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Letter

Hydrofluoroethers as heat-transfer fluids for OLEDs: Operational range, stability, and efficiency improvement

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ABSTRACT

In this work we introduce a simple yet very efficient method of heat dissipation by immersing OLED device into hydrofluoroether (HFE) fluids. It is shown that due to highly fluorous nature of this class of fluids, HFE do not damage organic semiconductors which are comprised in the OLED stack and therefore can be used as encapsulation media. HFE also have high thermal conductivity, low viscosity and can efficiently dissipate the heat by means of natural convection with laminar flow. By employing HFE we were able to significantly improve the OLED operating dynamic range. Lifetimes of OLEDs operating in HFE at high currents can be improved by about a factor of 8. Furthermore, HFE fluid significantly improves the light outcoupling by a factor of 70% due to higher than air refractive index ($n = 1.3$).

1. Introduction

One of the main reasons for the degradation and small operational range of organic light-emitting diodes (OLEDs) is Joule self heating [1–8]. Even though state-of-the-art OLEDs achieve impressive power efficiencies [9,10], more than 80% of the energy applied to OLED devices still goes into heat. In typical OLED devices with glass encapsulation (e.g. air/ITO/organic stack/thin metal (~100 nm)/nitrogen), no efficient heat sink is provided. This is especially true for large area devices, where the lateral heat flow is negligible. It was reported that operation temperatures of the electrode of the OLED can exceed 86 °C [2]. Highly disordered organic semiconductors have low thermal conductivity, so the actual temperature of the organic layers can be even higher. Joule heating induced by high current injection during operation reduces the luminance, shortens the lifetime and causes spectral shift of the OLEDs. Self heating of the OLED device also causes a roll off of the efficiency due to exciton-heat annihilation processes [11,12]. Furthermore, the OLED lifetime and stability strongly depend on temperature. OLED degradation processes are very complex and not very well understood. One of possible scenarios of the OLED degradation is irreversible electrochemical reaction of either transport or electroluminescent material [13]. In general such electrochemical process can be described by Marcus theory [14]. The rate of electron transfer is given by:

$$k_t = \frac{2\pi}{\hbar}|J^2|\frac{1}{\sqrt{4\pi\lambda k_b T}}\exp\left[\frac{-(\Delta G_0+\lambda)^2}{4\lambda k_b T}\right], \qquad (1)$$

where J is the electronic coupling between the initial and final states, λ is the reorganization energy, k_b the Boltzmann constant, and ΔG_0 is the total Gibbs free energy change for the electron transfer reaction. It is obvious that due to the exponential dependence, higher temperatures greatly accelerate electrochemical processes in the OLED including both carrier transport mechanism responsible for I–V–L curve shape and irreversible oxidation and reduction processes responsible for majority of degradation mechanisms.

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Joule self heating limits OLED operational range. At higher currents, due to certain irregularities in the electrode/organic interface local overheating occurs [3], causing formation of bubbles [15], melting of the metal electrode, and consequently electrical shorts of the device. Due to the issues mentioned above, it is crucial to efficiently dissipate heat generated inside the device. A few approaches have been suggested to address this problem including thin film encapsulation heat sink [7] and metal foil substrate [8].

Here, we introduce a simple yet very efficient method of OLED cooling by immersing it into hydrofluoroether (HFE) fluids. HFEs belong to a class of environmentally friendly, green solvents. HFEs are non-flammable, have zero ozone depletion potential, low global warming potential, and very low toxicity [16]. HFE have excellent dielectric properties and good heat conductivity. HFEs are orthogonal to most of other solvents and thus can be easily recycled. It was demonstrated before that HFEs are benign to wide class of solution processed organic semiconductors independently on the polarity [17]. This can be explained it terms of orthogonality of fluorous materials and solvents to non-fluorous organic materials [17,18]. One can use HFE fluids for solution processing of organic semiconductors without altering their properties. It was demonstrated before that HFEs essentially enable lithography for organic electronic systems [19].

In this work we demonstrate that not only HFE are fully compatible with typical materials used in high efficiency small molecule p–i–n OLED devices, but also provide an elegant and easy way to significantly improve OLED efficiency, lifetime, and operational range. Since HFE have a low refractive index of $n = 1.3$ the light outcoupling efficiency of OLED operated in HFE is increased by factor of 70%. Effective cooling with HFE fluids enables increasing the operational range by up to 16% (in terms of applied voltage). Lifetimes of OLEDs operating in HFE at high currents can be also improved by about eight times.

