Alkali & Alkaline-Earth Metal Sources for OLED Devices

S. Tominetti*, L. Cattaneo, G. Longoni, A. Bonucci, and L.Toia
SAES Getters S.p.A., 20020 Lainate (Milano), Italy
Phone: +39-02-931781, E-mail: stefano_tominetti@saes-group.com

Abstract

Low work function alkali metals and alkaline earths successfully lower the electron injection barrier and increase electron injection into the organic layer in OLED displays, but their implementation is not easy. AlkaMax technology can ensure the required metal evaporation rate in a fast, homogeneous and easily controllable way.

1. Introduction

Practical exploitation of Organic Light Emitting Diodes (OLEDs) still requires the solution of several scientific and technological issues. If we focus on the improvement of the cathode structure and the metal-organic interface, we can imagine achieving high electro-luminescence external quantum efficiency (η_{ext}), high power efficiency (η_E) and long-term stability through an extremely efficient electron injection. Low driving voltage, together with high electron mobility in the organic layer and thus high recombination efficiencies are required to achieve this goal[1]. Typically, OLEDs already use alkali metals, like Li and Cs, or alkaline-earth metals, like Mg and Ba, to improve the cathode performances; in the early stages of OLED development, Tang and Van Slyke[2] adopted a cathode structure based on composite MgAg alloy able to reduce the overall cathode work function and the barrier height for the electron injection.

More recently, the optimization of electron injection through the incorporation of an alkali metal inside the cathode structure is becoming more popular. The first appearance of alkali metals to obtain a low driving voltage OLED dates back to 1983, when Partridge used Na, K and Cs as efficient electron injection cathodes in a PVK based OLED[3].

Alkali metals incorporation in the OLED structure can be accomplished in two forms:

- ultra-thin layers (Li, LiAl, Li2O, LiF, Cs, CsAl, CsF and alkali-metal carboxilates) above the electron transport layer (ETL) and capped by an Al back electrode[4-8]
- co-deposition of Li or Cs with an ETL immediately prior to the cathode deposition[9-17] (also named “alkali metal doping of ETL”)

Both configurations have been shown to dramatically reduce the driving voltage and, in the meantime, increase the external quantum efficiency, the overall luminance and the long-term operational stability.

In the case of Top Emission OLED devices and Stacked structures (SOLEDs), the most promising transparent cathode layers can be obtained in two ways: 1) by co-deposition of a Mg:Ag layer above the ETL[18]; 2) by co-deposition of Li or Cs with ETL just before the deposition of ITO as cathode[4,18]. Transparent cathodes built up using CuPc or BCP capped with RF sputtered ITO, are conformal with the adoption of an alkali metal like Li.

Mg or Mg composite cathodes (using the co-deposition of Ag for instance) are the most widely cathode structures used for many OLED devices. Basically, Magnesium alloyed with Silver forms an efficient electron injecting contact on organic semiconductors: Magnesium is chosen for its low work function (3,7 eV) while Ag adds chemical stability to Mg layers and is also believed to increase the sticking coefficient of Mg during the deposition procedure. Mg is also found to partially diffuse into the organic layer (such as Alq3) leading to a broad “doped” interface made by organometallic complexes with a strong dipolar behavior[19,20].

In case of PLED devices, one of the most applied cathode layer is made of pure Ba. Alternatively, alkali metals have been successfully used also in PLED structures, mainly in conjunction with standard polymers like MEH-PPV, and with metallic cathodes like Al and Au[21-23].

As a side effect of the adoption of alkali metals inside the OLED structure, the organic materials experienced longer lifetime and stability due to the reduced electrical stresses. The device exploiting alkali metals can reach the same performances of a standard device using lower driving voltages and thus lower electric fields[13,24] (see Figure 1 below).

