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Resistivity Network and Structural Model of the Oxide Cathode for CRT Application

Abbass A. Hashim, David S. Barratt, Aseel K. Hassan, Jan H. Evans-Freeman, and Alexei V. Nabok

Abstract—In this paper, the electrical properties of oxide cathode and oxide cathode plus, supplied by LG Philips Displays, have been investigated in relation to different cathode activation regimes and methods. Oxide cathode activation treatment for different durations has been investigated. The formations of the compounds associated to the diffusion of reducing elements (Mg, Al, and W) to the Ni cap surface of oxide cathode were studied by a new suggestion method. Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) was used as analytical techniques.

Al, W, and Mg doping elements take place during heating to 1080 K (Ni-Brightness) under a rich controlled Ba–SrO atmosphere through an acceleration life test. The chemical transport of these elements was occurred mainly by the Ni cap grain boundary mechanism with significant pile-up of Mg compounds. Al and W show a superficial concentrations and distribution.

A new structural and resistivity network model of oxide cathode plus are suggested. The new structural model shows a number of metallic and metallic oxide pathways are exist at the interface or extended through the oxide coating. The effective values of the resistances and the type of the equivalent circuit in the resistivity network model are temperature and activation time dependent.

Index Terms—Ba and Sr oxides, electrical properties, electron emission, oxide cathode.

I. INTRODUCTION

Reducing the cathode coating resistivity by the incorporation of a conductive metallic phase enhances the emission current density. This is the main idea of the current generation of oxide cathode produce by LG Philips Displays component. One of the significant advances in the last few years has involved the work of this company on the development of new compositions for the emissive layer of their oxide cathodes. The oxide cathode comprises a top layer of Ba–SrO mixed with a 5% (oxide cathode) or 2.5% (oxide cathode plus) Ni powder cermet with surface area of 0.0165 cm² and layer thickness of approximately (65 ± 10) μm deposited onto a Nickel alloy cap [1]–[3]. This Ni cap contains low levels of W (2.98%), Mg (0.125%) and Al (0.1%) as activators in addition to small amounts of yttrium, zirconium, and iron.

Two different methods have been used to study the electrical properties and the formation of the interface layer. A special dummy tube was designed for this purpose. Numerous theories have been used for the conduction mechanisms of oxide cathodes in terms of the electron percolation and MS junction [4]. Scanning electron microscopy (SEM) and X-ray spectroscopy (EDX) analysis of oxide cathode samples with different treatments have been performed. SEM micrographic images give evidence that the conductivity is cathode type dependent ("S" or "N" types). EDX analysis proved that the conductivity is dependent on the amount of the Ba contaminant in the oxide layer. The analysis showed the penetration of the activators through the oxide, specifically the Al agents.

II. EXPERIMENTAL DETAILS

The Loosjes and Vink procedure was applied to measure the cathodes’ conductivity [5]. The cathode assemblies were mounted, face to face in pairs in a specially designed holder inside a glass chamber under vacuum of about 3 × 10⁻⁷ mbar [6]. A set of cathodes were activated at 1425 K, 1200 K, and 1125 K for different periods of time between 1 hour and 12 hours and the two oxide layers were combined to form a single layer with thickness of approximately 120 ± 10 μm as a result of conversion and activation processes.

Another set of two cathodes were used in a new method to investigate the interstitial growth of the interface layer. One of the cathode is a normal oxide coated cathode plus and the other is an uncoated cathode plus [4]. The two cathodes were assembled, face to face with an attach-contact between them. The entire assembly, as shown in Fig. 1, was mounted inside a dummy tube which was evacuated prior to and during the decomposition and activation process.

The dummy tube was sealed under vacuum of about 10⁻⁶ mbar. The filament temperature of the uncoated cathode was elevated to the accelerated temperature of 1080 K and
operated for different lifetime up to 1896 h (real-time \( \sim 14\,200 \) h) [4].

III. RESULT AND DISCUSSION

A. Electrical Measurement and Conduction Properties

Current-voltage characteristics of face to face cathodes in vacuum chamber were measured in the temperature range between (300–1200) K [1].

In Fig. 2(a), the dc conductivity of the 5% Ni cathode is found to be increase when sufficient oxide thickness is accelerated for 100 h in the temperature range 825–500 K [7]. This can be only understood by visualizing the \( \text{WO}_3 \) layer to provide a conduction path which is in parallel with the existing electrons conduction paths in the oxide. The specific resistivity of \( \text{WO}_3 \) is increased by two orders of magnitude from \( 10^{-10} \) to \( 10^{-8} \), when the oxygen concentration is increased from 5% to 30% [8], [9].

