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AlkaMax

SAES Solution for Alkali Metal Dispensing
in OLED Display Manufacturing

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OLEDs are an attractive and promising candidate for the next generation of displays and light sources (Tang, 2002). OLEDs have the potential to achieve high performance, as well as being ecologically clean. However, there are still some development issues, and the following targets need to be achieved (Bardsley, 2001).

- Lower the operating voltage—to reduce power consumption, allowing cheaper driving circuitry
- Increase luminosity—especially important for light source applications
- Facilitate a top-emission structure—a solution to small aperture of back-emission AMOLEDs
- Improve production yield

These targets can be achieved (Scott, 2003) through improvements in the metal-organic interface and charge injection. SAES Getters' Alkali Metal Dispensers (AMDs) are widely used to dope photonic surfaces and are applicable for use in OLED applications. This application note discusses use of AMDs in fabrication of alkali metal cathode layers and doped organic electron transport layers.

OLEDs

OLEDs are a type of LED with organic layers sandwiched between the anode and cathode (Figure 1). Holes are injected from the anode and electrons are injected from the cathode. They are then recombined in an organic layer where light emission takes place. Unfortunately, fabrication processes are far from ideal. Defects at the cathode-emission interface and at the anode-emission interface inhibit charge transfer. Researchers have added semiconducting organic transport layers to improve electron transfer and mobility from the cathode to the emission layer. However, device current levels are still too high for large-size OLED applications.

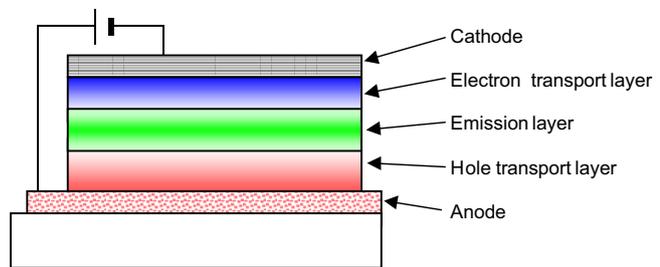


Figure 1

Alkali Metal Layer for cathodes

The carrier injection barrier at the electrode/organic interface is the greatest factor to determine the driving voltage. ITO, which is a transparent electrode material and it is proven for LCD and the like, is a comparatively suitable material for anode and it is commonly used. On the contrary, cathode materials are required to facilitate electron injection to organic layer and to be a reliable conductor as well, so that various materials for cathode have been proposed.

We should say that there is more room for improvement of electron injection efficiency on the cathode side than hole injection efficiency on the anode side.

By using low work function alkali metals and alkaline earth metals for cathode, the electron injection barrier is lowered and electron injection to the organic layer is increased, so that the operation at lower voltage becomes possible.

Alkali metals or alkaline earth metals are commonly used to build the cathode structure: MgAg alloy, AlLi alloy and technique to insert LiF or Li₂O, Ba or Ca between Al and the organic layer are typical in the OLED/PLED manufacturing.

There are, however, some critical issues associated to these materials: a proper control of the composition, flexibility in thickness limited by the conductivity of the compounds, which have also the function of conductors, the deterioration of the electrode material that can take place even in the case of alloys.

As an example, LiF and Li₂O are anticipated to be comparatively stable, but due to their insulating nature, their thickness is required to be maintained very thin so as not to increase driving voltage.

Features of the Alkali Metal Layer

Inserting a low work function alkali metal layer between cathode and electron transport layer is effective to realize lower driving voltage (Figure 2).

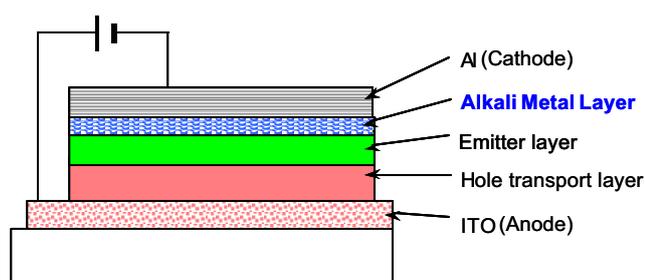


Figure 2

The lower the work function, the lower the voltage, so that it has been confirmed that Cs is the most effective alkali metal (Figure 3). Up to 30Å in case of Cs can work as high efficiency cathode: this is a clear advantage in terms of process control over LiF and Li₂O, which as we mentioned are insulators and require accurate deposition control so as to maintain 5Å range to avoid increase in film resistance.