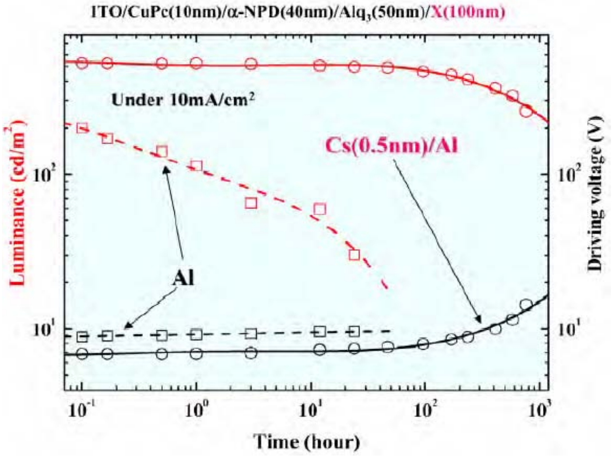

Figure 1: Luminance and driving voltage behavior over time at a constant current density (10 mA/cm^2) of an OLED structure with double layer cathode (Cs/Al) compared to the same structure with only Al cathode. ETL is Alq3. Organic lifetime seems to be increased by a factor more than 1000 using Cs layer (Courtesy of Prof. C. Adachi[24]).

The present work specifically discusses stable and reliable evaporation of Li, Cs, Mg and Ba through a novel technology for a controlled evaporation source.

2. Alkali and Alkaline-Earths in OLEDs

The electron injection mechanism at the interface between the organic layer and the metal cap is still unclear. The M-O interface is the key point to understand the behavior of different metals, not strictly related to their work functions only. The injection of electrons seems to be controlled by a density of states (DOS) created by interfacial dipoles due to the interaction of the alkali and alkaline-earth metals with the ETL molecules like Alq3[6,7,25-27], that are strongly polar molecules and easily react forming radical anions, due to a bonding of N (1s) with the alkali and alkaline-earth metal atom, as predicted by DFT and confirmed by XPS/UPS data[4,13].

The role of the alkali/alkaline-earth metal is now not only to reduce the barrier energy between the cathode and the ETL, but also to facilitate the creation the so called Gap States in the forbidden gap between the HOMO and LUMO of the organic material, thus increasing the Fermi level of the ETL and finally increasing the charge transport[4] (Figure 2). This phenomenon is similar to what happens inside inorganic n-type semiconductors.

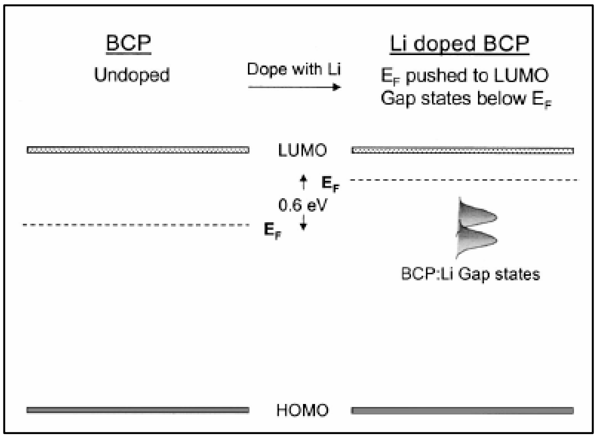

Figure 2: Proposed energy-level scheme of undoped (left) and Li-doped (right) BCP thin films. The lowest unoccupied and highest occupied molecular orbitals are labeled LUMO and HOMO, respectively.

Therefore alkali and alkaline-earth metals have their own intrinsic capacity to lower the barrier energy required for the electron injection, not exclusively dependent only on the work function. Due to the interfacial dipole layer formation, the power efficiency and the electro-luminescence efficiency are dependent also on the thickness of the deposited alkali metal layer, as figured out by the following pictures (Figure 3a) and 3b))[5,24].

