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by Merric Srour, Richard Fu, Steven Blomquist, Jianmin Shi, Eric Forsythe, and David Morton

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14. ABSTRACT

Low-work function metals, such as Lithium, Sodium, Potassium and Cesium, doped with suitable organic host materials as an electron injection and electron transport layer have been used in Organic Light-Emitting Diode (OLED) devices to lower device driving voltage. However, the practical process was greatly limited by lack of suitable organic host materials and difficult for using these active metals during device fabrication processes due to their extreme reactivity. In our designed OLED devices, we used alkaloid salt, cesium carbonate (Cs_2CO_3) which is very stable under environmental atmosphere, instead of extremely active low-work function metal, doped with widely used electron transport material 1, 3, 5-Tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBI) as an electron injection and transport layer. Our results demonstrated that OLED devices produce significant low voltage, and deep blue emission by using Cs_2CO_3 doped TPBI as an electron injection and transport layer; Alkaloid salt Cesium Carbonate can be used as an alternative for low-work function metal guest material in OLED devices to achieve low voltage, efficient electroluminescent (EL) devices instead of using hazard, highly reactive metals; Alkaloid salt Cesium Carbonate can be used in wide concentration range without significant affect driving voltage and EL efficiency of doped EL devices, which will gain significant yield for the OLED fabrication process.

15. SUBJECT TERMS

Organic Light-Emitting Diode, OLED, organic film, Cesium Carbonate, Cs_2CO_3

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1. Introduction

Alkaloid salt, cesium carbonate (Cs_2CO_3) is an organic chemical mostly used in fuel cells, solar panels, and medicine. However, there are many other applications for this versatile chemical. One application, for cesium carbonate is used to control the electron-injection capabilities in the electron transport layer of blue Organic Light-Emitting Diodes (OLEDs) (*1*). One can obtain the brightest and most efficient OLED, when the number of electrons injected at the cathode is equal to the number of holes injected in the anode (*2*). One reason for using cesium carbonate is the electron-injection ability can be directly controlled by the thickness of Cs_2CO_3 (*1*). One property found of alkaloid salt, cesium carbonate is it effectively facilitates electron injection from many different metal electrodes; this shows how cesium carbonate can be used to help increase the electron count in OLEDs. By increasing the electrons deposited, there is a higher possibility that an electron and a hole will recombine, and emit light. The more electrons and holes recombine, the more light there will be (*3*).

Cesium carbonate has been used in OLEDs because of its flexibility. Cs_2CO_3 can be applied by spin coating, or thermal evaporation. It is also highly soluble in liquids such as water or alcohol (*1*). Because it is so flexible, it has been used to increase the flux of electrons, in the electron transport layer. By using it in the electron transport layer, it eliminates the need to have a separate lithium fluoride (LiF) electron-injection layer (*4*). It has also been used in an interconnecting unit between an OLED stack (*5*), a replacement for low-work function metals (*6*), and as a connecting unit in tandem OLED cells (*1*).

Another reason cesium carbonate was chosen to be used as the control for the electron-injection capabilities is, when used it has a lower driving voltage, and therefore exhibits higher power efficiency (*1*).

One application that has not been tested directly, with regard to cesium carbonate and OLEDs, is the effects of Cs_2CO_3 when doped with 1, 3, 5-Tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBI). TPBI is an organic chemical used for the electron transport layer in blue OLEDs and is used to produce blue OLED’s.

2. Experiment

2.1 Cesium Carbonate Doping

An OLED was built on indium-tin oxide (ITO) patterned glass substrates that were cleaned using a 14-step process. The process included sonicating the glass in acetone, isopropyl alcohol, and soap water. After this, they were put through an O2 plasma treatment. The organic chemicals were then deposited on the glass substrates using a vacuum thermal evaporation system connected to a second glove box, which was used for the capping of the OLEDs.

Figure 1 is an OLED device structure. The ITO and glass perform as the anode. N,N'-Bis- (1-naphthalenyl)-N,N'-bis-phenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) was used for the hole injection layer, while TPBI was used as the electron transport layer. TPBI doped with different quantities of Cs_2CO_3 were used for the electron-injection layer. The magnesium doped with silver (10 parts magnesium [Mg] to 1 part silver [Ag]) acted as the cathode.

