Oxide cathodes
The effect of the coating-core interface on conductivity and emission


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In an oxide cathode a coating of Ba/Sr oxide is applied to a base consisting of nickel which may contain magnesium or aluminium. It is found that a potential barrier occurs at the interface leading to a rectifier action. This restricts the current flow when electrons pass from metal to coating. It is shown that in a well-aged and well-activated coating it is this restriction which determines not only the conduction current in the coating, but also the thermionic emission which can be drawn from it. The fact that the volt drop in the coating occurs primarily across a layer of thickness less than $10^{-4}$ cm, has important consequences as regards breakdown and the shape of the characteristic beyond saturation. The rapid decay of emission immediately following application of anode voltage is also to be associated with the barrier.

1. Introduction

A considerable amount of work has been done in the past on the electrical conductivity of oxide cathode coatings. A summary of earlier work was given by Blewett (1939a). The subject has become especially important more recently as attempts have been made to increase the current density drawn from these cathodes. High current density is necessary in space-charge control types of valve in order to achieve very high frequency operation (Bell, Gavin, James & Warren 1946). The highest current density which can be drawn from oxide coated cathodes continuously is at present of the order of 0.5 amp./cm.$^2$. When pulsed currents of a few microseconds’ duration are drawn, current densities of the order 5 to 10 amp./cm.$^2$ are typical, though higher values have been obtained experimentally under good conditions. In both cases, the limitation is frequently due to the establishment of conditions where arcing occurs between cathode and anode, rather than saturation of the emission. In pulsed operation the onset of arcing and the departure from space-charge limitation both occur at higher current density than in continuous operation. In the cavity magnetron used under pulsed conditions, the current density required is of the order of 10 amp./cm.$^2$ in designs for use at a wave-length of 10 cm., but may be three times as great in a magnetron for use at 3 cm. (Fisk, Hagstrum & Hartman 1946). In the magnetron the current from the cathode is enhanced by secondary emission, consequently the total current available remains space-charge limited to higher values than in the corresponding diode. The limitation to increase in power occurs almost invariably as a result of arcing rather than limitation of emission. This effect has led to considerable difficulties...
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in the development of the 3 cm. magnetron in view of the high current density required (Fisk et al. 1946; Griffiths 1946; Willshaw, Stainsby, Balls, Rushforth, Latham & King 1946). The arcing is a complicated phenomenon, but undoubtedly coating resistance is one important factor. In order to assist in achieving high current density operation, further study of coating resistance appeared desirable.

A particular point of interest is the question whether Ohm's law is obeyed, and whether the voltage gradient is uniform through the coating. The work of Becker and collaborators (Becker 1931; Becker & Sears 1931) indicated that this was the case. The work of Reimann and collaborators (Reimann & Murgoci 1930; Reimann & Treloar 1931), on the other hand, showed departures from Ohm's law, and indicated that an important part of the potential drop occurred across a potential barrier at an interface between metal and coating.

It appeared to the writer that some of the features of the behaviour of cathodes at high current density might be explained by the presence of such a potential barrier. Accordingly, measurements have been made on modern coatings in order to determine the shape of the current-voltage characteristic, and thereby to obtain information concerning interface effects. In addition, the theory of such barrier layers has been considerably modified since Reimann's results were obtained, and it is necessary to consider the later theories of the contact between a metal and a semi-conductor. The experiments have been carried out under continuous current conditions at low current density, and have been confined to the case of typical barium/strontium oxide coatings on a base of nickel containing magnesium. It is deduced from the results in the earlier part of the paper that an interface barrier layer is frequently present, and the general effects of such a layer when high current densities are drawn are discussed in the later part of the paper. It is found also that the interface is associated with the decay effects in emission and conduction currents. It is clear that the barrier layer will be greatly influenced by the composition of the base metal, and perhaps by the composition and physical properties of the coating. The effect of these details on high current density performance is under investigation.

2. Conduction and emission

In the practical case, electrons are drawn from a metal, through the coating, and through the vacuum to an anode. It is clear at once that certain types of mechanism governing current flow may affect both conduction current in the coating and thermionic emission from it. Thus Reimann observed a saturation of conduction current when two electrodes were used to apply a voltage across a coating, and there was a correspondence between this saturated current and the saturated thermionic emission current. Thus a common governing factor was postulated. The results of conduction-current measurements have therefore an important application to the theory of the mechanism of emission. The emission theory developed by Becker was essentially different from that of Reimann.
3. Earlier theory

In order to explain the characteristics for conduction current which he observed, Reimann (1934) used the Fowler-Wilson (1932) theory of passage of current through rectifying contacts. Now this theory supposes that at an interface between metal and semi-conductor, a potential barrier exists which electrons can penetrate by tunnel effect. If the conditions are such that rectification can occur, the difficult direction of flow for electrons is from semi-conductor to metal. Thus a condition for limitation of flow leading to a saturation effect can be present at the outgoing boundary from the semi-conductor to metal. Now while this theory could explain the limitation observed in conduction current, in the case of thermionic current the outgoing boundary is replaced by the vacuum between coating and anode. It is unlikely that this arrangement of semi-conductor surface, vacuum, and anode should behave in the same way as the barrier between the semi-conductor and an electrode in contact with it. Thus the observed correspondence between saturation of conduction current and of thermionic current has no simple explanation on this theory.

