

THE INFLUENCE OF THE CATHODE MATERIAL ON MEASURED BREAKDOWN STRENGTHS OF SOLID AND LIQUID DIELECTRICS*

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Summary

An outline is given of a general method of accounting for the effect of electronic and ionic space charge in the breakdown of solid and liquid dielectrics. Detailed calculations are performed for a special model of both a liquid and a solid dielectric, and the results are compared with recent experimental work. Exact calculation is not possible, but it is shown that for some substances an effect due to cathode material may well be measurable, and the factors influencing such an effect are examined.

I. INTRODUCTION

The intrinsic breakdown strength of certain dielectric materials has been calculated by Fröhlich (1937, 1939, 1947). The materials treated have been ionic crystals in the "low temperature" region, and "amorphous dielectrics". The latter term refers to the model assumed for the electronic structure of the dielectric and is taken to include ionic crystals in the "high temperature" region and various solids and liquids of more complicated structure. Attempts to measure this intrinsic breakdown strength experimentally are complicated by the fact that the theory takes no account of the finite size of the dielectric specimen, the finite rise time of the applied voltage, or the effect of electrode materials.

Various authors have discussed this latter effect, but opinions differ both as to its existence and to its mechanism presuming that it exists. Oakes (1948) obtained a significant difference between measurements on the electric strength of polythene using silver and graphite cathodes. von Hippel and Alger (1949) have performed experiments on the breakdown strength of potassium bromide (in its high temperature region) with gold, mercury, steel, and potassium bromide solution as cathodes, and claim much larger effects of this kind; it should be mentioned, however, that in the experiments by von Hippel and Alger the specimens with different electrode material were not conditioned in the same way so that the interpretation of the differences as due to electrode material cannot be considered as established. More recently Calderwood, Cooper, and Wallace (1953) have measured the breakdown strength of ionic crystals which were very carefully prepared and annealed. They found no significant difference in the breakdown strength of potassium chloride at room temperature using alternately graphite and silver electrodes; and a difference that was just about significant using graphite and potassium chloride solution alternately as cathodes.

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Similarly, Cooper and Grossart (1953) found no significant difference in the breakdown strength of potassium bromide using gold, graphite, and potassium bromide solution alternately as cathodes. This is in opposition to the earlier reported results of von Hippel and Alger.

Similarly, experimental results on the breakdown of dielectric liquids are conflicting. Various workers have measured the effect of different cathodes on the breakdown strength of *n*-hexane. Using a conventional sphere-sphere electrode system Edwards (1951), Salvage (1951), and Goodwin and Macfadyen (1953) all report the existence of such an effect while Lewis (1953*a*) reports that the effect does not exist. However, in further experiments using a point-plane electrode system, Lewis (1953*b*) found that the cathode material influenced the breakdown strength if the plane was the cathode, but that there was no measurable effect if the point was the cathode. The cathodes used in these experiments have been aluminium, chromium, silver, nickel, platinum, phosphor-bronze, and steel, and in all cases in which the existence of the effect is reported the measured breakdown strength increased with increasing cathode work function.

It is the purpose of the present work to interpret the possible influence of the cathode material on measured breakdown strengths, on the assumption that each material possesses an intrinsic electric strength. In the calculations below it is supposed that the specimen of dielectric under test is placed between two parallel metal electrodes and the applied potential altered so slowly that the charge distribution may always be assumed to be in a steady state. In approaching this steady state a space charge will have been built up in the dielectric, which will be so distributed as to give continuity of current across the specimen. The variation of potential will not be linear, and under certain conditions the maximum value of the field strength may be considerably greater than the average field strength. It is assumed that breakdown will occur when this maximum field strength exceeds the intrinsic breakdown strength.