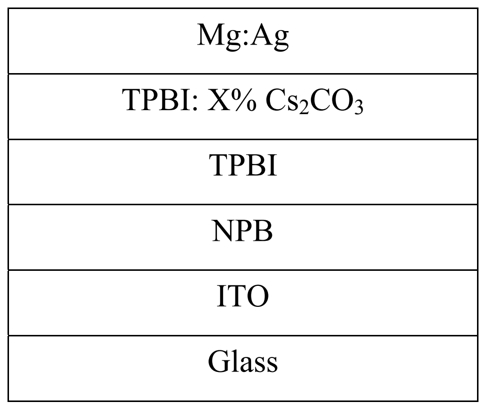

Figure 1. OLED device structure.

These specific wide arrays of thickness were chosen in order to test if there could possibly be a noticeable trend. The first sample had no TPBI and Cs2CO3 in order to make sure there was a difference when adding the co-doped layer of TPBI and Cs_2CO_3 (table 1).

Table 1. Thickness of each layer for six different runs using the same configuration of organic materials.

Sample	NPB (Å)	TPBI (Å)	TPBI + X% Cs_2CO_3 (Co-Doped, Å)
1	750	600	0% Cs_2CO_3 – 0
2	750	300	3.5% Cs_2CO_3 – 300
3	750	300	5.7% Cs_2CO_3 – 300
4	750	300	10.5% Cs_2CO_3 – 300
5	750	300	12.2% Cs_2CO_3 – 300
6	750	300	16.3% Cs_2CO_3 – 300

2.2 Stacking OLEDs

A second batch of OLEDs were tested to see if stacking double TPBI/ TPBI:X% Cs_2CO_3 layers of OLEDs would increase the brightness and voltage of the blue OLED (figure 2).

Mg:Ag
TPBI:X% Cs_2CO_3
TPBI
TPBI:X% Cs_2CO_3
TPBI
NPB
ITO
Glass

Figure 2. Stacked OLED structure.

Using this configuration we used the following quantities of the Organic Material to produce the stacked OLEDs (table 2).

Table 2. Thickness for each layer of the stacked OLEDs (bold run is standard).

Sample	**NPB (Å)**	**TPBI (Å)**	**TPBI + 7 % Cs_2CO_3 (Co Doped, Å)**	**TPBI (Å)**	**TPBI + X% Cs_2CO_3 (Co Doped, Å)**
1	750	300	300	300	300
2	750	300	300	0	0

3. Results and Discussion

3.1 Results of Cesium Carbonate Doping

A study was performed on OLEDs using NPB/TPBI/TPBI + X% Cs_2CO_3 / Mg:Ag, to test if a trend occurred when TPBI was doped with different quantities of cesium carbonate (table 3). Figures 3–5 showed device emission spectra curve, current-brightness (I-B) curve and current-voltage (I-V) curve, respectively.

Table 3. Results for the tested OLEDs (all numbers were taken from 20 mA/cm²).

Samples	Voltage (V)	Brightness (B) (cd/m^2)	CIE x	CIE y
NPB 750 Å/TPBI 600Å	5.27	110	0.16	0.09
NPB 750 Å/TPBI 300 Å/ TPBI + 3.5% Cs_2CO_3 300 Å	4.79	148	0.16	0.11
NPB 750 Å/TPBI 300 Å/ TPBI + 5.7% Cs_2CO_3 300 Å	4.77	143	0.16	0.10
NPB 750 Å/TPBI 300 Å/ TPBI + 10.5% Cs_2CO_3 300Å	4.67	143	0.16	0.11
NPB 750 Å/TPBI 300 Å/ TPBI + 12.2% Cs_2CO_3 300 Å	4.50	128	0.16	0.11
NPB 750 Å/TPBI 300 Å/ TPBI + 16.3% Cs_2CO_3 300 Å	4.44	156	0.16	0.11

The following was observed as a result of the tests.

- When using Cs_2CO_3 doping, the voltage is lowered.
- Cs_2CO_3 can be used in a wide range without significantly changing the voltage.
- Doping Cs_2CO_3 does not affect the color of the OLED.