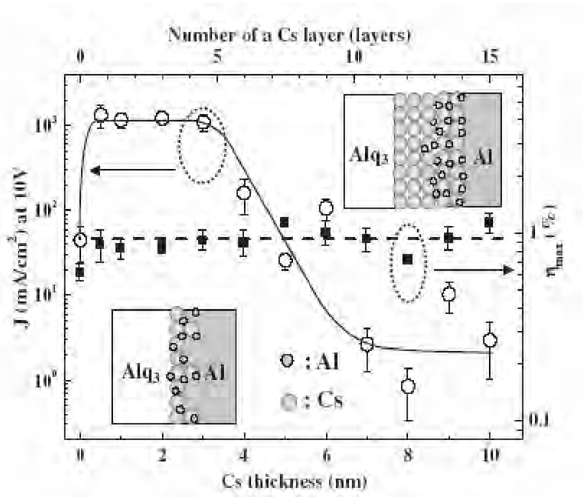

Figure 3a) current density (J) at 10V and maximum quantum efficiency(η_{ext}) depending on inserted cathode metal in ITO(110 nm)/α-NPD(50 nm)/Alq3(50 nm)/Cs(X nm)/Al (100 nm) device. Schematic view of Cs/Al configurations is shown[5].

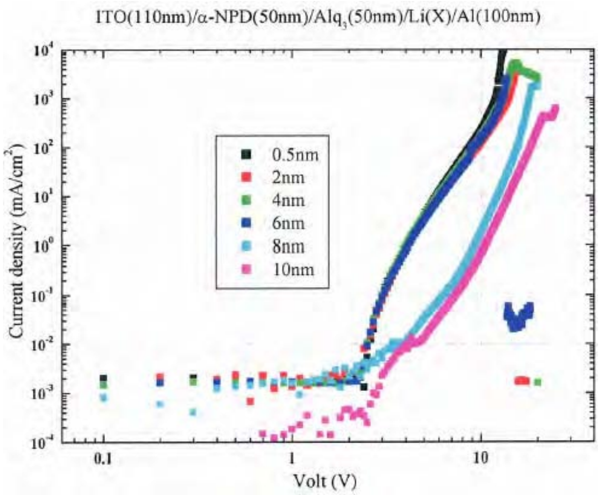

Figure 3b): current density- voltage (J-V) characteristics for the same device built up using Li instead of Cs for different Li thicknesses, from 0.5 nm to 10 nm (courtesy of Prof. C. Adachi)[24].

efficiency is achieved using a Cs layer between 5 and 30 Å and, inside the same architecture, using a Li layer thinner than 60 Å.

2.1. Technologies for dispensing Alkali Metals

Three main techniques can be identified to incorporate the alkali metals (e.g. Li) within the OLED architecture:

1) LiF dispensing through crucible
2) Li dispensing through crucible
3) Li dispensing through AlkaMax.

First, it's worthwhile discussing the main differences between the use of LiF and pure Li inside the OLED structure. From the scientific point of view, LiF is an insulator material and to create an active interfacial dipole layer between ETL and cathode its thickness should be extremely low (below 5 Å) and absolutely uniform to prevent shortcuts or electric field stresses within the device. On the other hand, if LiF is well deposited, it can prevent shortcuts between ITO spikes and the cathode and also any reaction between the cathode material and the organic leading to the formation of organo-metallic complexes able to quench the polarons[6,7,28]. But LiF can act only as interfacial dipole and it is not absolutely able to improve the ETL conductivity and also the recombination probabilities: pure Li, both as interlayer between ETL and cathode and as doping inside ETL, transfers the electron injection inside the bulk organic, creates the gap states and facilitates the electron mobility and finally the recombination efficiency, as shown in paragraph 2. Moreover Li thickness can vary between 5 Å and 60 Å, without strong constraints about uniformity and planarity. Therefore, from scientific point of view, Li would be preferable to LiF (see Figure 4).