II. GENERAL METHOD OF SOLUTION FOR CERTAIN SOLID DIELECTRICS

We consider now solid dielectrics in which the current is purely electronic. Continuity of current requires that the current of electrons leaving at the anode be equal to that entering at the cathode; the former is determined by the conductivity of the dielectric near the anode, and the latter by cold emission from the cathode into the conduction band of the dielectric. This can be expressed by

$$I_c(F_c, \alpha) = \sigma_a F_a, \quad \dots \dots \dots (1)$$

where F_c and F_a are the fields near the cathode and anode respectively, α represents parameters of the metal and the dielectric which are relevant to cold emission, and σ_a is the conductivity of the dielectric near the anode. The electronic space charge will be distributed to give the highest field strength near the anode and the lowest near the cathode. Near breakdown (1) thus becomes

$$I_c(F_c^*, \alpha) = \sigma^* F^*,$$

so that

$$F_c^* = F_c^*(\alpha, \sigma^*, F^*), \quad \dots \dots \dots (2)$$

thus determining the field near the cathode just before breakdown. The quantities σ^* and F^* are the conductivity and field strength just before intrinsic breakdown.

The conductivity of the dielectric will be increased by an electronic space charge, or a strong field applied to it, or both (cf. Fröhlich 1947) and we may write

$$\sigma = \sigma(\sigma_0, n, F, \beta), \quad \dots \dots \dots (3)$$

where σ_0 is the conductivity in the absence of a field, n is the space charge electron density, and β represents parameters of the dielectric.

Continuity of current gives

$$\begin{aligned} F\sigma &= \text{const.} \\ &= F^*\sigma^*, \quad \dots \dots \dots (4) \end{aligned}$$

so from equations (3) and (4) we have

$$n = n(\sigma_0, \beta, F, F^*). \quad \dots \dots \dots (5)$$

Poisson's equation can be written

$$\frac{dF}{dx} = 4\pi ne, \quad \dots \dots \dots (6)$$

where x is the position coordinate measured from the cathode. The variables are separable, so that integration of (6) gives

$$F = F(x, \beta, F^*, F_c^*) \quad \dots \dots \dots (7)$$

with the use of the boundary condition (equation (2)). If the anode and cathode are a distance d apart, then we can write for the apparent fractional decrease of breakdown strength

$$\left. \begin{aligned} D &= 1 - \frac{F_0}{F^*}, \\ F_0 &= \frac{\int_0^d F dx}{d}. \end{aligned} \right\} \quad \dots \dots \dots (8)$$

where

III. CALCULATIONS FOR AN AMORPHOUS DIELECTRIC

Since the detailed manner of variation of the number of conduction electrons with field strength is not known for a dielectric in its low temperature region (due to unsolved problems connected with internal ionization and recombination processes), we shall perform the explicit calculations for the case of an amorphous dielectric only. In this sense the term "amorphous" is taken to refer to the model of the electronic structure introduced by Fröhlich (1947). The electronic energy levels consist of a continuum of conduction levels immediately below which isolated shallow traps cover a range ΔV ; there are in addition deep traps whose energy is an amount W below the lowest of the shallow traps. For this model, the conductivity as a function of field strength has been calculated by Fröhlich, and his results will be required below.

Using a method similar to that given by Mott and Sneddon (1949) we can derive a Fowler-Nordheim type equation for the current emitted by the cathode into the conduction levels of the dielectric as

$$I_c = \frac{e^3 F_c^2}{8\pi\hbar\varphi} \exp\left(-\frac{4}{3}K\varphi^{3/2}/eF_c\right), \quad \dots\dots\dots (9)$$

where $K^2 = 8m\pi^2/\hbar^2$, e and m are the electronic charge and mass respectively, $\hbar$ is Planck's constant, and φ is the amount by which the energy of the lowest conduction level in the dielectric exceeds the energy of the top of the Fermi distribution in the metal. From equation (2) then

$$\frac{e^3 F_c^{*2}}{8\pi\hbar\varphi} \exp\left(-\frac{4}{3}K\varphi^{3/2}/eF_c^*\right) = \sigma^* F^*, \quad \dots\dots\dots (2a)$$

from which we can now find F_c^* , which is required as a boundary condition for the solution of the differential equation.

The number of electrons in conduction levels in the dielectric can be written

$$N_c(T) = k_1(T)(N+n) \exp\left(-\frac{W}{kT}\right), \quad \dots\dots\dots (10)$$

where T is the electronic temperature (assuming that electron-electron collisions are so much more frequent than electron-lattice collisions that an electronic temperature is attained—not necessarily the same as the lattice temperature T_0), k_1 is a factor which varies slowly with T compared with the exponential term, N is the number of trapped and conduction electrons, and n the number of space charge electrons. (It is assumed in the derivation of (10) that N is very much less than the total number of deep traps (cf. Mott and Gurney 1949).)