2. Results

In order to ensure that HFE solvents are really benign to all organic small molecule semiconductors used in the organic stack, we performed a simple dipping test. The tested sample was characterized and immersed in HFE7100 solution for one week. After that the same sample was dried in nitrogen atmosphere and characterized again. Results are presented in Fig. 1. It can be seen that virtually no influence of HFE solvent was observed during this time period. Similar tests were conducted for other HFE grades with essentially same result. However one has to be careful with sample handling to avoid excessive mechanical damage of the weakly bounded organic layers.

We performed a series of measurements for OLED operating in HFE fluids of different available grades. Current–voltage–luminance (*I*–*V*–*L*) curves were taken in DC regime by performing voltage sweeps with constant speed of 0.01 V/s. We identified this speed to be sufficiently slow for OLED to reach thermal stability. In the same time this speed is fast enough to avoid sample degradation until critical temperatures are reached. Fig. 2 shows measured *I*–*V*–*L* and efficiency curves for OLED immersed in HFE7100. Reference sample (no heat sink) performance is shown for comparison. As one may expect, at low voltages both *I*–*V* curves are essentially the same. We identify the onset of temperature rise at 4.2 V where the difference between pristine and cooled sample current density is about 10%. From this data we can conclude, that N_2 (air) cooling for tested devices is only efficient for applied power of not more than 220 mW/cm^2. This is an important value to keep in mind in case of accelerated degradation/lifetime measurements. For higher dissipated powers, temperature rise of the OLED device can switch on thermally activated mechanisms of OLED degradation, which were hindered for low power regime. In accordance with general expression (1) further increase of applied power causes exponential increase of current which flows in the device [20]. At about 6 V the breakdown of the pristine device occurs. On the other hand, the HFE7100 cooled device is able to operate at up to 9 V. However, at 7.5 V we observed boiling of the HFE7100 liquid indicating that a temperature of 61 °C is reached. It is useful to note that above 5.5 V, HFE7100 cooled sample *I*–*V* curve is essentially linear. The Ohmic regime holds until device breakdown. This data shows that one has to be careful with analyzing *I*–*V* plot without taking sample heating into account. From the *L*–*V* plot, one can determine operational range of the OLED. Similar to [5] we determine the OLED operational range as position of EL plateau in the *L*–*V* curve. Values of 5.5 and 6.4 V are obtained for the reference and HFE7100 cooled sample, respectively. The increase of the operational range is thus 16%. In the simple model of a Lambertian emitter external light coupling is proportional to $\sim n^2$. For HFE7100 the reported value of refractive index is $n = 1.3$ [21]. Therefore the light outcoupling factor is 1.69. This value agrees with maximum attained light intensity of the reference sample. The power efficiency roll-off curves for reference sample and cooled one shown in Fig. 2c and d are essentially the same (if the outcoupling is taken into account). We therefore conclude that exciton-heat annihilation effect on our device is negligible.

In order to justify our choice of the HFE7100 liquid, we performed similar tests with other available grades of HFEs. The results are summarized in Table 1.

It is known that fluorocarbons show a greenhouse effect which of course limits their application in industry. We therefore also include information on global warming potential (GWP) and atmospheric lifetime of tested liquids to emphasize possible environmental impact of HFEs. For comparison perfluorohexane (C_6F_{14}) which is commonly used cleaning solvent, refrigerant, and fire suppressant has GWP of 7400 and atmospheric lifetime of 3200 years.

In order to understand OLED HFE cooling mechanism we calculate Prandtl numbers (*Pr*) and Grashof numbers (*Gr*) (Table 1) according to [22]:

$$Pr = \frac{\upsilon}{\alpha}, \tag{2}$$

$$Gr = \frac{g\beta \Delta T L^3}{\upsilon^2}, \tag{3}$$

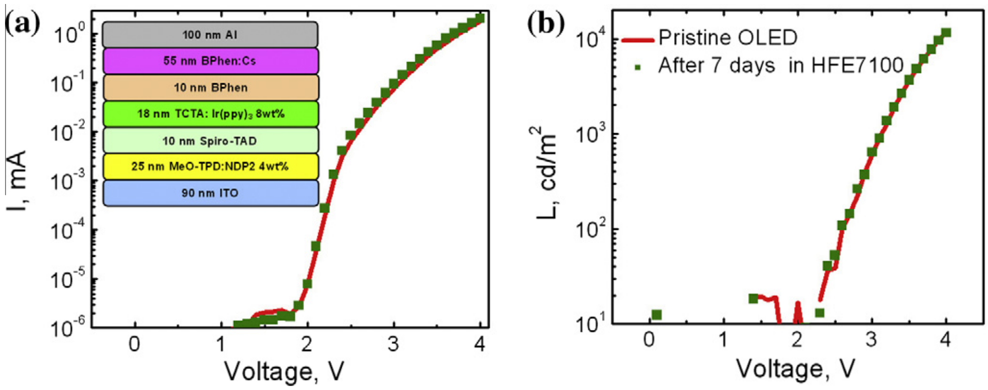

Fig. 1. (a) Current–voltage and (b) luminance–voltage plot of tested OLED devices. The dotted line represents the OLED immersed in HFE7100 for 7 days and solid line represents pristine sample data. Inset in (a) shows device structure.

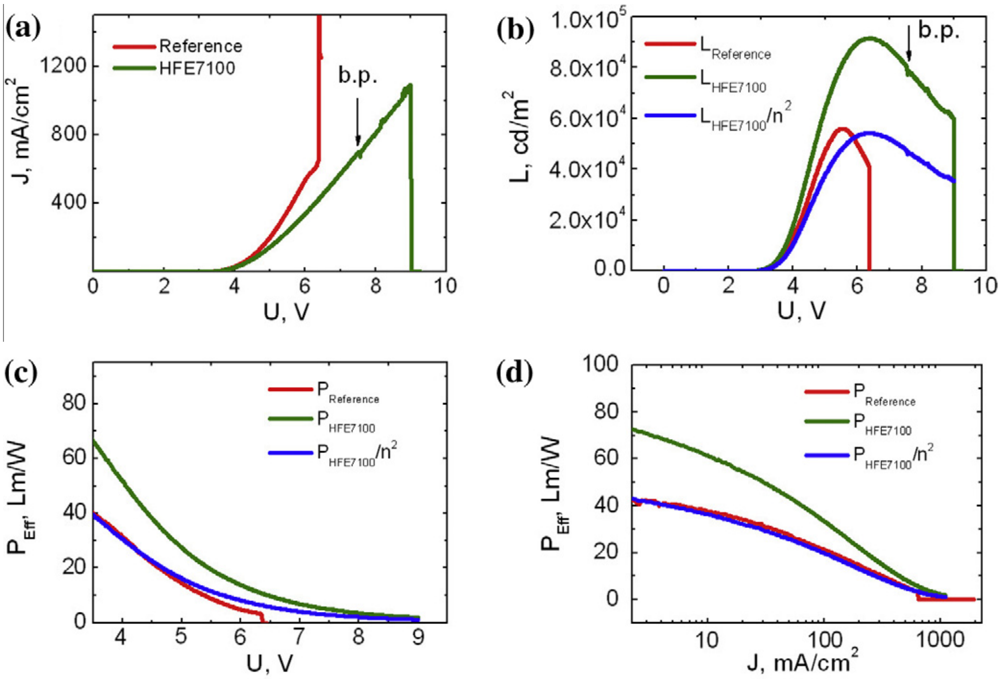

Fig. 2. (a) Current density–voltage, (b) luminance–voltage, (c) power efficiency–voltage and (d) power efficiency–current density plots of the HFE7100 liquid cooled (green) and reference (red) OLED devices. (b–d) also show cooled OLED values divided by square of refractive index ($n^2 = 1.69$) of HFE7100 liquid. Arrows show boiling point (b.p.) of HFE7100. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

where g is acceleration due to Earth's gravity, β is volumetric thermal expansion coefficient, T is difference between surface and bulk temperature, v is kinematic viscosity, α is thermal diffusivity and $L = (\text{device area})^{1/2}$. Since for all HFE grades Prandtl numbers are much higher than 1 and measurement vessel size is much large than the linear dimensions of the OLED device, we conclude that heat transfer mechanism is dominated by natural convection. Natural convection flow field is a self-sustained flow driven by the presence of a temperature gradient. As a result of the temperature difference, the density field is not uniform and buoyancy will induce a flow current due to the gravitational field and the variation in the density field. Product of Grashof number and the Prandtl number gives another important parameter, the Rayleigh number, $R_a = Gr \cdot Pr$. Rayleigh number is used to characterize the laminar to turbulence transition of a natural convection boundary layer flow. The laminar flow to turbulent flow transition typically occurs for $R_a > R_a^* = 10^9$. Since, for all tested HFEs we calculate $R_a \ll R_a^*$ (Table 1), we conclude that the boundary layer of the HFE liquid is always laminar.