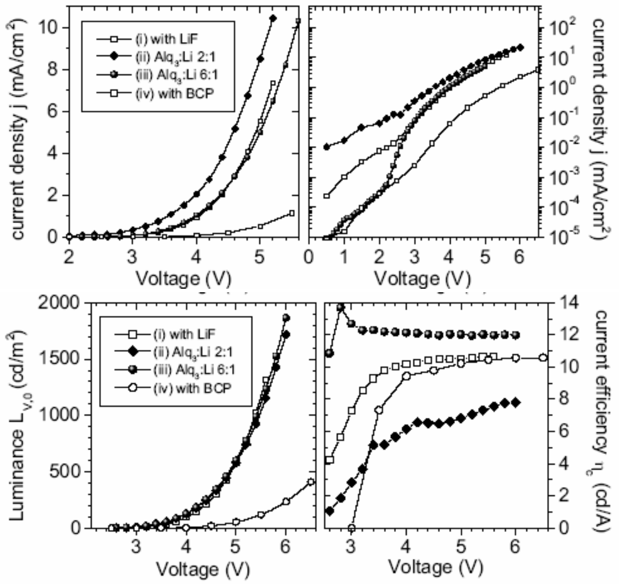

Figure 4: Current density j vs. voltage V in a linear scale (top left) and a log-lin scale (top right). Luminance in forward direction L vs. voltage V (bottom left) and current efficiency η_c vs. voltage (bottom right)[29].

In spite of these scientific results, many OLED manufacturers are exploiting the usage of LiF because it is stable in air and easier to be handled. But even LiF evaporation inside a crucible is sensitive to temperature variation, with a consequent unstable behavior during the deposition if the temperature control is not extremely accurate and highly efficient, even if the is not as critical as for conventional pure Li evaporation using crucibles.

In fact, the deposition of alkali (and alkaline earth) metal layers can be performed through the metal itself in a conventionally heated crucible. However these metals are very reactive and should be handled in inert atmosphere throughout the entire process, since free metals easily react with gaseous impurities, leading to several instabilities, like splash evaporation, due to reaction at solid-liquid interface, or increased sensitivity to the temperature equilibrium. An innovative metal dispensing technology has been developed to overcome these problems and ensure OLED metal cathode reliability as well as stable and accurate deposition rates for the cathode structures.

3. The AlkaMax technology

The working principle of AlkaMax is a chemical reaction which involves a non toxic precursor of the metal and/or a metallic alloy: it is extremely stable at room temperature and at standard atmosphere. Before evaporation the metal is present in a stabilized form and can be evaporated "on demand": the evaporation could be stopped and re-started without loosing metal yield because the residual metal, not yet released, remains in its stable form.

3.1 Lithium and Cesium evaporation

The alkali metal dispensers have different configurations related to material content and to the production scale-up. Laboratory scale tests can be performed with small wires (to evaporate a few milligrams of metal), pilot line test can be carried out with an "evaporation boat" (to evaporate hundreds mg of Lithium) and mass production test can run with a bigger evaporation boat (Figure 5).

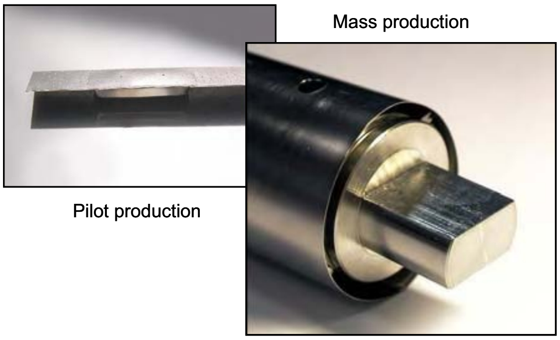

Figure 5: AlkaMax configurations

The cylindrical configuration will be deepened here: it has been optimized for Lithium evaporation in mass production case. The material and layout of this container have been designed so as to provide low outgassing throughput (H_2, CO) during heating, to withstand embrittlement (due to H_2 at high temperature) and feature minimum radiative heating (evaporation chamber, target substrate, Quartz Crystal Microbalance).