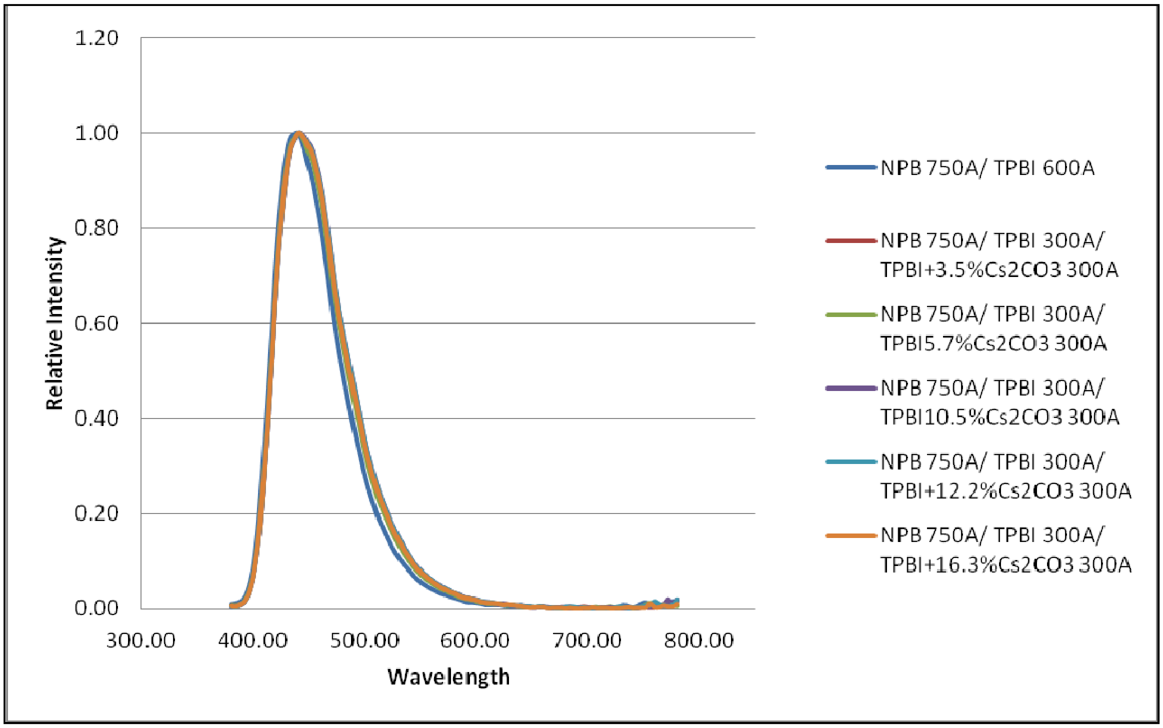

Figure 3. Emission spectra curve.

