7.1 Introduction

Presently available powder EL devices are of two types: (1) AC Powder EL cell and (2) DC Powder EL cell, [1]. The AC powder cells are the earliest and the most common. These are essentially Destriaau type cells which consist of the electroluminescent phosphor suspended in a dielectric sandwiched between two electrodes. An efficient DC powder EL device, which is the subject of discussion in this Chapter was first reported by Vecht et al. [2]. Their results triggered the interest of many workers in this field. Vecht et al. have developed information display panels using ZnS:Cu,Mn [3] and, recently, CaS:Ce [4] phosphors. Yashiyama et al. [5,6] have successfully fabricated a TV display panel based on DC powder technology. Hiroshi Kawarada et al. have fabricated a TV display panel of 50176 picture elements [7]. It is reported that, compared to the AC powder panels, DC devices can be excited to higher (excitation) levels in the pulsed excitation mode thus producing higher brightness level. Cross talk effect is less in this type of panels because of their highly non-linear brightness-voltage characteristics. Moreover, the scanning circuit of these devices will be simpler due to the DC mode of operation. The green emitting CaS:Ce system is
very significant in this context due to its fairly broad band emission ranging from 450 nm to 650 nm, which when used with appropriate filters can produce red, yellow, green and blue displays [4]. So, some attempts were made to fabricate a few such devices using ZnS:Cu,Mn and CaS:Ce. Eventhough the conventional ZnS:Cu,Mn cells have been prepared, no detailed investigations on these devices are presented here, since their characteristics are quite well known [2,8]. This chapter essentially contains the preparation details of a ZnS:Cu,Mn device and of CaS:Ce device together with the results of some investigations made on the latter. In addition a brief outline of the DC powder EL device fabrication technology, the DC forming process and an analysis of the various electrical characteristics of such devices are also given.

7.2 DC powder cell fabrication

The phosphors for the preparation of DC powder EL cells of ZnS:Cu,Mn can be prepared either by the conventional slurring technique or by the simultaneous activation; i.e. by precipitating the phosphor from solution containing appropriate amounts of Cu and Mn. The latter method is found to be more suitable for DCEL cells. This is because the phosphors thus obtained have virtually no particle size distribution unlike those obtained from the slurry technique [9]. Moreover, these samples will have an even spreading of Cu and Mn, which will improve the visual appearance of the
device. The doped samples obtained by (any one of) the above methods were then treated with cuprous or cupric salt solution to form a high conductive skin of \( \text{Cu}_x \text{S} \). The most suitable method found was to treat it with a cupric salt solution rather than with a cuprous salt solution since phosphors obtained from this technique showed better reproducibility. The \( \text{Cu}_x \text{S} \) coating thus obtained is a p-type semiconducting layer. So, a heterojunction will be developed between the doped ZnS and \( \text{Cu}_x \text{S} \) suitable for the formation of high field region for the injection of charge carriers [7].

These \( \text{Cu}_x \text{S} \) coated phosphor particles were then dispersed in a suitable binder with appropriate phosphor-binder ratio. It was then spread on a suitably etched transparent electrode by one of the following methods, viz. silk screen printing, doctor blading or spraying. Because of variation in the thickness of large area glass substrates, doctor blading has been used only for test areas and small display panels. The phosphor-binder mixture is diluted with large volumes of solvents to obtain a solution useful for spraying. Silk screen printing gives controlled thickness layers of high packing density with little waste, provided a suitable binder and solvent mixture to give screen stability can be compounded. It is observed that devices of thickness in range 30-100 \( \mu \text{m} \) have the same electrical characteristics and brightness [3]. The back electrode is usually provided with an evaporated aluminium or with a graphite paint. The binder
is used to hold the phosphor particles in contact with each other and to the glass substrate. It occupies less than 5 percent of the total volume of the layer [9].