It was shown later, however, that rectification usually occurs in the opposite direction to that predicted by the Fowler-Wilson theory. That is, the difficult direction of flow for electrons is from metal to semi-conductor when the semi-conduct is of the excess type. This is the case for barium oxide. Thus a limitation of current can be imposed by the interface where electrons pass from metal to semi-conductor, and this interface is common to both cases, whether the current is conduction current drawn to another electrode in the coating, or thermionic emission drawn to an anode outside the coating. Thus it is reasonable to expect that under some conditions both conduction current and thermionic emission may be limited by the effect of this interface, causing saturation at corresponding values. This would explain Reimann’s observations.

4. Later theory

The rectification observed at boundaries between metal and semi-conductor has been the subject of later theories which do predict the correct direction of the limited current. Schottky (1939) has shown that in the absence of any intervening layer of different composition, there will be a potential barrier at the boundary due to the space charge created when equilibrium is established between metal and semi-conductor. The height of this barrier is φ, the difference between the work functions of the metal and semi-conductor, and its width is

\[ x = \sqrt{\frac{K\phi}{2\pi N \varepsilon^2}} \tag{1} \]

where \( K \) is the dielectric constant of the semi-conductor, \( N \) is the number per c.c. of impurity centres, and \( \varepsilon \) is the electronic charge (Mott & Gurney 1940, p. 174).
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In many cases \( x \) is so large that negligible tunnel effect penetration is possible, and the only flow is that of electrons with sufficient energy to overcome the barrier of height \( \phi \).

Mott (1939) has shown that if an insulating interface layer is formed between the metal and semi-conductor, this will also lead to a barrier of height \( \phi \), though its width is nearly that of the insulating layer. Such a barrier can again only be passed by electrons with sufficient energy, and in both cases flow of this type leads to a limitation of electron current from metal to semi-conductor.

The complete expression for current flow derived by Mott is

\[
i = e v \left( \frac{\phi - V}{d} \right) \left[ 1 - e^{eV/kT} \right] B e^{-e\phi/kT}.
\]

Here \( v \) is the electron mobility in the insulating layer, \( d \) is the width of this layer, \( V \) is the applied voltage across the layer, and \( B \) is the term \( \frac{2(2\pi m kT)^{\frac{3}{2}}}{h^3} \).

For the direction of difficult flow, \( V \) takes negative values in this formula. Thus current should increase rapidly with voltage provided \( eV \) is less than \( kT \). When \( eV \) exceeds \( kT \) the square bracket approaches unity, so that there is a ‘knee’ in the curve, after which current varies linearly with voltage. Extrapolation of the plot when it becomes linear should give an intercept on the voltage axis equal to \( -\phi \). The slope of the linear part of the plot will vary with temperature primarily in accordance with the term \( e^{-e\phi/kT} \); thus a resistance defined from this slope has activation energy equal to \( \phi \). This energy is greater than is typical for the activation energy of the resistance of semi-conductors. When \( V \) becomes sufficiently great, the Schottky effect and later field emission will increase the current above the linear plot. Thus the resistance of the barrier will finally become so small that the effective resistance is that of the semi-conductor itself, unless dielectric breakdown occurs in the barrier leading to disruption of the semi-conductor.

This type of characteristic was observed by Reimann for the conduction current between electrodes in oxide coatings, and also for thermionic emission from a coating.

The theory in the case of a barrier of the Schottky type has been developed in particular by Davydov (1939, 1941). The shape of the characteristic deduced is similar to that found by Mott, except that above the ‘knee’, current varies with the square root of applied voltage.

5. Experimental arrangement

In order to examine the behaviour of modern coatings in the light of the above theory, tests were made using a method similar to that of Becker & Sears (1931). A cylindrical cathode of nickel containing 0·07 to 0·15 % Mg* was coated over a length 12 mm. with oxide coating by spraying on a mixture in equimolecular

* For footnote see p. 398.
proportions of barium and strontium carbonates. After spraying to a depth of the
order 0·05 mm. the depth was determined, and five turns of 0·03 mm. diameter wire
were wound over the coating surface. This wire consisted of nickel with 0·4 % of Al.*
Further coating was then sprayed on to give a total coating thickness of about
0·1 mm. This thickness was measured. The cathode diameter was 1·7 mm., and the
coated area 0·65 cm.². The projected area of the spiral winding on the cathode was
0·01 cm.². The difference between this arrangement and that of Becker & Sears lay
in the high ratio of 65 to 1 between these two areas—in their arrangement more
turns of wire were employed so that the electrodes were more nearly symmetrical.
The cathode was mounted inside a cylindrical bright nickel anode giving an anode
to coating surface clearance of 0·5 mm.

6. Coatings used

Two types of coating were tested, coating (i) was a mixture of barium and
strontium carbonate of commercial origin, particle size in the range 1 to 3μ, and
coating (ii) was a double carbonate formed by precipitation from the nitrate with
ammonium carbonate. (ii) had a larger particle size, in the range 10 to 15μ.

7. Pumping and Ageing

The diodes were pumped on a mercury in glass diffusion pump with liquid air
trap. The following treatment was given in high vacuum:
Bake 400° C 10 min.
Anode and getter outgas. Anode temp. about 850° C for 45 sec.
Cathode outgas. Cathode temp. about 1050° C for 1 min.
Anode outgas at 950° C with cathode at 1050° C, disperse getter 5 sec.
Seal off.
The anode temperature was raised by eddy-current heating. An ageing treatment
followed the seal off:
Heat cathode to about 1100° C for 1 min.
With cathode at 950° C, apply 20 V d.c. to anode.
This gave an anode current of the order of 200 mA. All diodes had this run for
at least 20 min. before any measurements were made. The results recorded below
followed long runs under this condition, as listed in § 8.