If there is no field and no space charge the electronic temperature will equal the lattice temperature and

$$N_c(T_0) = k_1(T_0)N \exp\left(-\frac{W}{kT_0}\right). \quad \dots\dots\dots (11)$$

Combining equations (10) and (11) and treating k_1 as constant, we have for the ratio of the conductivities

$$\frac{\sigma}{\sigma_0} = \left(1 + \frac{n}{N}\right) \exp\left(-\frac{W}{kT} + \frac{W}{kT_0}\right). \quad \dots\dots\dots (12)$$

Fröhlich (1947) has shown that

$$\frac{W}{kT_0} - \frac{W}{kT_1} \simeq \frac{F^2}{F^{*2}} \frac{W}{\Delta V}, \quad \dots\dots\dots (13)$$

provided that $F \lesssim F^*$ and where T_1 is the steady electronic temperature built up under the influence of a field F . Equations (12) and (13) then give

$$\frac{\sigma}{\sigma_0} = \left(1 + \frac{n}{N}\right) \exp\left(\frac{W}{\Delta V} \frac{F^2}{F^{*2}}\right). \quad \dots\dots\dots (3a)$$

Substituting (3a) into (4) gives at once

$$\frac{n}{N} = \frac{F^*}{F} \exp\left\{\frac{W}{\Delta V} \left(1 - \frac{F^2}{F^{*2}}\right)\right\} - 1. \quad \dots\dots\dots (5a)$$

Using (5a) in (6) and separating the variables we find

$$x = \frac{1}{4\pi Ne} \int \frac{dF}{\frac{F^*}{F} \exp \left\{ \frac{W}{\Delta V} \left(1 - \frac{F^2}{F^{*2}} \right) \right\} - 1}.$$

For values of $F \lesssim F^*$ the exponential can be well approximated by two terms and elementary integration gives

$$x = \frac{\Delta V}{W} \frac{F^*}{4\pi Ne} \left[-\ln \left(\frac{F}{F^*} - 1 \right) + \left(\frac{\Delta V}{W} + 1 \right) \ln \left(\frac{F}{F^*} + \frac{\Delta V}{W} + 1 \right) \right]. \quad (14)$$

The quantity $(1 + \Delta V/W)$ is of order unity, so for $F \lesssim F^*$ the first term of (14) will be very much greater than the second. Neglecting this second term and applying the boundary condition $F = F_c^*$ at $x = 0$ when breakdown is about to commence at the anode, we have

$$\frac{F}{F^*} = 1 - \left(\frac{F^* - F_c^*}{F^*} \right) \exp \left(- \frac{4\pi Ne}{F^*} \frac{W}{\Delta V} x \right), \quad (7a)$$

which gives the field strength at any point when the dielectric is about to break down. Performing the averaging and substituting in (8), we have for the apparent fractional decrease of breakdown strength

$$\begin{aligned} D &= \frac{F^* - F_c^*}{4\pi Ned} \frac{\Delta V}{W} \left[1 - \exp \left(- \frac{4\pi Ned}{F^*} \frac{W}{\Delta V} \right) \right] \\ &= \frac{F^* - F_c^*}{\beta} \left[1 - \exp \left(- \frac{\beta}{F^*} \right) \right], \quad (8a) \end{aligned}$$

where we have written

$$\beta = 4\pi Ned \frac{W}{\Delta V} \quad (15)$$

as a parameter which has the dimensions of a field strength and is characteristic of the specimen under test.

IV. GENERAL METHOD OF SOLUTION FOR LIQUID DIELECTRICS

We consider now a liquid dielectric in which the electronic current emitted from the cathode is

$$I_c = I_c(F_c, \alpha), \quad (16)$$

where again α represents parameters of the metal and dielectric which are relevant to cold emission.