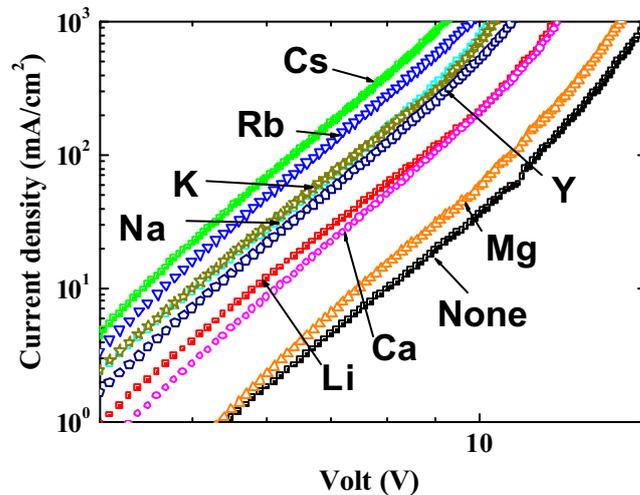


Figure 3 J-V characteristics depending on a work function of cathode, ITO(110nm)/a-NPD(50nm)/Alq3(50nm)/Metal Layer(0.5nm)/Al(100nm) (Oyamada, 2003)

Alkali Metal Doped Organic Layer

Current cathode electron transport systems do not achieve the same level of performance as hole-transport systems. This limits luminescent emission due to electron-hole recombination in the emitting layer. The AMDOL (Figure 4) consists of pure alkali metal doped into the organic layer interface between the cathode and emitter layers (Kido, 1998). AMDOLs have attracted attention as a possible method to provide the benefits of LiF and Li₂O while avoiding the problems they induce.

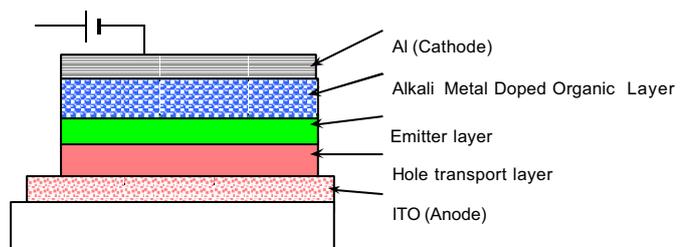


Figure 4

While the alkali metal itself is reactive and unstable, alkali metal co-doped in an organic layer (AMDOL) is considered as stable as the non-doped organic transport layer itself. The stability of the device then depends on the nature of the host organic compound, not the alkali metal (Kondo, 2000). Several organic compounds have been evaluated in conjunction with alkali metal doping. The most successful are Alq3, Bphen, BCP, Distyrylarylene derivative, and DSA amine.

Features of the Alkali Metal Doped Organic Layer

➤ Lowering the Operating Voltage to reduce power consumption

Doping alkali metal into the organic layer at the interface of the cathode lowers the operating voltage of the OLED. In the AMDOL, the alkali metal supplies a radical anion, which works as an internal carrier. Electron injection at the interface and the electron mobility in the layer is improved (Matsumoto, 2000).

The relationship towards lower voltage correlates with moving to a metal with a lower work function. While Rb (2.16eV), K (2.32eV), Na (2.75eV), Li (2.90eV), Ca (2.87eV), Mg (3.66 eV), Sr (2.59 eV), Y (3.1 eV), and Sm metals have been evaluated (Nakamura, 1999; Matsumoto, 2000; Adachi, 2003), doping with Cs (2.14 eV) has been found to be the most effective alkali metal in lowering the operating voltage and improving the current efficiency. Compared with Li, the operating voltage is lowered by ~2 Volts and current efficiency is improved from 7 mA/cm² to 40 mA/cm². Resistivity is lowered from 10⁶ Ωcm for Li to 10⁵ Ωcm for Cs-doped Bphen (Figure 5).