* The specification of the nickel was:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0·07 to 0·15%</td>
</tr>
<tr>
<td>Co</td>
<td>&lt;0·5%</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0·15%</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0·2%</td>
</tr>
<tr>
<td>Si</td>
<td>&lt;0·1%</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0·1%</td>
</tr>
<tr>
<td>S</td>
<td>&lt;0·005%</td>
</tr>
</tbody>
</table>

Spiral wire Ni: Al 0·4 % (Al 99 % pure).
C, Fe, Cu of the order 0·05 %.
Si and S of the order 0·005 %.
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8. Diode details

Six diodes were investigated in detail. The spiral-core clearance and total time of ageing run with cathode at 950°C and 20 V on the anode are listed:

<table>
<thead>
<tr>
<th>tube number</th>
<th>coating</th>
<th>spiral-core clearance (mm.)</th>
<th>coating thickness (mm.)</th>
<th>time of ageing run (min.)</th>
<th>emission (amp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B13</td>
<td>(i)</td>
<td>0.05</td>
<td>0.10</td>
<td>260</td>
<td>15.2</td>
</tr>
<tr>
<td>B21</td>
<td>(i)</td>
<td>0.09</td>
<td>0.11</td>
<td>260</td>
<td>25.0</td>
</tr>
<tr>
<td>C21</td>
<td>(i)</td>
<td>0.06</td>
<td>0.10</td>
<td>950</td>
<td>5.6</td>
</tr>
<tr>
<td>A9</td>
<td>(ii)</td>
<td>0.06</td>
<td>0.10</td>
<td>180</td>
<td>12.8</td>
</tr>
<tr>
<td>A20</td>
<td>(ii)</td>
<td>0.09</td>
<td>0.11</td>
<td>180</td>
<td>7.6</td>
</tr>
<tr>
<td>A17</td>
<td>(ii)</td>
<td>0.09</td>
<td>0.11</td>
<td>180</td>
<td>7.6</td>
</tr>
</tbody>
</table>

The last column headed emission gives the peak emission measured on a 2 μsec pulse with the cathode at 730°C, the measurement being made after the ageing time quoted. The emission was approximately saturated, i.e. values are a little above the 'knee' of the amps-volt plot. These measurements show that the cathodes were in good condition from the emission point of view, the values being higher than typical for commercial tubes, but normal for simple diodes and good pumping conditions. The observed spread is also typical.

9. Experimental procedure

Three types of experiment could be carried out using the diodes described:

1. It was possible to apply a voltage between spiral and cathode core, and to draw conduction current through the coating in either direction. The anode was left floating in these measurements.

2. It was possible to use the spiral as cathode, and draw thermionic emission to the diode anode. In this case the cathode core was floating.

3. The tube could be used as a normal diode, applying a positive anode potential and drawing thermionic emission using the cathode core as cathode. The spiral was used as a probe, indicating the potential at a depth in the coating determined by the spiral-cathode core spacing.

The measurements were made on d.c. so that it was necessary to limit the range of voltage and current explored in order to avoid heating effects. For this reason most of the detailed measurements were made at temperatures lower than normal operating temperatures. The potential of the probe in experiment (3) was determined using an electrometer triode.

In all the tubes and in all three types of experiment it was found that as current was increased, a stage was reached where current changed with time after application of voltage. The normal procedure in all experiments was therefore to pre-set the voltage required, apply it to the electrode and observe the current-time variation at constant voltage until the current was substantially stable. The current in all cases decreased with time, most of the decrease occurring in the first 15 to 30 sec.
after applying the voltage. The current continued to decay slowly in most cases, but after 3 min. the rate of fall was very slow; 3 min. was therefore the usual length of run with voltage on. After this run, the voltage was removed and an off-period allowed for recovery before applying a different voltage. The recovery was almost complete in 15 to 30 sec., but again 3 min. was the normal time allowed. After this time, if the previous voltage was applied, the current behaved as in the previous run.

When the initial rate of fall was not too rapid, it was possible to extrapolate back to zero time and so determine a zero-time current-voltage characteristic. The values of current which were reached after 3 min. decay defined a steady-state characteristic, which could be explored over a greater range than the zero-time characteristic. At sufficiently high currents heating effects appeared; thus after switching on the voltage, the current fell for a few seconds and then began to rise. It was found to be generally true that after establishing the steady state at a chosen current density, the voltage could be varied over a considerable range causing changes in current which did not show further time effects. There was the upper limit at which heating appeared, and a lower limit below which recovery occurred tending to re-establish the zero-time state, but over the range between there were no further changes with time on altering the current after establishing the steady state at a particular current. This was true accurately in the case of the conduction current measurements; in the case of the emission current there were small changes in the steady state after altering the current density owing to small changes in temperature. These were the results of a rebalancing of the cooling due to electron evaporation and the heating due to $i^2R$ loss. They were small compared with the total decay between the zero time and steady state.

It was noted that an e.m.f. was always present between spiral and cathode core. This was due primarily to temperature difference. The potentials of the spiral measured in experiments of type (3) were the changes in potential produced by the current flow, taking as zero the potential with zero-anode voltage and therefore zero current. In experiments of type (1) on conduction current there was a current flow if the circuit was closed with zero applied potential. The characteristics of current against voltage were plotted, taking as the voltage zero the voltage at which zero current flowed. The voltage necessary to give zero current varied from 0.1 to 0.4 V according to temperature.

