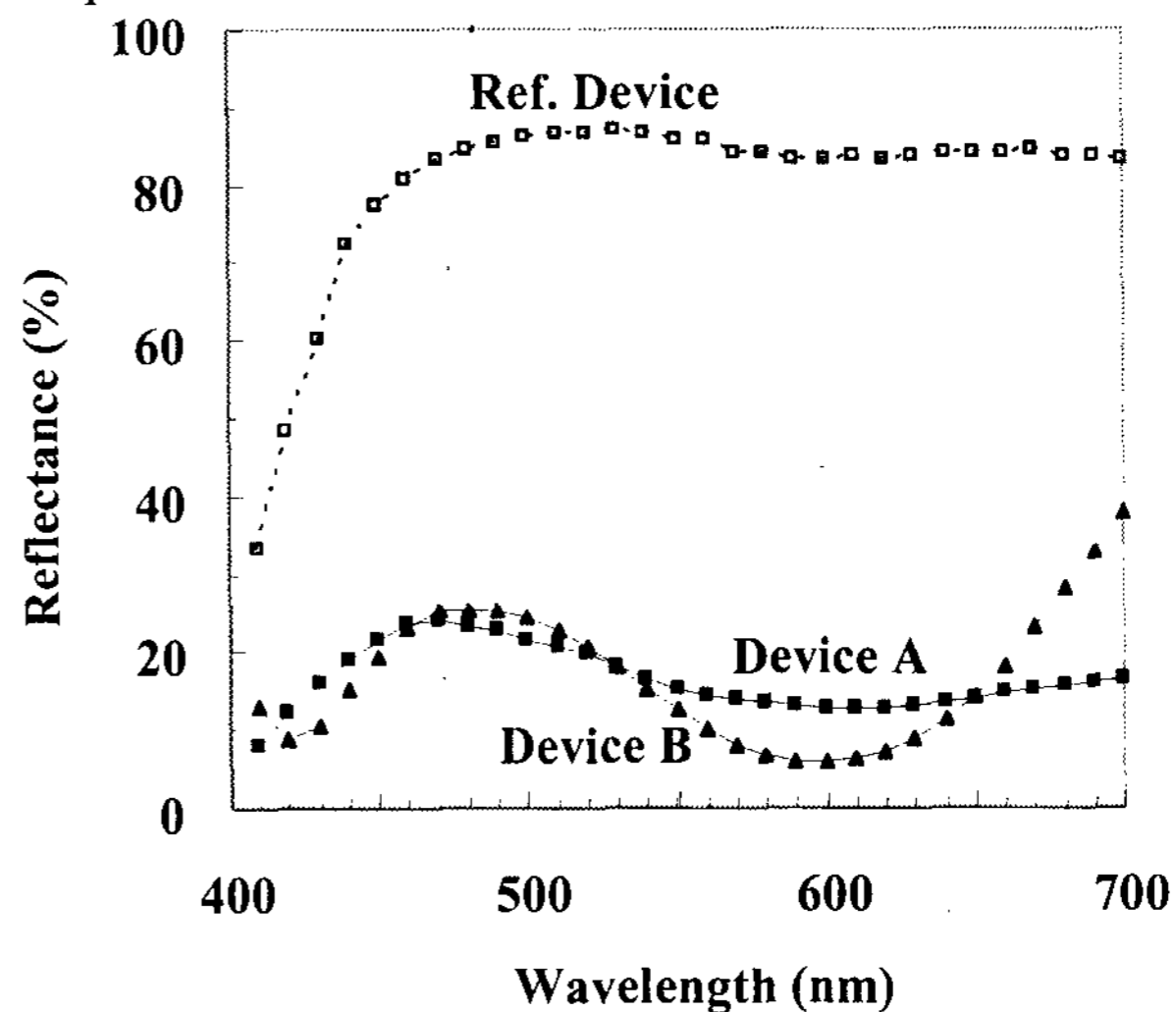


Figure 4. Comparison of reflectance of the reference device with devices A and B described in Table 1.

Device	MOML Composition (vol. %)	SEIR (%)	EL (cd/m ²)
A	AlQ ₃ :Mg:Ag (47.5 : 47.5 : 5)	11.9	968
B	AlQ ₃ :Ag (80 : 20)	9.1	576
C	AlQ ₃ :Ag (80 : 20)	9.2	959
Ref	-	80.9	1778

Table 1. Device SEIR and electroluminescence (EL) properties at 25 mA/cm² of OLEDs with different cathode compositions. All MOML thicknesses are 150 nm. A – MOML is capped with 100 nm 9:1 Mg:Ag alloy. B – capping is 100 nm of pure Ag. C – same as B, but with 2 nm thick Ca layer between the MOML and AlQ₃. Reference device has a standard Mg:Ag cathode.

4. Conclusion

We described mixed emitter layer devices, which show excellent stability when operated at elevated temperatures. This characteristic of mixed emitter layer devices is strongly dependent on the hole transport molecule used. The results can be understood within the framework of unstable AlQ₃ cationic species. Extraordinary stability of devices with NPB in the mixed layer is a result of proper HOMO energy level difference between NPB and AlQ₃. It is large enough to substantially reduce

2.1 / Plenary

formation of cationic AlQ_3 , but still energetically allows efficient direct recombination of AlQ_3^- and NPB^+ species to form excited state AlQ_3^* .