7.3 **DC forming of the cell**

Two essential features of any DC EL panel are that the phosphor particles are in contact with each other and with the electrodes. On the initial application of a DC voltage, a high current flows and no light emission is observed. This is because the high conductivity of the phosphor surface and the interparticle contacts precludes any current flow through the ZnS particles themselves. At a critical power density the current falls and light emission appears at the positive electrode. An increase in applied voltage produces a temporary rise in current density but this falls rapidly and the panel brightness increases. This is termed as the 'forming process'. A study of the EL cells with a planar electrode configuration gap cell showed that virtually all the applied voltage appears across the light emitting region. The remaining phosphor retains its high surface conductivity and acts as an extension of the electrode [9]. The forming process does not occur simultaneously over the whole of the panel area but usually begins where the shortest current path exists between the electrodes. This represents the region of highest current density. When forming takes place, the resistance of the phosphor increases and the current density falls. This increases the current
density in adjacent unformed areas and forming will take place at this region. Thus the formed region will spread across the panel area until a complete plane of high resistance phosphor develops between the electrodes. These devices, except when pulsed, are invariably operated at a final forming voltage. The forming process results from the diffusion of copper from the copper sulphide surface coating into the bulk of the zinc sulphide particle. Considerable heating of the panel takes place during the forming process and a phase change in the copper sulphide coating seems to contribute to the development of a high resistance region [10]. Since the EL brightness is field dependent, the localization of the applied field in the formed layer gives an important advantage in these devices. High fields can be generated at relatively small applied voltage provided the applied voltage has reached a value where the current has dropped by an order of magnitude or more. The forming process is irreversible, as the high resistance of the phosphor permanently reduces the power density.

7.4 Structure of a typical cell and its analysis

Figure 7.1 shows the cross sectional view of a typical DCEL powder cell. Details of the fabrication are given by Alder et al. [10]. It consists of a tin oxide coated glass substrate which acts as the positive electrode. The active layer is ~25 μm thick and of area 4 x 7 cm², spread on the transparent electrode. The structure is completed with
Fig. 7.1. Structure of a DCPET cell

Fig. 7.2. Depicts the formed and unformed regions
the rear Al electrode. The whole assembly is then encapsulated with a proper dessicant to exclude water vapour from the atmosphere.

Physically, the phosphor layer in the formed device consists of at least two regions, the formed and the unformed (Fig. 7.2). It has been shown that the unformed layer is quite conducting while the formed region is far more resistive [9].

Abdalla et al. [12] have assumed that a concentric multi-hetero structure exists for each powder particle with the configuration

\[ P-Cu_xS \quad -\quad -\quad n-ZnS:Mn \quad -\quad -\quad p-Cu_xS \quad \ldots (1) \]

where the \( n-ZnS:Mn \) is known to be an insulator. For the assembled device this configuration then becomes,

\[ \text{Anode (ITO) } \sum\{p-Cu_xS \quad -\quad -\quad n-ZnS:Mn \quad -\quad -\quad p-Cu_xS\} \quad \text{Cathode (Al)} \quad \ldots (2) \]

When voltage is applied to the device, a high current defined as the forming current is found to pass through the device. This current has been attributed to the high surface conductivity of \( Cu_xS \) surrounding each powder particle. The current voltage characteristics of the device during the initial forming stage resemble that of pure resistance. The configuration of the luminescing device has been proposed as [13]
Anode-doped ZnS- \( \sum (p-Cu_xS \rightarrow n-ZnS:Mn \rightarrow p-Cu_xS) \)-Cathode ... (3)

Thin luminescing active region

Extended cathode (globally p-type)

which shows that the luminescing device can always be regarded as reverse-biased. The current voltage characteristics of such a luminescing device is similar to that of a leaky diode [13].

Reversal of the device polarity results in another forming process, which is terminated by the appearance of luminescence localized at the new as well as the old anode. The current-voltage characteristics of the device then resemble that of two diodes connected back to back. But the brightness in this case is lower since the applied voltage has to be divided between the two localized regions.

7.4.1 Current voltage characteristics of freshly prepared devices and the conduction mechanism

A freshly prepared device which has not undergone any detailed life tests shows two conduction process. The first one occurs in the voltage range extending approximately to a value corresponding to the emergence of EL while the other at a voltage beyond this value. The logarithm of the current is found to increase in proportion to the square root of the applied electric field in the first range. Such a behaviour can be interpreted as either due to the Poole-Frenkel effect or the Schottky effect [14]. Both effects are characterized
by the reduction of the height of the potential barrier due to the applied electric field. In order to distinguish between these two effects, the current at constant voltage is recorded at different temperatures. It is observed that a plot of the log I versus 1/T is a straight line. This confirms that in this voltage range the conduction process is dominated by Poole-Frenkel effect since the Schottky effect is described by a 1/T² dependence of log I/T [13].