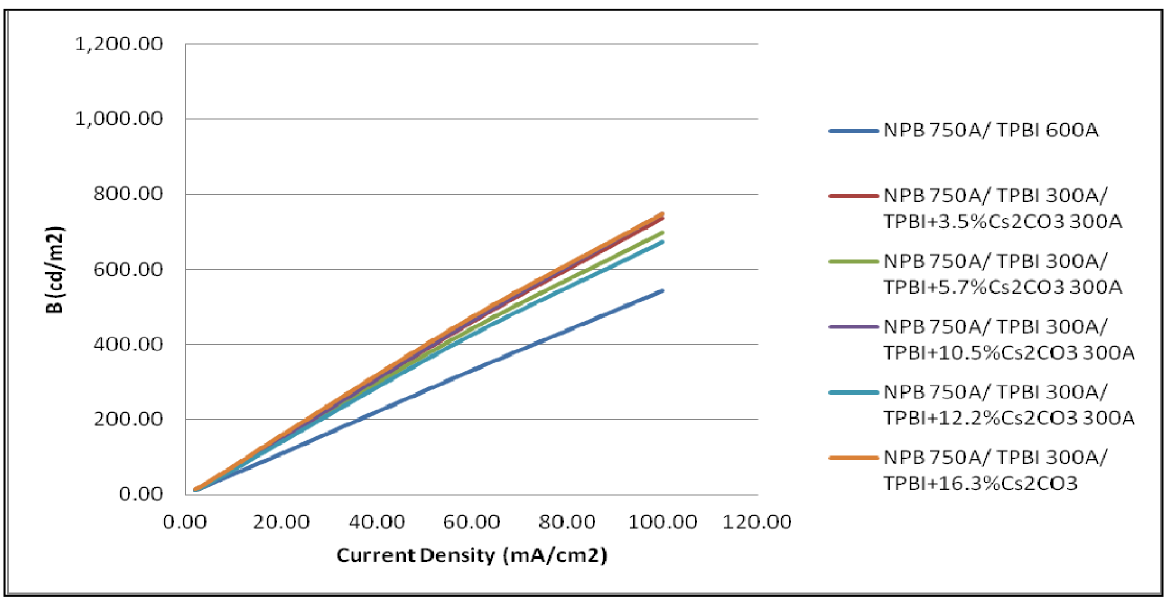

Figure 4. Current (I)-B curve.

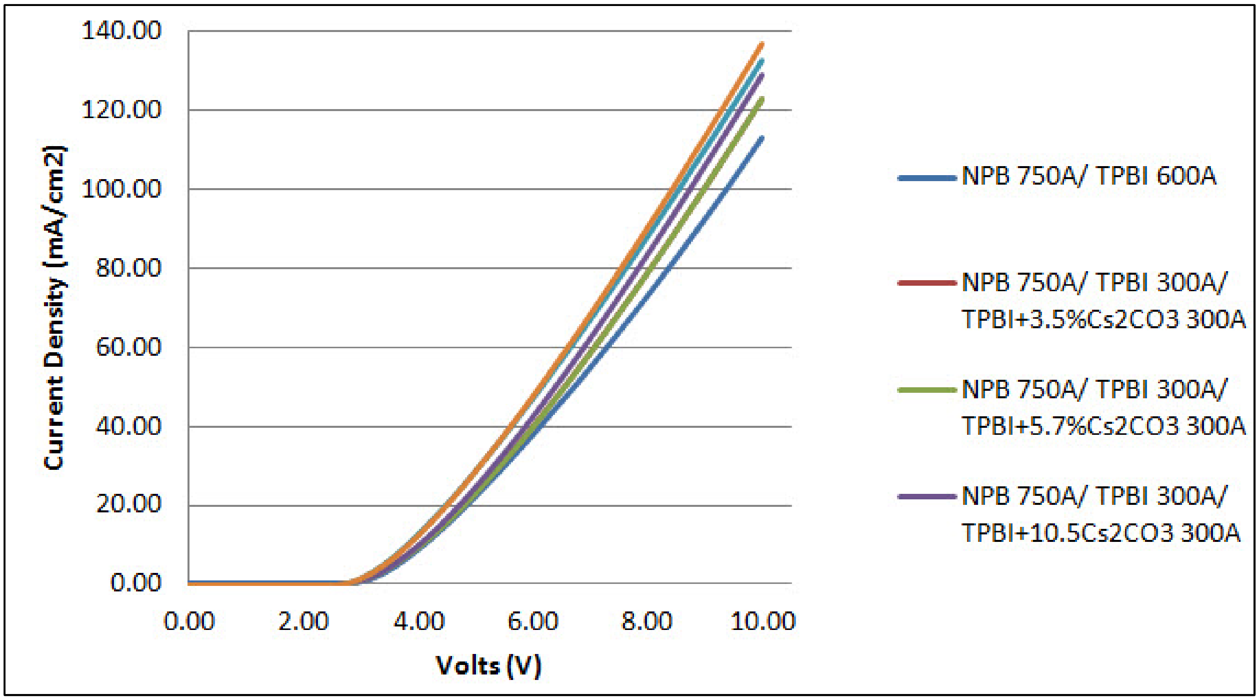

Figure 5. I-V curve.

3.2 Results of Stacking OLEDs

This study was preformed to see what the effects would be when stacking a second OLED on top of the first one (table 4).

Table 4. Results for the tested stacked OLEDs (all numbers were taken from 20 mA/cm²).

