

An explanation of the results of experiments on surface roughness and oxidation may be attempted with the aid of a simplified arc model. The cathode 'spot' is believed to consist of a number of emitting sites, electrons from which are accelerated through the fall region and ionize at the base of the arc column. The ions so formed drift to the cathode, but because of the transverse magnetic field they strike the cathode on the Amperian side of the spot. (For modification of this model to account for behaviour at low pressure where retrograde motion occurs, see ref. 4). This ion bombardment ahead of the existing cathode spot conditions suitable sites to take over the arc current when the emission efficiency of the existing sites decreases. Thus arc movement would occur by a series of micro-jumps of the individual sites and the magnitude of the arc velocity should be a function of the ease of conditioning new sites, and of the rate of decay of emission efficiency of the existing sites. It should be pointed out that the mechanism of electron emission from a site at the instant of current transfer to it need not necessarily be the same as that when the site has become established. It is believed that the conditioning of new sites occurs by a process of surface charging due to positive-ion bombardment, which lowers the effective work function, and that at the instant of current transfer a field emission process predominates. Thus a roughening of the cathode surface could lead to localized high-field regions due to asperities and the sites ahead of the existing spot should then require less conditioning. In addition, surface oxide layers which alter the effective work function will also control the emission. The rate of surface charging for various thicknesses of oxide layer cannot be explained simply, and to obtain a realistic picture it is necessary to consider the mode of electron transfer through a semiconductor oxide film with a surface charge of positive ions. It is then possible to explain the shape of the velocity and breakdown voltage curves shown in Fig. 2.

Further experiments on stainless steel, copper and platinum, in air, nitrogen and hydrogen, for both Amperian and retrograde motion, have yielded considerable evidence in support of the mechanism of motion postulated. It is hoped to publish a far more detailed account of these investigations elsewhere.

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advice and encouragement, are gratefully acknowledged. One of us (P. E. S.) wishes to thank the Department of Scientific and Industrial Research for a maintenance allowance and the Institution of Electrical Engineers for the recent award of an I.M.E.A. Scholarship.

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¹ Guile, A. E., Lewis, T. J., and Mehta, S. F., *Brit. J. App. Phys.*, **8**, 444 (1957). Secker, P. E., and Guile, A. E., *Proc. Inst. Elec. Eng.*, **106**, A, 311 (1959).

² St. John, R. M., and Winans, J. G., *Phys. Rev.*, **98**, 1664 (1955).

³ Davies, D. E., and Fitch, R. K., *Brit. J. App. Phys.*, **10**, 498 (1959).

⁴ Ecker, G., and Muller, K. G., *J. App. Phys.*, **29**, 1808 (1958).

Bulk Conductivity in Organic Crystals

ONE of the basic problems in the study of bulk conductivity phenomena (dark- and photo-conductivity) in organic crystals is the apparent energy deficit in the difference between the ionization energy of the molecule in the crystal and the energy supplied by the exciting radiation. An excellent review of this problem is given by Garrett¹. All current efforts to resolve this difficulty have been concerned with the energy balances within the crystal, excluding the electrodes, with the goal of explaining how a charge separation is produced inside the crystal.

There is, however, another mechanism for explaining the observed conductivity, and that is to assume that the carriers are produced at the electrodes. This process in organic crystals would be classified mainly as one of hole injection into the adjacent crystal from the electrode. The experimental basis for this picture has been given in a preceding paper².

In these experiments an anthracene crystal was provided with electrolyte electrodes. One electrode compartment was filled with 1 M sodium iodide solution saturated with iodine, while the other electrode compartment was filled with 1 M sodium iodide solution without iodine. The dark current which flowed when the iodine compartment was made electrically positive was 22 times that when the iodine compartment was negative and 80 times the dark current when neither compartment had any iodine. These results were explained by assuming that the iodine extracted an electron from the adjacent anthracene crystal, becoming an I⁻ ion, thereby injecting a positive hole into the anthracene.

The energy balance for the process of hole injection can be described as follows: I_A is the energy required to take an electron out of solid anthracene, creating a positive hole A^+ (s) in the solid and freeing an electron e^- in the gas. If, further, W_E is the energy required to remove an electron from the electrode and E_X the energy externally supplied (optically or thermally), we

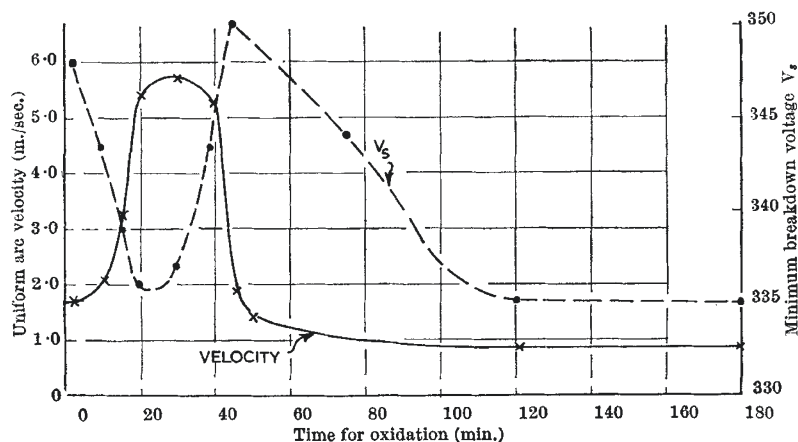


Fig. 2. Variation of uniform arc velocity and minimum breakdown voltage with time of cathode oxidation. Arc current, 70 amp., air pressure, 25 mm. mercury, magnetic flux density, 0.024 Wb./m.², inter-electrode gap, 6.4 mm.

have the following energy balance for the process of hole injection :

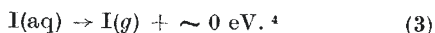
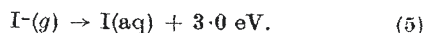
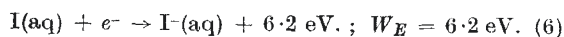
$$W_E + E_X - I_A > 0 \quad (1)$$

In the same way, one can describe the condition for electron injection into anthracene. If W is the energy freed when an electron is absorbed in anthracene, then the condition for electron injection is :

$$W_A + E_X - W_E > 0 \quad (2)$$

I_A is given in the literature¹ as about 6 eV. ; our estimate is between 5 and 6 eV.