10. **Conduction current between spiral and cathode core**

Figure 1 shows current-voltage characteristics using d.c. for several of the tubes over a range of temperature, including in some cases the typical operating temperature of 730° C. The plots cover the range of voltage and current where the current was either stable with time or where the change with time was so slow that zero-time readings could be accurately estimated. It will be noted that the characteristics of the tubes differ in detail, but are in agreement in showing departures from Ohm’s law. There is a lack of symmetry about the origin, and most of the plots are not
linear. Tubes A9 and B21 show a very clear rectifier characteristic, where the current limitation with the spiral negative is very pronounced. With the spiral negative, all the curves show a slight initial curvature towards the voltage axis, and afterwards become linear, that is they follow a law similar to that of equation (2). With the spiral positive at low temperature the curves have a form closely resembling a diode characteristic. Near the origin there is in some cases an exponential rise, followed by a square law, after which the saturation effect appears. After saturation, especially in A17, the curvature reverses, as in the case of a diode characteristic in a strongly accelerating field. The square law probably corresponds to the presence of space charge in a semi-conductor (Mott & Gurney 1940, p. 172). The behaviour is thus as though the spiral were an anode collecting thermionic emission from the
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cathode. Some features of the curves with spiral positive are probably due to the lack of symmetry; thus with increasing voltage on the spiral current may be drawn from an increasing area of cathode core. The fact that with the spiral negative the

![Figure 2a](image1)

![Figure 2b](image2)

![Figure 2c](image3)

**Figure 2a–c.** Variation of conduction current with voltage applied between spiral winding and cathode core. \(I_0\), zero-time currents; \(I_s\), steady-state currents.

law resembles equation (2) indicates a potential barrier at the surface between spiral and coating. This is especially effective in A9 and B21. We conclude that in these tubes a thick barrier is present, representing a chemically different interface rather than a Schottky barrier. This is probably associated with the aluminium content.
of the nickel. With tube C21, however, where the curves were more nearly linear, a thin barrier only is present. The shape of the characteristic with spiral positive indicates that a barrier is also present at the surface between cathode core and coating, and the conduction current which can flow is the thermionic emission which can be drawn over this barrier. It is clearly possible that the thermionic emission from the cathode coating may in some cases be determined by the emission over this barrier. This will be discussed further below.

The steady-state curves resembled in form the zero-time curves for each tube. The slope was, however, reduced, corresponding with an increased effective resistance. The curve in the steady state at a given temperature resembled closely the zero-time curve at a temperature 20 or 30° lower. This is illustrated by the curves in figure 2 for A9 and B21. In B13 the onset of the current decay occurred at less than half a volt with spiral positive, a fact which explains the small range in voltage in the plots of figure 1 (d). The steady state could, however, be explored over a greater range as in figure 2. Tube B13 gave the best illustration of a general feature, that is, that the instability of current set in at widely different currents in the two directions of flow. Thus the curves with spiral negative for B13 were stable over the whole range examined, so that steady-state curves with spiral negative were identical with the zero-time curves of figure 1 (d). Thus the shape of the characteristic, current at the knee and current at the onset of instability all depend on the direction of flow.

After establishing the steady state, it was found that no reverse current could be detected on short-circuiting the coating, and no back e.m.f. could be measured on opening the circuit. Thus if any back e.m.f. were present, it decayed very rapidly an open circuit. But it was found that to restore the zero-time state on open circuit required at least half a minute. Thus a back e.m.f. could not be the main factor in decreasing current flow during the establishment of the steady state. The time constants for the decay were similar to those of emission current below, and it is probable that the same mechanism was the cause of both.

If the experimental procedure was altered so that the voltage was increased from zero in stages without intervening recovery periods on open circuit, the current followed at first the curves of figure 1. After passing the onset of instability the current increased less rapidly with voltage, and at higher voltages became asymptotic to the steady-state curves of figure 2. This resulted in curves as in figure 3 for B13. The reason for this type of characteristic is indicated by some typical decay curves. With increasing current density the total current decay increased, but the initial rate of decay also increased and the stable state was reached more quickly. The details of figure 3 depend on the time interval between readings, and the longer the delay, the flatter the section (a). Thus curves obtained in this way indicate a saturation of current which is not a true saturation effect, but depends on the time changes. When the voltage was decreased in stages before reaching the steady-state hysteresis loops were traced as indicated by the arrows. When once the steady-state curve (b) was reached, this curve was traced on raising or lowering voltage provided neither heating at high voltage nor recovery at low voltage was permitted.
Figure 3. Tube B13. Variation of current with voltage, with spiral positive, and decay of current with time. Curves (a) show the variation of current as voltage is increased continuously from zero, contrasted with (b) the steady-state curve, and (c) the zero-time curve.

11. Spiral as cathode

It has been shown that current limitation occurs indicating a rectifier action. It has also been pointed out that the theory suggests that with the spiral negative, current limitation occurs due to a barrier between spiral and coating, and with the spiral positive, due to a barrier between cathode core and coating. If the flow of thermionic emission is also limited by the flow from metal to coating, correspondence in behaviour with the conduction current is to be expected.

It was found that the emission current was, in fact, determined by the cathode in use, and that the emission current from the spiral behaved in the same way as
conduction current with spiral negative as discussed in the previous section. On
the first point, if the cathode emission were determined by the outer coating surface
only, the emission with the spiral as cathode should be $1/65$ of that with the cathode
core as cathode. This was not the case, as shown in table 1. In A9 and B21 the
ratio was greater than 1000, in C21 it was about 100, and in B13 as low as 30. This
is in contrast to the results of Becker & Sears, and shows that in the present cathodes
the emission is limited by the flow of current from cathode to coating. It should
be noted that reference here is to well-aged cathodes with high emission, so that
adequate barium is no doubt present on the surface of the coating and dispersed
through it. Further, the nickels forming both core and spiral contain additives
which may form insulating oxides. These additives are, of course, intended to assist
in the reduction of barium oxide to give adequate free barium.