Samples	Voltage (V)	B (cd/m^2)	CIE x	CIE y
NPB 750 Å / TPBI 300 Å / TPBI+7.4% Cs_2CO_3 300 Å / TPBI 300 Å / TPBI+6.4% Cs_2CO_3 300 Å	7.04	291	0.16	0.15
NPB 750 Å / TPBI 300 Å / TPBI+5.7% Cs_2CO_3 300 Å	4.77	143	0.16	0.10

The reason a second layer of NPB was not added to the stacked OLED, was because it would block the electrons from combining with the first layer of NPB.

The results in figures 6–8 showed with regard to our stacked OLED, that the voltage from the regular OLED to the stacked OLED increased by approximately 2.27 V. However, with the increase of voltage on the stacked OLED came the increase of the brightness, which doubled from the original OLED. Another characteristic of the stacked OLED that was noticed is, that even with the increase of the voltage and brightness, the color remained around the same as the regular OLED.

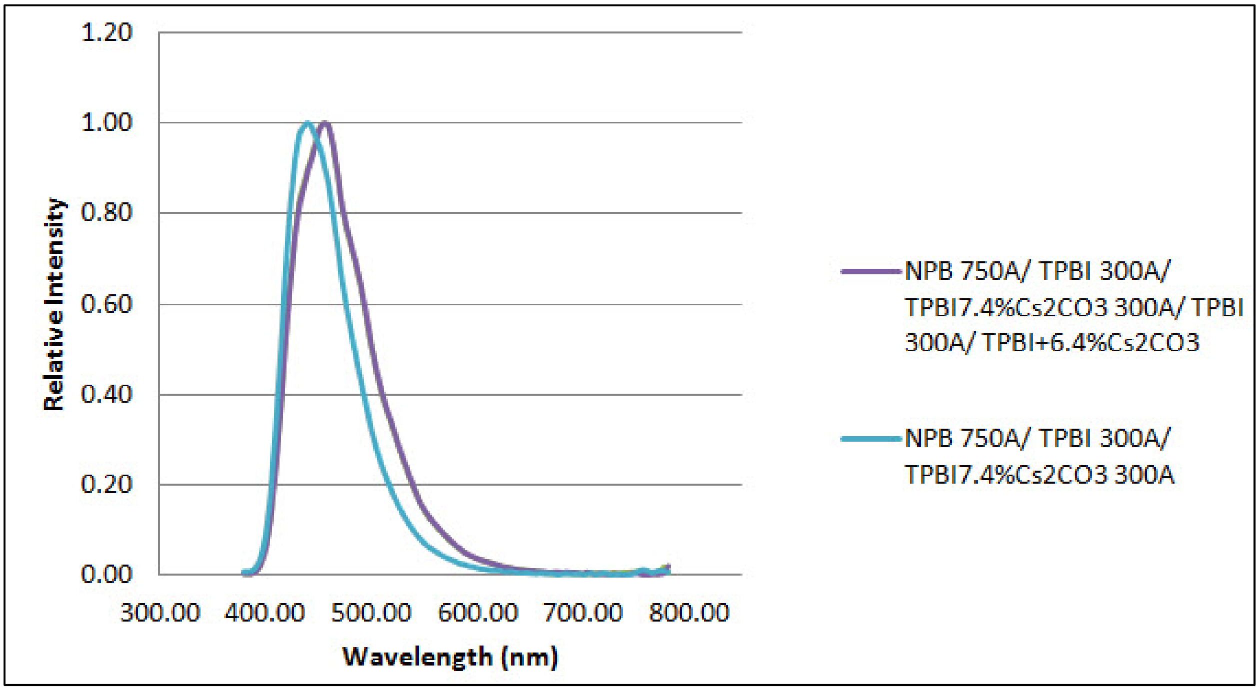

Figure 6. Emission spectra curve for the stacked OLED.