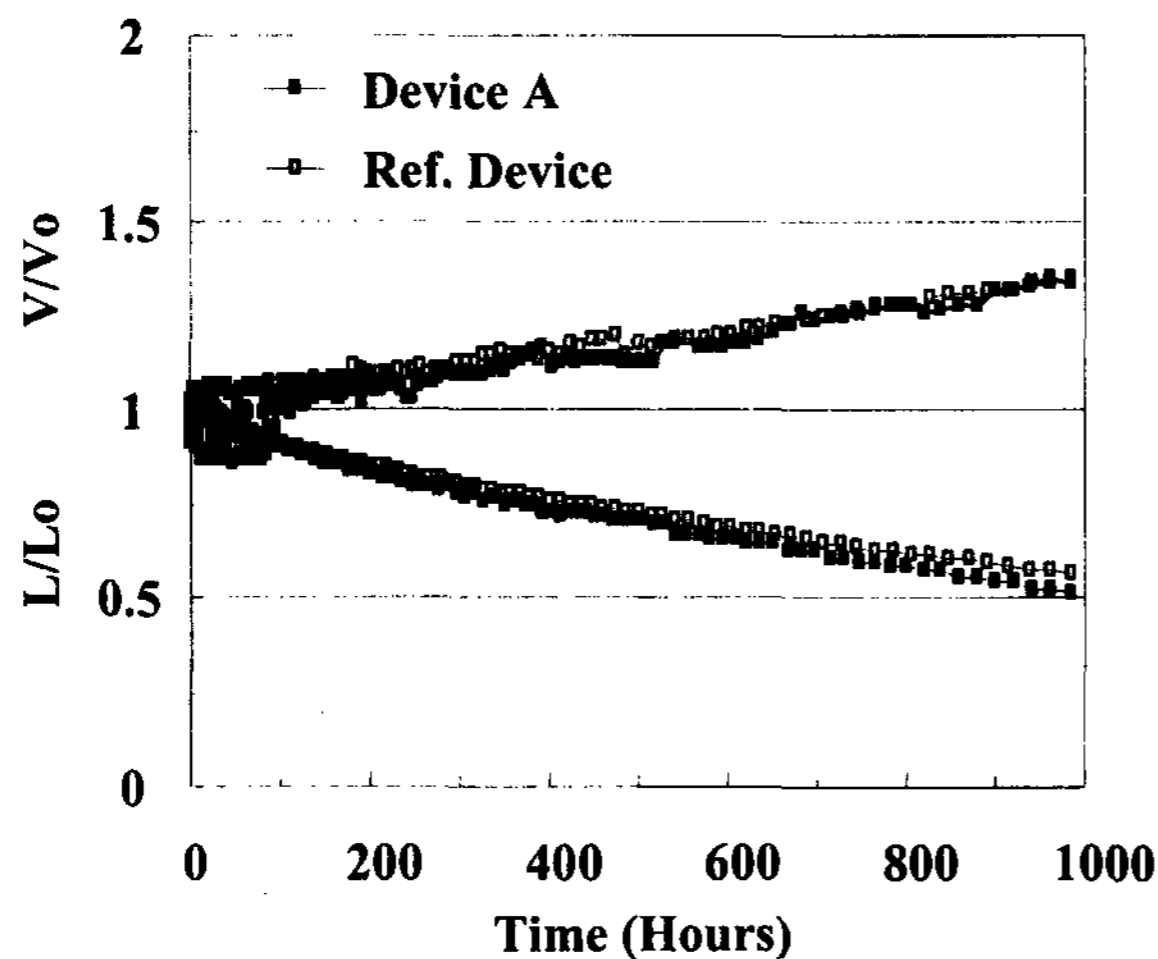


Figure 5. Normalized luminance (L/L_0) and normalized driving voltage (V/V_0) versus time of operation at 90°C of device A and the reference device at an average constant current density of 31.25 mA/cm^2 . L_0 is 1210 cd/m^2 and 2220 cd/m^2 , and V_0 is 8.7 V and 8.8 V for device A and the reference device, respectively.

Introduction of cathodes based on mixed organic metal layers (MOML) lead to substantial reduction of OLED device reflectivity without any impact on device temperature stability. MOMLs are produced by the same vacuum evaporation method used for

making OLED organic layers and are therefore expected to be easily scaled to a manufacturing process.

5. References

- [1] H. Aziz, Z. D. Popovic, N. X. Hu, A. M. Hor and G. Xu, *Science* **283**, 1900-1902 (1999).
- [2] Y. Hamada, T. Sano, K. Shibata and K. Kuroki, *Jpn. J. Appl. Phys.* **34**, pp.L824-L826 (1995).
- [3] S.A. Van Slyke, C.H. Chen and C.W. Tang, *Appl. Phys. Lett.* **69**, pp. 2160-2162 (1996).
- [4] Z. D. Popovic, H. Aziz, C. P. Tripp, N. X. Hu, A. M. Hor and G. Xu., *Proceedings of the SPIE, Volume 3476, Organic Light-Emitting Materials and Devices II*, San Diego, CA, July 19-24, 1998, pp. 68-73.
- [5] H. Aziz, Z.D. Popovic, and N-X Hu, *Appl. Phys. Lett.* **81**, 370 (2002).
- [6] Z. D. Popovic, G. Vamvounis, H. Aziz, and N.Hu, *Proceedings of SPIE Conference on Organic Light Emitting Materials and Devices VI*, Seattle WA, July 8-10, 2002, Vol. 4800, pp 87-92 (2003).
- [7] Z. D. Popovic, H. Aziz, A. Ioannidis, N. Hu, P. N. M. dos Anjos, *Synth. Met.* **123**, 179-181 (2001).
- [8] Z. D. Popovic, H. Aziz, N. Hu, A. Ioannidis, P. N. M. dos Anjos, *J. Appl. Phys* **89**, 4673-4675 (2001).
- [9] V. Choong, J. Shen, J. Curless, S. Shi, J. Yang and F. So, *J. Phys. D., Appl. Phys.* **33**, 760 (2000).