Another type of conduction process occurs at applied voltages beyond the first region. In their studies on reverse biased heterojunction devices, Riben and Fencht [15] showed that the current density can be explained by means of Zener tunnelling model where the current is expressed as

\[ I \propto AV \exp \left( BV - \frac{1}{2} \right) \]

where A and B are constants. In the present case it is observed that in the second range a plot of log I/V versus 1/\sqrt{V} is a straight line which means that such a relationship exists in this region. So it can be assumed that the heterojunction occurs between the thin luminescing active region (n-type) and the extended cathode (globally p-type) region. Furthermore, measurements at different temperatures gives straight lines with almost similar slopes, which is characteristic of the tunnelling process [14]. So, it can be concluded that, in freshly prepared devices, there exists a reverse biased heterojunction, as given by the configuration depicted by equation (3) which is responsible for the conduction mechanism.
7.4.2 Current-voltage characteristic of degraded devices

The degraded device shows ohmic conductivity at lower voltages. At higher voltages space charge limited conductivity (\( \log I \propto V^2 \)) predominates which indicates that the electrical conduction mechanism seems to have undergone modification due to degradation.

7.4.3 The electrical equivalent circuit of the device and the effect of degradation on the circuit parameters

The evaluation of the equivalent circuit consists of applying a unidirectional voltage pulse of amplitude \( V \) and analysing the corresponding current waveform. A typical current waveform for a square wave applied voltage is shown in Fig. 7.3. The instant voltage is applied, current decreases exponentially from a maximum value \( I_o \) to reach a constant value \( I_R \). Therefore, current at any instant \( t \) can be expressed as

\[
i(t) = I_R + (I_o - I_R) \exp\left(-\frac{t}{\tau}\right)
\]

The first term in the above equation can be regarded as due to a resistance of value \( R_p \) given by

\[
R_p = \frac{V}{I_R}
\]

The second term is due to a charging current in a capacitor of value \( C \) in series with a resistance of value \( R_S \) given by

\[
R_S = \frac{V}{(I_o - I_R)}
\]

with a time constant \( T = R_S C \). The equivalent circuit of the device is shown in Fig. 7.4.
Fig. 7.3. Typical current waveform of a DCPEL cell.
In order to study the effect of degradation on the equivalent circuit parameter a plot of the $R_s$, $R_p$ and $C_s$ as a function of time is usually drawn. A typical plot is shown in Fig. 7.4. It is seen that for a fresh device the value of $R_p$ is higher than $R_s$. But when the device is operated for extended periods $R_s$ is found to increase more rapidly than $R_p$ and it even assumes values greater than $R_p$. The value of $C_s$ is found to decrease due to degradation [14]. A detailed analysis of these parameters shows that for DC EL powder devices to operate at reasonable brightness levels for extended periods of time, the $R_s$, $R_p$ and $C$ values must be stabilized. This can be achieved only by stabilizing the thickness of the localized region by keeping Cu ion migration to a minimum.

7.5 Preparation of ZnS:Cu,Mn DCPEL cells

In the present case powder phosphors required for the fabrication of DCPEL cells of ZnS:Cu,Mn were prepared by the slurring technique. For this, a weighed amount of luminescent grade ZnS (BDH Poole, England) was mixed with cupric acetate containing 0.5 wt percent copper and Manganese acetate containing 1 wt percent of Mn. A slurry of the mixture was then prepared in aqueous solution. It was then slowly dried and then fired at 1000°C for 90 minutes at $10^{-2}$ torr, by introducing the phosphors into the high temperature zone of a horizontal furnace. The fired phosphor was then treated with cupric acetate solution containing 2 wt percent copper.
Fig. 7.4(A). Variation of $R_s$, $R_p$ and $C$ as a function of time of operation.

(B). The equivalent circuit.
The treated phosphor was black in colour indicating the formation of black copper sulphide layer on the phosphor particles. The powder thus obtained was then mixed with a polymethyl methacrylate solution prepared in chloroform. The mixture was then agitated ultrasonically by suspending the mixture container in an ultrasonic cleaning tank. This uniformly dispersed the powder particles in the binder.