AlkaMax container is treated with a firing procedure that enables it to withstand strong thermal and mechanical stresses. The selected material of the dispenser is SS AISI 304L (140 mm length x 37 mm diameter).

The final configuration has been optimized with an external shield[30] which allows minimizing the heat exchange with the surrounding elements, a better controlled, stable and reproducible evaporation rate and finally reducing power consumption. AlkaMax is simply mounted to appropriate electrodes and heated by Joule effect. The heating process comprises two steps: 1) preliminary degassing (around 30-40 minutes) at a temperature lower than the starting of evaporation; 2) evaporation and deposition step controlled on line by means of QCM (Quartz Crystal Monitor) and/or AAS (Atomic Absorption Spectroscopy)[31].

During the long term evaporation the deposition rate obtained was stable and reproducible for several setting in the range 0.05-0.6 Å/s. Figure 6 shows a constant deposition rate of Lithium at 0.3 Å/s for 80 hours and the corresponding current applied during evaporation. Generally, the operating voltages and currents applied to obtain Lithium evaporation from the configuration suitable for mass production use are: 0.8-2 V and 170-300 A.

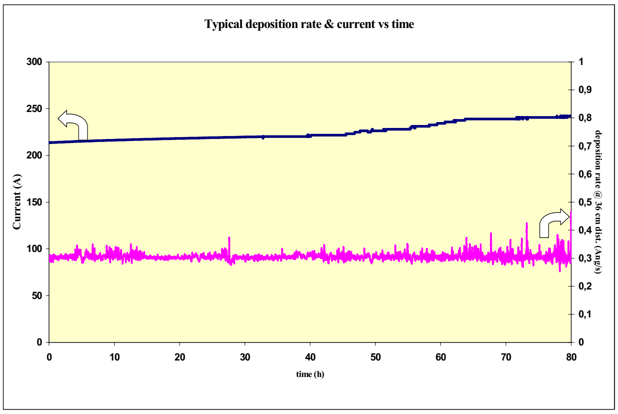

Figure 6: Li evaporation rate and AlkaMax heating current vs. time.

For Cesium, similar characteristics are obtained at lower currents, since the temperature required for deposition is lower. AlkaMax operating temperature does not affect the substrate temperature thanks to the presence of a shield as shown in Figure 5. The uniformity of the deposited layer has been verified in the case of Lithium, but theoretical evaluations lead to the same results also with the Cs source. The thickness was set at 200 Å at a distance source-substrate of about 40 cm and the variation was below

15% over a glass substrate measuring 300x400 mm^2 (see Figure 7)[32].

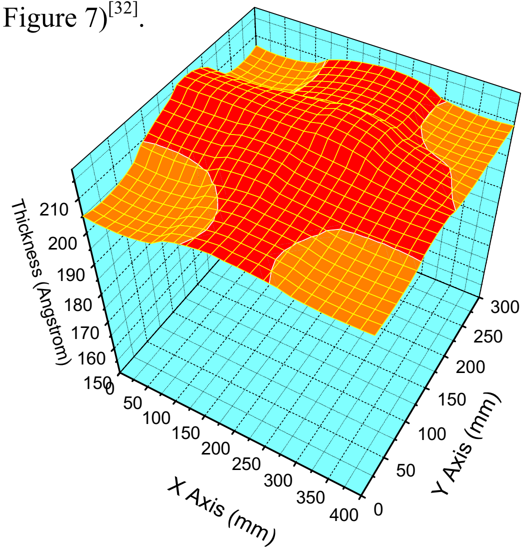

Figure 7. Surface contour plot of the deposition uniformity of Li on glass substrate 300x400 mm^2.

3.2 Magnesium evaporation

Also with Mg, stable and reproducible evaporation rates have been obtained as shown in Figure 8.