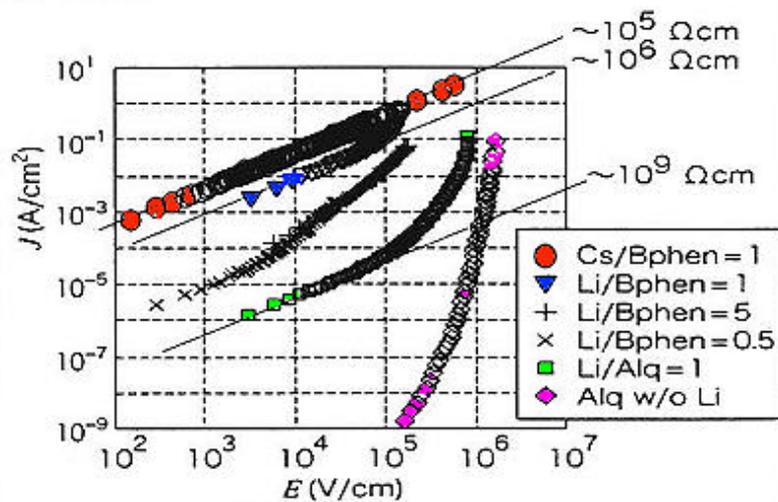


Figure 5 (Matsumoto, 2000)

➤ The AMDOL's properties facilitate a top-emission AMOLED structure

Typical Active-Matrix OLEDs (AMOLED) are bottom-emitting (Figure 6). A metal-cathode electrode such as aluminum is used and all light is emitted through an aperture between the TFTs. Because the available sub-pixel emission aperture is reduced by the TFT, the OLED is not as bright as possible. In order to capture all emission (at least 3 times improvement), one must construct a top-emission AMOLED. However, to accomplish this goal, a stable transparent cathode system must be developed. The AMDOL is transparent, and it promotes high electron-injection efficiency (Parthasarathy, 1998; Parthasarathy, 2000).

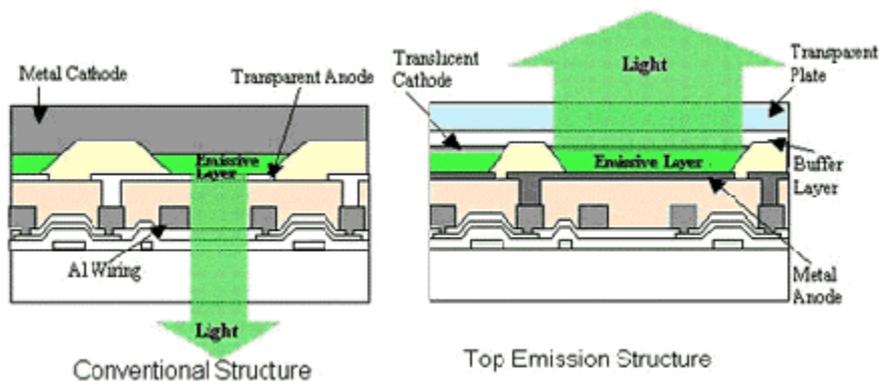


Figure 6 (Sasaoka, 2001)

These properties allow the use of a high-work-function cathode material, such as ITO or other transparent organic conducting cathode electrodes (Fukase, 2002). Therefore, the AMDOL enables a top-emission OLED structure.

➤ **The AMDOL can be thick enough to prevent short circuits in the device**

Conventional AMOLED and Passive Matrix OLEDs use ITO as the bottom electrode and hole injection source. Increased OLED emission efficiency requires a high-work-function hole injection layer like ITO that must have a low sheet resistance, and be very smooth (Kim, 2002). The surface must be much smoother than for LCDs. Typical parameters are <1nm RMS with spikes <30nm in height, with a frequency of 0.2 spikes/ μm^2 . Conventional ITO has 50nm high spikes averaging 2 spikes/ μm^2 which cause high leakage paths between anode and cathode, and increase the incidence of short circuits (Boehm, 2001).