This specific resistivity is also decrease in other manners like temperature elevation. This seems to have happened at the interface layer of hot cathodes at the acceleration temperature due to the fact that the Debye temperature of the barium oxide is quite low \( (\theta_D(\text{BaO}) = 525 \) K) [10]. Therefore, the increase can be explained by the lowering of the total cathode resistance as the conductivity of \( \text{WO}_3 \) increases by two orders of magnitude giving activation energy of 1.05 eV and the system becomes more conductive at temperature range 500–625 K [11]. This activation energy is slightly larger than 0.77 and 0.84 eV for amorphous and crystalline tungsten oxide, respectively [8].

On the other hand, we think that there is an influence of \( \text{Al}_2\text{O}_3 \) resistance on the oxide cathode network. The resistance of \( \text{Al}_2\text{O}_3 \) decreases from \( 10^{12} \) to \( 10^9 \) when the temperature is increased from (670–825) K [12]. Thus, the activation energy of 1.05 eV observed in Fig. 2(a) at the temperature ranges 690–825 K may be described in terms of the effect of the aluminum resistance on the resistivity network.
Approximately same activation energy value ($E_a \approx 1$ eV) is observed again at the operation temperature range of (950–1050) K. This conduction can be interpreted in term of the surface conduction via Ba on BaO monolayer [6], [7]. The accumulation of the Ba as an effective layer is a result of the long operation time of this semi-closed system [7]. These adsorbed layers on the Ba–SrO grain surfaces inserted another resistance to the resistivity network of the oxide cathode. This resistance is most likely to be in parallel [1]. The effect of the Ba layers on the oxide conductivity can be viewed at low temperature range (300–600) K and high temperature range (1000–1200) K very clearly after several hundreds hours of operation, as shown in Fig. 2(b) [1]. At the high temperature range, the pores contribution was disappeared due to the effect of the Ba multi-layers contamination [13].

Fig. 3 shows the conductivity follows the resistivity network in the oxide cathode plus (2.5% Ni powder). This network is changed due to the equivalent circuit (series or parallel type) between the resistance contents of the oxide cathode. The effective values of these resistances and the type of the equivalent circuit are temperature and activation time dependent. The figure shows, precisely, that the activation of the cathode for 12 h at 1200 K results in the formation of Ba metallic pathways, which percolate through the oxide and cause a decrease in the pores conductivity contribution. This is exactly what has happened in Fig. 2(b) after accelerating the (5% Ni powder) oxide cathode to 200 h. However, the activation of the cathode for the same duration at lower temperature (1125 K) caused a conduction path which is in series with the existing electrons conduction paths (grain-grain) in the oxide. The electron is prompted to pass to the pores (electron gas) at the threshold temperature of 600 K [5].

The metallic pathways increased the conductivity about 4 orders of magnitude at the RT range when the activation temperature was elevated from 1125–1200 K, whereas the high activation temperature (1425 K) shows a limited effect for the contaminated Ba on the oxide conductivity at the temperature range (300–450) K. It also shows a clear pores conductivity contribution at high operation temperature (1000–1300) K.

The conductivity and the activation energy characteristics are strongly dependent on the life test condition. The conductivity of an activated (Ba,Sr)O coating is reported to be of the order of $10^{-2}$(Ω cm)$^{-1}$ [14], but the value for the new cermet oxide cathode plus with 2.5% Ni powder addition is increased to $10^{-2}$(Ω cm)$^{-1}$ at the operating temperature [15].

Fig. 4 shows the dc electrical characteristic which indicates very strong rectifying behavior through the M-S junction particularly after 144 h lifetime inside a dummy tube test [4], [16].

The coated-uncoated cathode assembly in a dummy tube showed reversible and reproducible characteristics and showed a rectification ratio ($r$) of 100. The ideality factor was calculated to gives a consistent value of about ($n \approx 9.6$) [4]. The higher value of $n$ ascribed to the tunnelling in the junction area as a result of the increasing in the electron space charge (thermionic emission) and the increasing in the Schottky effect [17], [18]. This approves the formation of the interface layer in between the oxide coating and the Ni cap. The interface layer thickness grows to 6 µm after accelerating the cathode to 1896 h (real time ~14 200 h) [4]. The 6-µm value seems to be an effective thickness which may increase the reduction reaction area between the Ni surface cap activators and the oxide grains. Such a high value of the interface layer thickness indicates a nonuniform shape of interfacial layer. However, it may also prove that the interface layer grows inside the Ni cap grain boundaries and penetrates in between oxide grains [4], [19]. It may be explained in term of the influence of the interface layer in the pores space between the grain boundaries, as shown in Fig. 5.