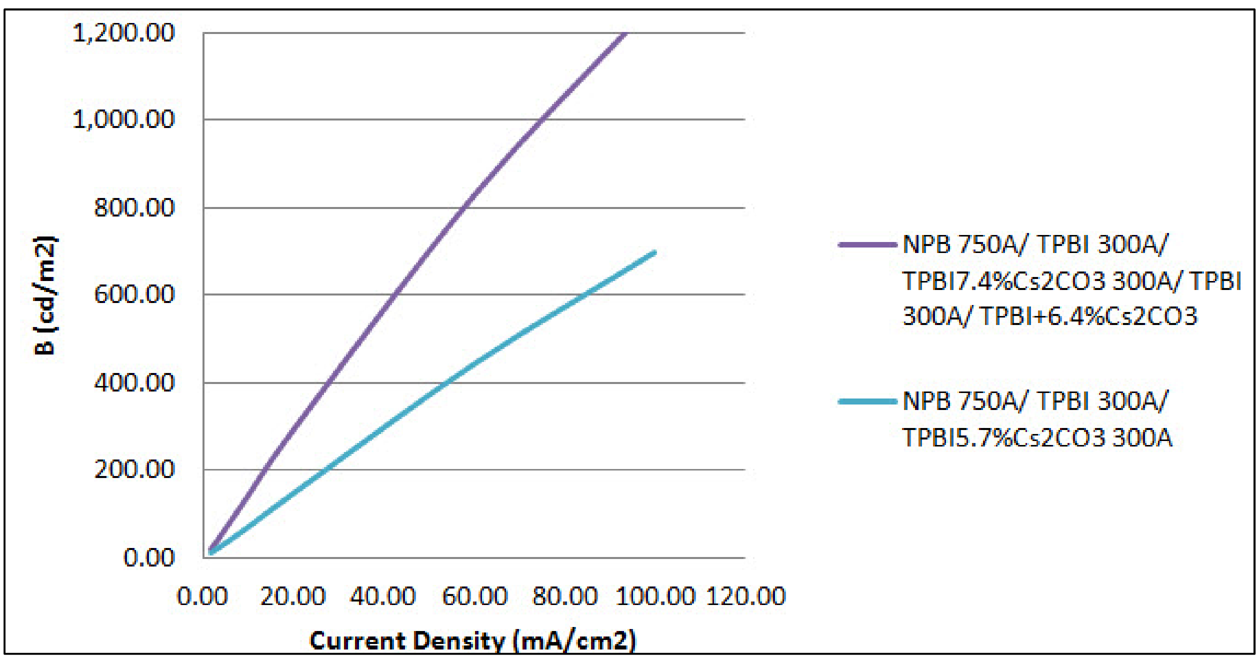

Figure 7. I-B curve for the stacked OLED.