LiF or Li_2O cathode layers must be very thin (<0.8nm) as they are insulating materials. Spikes of ITO can penetrate deeply into the thin organic and LiF or Li_2O layers causing shorts or breakdown points with the aluminum electrode at the cathode. Many in the field have added a >100nm layer of SiO_2 to planarize the hole-injection layer and solve this problem.

Since the resistance of the AMDOL is about five orders of magnitude lower than the LiF or Li_2O cathode layers and other organic injection layers (Matsumoto, 2000), the AMDOL can be sufficiently thick to eliminate ITO penetration to the Al cathode electrode. This will eliminate the need for a planarization layer and facilitate using lower quality ITO increasing production yields.

➤ **Towards current efficiency over 100%**

New possibilities for device configuration have been reported due to the features of the AMDOL, namely transparency and high electron injection (Kido, 2002; Kido, 2003; Matsumoto, 2003). As shown in Figure 7, a stacked structure can be fabricated separated by a Charge Generation Layer (CGL). In the device, each CGL generates electrons and holes upon voltage application at the anode-cathode electrodes. The result is Multi Photon Emission (MPE) for a given current in the device. The use of the transparent AMDOL was the key to success of this novel OLED structure.

It has been confirmed (Matsumoto 2003) that the current efficiency of the MPE Device is more than 100% and very high luminosity is achieved with very low current. OLED lifetimes are strongly affected by the current level required to operate them. Consequently, lowering the current may result in longer device lifetime. In addition, it is reported that the risk of short circuits can be reduced due to the stacked configuration.

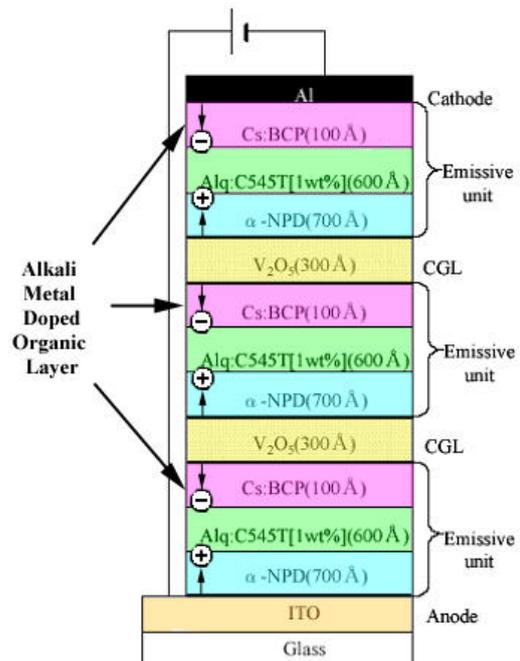


Figure 7 (Matsumoto, 2003)

Using AlkaMax, SAES Alkali Metal Dispenser for OLED

➤ **Alkali Metal Dispensers (AMDs)**

In order to fabricate an AMDOL, pure alkali metal must be deposited. It is not possible to deposit pure alkali metal vapor by conventional methods. SAES Getters Alkali Metal Dispensers (AMDs) solve this problem. Ultra-pure alkali metal vapor can be easily obtained. Li, Na, K, Rb and Cs can be deposited from AMDs. AMDs can be easily handled in the fab environment. SAES Getters' AMDs have a long history of use in purity sensitive applications like photo and electron multipliers. Traditional AMD formats dispense a few milligrams alkali metals and are suitable for laboratory-scale tests in the OLEDs. SAES Getters has developed new AMD formats to support full-scale production of AMDOLs. AlkaMax, the new AMD configuration by SAES, is capable of releasing up to a few grams of alkali metals.

➤ **The mechanism of Alkali Metal deposition**

The alkali metal is stabilized as a salt and mixed with a zirconium alloy based non-evaporable getter material (SAES St 101 alloy) in SAES Getters' AMD. The mixture is then loaded into the dispenser structure. This configuration, allows AlkaMax to be easily handled in air. No special protected environment is necessary for handling SAES AlkaMax dispensers.