<table>
<thead>
<tr>
<th>tube number</th>
<th>cathode temp. (°C)</th>
<th>cathode core as cathode (mA)</th>
<th>spiral as cathode (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B21</td>
<td>480</td>
<td>22</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>200</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>630</td>
<td>1200</td>
<td>~0.1</td>
</tr>
<tr>
<td>A9</td>
<td>480</td>
<td>20</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>90</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>630</td>
<td>220</td>
<td>0.09</td>
</tr>
<tr>
<td>C21</td>
<td>480</td>
<td>8</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>50</td>
<td>0.35</td>
</tr>
<tr>
<td>B13</td>
<td>480</td>
<td>15</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>560</td>
<td>120</td>
<td>3.0</td>
</tr>
<tr>
<td>A17</td>
<td>560</td>
<td>20</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>630</td>
<td>110</td>
<td>0.25</td>
</tr>
</tbody>
</table>

On the second point, the plots of emission current against voltage were similar
to the conduction current plots of figure 1 with spiral negative. Comparisons are
shown in figure 4 for tube A17. The emission current follows at first a $3/2$ power
law, and later departs from this law at the onset of saturation, whereas the conduction
current follows the equation (2) law, i.e. it shows a saturation effect following
a steeper rise from the origin. The important point is that the onset of saturation
occurs at approximately the same current density with both types of current. This
was true in all the tubes, though the separation between corresponding curves in
the saturation region varied from tube to tube. Thus corresponding curves were
almost coincident in B21 and A9, while in C21 the separation was slightly greater
than that shown in figure 4 for A17. The curves are so steep following the change
in curvature that it is necessary to show that saturation is in fact occurring. A test
was made which proved this to be the case. Measuring the current in the lead to the spiral, the positive voltage was first applied to the anode only, then to the cathode core only, and thirdly to the two together. In the case of C21, which was typical, the results are shown in table 2.

![Graph showing current-voltage characteristics for cathode and anode with different temperatures.]

**Figure 4.** Tube A17. Comparison of conduction current to cathode core with emission current to anode, using spiral winding as cathode. *(b)* shows detail near origin in low-temperature curves of *(a).*

**Table 2**

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Cathode Only</th>
<th>Anode Only</th>
<th>Anode + Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>cathode temp. 560°C</td>
<td>0.5</td>
<td>0.25</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.66</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.05</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>2.2</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>3.4</td>
<td>3.1</td>
</tr>
<tr>
<td>cathode temp. 630°C</td>
<td>2.0</td>
<td>2.45</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>4.7</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Thus the effect was not additive as low as 0.5 V, while at higher voltages the saturation was very marked. It is thus established that both currents show a saturation effect, and that in the tubes tested the saturation of both currents occurs at the same current density. This current density is determined by the cathode-coating boundary.

It was found also that the onset of instability occurred at the same current when drawing emission to the anode as when drawing conduction current to the cathode.
core. It has been shown above that the onset of decay is dependent on the direction of current flow, and is therefore not a phenomenon of the coating itself. The correspondence between the two types of current shows that the decay effect also is associated with the boundary between the coating and the metal acting as cathode.

12. EXPERIMENTS USING SPIRAL AS PROBE

It has been shown that the behaviour when drawing emission current from the spiral closely resembles that when conduction current flows with the spiral negative. The question remaining is whether there is similar correspondence when drawing emission from the whole coating using the cathode core as cathode. The results of this section show that this is the case. The measurements were made with the cathode at low temperature, so that emission could be saturated without excessive anode heating. Heating effects in the coating itself did not become significant until the current was greater than 100 mA. The anode current-anode voltage characteristics were normal, though the 'knee' was not well defined. Beyond the knee the current continued to increase with voltage as in the curves of figure 4.

It was found that the plot of current against probe potential was of the same form as the plot of current against anode potential, with a knee which was more sharply defined in most cases. The knee occurred as in the previous section at the same current density in both plots. In the case of A 9 and B 21, where the curvature near the origin was very marked in figure 1 with the spiral positive, a similar curvature appeared in the current, probe potential plot, as shown in figure 5. The other tubes giving a more linear plot in figure 1 gave a nearly linear plot below the knee in figure 5. Thus the correspondence is close. The results confirm the view that a barrier is present between cathode core and coating. It will be noted that with space-charge limited anode current, the potential drop does not exceed a value of the order of 1 V in figure 5, but with saturated anode current this value can increase rapidly. Similar results to those obtained at 480° C as in figure 5 were obtained at 560° C.

It was shown that the volt drop depended on the passage of current by applying negative volts to the diode anode. The probe did not take up a negative potential.

Some details of the time changes may be recorded. The general behaviour was discussed in § 9, and details for conduction current in § 10. In the case of emission current the decay set in when a certain current density was reached, and higher initial currents decayed more rapidly as in the case of conduction current. Whereas conduction current continued to increase with voltage in the steady state, this was not usually the case with emission current. Frequently the higher initial currents decayed to steady values similar to the current at onset of instability, so that the steady-state characteristic became horizontal with a well-defined knee at the onset of instability. In some cases, however, the higher initial currents decayed to values lower than that at the onset of instability. Thus if the current at the end of the 3 min. run was plotted against voltage, there was a region where current decreased as voltage increased. This behaviour is similar to that observed by Blewett (1939).
It was noted that while the probe potential fell during current decay, the fall in potential was less than the fall in current, so that compared with the zero-time value, the resistance increased during the decay. With the coatings of type (i), the decay appeared at 480 and 500°C at about a quarter of the knee value on the zero-time characteristic. Correspondingly the knee value in the steady state was about a quarter of that in the zero-time state. The volt drop fell to about half its value at the knee of the zero-time characteristic. With coatings of type (ii) the decay did not appear until the current was from a half to three-quarters of the knee value, so that the knee value in the steady state was correspondingly greater than with coatings of type (i).