Phosphor binder mixture thus obtained was spread on a suitably etched transparent conducting electrode. For this a mica mask 100 μm thick with a groove of size 4 x 2 cm² was cut, and placed on the transparent electrode. Then the phosphor mixture was poured in the groove, carefully filling it with a flat glass or metal strip. Then the solvent was allowed to evaporate from the mixture. When the solidification was complete the mask was removed, and a thin phosphor layer embedded in the polymer matrix resulted. The thickness of the layer could be changed by altering the binder solvent ratio. It was observed that a fast evaporation rate of the mixture resulted in a foggy phosphor layer. So the whole preparation procedure was done in an atmosphere which favoured slow evaporation of the solvent. After evaporation of all the solvent the device was introduced into a vacuum chamber and an aluminium metal electrode was deposited as the rear electrode through proper mask. The device thus fabricated is of the type as shown in Fig. 7.1.
7.6 Preparation and study of CaS:Ce DCPEL Cells

The CaS:Ce phosphor used for the fabrication of the cell was prepared by the slurrying technique. For this, to a weighed amount of CaS, 2.5 wt percent of Ce in the form of ammonium ceric sulphate and 5 wt. percent Na$_2$S$_2$O$_5$ was added. A slurry of the mixture was then prepared in aqueous solution. It was then slowly heated and dried. The resulting mass was then crushed and mixed with equal amount of sulphur. The mixture, taken in a quartz test tube with close fitting cap, was introduced into the high temperature zone of a horizontal furnace kept at 1000°C. The firing was done for 90 minutes. This resulted in a pale yellow powder which was then suspended in a cupric acetate solution containing 2.5 wt. percent of copper. The solution was boiled until the phosphor particles turned black in colour. It was then dried and mixed with methyl methacrylate solution prepared in trichloroethylene. The rest of the fabrication procedure was the same as that adopted for the fabrication of ZnS:Cu,Mn cells.

On the first application of the electric field, it is observed that a large current flows through the device. As the voltage is increased, the current increases and after attaining a certain value the current drops with the simultaneous appearance of the EL emission. For a cell of area 0.5 x 2 cm$^2$ this transition occurred at 100 mA. On further increasing the voltage the current increases but levels off again with increase in brightness. The B-V characteristic
of the device measured with a current limiting resistance of 47 K ohm included in the circuit is shown in Fig. 7.5. The brightness wave of the cell under square wave excitation is found to have two brightness peaks, corresponding to the rise and fall of the square pulse. This can be easily understood on the basis of the equivalent circuit as shown in Fig.7.4. Under very low excitation frequency, in addition to the brightness peaks, a flat portion of low amplitude is also observed corresponding to the flat portion of the excitation pulse (Fig.7.6).

Eventhough the cell can be excited to a moderately high brightness level it consists of large bright spots as well as small feeble emitting points. This, evidently, is due to the variation in size of the phosphor particles. Moreover, it is observed that the metal electrode at the back of the most intense spots gets destroyed in course of time. So it is not possible to improve the brightness level beyond a limit. It is felt that the most serious drawback of the cells thus prepared arises from the lack of control of the particle size. Since the performance of the cell was not very satisfactory, no detailed investigation on their electrical characteristics was carried out.

7.7 Conclusion

This chapter consists of a brief discussion of the DC powder electroluminescent devices and their DC forming process. An analysis of the DC electrical
Fig. 7.6. B-V characteristic of the CaS:Ce DCPBL cell drawn (A) with initial reading (B) with readings taken after 30 minutes of continued operation.
Fig. 7.6. The brightness waves of a CaS:Ce DC cell under square wave excitation of different amplitudes.
conductivity is also included. Attempts made to fabricate DC powder cells using ZnS:Cu,Mn and CaS:Ce are outlined. The characteristics of the ZnS:Cu,Mn cells are found to be almost the same as those described extensively in the literature. The CaS:Ce cells prepared are found to be of poor quality mainly due to the lack of control of the particle size. However, some of the results of the investigations made on this new type of cells are presented.

References


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