When AlkaMax is heated (generally by resistive heating) in a vacuum, alkali metal evaporates as the result of a reduction reaction between the alkali metal salt and the getter material. The getter alloy sorbs gases released during the decomposition of the alkali metal salt preventing them from escaping from the AlkaMax dispenser (della Porta, 1968). A pure alkali metal vapor is emitted from the dispenser.

Figures 8(a) and 8(b) illustrate two heating profiles for using AlkaMax. The profile chosen depends on the history of the dispenser before use. Figure 8 (a) illustrates the process used in an initial "activation" or "outgassing" whenever the new dispenser is mounted in the chamber or after the dispenser has been exposed to air.

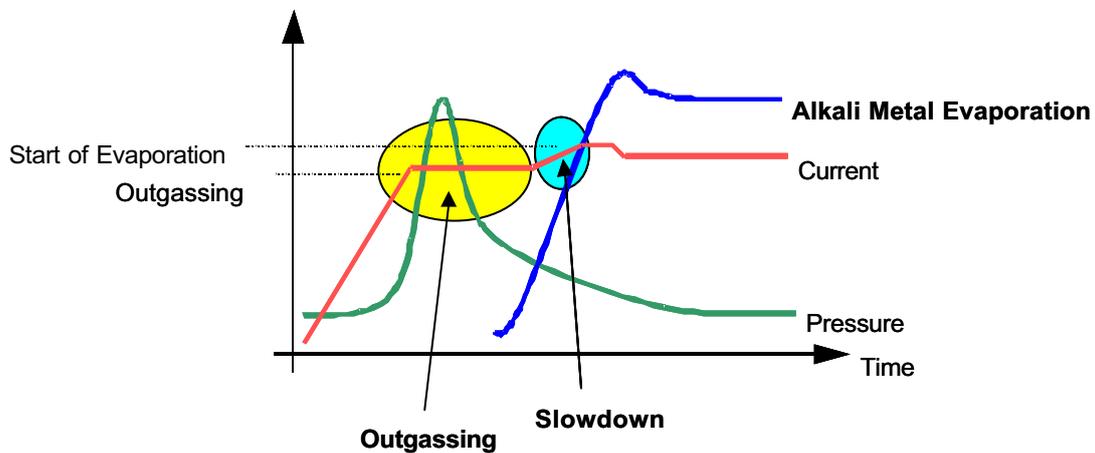


Figure 8(a)

During the outgassing step, AlkaMax is heated via resistive heating to decompose the alkali metal salts and remove residual moisture. For a new dispenser, the current level is specified as the "outgas current". By monitoring the pressure rise in the vacuum chamber, then subsequent decline, the user knows that the dispenser has been "outgassed". When the pressure decreases, the current should be slowly increased to the current shown in the specification as "Start of Evaporation". The current is adjusted slightly down when evaporation begins. During the evaporation, the pressure of the chamber remains very low due to the activated getter, which sorbs the gaseous impurities. The process shown in Figure 8(a) is used each time AlkaMax has been removed from the vacuum chamber.

Figure 8(b) illustrates the process for evaporation when AlkaMax has already been outgassed, and has not been exposed to atmosphere or moisture.

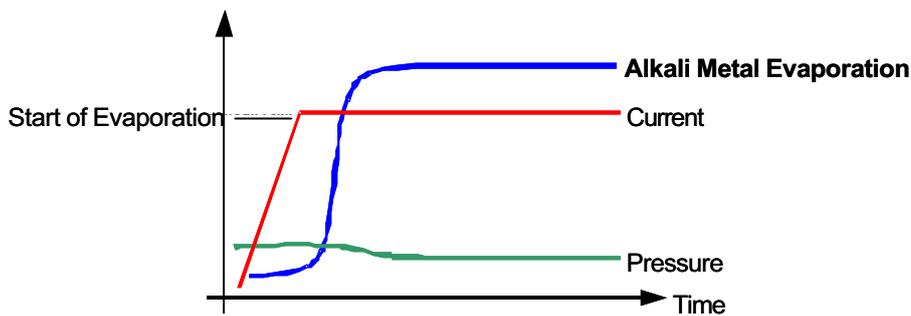


Figure 8(b)

When a dispenser has not been exposed to air after a previous evaporation, it is not necessary to perform the outgassing process. The current can be increased to the current shown in the specification as “Start of Evaporation” to start the deposition. It is important to point out that the current setting should be adjusted during evaporation process in order to maintain the desired deposition rate.