![Figure 5. Spiral winding used as probe. Variation of spiral potential with emission current from cathode core to anode.](image)

The fall in current was reversible, that is, recovery occurred rapidly at zero-anode voltage, the recovery curve being approximately a reflexion of the decay curve as in the case of conduction current. The cycle could then be repeated. The onset of decay occurred at small current and anode voltage, especially with coatings of type (i), and it is very unlikely that this reversible decay was due to gas from the anode. At high-anode voltage irreversible decay has been encountered. The rapid increase in rate of decay with increasing current density indicates that at the higher currents obtainable at higher cathode temperatures, the effect could best be studied using short pulse technique. Such studies have been made, in particular by Sproull (1945) who observed decay effects which correspond with those observed by Blewett.
(1939b) and in the present work. Thus the decay phenomenon is of widespread occurrence. It is responsible for decay of peak pulsed emission during a long pulse, for decrease in peak pulsed emission if d.c. is superposed, for the fact that emissions available continuously are less than those available in short pulses, and for the decay of d.c. emission discussed above.

The mechanism will be discussed further below.

13. Values of resistance

The results of §11 showed that the current-voltage plot had no change of slope at the origin. A resistance could therefore be specified by the slope of the plot between $-0.1$ and $+0.1$ V. This is the resistance which has been specified by other writers, though it is clear that for the present cathodes it cannot be used to predict voltage drop at higher current densities. In B21 especially, the slope at the origin is of no value for this purpose.

In figure 6 the log of resistance is plotted against the reciprocal of absolute temperature. The plots have similar slopes with a mean value of $0.57$ eV. Tubes B21 and A20 were first tested after ageing runs of 260 and 180 min. respectively. After a total ageing of 950 min. the resistances were not appreciably changed.

The slope of the plots of figure 1 with spiral negative becomes approximately linear above about half a volt. This slope defines a resistance whose value is higher than the resistance at zero. The difference is not large at $730^\circ$ C, but increases at lower temperatures. Thus the plots of the log against $1/T$ have an increased slope with a mean value of $0.67$ eV. According to equation (2) this should represent the barrier height $\phi$ which is the difference in work function between the metal and the semi-conductor. The extrapolation of the linear part of the characteristic should cut the voltage axis at $\phi$ V. The intersection occurs at about $0.7$ V with A9 and B13, but in C21 and A17 the intersection is at a lower value.

It will be noted from figure 6 that there is no correlation between values of resistance and spiral-cathode spacing. This would be expected according to the view that the volt drop is largely in the interface layers. There is no systematic difference between the two types of coating.

It was noted that the current at less than 1 V in figures 5 and 6 was about 50 times that at the same voltage with the spiral positive in figure 1. This is consistent with the area ratio of 65 to 1. It is thus possible to deduce from figures 1, 5 and 6, a figure for the resistance per cm.$^2$ of coating which will apply to space-charge limited currents, and serve as a rough indication of the volt drop which may be expected during the operation of a cathode. We have determined the current at $0.5$ V drop at $630^\circ$ C as a mean for all the tubes taking all the information available with the spiral positive. The mean value is 6 ohms/cm.$^2$. From the slope of figure 7 we can find the corresponding figure at other temperatures. The figures are shown in table 3. These will apply for currents which are small at the higher temperatures compared with the knee values. Thus in a cathode at $780^\circ$ C a peak current may be drawn for
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**Figure 6.** Plot of coating resistance on logarithmic scale against reciprocal of absolute temperature.

**Figure 7.** Energy levels in coating.
a few microseconds which remains space charge limited up to 50 or 60 amp./cm.$^2$. Here the volt drop will approach 100 V, and the voltage gradient in the interface layer will be of the order of $10^6$ V/cm. Thus the conditions for dielectric breakdown are approached.

<table>
<thead>
<tr>
<th>cathode temp. (°C)</th>
<th>resistance/cm.$^2$ (ohm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>480</td>
<td>27</td>
</tr>
<tr>
<td>560</td>
<td>11</td>
</tr>
<tr>
<td>630</td>
<td>6</td>
</tr>
<tr>
<td>680</td>
<td>4</td>
</tr>
<tr>
<td>730</td>
<td>3</td>
</tr>
<tr>
<td>780</td>
<td>2.2</td>
</tr>
<tr>
<td>820</td>
<td>1.6</td>
</tr>
</tbody>
</table>

14. **Interpretation of results**

The results are consistent with the view that when saturation of current occurs, the restriction is imposed by the passage of current from the metal to the coating through a barrier which is too thick for tunnel-effect penetration. Such a barrier could occur (a) according to the Schottky theory without any variation in chemical composition near the boundary, (b) according to Mott's theory if an insulating layer is present forming an interface between metal and coating, or (c) if an interface layer is present which is not an insulator, but a semi-conductor with higher resistance than that of the bulk coating. This could be formed by chemical reaction between the cathode core and the coating, or by reduction in the concentration of excess barium in the oxide near the cathode core. The energy-level diagram for the system core metal-coating-vacuum is indicated in figure 7, where linear variation of potential energy has been drawn through the interface, which corresponds with an insulating layer. If the layer is a semi-conductor with higher resistance than that of the coating, the potential-energy plot in the layer will be concave upwards. It is not possible to deduce definitely what type of barrier is present in the above experiments, but the semi-conducting layer with higher resistance than that of the bulk coating is most probable. There is direct evidence (Rooksby 1940) that nickel containing silicon or aluminium forms interface layers of barium silicate or barium aluminate, which are probably semi-conductors. On nickel containing magnesium an interface layer has been observed, in which magnesium oxide has been identified.