The liquid molecules will be ionized by the electrons and the steady state field distortion will be due to the space charge of both electrons and positive ions. Poisson's equation will then be found to take the form

$$\frac{dF}{dx} = \frac{dF}{dx}(I_c, \beta, F, x), \quad (17)$$

where β again represents parameters of the dielectric specimen under test (e.g. its size and shape, the mobilities of electrons and positive ions, and ionization and recombination coefficients). If (17) can be integrated the result will be

$$F = F(I_c, \beta, F_c, x), \quad \dots \quad (18)$$

where $F = F_c$ when $x = 0$ has been introduced as a boundary condition. Using (16) in (18), we have immediately

$$F = F(\alpha, \beta, F_c, x). \quad \dots \quad (19)$$

In the case of the liquid dielectric the lower mobility of the positive ions as compared with the electrons will result in the field strength being greatest near the cathode and falling away towards the anode. Breakdown will thus occur when $F_c = F^*$ so that the breakdown field at any point is

$$F = F(\alpha, \beta, F^*, x). \quad \dots \quad (20)$$

The apparent fractional decrease in breakdown strength is then given by equation (8) as previously.*

V. CALCULATIONS FOR A LIQUID DIELECTRIC

The case of a liquid dielectric can also be made amenable to calculation if certain assumptions are made. It will be assumed that the electron current I_c from the cathode produces positive ions by collision-ionization with a multiplication coefficient η which will be strongly dependent on the field strength. Recombination will be neglected as being negligible compared with ionization. If in addition the mobility of the electrons is very much greater than the mobility of the positive ions it can be shown that Poisson's equation gives (cf. Loeb 1939)

$$F \frac{dF}{dx} = -\frac{4\pi I_c}{k_+} \left\{ \exp \left(\int_0^d \eta dx \right) - \exp \left(\int_0^x \eta dx \right) \right\},$$

where k_+ is the mobility of the positive ions. (This equation is standard for the case of discharge in a gas.) It can be taken that

$$\eta = \eta_0 F^2 \quad \dots \quad (21)$$

* Goodwin and Macfadyen (1953) combine equations (16) and (18) to produce a breakdown criterion. They do this by showing that, for sufficiently large F_0 (average field strength across the specimen), no simultaneous solution for I_c and F_c can be obtained from these equations. This procedure, however, seems unsound for several reasons. Firstly, the possibility that the liquid possesses an intrinsic breakdown strength is ignored, and in view of the relative constancy of measured breakdown strengths it seems very probable that the concept of the intrinsic breakdown strength applies to a liquid. This would be calculated as that field strength for which no equilibrium is possible between the rate at which the charge carriers in the liquid receive energy from the field and the rate at which they can transfer this excess energy to the bulk of the liquid. Secondly, the constants used by these authors in the Fowler-Nordheim equation correspond to values of ϕ for which not cold emission but thermionic emission would be the dominant effect. This is in the main due to the method by which they determine these constants from experiment by extrapolation of current *v.* gap length curves (for a given average field strength) to zero gap length. This is not permissible since the field distortion near the cathode is such that the average field strength in a large gap may be very much lower than the field strength immediately in front of the cathode.

over a wide range of field strengths (cf. Goodwin and Macfadyen 1953). Introducing a new variable

$$u = \int_0^x \eta_0 F^2 dx, \quad \dots\dots\dots (22)$$

and a constant (with respect to x)

$$u_d = \int_0^d \eta_0 F^2 dx, \quad \dots\dots\dots (23)$$

we have from (17)

$$\eta_0 F^3 dF = -\frac{4\pi I_c}{k_+} (\exp u_d - \exp u) du. \quad \dots\dots\dots (17a)$$

Integration and use of the boundary conditions yields

$$F^4 - F_c^4 = -\frac{16\pi I_c}{\eta_0 k_+} (u \exp u_d - \exp u + 1). \quad \dots\dots (18a)$$

Equation (16) will again be given by (9) as

$$\left. \begin{aligned} I_c &= a F_c^2 \exp\left(-\frac{b}{F_c}\right), \\ \text{where } a &= \frac{e^3}{8\pi h \varphi}, \\ \text{and } b &= \frac{4K\varphi^{3/2}}{3e}. \end{aligned} \right\} \quad \dots\dots\dots (16a)$$

Substituting in (18a) we find

$$F^4 - F_c^4 = -\frac{16\pi a F_c^2 \exp(-b/F_c)}{\eta_0 k_+} (u \exp u_d - \exp u + 1). \quad \dots (19a)$$