The heating profiles shown are for an ideal case. They must be optimized for each individual deposition system as they can vary depending on operating conditions such as environment during handling, air exposure and chamber configuration.

AlkaMax dispensers are supplied in a sealed metal can filled with dry nitrogen. As long as the can has not been breached or otherwise opened the can may safely be stored until the shelf life has expired. An expiration date is given on the can’s label. After the can is opened, the dispensers should not be left in air for an extended period of time in order to prevent deterioration due to humidity and dust. Air exposure should be as short as is practicable. Store AlkaMax in a vacuum or dry environment, like a desiccator or nitrogen dry box. Dispose of used dispensers according to the instructions in the MSDS.

➤ **Controlling Organic and Alkali metal evaporation during fabrication of AM DOL films**

It is very important to maintain a specific molecular ratio between the alkali metal and organic material in a co-deposition process during AMDOL fabrication. Typically, a quartz-crystal deposition monitor is sufficient for monitoring the evaporation rate of organic compounds. In the case of alkali metals, however, more precise monitoring and process controls are needed.

It is well known that the deposition rate of the organic material is difficult to be maintained at a steady rate. Therefore, the deposition rate of the alkali metal should be adjusted to keep pace with the deposition rate of the organic material. Experimental data (Figure 9, Feedback off) shows that the deposition rate from an AlkaMax dispenser can be quickly controlled. Consequently, the deposition rate of the alkali metal can easily be adjusted to match the fluctuation of the deposition rate of the organic material in order to maintain the targeted molecular ratio.

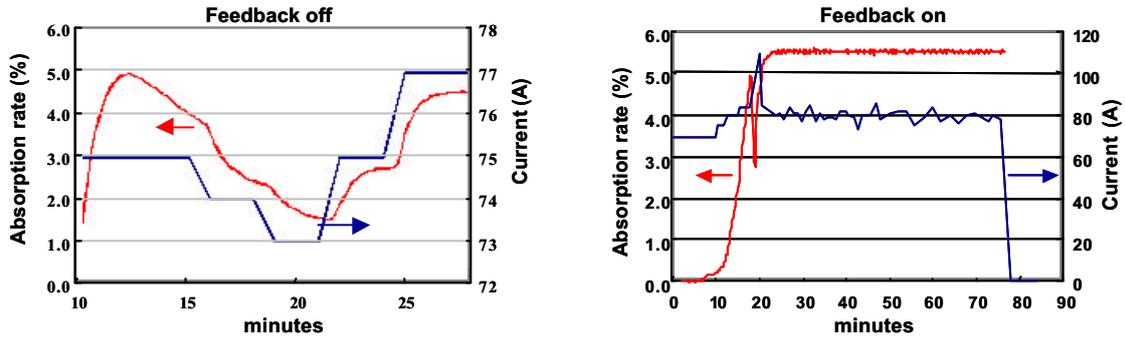


Figure 9 (Courtesy of IMES Co., Ltd; and, R-DEC Co., Ltd)

Alkali metal deposition rates can be monitored using an Atomic Absorption Spectroscopy (AAS) control system with a feedback control loop (Succi, 1985; Maeda, 2002). By selecting a suitable wavelength (for example, 852nm for Cs), the deposition rate of the alkali metal vapor mixed in an organic vapor can be monitored. (Figure 9, Feedback on). Deposition rate is controlled to within $\pm 2\%$ during the 1-hour deposition time. Response time is dependent on AlkaMax size and configuration. The example in Figure 9 represents refers to an AlkaMax dispenser with a 1-gram Cs total yield.

AlkaMax dispensers deposit very uniform alkali metal layers. A deposition test on a 200mm \times 200mm glass substrate is shown in Figure 10. A $\pm 5\%$ uniformity in Cs deposition was achieved without rotating the substrate.