The limitation of current at such a barrier produces the knee in the current-volt plot, whether the current is conduction current between one electrode and another in the coating, or emission current to an electrode outside the coating. The potential drop occurs primarily in the barrier, a fact which has consequences as regards breakdown which will be discussed below, while the decrease in current with time is also to be associated with the barrier layer. Before we discuss this feature it
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should be emphasized that the results apply to coatings which have been well aged and have high thermionic efficiency, and to core metals containing additives which form insulating oxide layers. Corresponding with the high emission there is probably an optimum covering of Ba on the outer surface of the coating, and a high concentration of Ba in the coating. Thus conduction through the bulk of the coating and thermionic emission from its outer surface are both high, and do not have a limiting effect on the emission which can be drawn. This may be expressed in terms of the energy levels.

In figure 7 $E_0$ is the top of the Fermi distribution for the metal at 0°K, $A$ is the bottom of the conduction band of the coating, $C$ is the impurity level in the coating caused by the presence of free barium in it, $D$ is the energy level in vacuum at a great distance from the surface. $B$ is approximately half way between $A$ and $C$, and is level with $E_0$. The highly activated state corresponds with a small value of $(D - B)$, in which case the barrier height $\phi$ may take control. $\phi$ is the difference between the work functions of the metal and the coating as already defined. The coating work function involved here is, of course, the value for the coating without an adsorbed layer on its surface.

There must clearly be conditions under which either emission from the outer surface or conduction through the bulk coating can take control. This would apply if the coating is not well activated, in which case $(D - B)$ would be greater; or if in a well-activated coating the barrier at the metal-coating interface is very thin. If there is no ‘chemical’ barrier, i.e. layer of different composition between metal and coating, the Schottky barrier only will occur, and in a well-activated cathode, $N$ in equation (1) § 4 will be large, so that the barrier may be thin enough for tunnel-effect penetration. In this case the current-voltage plot might well be ohmic, and the emission would be determined by the outer coating surface. This would presumably be the case in the experiments of Becker & Sears. In the present experiments and in those of Reimann a chemical barrier was probably present. The behaviour of oxide cathodes in a number of practical devices indicates that the barrier is of common occurrence.

15. Decay effects

With regard to the decay of emission, it does not appear that any theory of electron trapping can be invoked as an explanation. It seems necessary to suppose that, superposed on the electron flow which has been considered so far, there is an electrolytic flow of barium or oxygen ions. Now Sproull (1945) interpreted his results as due to electrolytic depletion of barium concentration on the outer surface of the coating. The theory and results were consistent except that the rate of depletion was found to be independent of coating thickness. Sproull considered that the flow of barium ions occurred only in the outer layer of crystallites. This does not seem probable to the writer. The present results predict without any further assumptions that the rate of depletion will be independent of coating thickness, since the coating
approximates to a high interface resistance in series with a low coating resistance. The potential difference across the whole coating which determines the electrolytic flow is therefore only slightly greater than that across the interface, and thus varies little with coating thickness. However, the present results suggest that the concentration of barium on the outer surface is not the important factor, since the cathode determines the behaviour, and conduction current and emission current decay in the same way. Thus while decay may be due to the electrolytic flow of barium or oxygen ions, the consequent changes are important in so far as they affect the inner boundary between metal and coating, and not the outer coating surface. For example, barium-ion accumulation at the metal surface may change the shape of the barrier, leading to a decrease in current, or there may be a change in barium concentration in the interface layer.

The occurrence of ion flow which is suggested by the decay effects has important implications which we shall discuss briefly. The theories of Schottky and Mott referred to above deal with the case where electronic flow occurs unaccompanied by electrolytic flow. In consequence, the barrier height is equal to the difference between the work functions of the metal and coating. If ion flow across the interface is postulated in order to explain decay effects, it is clear that such flow could also occur initially during the establishment of the equilibrium conditions. Thus these conditions will be considerably modified. The electron equilibrium leads to the formation of a barrier with a potential gradient in it as shown in figure 7. This potential gradient will cause a flow of positive ions to the cathode metal surface. It is therefore possible that an adsorbed film of barium is present on the nickel surface in equilibrium, which would reduce the work function of the nickel and consequently reduce the height of the barrier. The barrier height $\phi$ will now be the difference between the work function of the coating and that of the base metal with an adsorbed barium layer. The formation of such a layer may be an important part of the activation process. Further, the height of the barrier will not be very dependent on the base metal, since the work function of a metal with barium adsorbed on its surface does not vary greatly with the work function of the metal itself. This is in contrast with the situation in the theories of Schottky and Mott in which the barrier height varies directly with the work function of the base metal. It is to be expected that there are many cases where ion flow can occur in a semiconductor, leading to effects of this type. These features require further investigation, both theoretical and experimental.