Owing to the complicated form of this equation a simple expression for F as a function of F_c cannot be obtained in general. However, in the vicinity of the cathode $u \ll u_d$, so that we have with the use of (22)

$$F^4 \simeq F_c^4 - \frac{16\pi a F_c^2}{k_+} \exp\left(-\frac{b}{F_c} + u_d\right) \int_0^x F^2 dx. \quad \dots\dots (19b)$$

Assuming a trial solution for (19b) of the form

$$F = F_c \exp(-\gamma x), \quad \dots\dots\dots (24)$$

for sufficiently small values of x we find

$$\gamma = \frac{4\pi a}{k_+} \exp\left(-\frac{b}{F_c} + u_d\right). \quad \dots\dots\dots (25)$$

For larger values of x a very approximate solution gives $F \propto 1/x^{\frac{1}{2}}$, but, since the neglected effect of recombination will be becoming more important for larger distances from the cathode, it is reasonable to suppose that the field strength becomes practically constant for sufficiently large values of x . It is thus not

possible to derive an accurate expression for the apparent percentage decrease in breakdown strength, but sufficient calculations have been done to show whether the mechanism discussed could produce a measurable effect.

VI. DISCUSSION

(a) Solids

If any effect due to the cathode material is to be measurable, equation (8a) shows that not only must the field near the cathode be significantly lower than the breakdown field, but also that the field must be maintained at a lower value than breakdown for an appreciable distance across the specimen. Thus, in addition to the obvious condition $F_c^* < F^*$, we must have a condition on β (which measures the ability of the dielectric to maintain a reduced field). Three main cases can be distinguished for which (8a) gives

$$\left. \begin{aligned} D &\simeq 1 - \frac{F_c^*}{F^*}, & \text{if } \beta \ll F^*, \\ D &= \frac{F^* - F_c^*}{\beta} \left[1 - \exp \left(-\frac{\beta}{F^*} \right) \right], & \text{if } \beta \sim F^*, \\ D &\simeq 0, & \text{if } \beta \gg F^*. \end{aligned} \right\} \quad \dots (8b)$$

It appears then that the conditions for a measurable effect of the cathode material reduce most simply to

$$F_c^* < F^* \quad \text{and} \quad \beta \lesssim F^*. \quad \dots \dots \dots (26)$$

Before endeavouring to decide whether these conditions can apply to real solids we rewrite (2a) and (15) substituting numerical values for universal constants, and in the case of (15) assuming that $W/\Delta V \sim 5$. This gives

$$1.55 \times 10^6 \frac{F_c^{*2}}{\varphi} \exp \left(-66 \frac{\varphi^{3/2}}{F_c^*} \right) = \sigma^* F^*, \quad \dots \dots \dots (2b)$$

and

$$\beta \sim 10^{-11} N d, \quad \dots \dots \dots (15a)$$

in which β , F_c^* , and F^* are in MV/cm, φ is in eV, σ^* in micromho cm^{-1} , N in electrons/c.c., and d in cm.

Working on polythene, Oakes (1948) gives $F^* \simeq 5$ with $d \simeq 5 \times 10^{-3}$, from which data using (15a) and (26) we find $N \lesssim 10^{14}$ if any such cathode effect is to be measurable. This seems a reasonable value for a substance such as polythene, and if $F_c^* < F^*$ the effect should be observable. Turning to (2b) we find that, on account of the extreme sensitivity of the exponential term to small changes in φ and F_c^* , a wide range of reasonable values can be covered. Thus the most that can be said in this case is that, for reasonable values of the parameters involved, the explanation given for the apparent decrease in the breakdown strength of polythene could be correct.

Taking the experiments of Cooper and co-workers (Calderwood, Cooper, and Wallace 1953; Cooper and Grossart 1953) on alkali halides we find $F^* \simeq 1$ for $d \simeq 5 \times 10^{-2}$. This would require $N \lesssim 2 \times 10^{12}$ if there is to be any measurable effect due to cathode material. This would appear to be very much too low a

value for the number of conduction and trapped electrons in an alkali halide at room temperature. It thus appears that an effect of the type discussed here would probably not be measurable in experiments on alkali halides—a conclusion which is in agreement with the findings of Cooper and his co-workers. It may be argued that the effect should be found in experiments on thinner specimens, but it seems from the figures that the thickness of the specimen would have to be reduced so much as to be impracticable. Furthermore, in the case of alkali halides, ionic currents and space charges would be expected to intervene, and their effect would be opposite to that of electronic currents and space charges in producing any cathode dependence of the breakdown strength.