### B. Morphological and Elemental Analysis

1) Cathode Activated in a Glass Chamber: The cathode that decomposed and activated under this condition (with enough
compression between the two attached cathodes and a very high temperature) is most likely to be an “S” type cathode [1]. This cathode always has low emission, and the oxide particles are considered to be sintered and have short grain-to-grain boundaries, and the very low contact potential barrier [11]. It can be assumed that the semiconductor-type conduction through the grains will be predominant in the “S” type cathode [11]. The morphological analysis shows that the oxide became more sintered, the grain size increased from approximately 6 μm to 10 μm after twelve hours of activation at 1200 K activation temperature. It is also apparent that the porosity decreased with the increasing of the activation time.

In such case, the EDX analysis for the Ni cap surface shows that tungsten was the first element to diffuse through the Ni boundary grains, forming one of the tungsten oxide compositions [15]. The presence of Al was observed in an appreciable quantity after 3 h of activation at 1200 K. The decrease in the Al on the Ni cap surface is followed the cathode activation for more than two hours at 1425 K. This observation indicates that the Al left the interface and transported through the oxide layer. Fig. 6 shows the Al proportion quantities on the Ni cap for different period of activation time and temperature. Obviously, for the time period of 4–12 h at the activation temperatures 1125 and 1200 K, the Al proportion values are most likely to be temperature independent. The reality is that the Al diffusion depended on temperature and time when the cathode activated to 1425 K. The behavior may be taken as a strong evidence of the percolation of the Al through the oxide. These atoms can reduce the oxygen from the oxide grains directly and causes a Ba adsorption layer on the grain surface. The evidence for this description is the Al element which was found to be distributed on the surface of the oxide layer [15], [20], [21].

After a long time of activation of about 12 h at 1200 K. These particles are believed to remain in their respective oxide forms (e.g., Al₂O₃ for Al and MgO for Mg) distributed on the surface of the capac, concentrated in the Ni grain boundaries. Mg may also be present in the MgAl₂O₄ form [19].

The sintering ratio, the oxide grain size, and the pores density are activation temperature dependent, as clearly shown in Fig. 7. The grouping ratio (oxide grains grouped together) in the oxide material activated at 1425 K is more than the sintering ratio. The figure shows also the differences in the coarsening of the Ni additives phase between the Ba/SrO grains due to the activation temperature.

2) Cathode Activated in a Dummy Tube: The dummy tube morphological analysis shows the following:

- X-ray spectrum indicates some Al and Zr elements are diffused on the surface of the oxide.
- Mg was found to be diffused on the Ni cap surface initially very clearly, as shown in Fig. 8. Actually, this is in opposition with the EDX and SEM results for the cathode activated in a vacuum chamber to 1200 K [15].
Fig. 6. Al activator element EDX analysis distributed on the Ni cap surface through period of time and activation in a vacuum chamber test. (Color version available online at http://ieeexplore.ieee.org.)

Fig. 7. SEM images for oxide cathode activated in a vacuum chamber (a) the surface of the oxide, (b) the distribution of the Al on the same location. (Color version available online at http://ieeexplore.ieee.org.)
These results can be accepted if it is supposed that the Mg was initially diffused to the surface then transported through the oxide quickly but with a very short path. This is explained the disappearance of the Mg from the Ni cap surface images and EDX test (Section III-B-1).

C. New Structural Model

By highlighting some points from the previous literature results, using the conclusions above, it help to build a new network model for the new generation of oxide cathode. The highlighted points can be summarized as follows.

- According to the Looose and Vink experiments in the oxide coating, there is a dependence on temperature given by [5]

\[
\sigma = \sigma_{\text{oxide}} + \sigma_{\text{pore}} + \sigma_{\text{metallic}} = A \exp \left( \frac{E_o}{kT} \right) + B \exp \left( \frac{E_p}{kT} \right) + C \exp \left( \frac{E_m}{kT} \right)
\]

where \( E_o \) is the oxide activation energy, \( E_p \), the pore activation energy and \( E_m \), the metallic pathway activation energy.