Table 1
Heat transfer properties of different grade HFEs.

	HFE7100	HFE7200	HFE7300	HFE7500	HFE7600
OLED DC operational range increase (%)	16	16	11	11	9
b.p. (°C)	61	76	98	128	131
Thermal conductivity[a] W/(mK)	0.069	0.068	0.063	0.065	0.071
Prandtl number[a]	9.84	10.4	21.3	21.6	31.5
Grashof number	1.31×10^5	1.00×10^5	2.71×10^4	2.31×10^4	9.56×10^3
Rayleigh number	1.29×10^6	1.05×10^6	5.78×10^5	4.97×10^5	3.01×10^5
GWP	297	59	210	100	700
Atmospheric lifetime (years)	4.1	0.77	3.8	2.2	9

[a] At 300 K and ambient conditions.

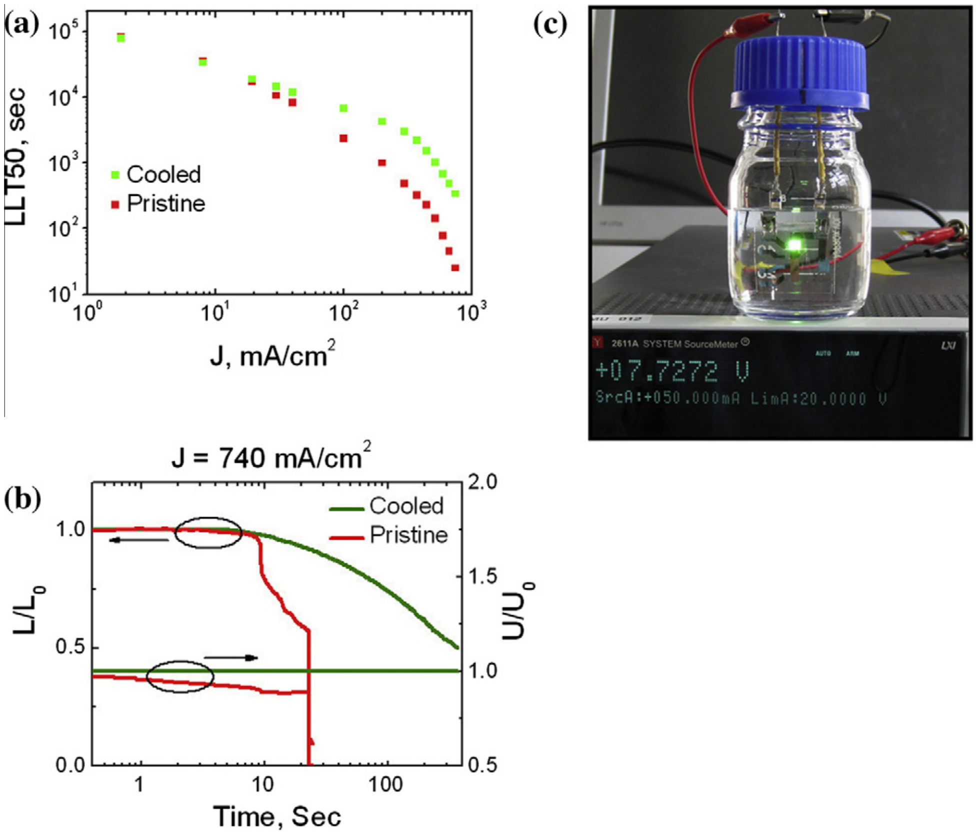

Fig. 3. (a) LLT50 dependence on applied current density. (b) Relative luminance and voltage drop (normalized with initial values) with time at constant DC current density of 740 mA/cm^2. Data is shown for HFE7100 liquid cooled (green) and reference (red) OLED devices. (c) OLED device stably operating at 740 mA/cm^2 in HFE7100 liquid. OLED device area is 6.76 mm^2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