(b) *Liquids*

From (24) the condition for a measurable effect of the cathode material will be

$$\left. \begin{array}{l} \gamma^* x \sim 1, \text{ for } x < d, \\ \gamma^* d > 1, \end{array} \right\} \dots\dots\dots (27)$$

or

where γ^* is the value of γ when breakdown is about to commence at the cathode. Using (25) and (27) and substituting numerical values for universal constants we obtain

$$\frac{19.5 \times 10^{-6} d}{\phi k_+} \exp \left\{ -66 \frac{\phi^{3/2}}{F^*} + u_d^* \right\} > 1, \quad \dots\dots\dots (27a)$$

where u_d^* is the value of u_d when breakdown is about to commence at the cathode. (Note that equation (27a) may not be satisfied by indefinitely increasing d since then the neglect of recombination introduces serious error.)

Owing to the extreme sensitivity of (27a) to factors in the exponential term no definite predictions can be made but it is interesting to investigate orders of magnitude. Thus the various experimental workers previously quoted give for *n*-hexane: $F^* \simeq 1$ MV/cm, $d \sim 5 \times 10^{-3}$ cm, $k_+ \sim 10^{-3}$ cm² V⁻¹ sec⁻¹, and $\eta \sim 10^4$ cm⁻¹ near breakdown. Substituting these values in (27a) we find that $\gamma^* d \gtrsim 1$ if $\phi \lesssim 1$ eV, which is a most reasonable value.

These calculations tend to support the opinion that the differences between the work of Lewis (1953a) (who found no measurable effect of cathode material) and that of Edwards (1951), Salvage (1951), and Goodwin and Macfadyen (1953) (who did find such an effect) may be well due to differences in the polish and cleanliness of the cathode surface. This seems to be so since the precise value of ϕ is very critical and any variation of it (such as that leading to emission from spots on the cathode) would completely alter the situation. In addition, some light is thrown on the experiments of Lewis (1953b) with a point-plane electrode system. With the point negative the non-uniformity of the field would be increased and the breakdown voltage decreased, while with the point positive the reverse would hold. This was in fact observed by Lewis, who concluded that the liquid was therefore stressed more highly when the plane was negative. However, this is not necessarily so, since space charge effects of the type discussed above would modify the maximum field strengths calculated by Lewis in such a way as to render them more nearly equal.

VII. REFERENCES

- CALDERWOOD, J. H., COOPER, R., and WALLACE, A. A. (1953).—*Instn. Elect. Engrs. Paper No.* 1457.
- COOPER, R., and GROSSART, D. T. (1953).—*Proc. Phys. Soc. Lond.* B 66 : 716.
- EDWARDS, W. D. (1951).—*Canad. J. Phys.* 29 : 310.
- FRÖHLICH, H. (1937).—*Proc. Roy. Soc. A* 160 : 230.
- FRÖHLICH, H. (1939).—*Proc. Roy. Soc. A* 172 : 94.
- FRÖHLICH, H. (1947).—*Proc. Roy. Soc. A* 188 : 521.
- GOODWIN, D., and MACFADYEN, K. (1953).—*Proc. Phys. Soc. Lond.* B 66 : 85.
- VON HIPPEL, A., and ALGER, R. S. (1949).—*Phys. Rev.* 76 : 127.
- LEWIS, T. J. (1953*a*).—*Instn. Elect. Engrs. Paper No.* 1488.
- LEWIS, T. J. (1953*b*).—*Proc. Phys. Soc. Lond.* B 66 : 425.
- LOEB, L. B. (1939).—"Fundamental Processes of Electrical Discharge in Gases." (John Wiley & Sons: New York.)
- MOTT, N. F., and GURNEY, R. W. (1949).—"Electronic Processes in Ionic Crystals." (Oxford Univ. Press.)
- MOTT, N. F., and SNEDDON, I. N. (1949).—"Wave Mechanics and its Applications." (Oxford Univ. Press.)
- OAKES, W. G. (1948).—*J. Instn. Elect. Engrs.* I 95 : 36.
- SALVAGE, B. (1951).—*Proc. Instn. Elect. Engrs.* IV 98 : 15.