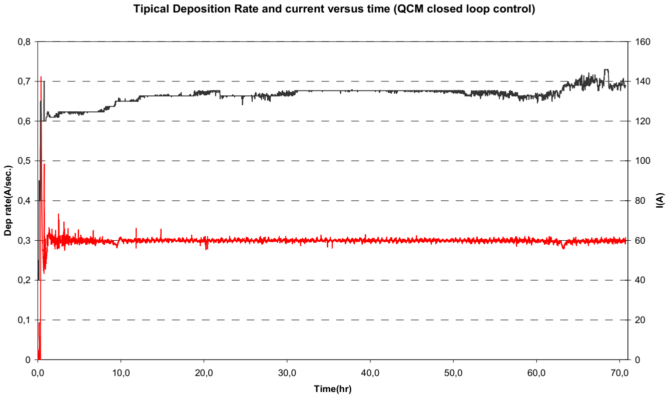

Figure 8. New Magnesium source: deposition rate (red) and current (black) vs. time.

The deposition rate was continuously adjusted through the closed-loop control. During the long term evaporation the deposition rate obtained was stable and reproducible for several settings in the range 0.05-1 Å/s. For example Figure 8 shows a constant deposition rate of Magnesium at 0.3 Å/s for 70 hours and the corresponding current applied during evaporation. The control loop acts onto the power supply in order to keep the deposition rate constant. The obtained yield was more than 5 grams of Magnesium.

The heating procedure is similar to the one described in 3.2 and the entire process is monitored by means of QCM (Quartz Crystal Monitor).

The operating voltages and currents are related to the material type and to the dispenser configuration; they can vary in the following ranges: 0.3-1.5 V and 100-250 A. The preferred Magnesium source developed at SAES laboratories operates at the reasonable lowest currents and temperatures, guaranteeing very high Mg yields: up to 6 grams. Before evaporation Magnesium is present in a stabilized form and it can be evaporated "on demand": the evaporation could be stopped (exposed to air if necessary) and re-started without losing metal yield because the metal not yet released remains in its stable form.

3.3 Controlling the deposition rate

The measure of deposition thickness and rate is generally performed with a quartz microbalance (QCM). It's also possible to use an in-situ closed-loop control because, in case of Lithium AlkaMax, the variation of the deposition rate F with the temperature

T is $\frac{\partial F}{\partial T} \approx 10^{-4} \div 10^{-3}$ Å/sec °C.

AlkaMax therefore exploits a much more stable evaporation rate and less sensitive temperature variation, compared to other dispenser designs or crucibles dispensing raw materials. This is mainly due to the adopted alkali metal precursor and also the AlkaMax container design. The low value of first derivative $\delta F/\delta T$ allows an easy tuning of the automatic feedback control on the power supply to heat AlkaMax.

In case of Magnesium, the in-situ closed-loop is applicable to different dispensers' designs thanks to the high controllability of the raw material itself (Magnesium precursor).

4. Conclusion

In the quest for more efficient and performing devices, many OLED manufacturers are exploiting the usage of Lithium or Cesium insulating compounds (such as LiF or CsF) because they are stable in air and easy to be handled even if, from the scientific point of view, pure Li or Cs would be preferable. The use of pure alkali metals in conventional evaporation systems still gives rise to several technological problems (see 2.1) and AlkaMax can solve all these issues.

In Top Emission OLEDs (but generally for all Active Matrix structures), Mg:Ag seems the most promising cathode material, whilst Ba is a good candidate for PLED due to its low work function and its compatibility with the most widely used conductive polymers. Both Mg and Ba can be deposited by a thermal evaporation of the metals from a heated crucible; but also Mg and Ba are strongly reactive and can easily and rapidly undergo oxidation in a non-inert atmosphere. The reactions at the solid-liquid interface lead to several typical instabilities like splash evaporation and to technological problems related to the purity of the deposited films and to the controllability of the deposition rate. The novel metal dispensing technology described in the present work is based on materials and configurations stable in air and during the evaporation procedure, allowing the solution of the already described manufacturing issues and therefore enabling the establishment of a reliable mass-production process.

5. References

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