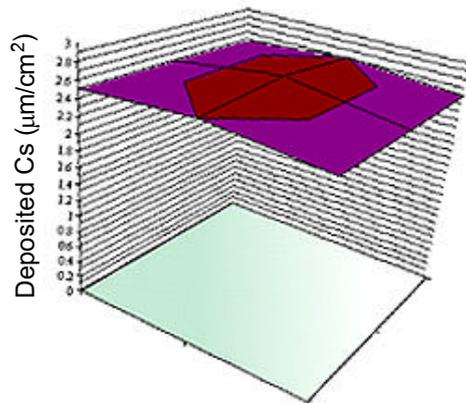


Figure 10 (Courtesy of IMES Co., Ltd; and, R-DEC Co., Ltd)

Products & Prototypes Details

➤ Dispensers for laboratory use

For laboratory use, SAES' traditional line of dispensers with yields in the milligram range is available. Li, Na, K, Rb and Cs are available in small laboratory AMDs. Figure 11, and Table 1 summarize the performance and operating conditions for various alkali metals. When the dispenser is heated with constant current, the quantity of evaporated alkali metal smoothly increases as time goes by. In Figure 12, the yield vs. time curve for Cs dispenser (CS/NF/16/50 FT10+10) is shown for typical operating currents of 6.5A and 7.5A.

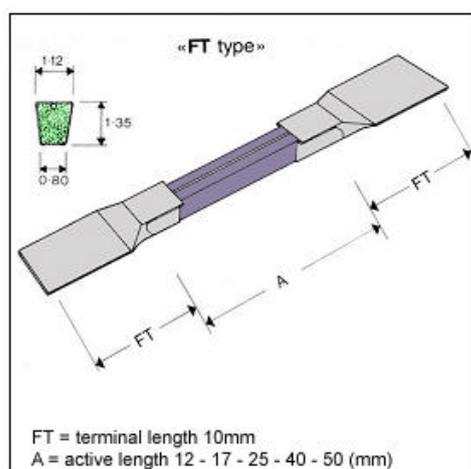


Figure 11

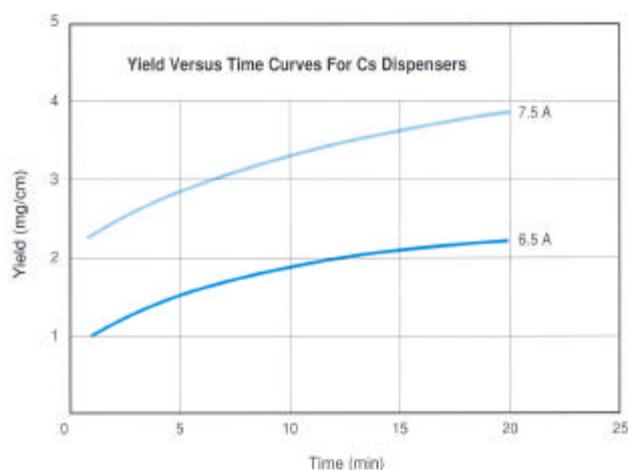


Figure 12

Table I. Specifications for some FT type AMDs

Element	Model	Code	Content (mg)	Outgas Current (A)	Start of evaporation (A)
Li	LI/NF/2.5/50 FT10+10	5G0080	3.5	3.0	7.3 ± 0.2
Na	NA/NF/6/50 FT10+10	5G0105	7.0	3.0	6.0 ± 0.2
K	K/NF/9/50 FT10+10	5G0030	12.0	3.0	5.3 ± 0.2
Rb	RB/NF/14/50 FT10+10	5G0120	18.5	3.0	5.3 ± 0.2
Cs	CS/NF/16/50 FT10+10	5G0040	22.0	3.0	4.7 ± 0.2

➤ **AlkaMax dispensers for OLED mass production**

At present, dispensers with yields of 1g and 10g of Cs are available (Figure 13). These are prototypes and their configurations (dimensions, hole location, etc) may be modified during optimization and industrialization phases.