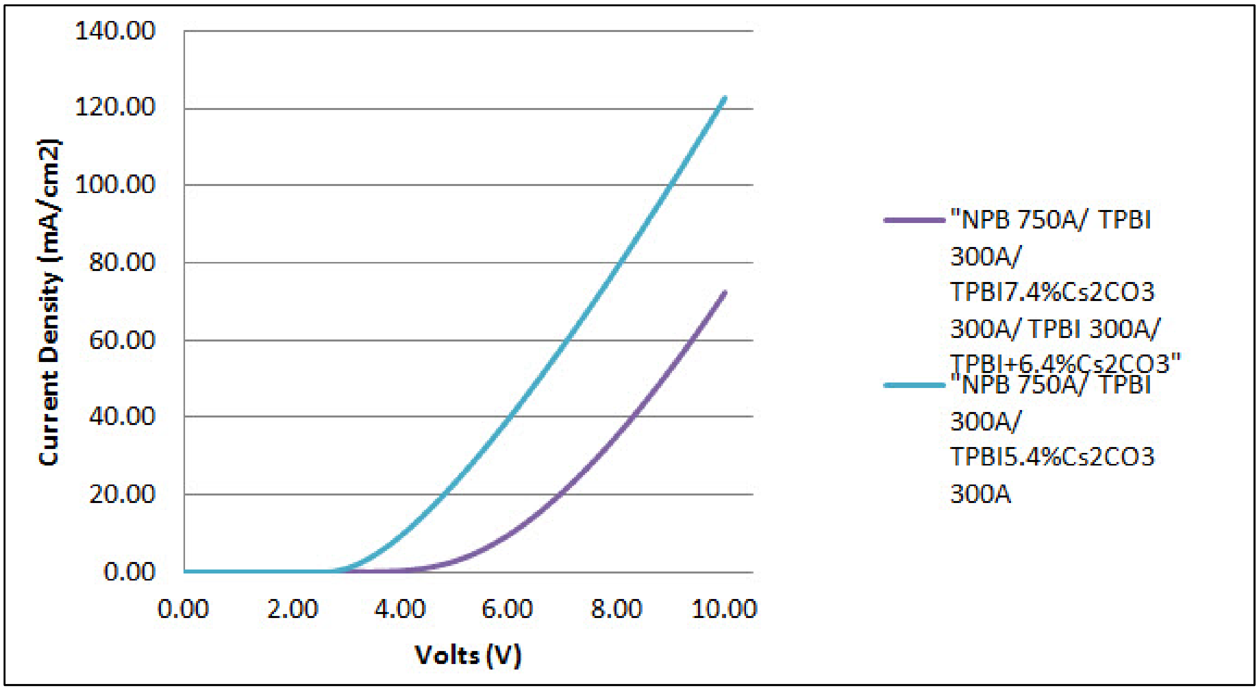

Figure 8. I-V Curve for the stacked OLED.

4. Conclusions

These results will help mainly for manufacturing purposes. The reason is because when different amounts of Cs_2CO_3 are added to a single OLED the voltage and brightness do not dramatically change. Therefore, since there is a large margin of error, it is easier for manufacturers to produce OLEDs.

By a stacked OLED, the results show that when a second layer of TPBI, and TPBI doped with Cs_2CO_3 is added, the brightness and voltage are increased without dramatically affecting the color of the OLED.

5. References

1. Huang, J.; Xu, Z.; Yang, Y. Low-Work-Function Surface Formed by Solution-Processed and Thermally Deposited Nanoscale Layers of Cesium Carbonate. *Adv. Funct. Mater.* **2007**, *17*, 1966–1973.
2. Nguyen, T.; Destruel, P. Electroluminescent Devices Based on Organic Materials and Conjugated Polymers. *Handbook of Luminescence, Display Materials, and Devices,* 2003, 56–68.
3. Wu, C.-I.; Lin, C.-T.; Chen, Y.-H.; Chen, M.-H.; Lu, Y.-J. Electronic Structures and Electron-Injection Mechanisms of Cesium Carbonate-Incorporated Cathode Structures for Organic Light-Emitting Devices. *Applied Physics Letter,* **2006**, 2–4.
4. Swensen, J. S.; Rainbolt, J. E.; Wang, L.; Koech, P. K.; Polikarpov, E.; Padmaperuma, A. B.; Gaspar, D. J. Blue Phosphorescent Organic Light-Emitting Devices Utilizing Cesium–Carbonate-Doped 2,4,6-tris(2_,4_-difluoro-[1,1_- biphenyl]-4-yl)-1,3,5-triazine. *Journal of Photonics for Energy,* **2011**, 011008-9 Vol. 1.
5. Hamwi, S.; Meyer, J.; Kroger, M.; Winkler, T.; Witte, M.; Riedle, T.; Kahn, A.; Kowalsky, W. The Role of Transition Metal Oxides in Charge-Generation Layers for Stacked Organic Light-Emitting Diodes. *Adv. Funct. Mater*, **2010**, *20*, 1762–1766.
6. Chen, M.-H.; Lu, Y.-J.; Wu, C.-C.; Wu, C.-I. Effectiveness of tris–(8-Hydroxyquinoline)–Aluminum Doped with Cesium-Derivatives in Organic Light-Emitting Diodes; *Thin Solid Films,* 2010, *518*, 3942–3944.

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List of Symbols, Abbreviations, and Acronyms

Ag	silver
B	brightness, cd/m^2
Cs_2CO_3	cesium carbonate
EL	electroluminescent
I	current
ITO	indium−tin oxide
LiF	lithium fluoride
Mg	magnesium
NPB	N,N'-Bis- (1-naphthalenyl)-N,N'-bis-phenyl-(1,1'-biphenyl)-4,4'-diamine
OLED	organic light-emitting diode
TPBI	1, 3, 5-Tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl
V	voltage

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