16. Breakdown

If a well-activated diode cathode is operated at 750°C or higher, and pulsed emission is drawn, currents of the order of tens of amp./cm.$^2$ can be obtained under space-charge limited conditions. A limitation is usually reached between 50 and 100 amp./cm.$^2$ owing to breakdown of the coating. This leads to local disruption of the coating and arc discharges between coating and anode, causing the formation
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of craters which penetrate the whole coating thickness. If the temperature of the cathode is lowered, or if it is inherently a poorer emitter, discharges of this type do not appear until saturation has occurred, thus the anode voltage is higher and the current lower at the onset of breakdown. The measurements made above indicate that the volt drop in the coating when drawing space charge limited current will be of the order of some tens of volts. If the potential gradient were uniform across the coating, volt drops of this order would not be expected to lead to breakdown. If, however, the volt drop occurs across the barrier layer of thickness of the order of $10^{-5}$ to $10^{-4}$ cm, breakdown under these conditions is to be expected. The rapid increase in volt drop when saturated emission is drawn explains why at lower currents breakdown occurs on increasing the anode voltage to draw saturated emission.

It is clear from equation (2) that if barrier width varies from cathode to cathode, and if breakdown strength is independent of thickness, then $(\phi + V)$ will be proportional to barrier width $d$, and breakdown will occur at constant current but at a voltage increasing with $d$. The larger $d$, the smaller the current at the ‘knee’ and the further up the characteristic is the breakdown. However, breakdown strength is known to decrease rapidly with increasing thickness at small thicknesses of insulator, so that the voltage at breakdown will increase less rapidly than as given by $(\phi + V) \propto d$. Consequently the current at breakdown should decrease as the barrier width increases. It thus appears that varying barrier width can lead to the observed variations from tube to tube in knee value of emission current, and to the observed variations in breakdown voltage and current, at a constant temperature.

As temperature varies in a cathode with a fixed barrier width, if breakdown strength is independent of temperature it is clear that breakdown should occur at constant voltage. The fact that at lower temperatures breakdown occurs at increasing voltage shows that the dielectric strength of the insulating layer increases as temperature falls. This is consistent with the theories of Fröhlich (1945).

17. Schottky region

It is frequently observed with oxide cathodes that the emission current increases with anode voltage beyond the ‘knee’ in a manner similar to the increase of conduction current with spiral positive. For example, the case of A17, figure 1(c) would be typical. The curves may obey a law of the type $\log i$ proportional to square root of anode voltage, but the gradient is much greater than would be expected from the field at the cathode surface. This is again explained, however, if the increase in emission current is due to the potential gradient in the barrier layer. The Schottky effect and later field emission will occur with voltage drops across the barrier of the order of tens of volts, which can be produced with comparatively low anode voltage.
18. \( A \) value

The theoretical formula for saturated thermionic emission is

\[
I = aA T^2 e^{-\phi/kT},
\]

where \( A \) has the value 120 amp./cm.\(^2\) and \( a \) is a term arising from the reflexion at the surface. Clean metals give values of \( aA \) lying between 30 and 150. Metals with adsorbed layers of other electropositive metals give values of the order 2 to 10. Oxide cathodes, however, have values of \( aA \) in the range \( 10^{-3} \) to 1, and it has been assumed that these low values are not simply due to low values of the term \( a \). Thus de Boer (1935) supposed that the value of \( aA \) was determined by the proportion of the outer surface covered with barium, and by the rate of supplementation of electrons to the surface by flow through the coating. If flow through the coating becomes the main factor, as appears to be the case in the present experiments, the current will be determined by equation (2).

Now at the knee the second bracket in (2) has become unity, and the value of \( V \) is only a fraction of a volt. Therefore approximately

\[
I = 10^{-3} v/d T^2 e^{-\phi/kT} \text{ amp./cm.}^2,
\]

since \((\phi + V) \sim 1 \text{ V.}\)

Thus at 1000° K

\[
I = 32v/d e^{-\phi/kT},
\]

while the emission formula gives

\[
I = a \times 1.2 \times 10^8 e^{-\phi/kT}.
\]

Thus to explain apparent values of \( 'a' \) of the order \( 10^{-3} \) to \( 10^{-2} \), values of \( v/d \) of the order \( 10^4 \) must be supposed. Such values are quite reasonable; thus if \( d \) is from \( 10^{-5} \) to \( 10^{-4} \) cm., \( v \) will be from \( 1/10 \) to 1 cm./sec./unit voltage gradient.

19. Cavity magnetrons with oxide cathodes

In most thermionic devices the current from the cathode is of thermionic origin and is space-charge limited in the operation of the device. Thus except in highly emitting cathodes voltage gradients will not be sufficient to cause breakdown. In magnetrons, however, the cathode current is enhanced by secondary emission. Frequently the thermionic emission of a magnetron cathode is poor, and the operating current is several times larger than the knee value of the emission. This increase is due to secondary emission. It is clear that if the limitation in thermionic emission is imposed at the metal-coating interface, then in order to supplement the secondary emission from the outer layers of the coating, the potential gradient in the interface must increase along the saturated part of the characteristic of figure 5. Thus the voltage gradient will be much greater than when drawing space-charge limited emission of the same magnitude as the operating current. The tendency to breakdown at a given current will therefore be greater in a magnetron.
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than in devices which do not employ secondary emission. This may explain the breakdown effects frequently observed in the operation of cavity magnetrons with oxide cathodes under pulsed conditions, especially when the operating current density is increased beyond about 10 amp./cm.².

In conclusion the author desires to tender his acknowledgements to the General Electric Co. and the Marconiphone Co., on whose behalf the work was done which led to this publication. The author is also grateful to Professor Mott for helpful discussion.

Note added 6 December 1946. Since the preparation of the above paper, a group of papers has appeared discussing high current density pulsed emission from oxide cathodes, and showing the presence of interface layers:


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