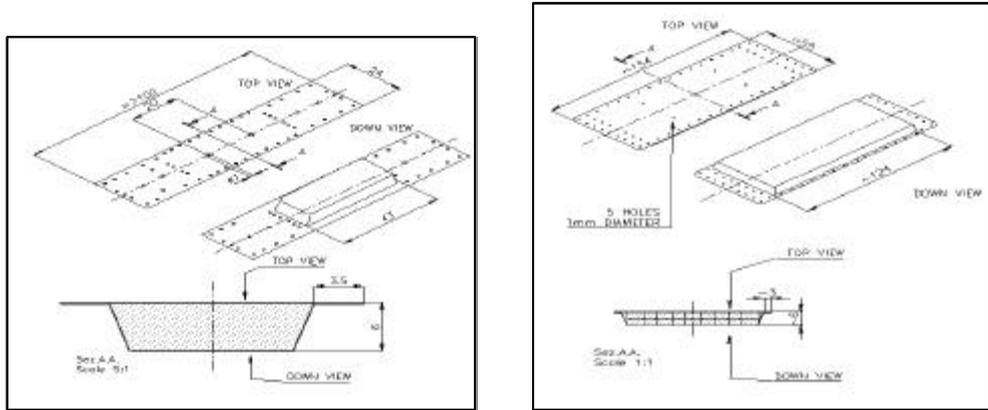


Figure 13

Table II. Specifications of AlkaMax dispensers for Mass Production

Element	Model	Code	Cs Content (mg)	Outgas Current (A)	Start of Evaporation (A)
Cs	CS/BD/MO/100x24x6/1000	4G0021	1,000	45 ± 5	55 ± 10
Cs	CS/BD/MO/154x59x6/10000	4G0022	10,000	75 ± 5	85 ± 15

As with the small AMDs, when the AlkaMax is heated with constant current, the quantity of the evaporated alkali metal increases smoothly as time goes by. In Figure 14, the yield vs. time curve for AlkaMax Cs dispenser (CS/BD/100x24x6/1000) is shown for typical operating currents, 65A and 75A. If the alkali metal dispenser is used many times for different evaporation tests, the operating current may slightly change: it typically increases for subsequent evaporations.

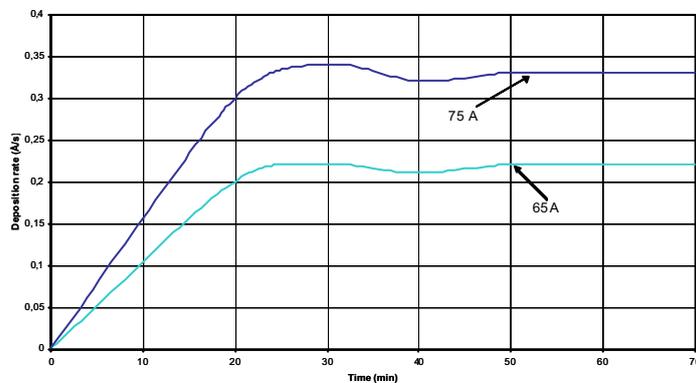


Figure 14

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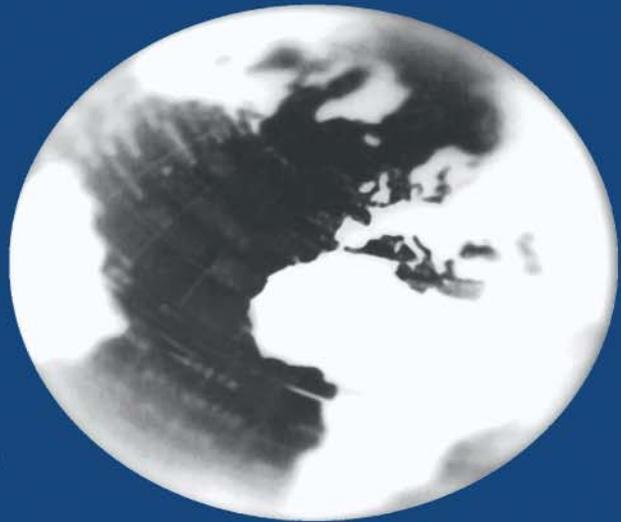
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