If these mechanisms are connected parallel to each other the resultant conductivity will be at every temperature determined mainly by the mechanism with the highest conductivity. The resultant conductivity is in that case, the sum of the conductivities of the separate mechanisms.

- In oxide-coated cathodes, Dearmaley proposed that the presence of reducing agents at the activation temperature results in the removal of some oxygen from the coating [10]. At certain favorable points on the metal-oxide interface the oxygen may locally become conducting, perhaps owing to an aggregation of oxygen vacancies, which may occur particularly at grain boundaries in the polycrystalline structure. If an electric field is applied during activation the filament will then tend to grow through the oxide coating.

The far heavier barium atoms are remaining relatively undisturbed. In the conducting chain created by a high concentration of oxygen vacancies and terminating at the metal base, the applied field will cause a very large electric stress at the other end, extending as it does into the insulating oxide. Under such a stress, and at the activation temperature, Dearmaley supposed that further oxygen vacancies migrate to this tip and cause it to grow until the chain penetrates the oxide layer. The increased conductivity of the layer will eventually reduce the electric field and filament growth will come to an end [10].

The conclusion taken from the experimental results covered by these specific theories may lead to a dependent model, which is build up in the structure of the oxide cathode through the activation and operation process (acceleration). By the effect of the electrical field, the free oxygen formed a filament chain percolated in the oxide layer and ended at the Ni cap surface and oxide top layer.

At the high operation and activation temperature, the activators such as Al, W, and Mg move to the Ni cap surface. These activators reach the oxygen filament depending on their reaction-reduction activities to be oxidized. The high oxygen concentration prompts these elements to follow the high concentration points. Because of that, the activators moved away from the Ni cap surface and transport through the oxide layer creating different kinds of oxides filaments. This is also the reason for the existence of the Al or Zr on the top surface of the Ba–SrO. Free Ba atoms and oxygen vacancies move to the grain surface cre-
ating conduction or emission electron and an adsorbed mono-
layer or multilayer of Ba.

All these processes form thermal resistances which are con-
ected with each other in a complicated way. It is believed that
the conductivity changes occurring during the activation process
can be attributed to this structural rearrangement. The coars-
ening of the Ni phase between the Ba–SrO grains and in between
these activator oxides make a short pathway for the electron to
transport in between. The electron follows the lower resistance
and reduces the number of continuous electronic pathways.

Fig. 9 shows this new model taking into account all these
processes which were shown in the experimental results of this
study. This model shows a number of metallic and metallic
oxide pathways are exist at the interface or extended through the
oxide coating. The experimental results proved few facts which
can be summarized as follows.

1) Aluminum and zirconium oxide filaments have started
from few microns inside the Ni cap grain boundaries [22]
and percolated the oxide coating reaching the top surface.
2) Tungsten and magnesium oxides filaments have also
started from few microns inside the Ni cap [22] and per-
colated the oxide coating with short pathways. We have
no idea how many microns are these filaments long.
3) The mono or multilayers containing free Ba and Ni coars-
ening powder provided the lowest resistivities pathways
which may act as conductive links between the grains of
the main oxide material.

IV. CONCLUSION

The resistivity network of the oxide cathode and the structure
are changed due to number of factors. The most important fac-
tors are activation temperature, operation, or acceleration tem-
perature and time. These factors are controlled by the activa-
tors (Al, W, ...) movement and distribution through the oxide
coating and leads to changed the resistivity network or conduc-
tivity pathways map of oxide coating.

The experimental result indicates that the Al left the interface
and transported through the oxide layer and aluminum oxide
concentrated in some bright points on the top surface of the
oxide cathode. This observation was interpreted depend on
Dearnaley filament theory, where the Al follows the oxygen
filament ended inside the Ni cap to the top of the oxide material.
This novel phenomenon was proved by the X-ray spectrum,
which indicates some Al and Zr elements are diffused on the
surface of the oxide. The Mg is initially diffused to the surface
then transport through the oxide quickly but with a very short
path and this seems has happened with the other elements like
tungsten.

These activators reduces the oxygen from the oxide grains
directly causing a Ba adsorption layer on the Ba–SrO grain sur-
faced, and inserts another resistance to the resistivity network
of the oxide cathode. All these filaments were taken into account
to build a new oxide cathode structural model. This model jus-
tifies the main concept of this work.

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