In order to study the influence of the cooling on the stability of OLED devices, we performed a series of aging tests. Samples were aged at constant current densities until they reached 50% (LLT50) of initial luminance (L_0). The results of stability test for HFE7100 cooled and reference OLEDs are shown in Fig. 3. As expected from expression (1) the temperature has very significant effect on OLED stability. While for low power regime the lifetime data for both experiments coincide within experimental error, about an order of magnitude LLT50 improvement can be achieved (by efficient heat dissipation with HFE7100) for high power regime. Also, we observe that HFE7100 prevents so-called "sudden death" of the OLED, which is caused by local overheating, melting, and eventual shortage of the OLED device. This is illustrated in Fig. 3b. The following scenario is typical for such sudden death mechanism. Once current is applied it causes an initial drop of applied voltage. This is due to heating, which increases device temperature and consequently increases mobility of transport layer and charge injection from electrodes into transport layers and between organic layers. Eventually, the temperature reaches a critical value which causes device failure.

The abrupt cessation of light emission is accompanied by a sharp drop of the voltage and bursting of the metal film above the damaged spots. On the other hand HFE liquid stabilizes the temperature and effectively prevents thermal breakdown. We believe, that described heat dissipation method, can be applied for cooling of commercial OLEDs for accelerated lifetime testing. Such accelerated lifetime measurements are typically done at rather high currents to be able to test the OLED in a reasonably short time frame. This, however, may lead to overheating of the device, so the degradation mechanisms are different from that ones at lower currents. Described cooling method can significantly alleviate the heating of the device, which would improve the dynamical range and make such measurements more relevant.

3. Conclusions

In conclusion, we show that highly fluorinated fluids and particularly hydrofluoroethers can be effectively used for OLED heat dissipation. Simple immersion of OLED into HFEs fluids significantly improves OLED stability and dynamic range. We found that particularly HFE7100 seems to be most effective OLED coolant. OLED operating dynamic range is increased up to 16%. Comparison of *I*–*V*–*L* curves for reference and HFE cooled samples gives an upper limit for stable OLED operation in N_2 (air) of 220 mW/cm^2. Evaluation of fluid mechanics numbers for tested liquids allows us to conclude, that the main mechanism of cooling is natural convection with laminar flow (until boiling point is reached).

We show that, lifetimes of OLEDs operating in HFE at high currents can be improved by about eight times. HFE fluids also significantly improves light outcoupling by factor of 70% due to higher than air refractive index ($n = 1.3$). In summary, we believe HFE7100 to be very promising replacement for N_2 as OLED encapsulation media.

4. Experimental

A set of identical p–i–n OLED devices was prepared by vacuum deposition. The OLEDs are evaporated in a multichamber ultrahigh vacuum of 10^{-8} mbar on top of clean glass/indium tin oxide (ITO, 90 nm) substrates. These devices consist of a 25 nm thick *N*,*N*,*N*′,*N*′-tetrakis 4-methoxyphenylbenzidine (MeO-TPD) doped with 2 wt.% of NDP2 (Novaled AG), a hole injection and transport layer, followed by 10 nm 2,2′,7,7′-tetrakis-(*N*,*N*-diphenylamino)-9,9′-spirobifluoren (Spiro-TAD) electron blocking layer, 18 nm 4,4′,4″-tris(*N*-carbazolyl)-triphenylamine (TCTA) doped with 8 wt.% of tris(2-phenylpyridine) iridium ($Ir(ppy)_3$) emitter layer, 10 nm 4,7-diphenyl-1,10-phenanthroline (BPhen) hole blocking layer, 55 nm BPhen doped with Cs electron transport layer and a 100 nm Al top electrode. This particular device structure is well known to be stable and efficient [23]. All OLEDs have device area of 6.76 mm^2. Devices are immersed in fish-bowl like container filled with HFE fluids and current–voltage–luminance characteristics were taken. The dimensions of the container are much higher than those of OLED device. Five different grades HFE7100, HFE7200, HFE7300, HFE7500 and HFE7600 are tested. Before use, HFE fluids were purged for 24 h with nitrogen to remove dissolved oxygen. Electrical characterization is done using Keithley 2611A SMU and light intensity is recorded using calibrated photo-diode. For the pristine sample the very same measurement schema is used with empty container. For the calibration of photo diode, we used the setup, used before [9] and pristine OLED with glass encapsulation. All measurements were done in nitrogen atmosphere, to prevent samples degradation. The background temperature for both experiments is kept at 25 °C.

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