Applying equation (1) to the case of hole injection from an unilluminated I_2 electrode, E_X is small, of the order of thermal energy : W_E is about 6.2 eV., calculated as follows :



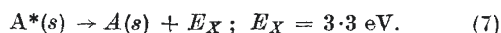
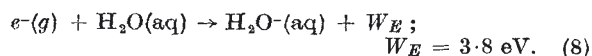
The energy balance is seen to be favourable for the extraction of an electron from the anthracene, and the injection of a positive hole into the anthracene. At the opposite electrode, the process is the discharge of the positive hole, similar to the discharge of an ion at a metal electrode, probably producing free iodine.

When external radiation is absorbed by I_2 (and also I_2^-), its dissociation into iodine atoms is greatly increased³; on the above basis, hole injection should also be increased, as is indeed the case². Thus, when 4360 Å. radiation was used, the enhanced dissociation when the iodine electrode was at a positive potential increased the current by a factor of 16,000 over the dark current.

This radiation does not excite the anthracene crystal and need not contribute directly to the electron extraction process. This process of hole injection can occur with any electrode, for which the energy balance is positive as indicated in equation (1). For example, the replacement of I_2 by Ce^{4+} solution produces a large increase in the dark current.

The case where the external radiation is absorbed by anthracene in contact with salt solutions containing no iodine produces hole injection in a similar way. It is assumed that when the exciting radiation is absorbed (3650 Å.), excitons are produced. Most excitons are found near the illuminated electrode, frequently colliding with the electrode. During a collision, the injection of positive holes is possible if equation (1) is satisfied.

The energy balance at the electrode in contact with the excited anthracene (A^*) surface is :



If these values are placed in equation (1), using a value of 5.5 eV. for I_A , there is an excess in energy of about 1.5 eV. for the injection of a positive hole into the anthracene.

Step (8) involves the capture of an electron by a water molecule⁴. The resulting ion is unstable and will dissociate, probably forming hydrogen and

hydroxyl. At the opposite electrode, the discharge of the positive hole is accomplished as at an ordinary electrode.

The major influence of the positive electrode on the bulk conductivity is further indicated by the comparison of the electrode efficiencies of Cl^- and I^- solutions⁵. The replacement of Cl^- by I^- decreases the positive current flowing away from the adjacent anthracene surface by a factor of 13. This reduction clearly indicates that most of the current is produced at the electrode adjacent to the excited region of the crystal.

Some conclusions may also be drawn about the nature of the current (i^-) which flows when the illuminated side of the crystal is at a negative potential. The injection of negative carriers into the anthracene is probably also energetically feasible, but apparently this process is not probable (i^- is small). This may be due to the low mobility of the electron in anthracene. Our results, moreover, lead to the conclusion that most of this negative current is actually due to the interaction of fluorescent light with the electrode-anthracene surface not directly illuminated by the incident light. This interaction produces positive holes which then flow to the negative electrode.

This conclusion is based on the following observations : the magnitude of i^- is markedly affected by the nature of the electrode distant from the light, and in the same way that the positive current is affected ; the i^- has almost the same dependence on the exciting light intensity as the positive current : both negative and positive currents are saturated at about the same voltage, although at greatly different currents. The latter result cannot be explained by assuming the formation of an internal space charge, since in this case an increase of the field would cause a large increase in the photocurrent ; this does not occur.

The existence of a true negative current within the anthracene is, however, not excluded. Internal polarization experiments by M. Silver⁶ and M. Pope⁷ on polycrystalline layers and single crystals, respectively, of anthracene can best be explained by assuming the existence of trapped negative charge within the crystal. No equivalent positive charge distribution was ever observed. These results, in conjunction with those on photoconductivity, show that the true negative current carried by electrons exists but is exceedingly small.

Most dark currents differ in behaviour from the conductivity described in this communication. They do not become saturated, as do the photocurrents and the dark currents with I_2 electrodes, and they also do not depend on the nature of the electrode.

For the normal dark current, the criterion for positive hole injection would be satisfied if the difference between W_E and A_A can be supplied by thermal action. The extent to which this occurs is as yet unknown.

These considerations do not exclude the possibility of hole and electron production within the anthracene itself by some process of charge separation. Internal polarization experiments indeed indicate that charges are also produced inside the crystal to some extent. However, the findings of this communication show that charge injection can easily occur and is frequently responsible for the large currents observed. For organic materials other than anthracene, calculations also show the possibility of hole injection.

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¹ Garrett, C. G. B., in "Semiconductors", Hannay, N. B., 634 (Reinhold Pub. Co., 1959).

² Kallmann, H., and Pope, M., *J. Chem. Phys.*, **32**, 300 (1960).

³ Kistiakowsky, G. B., "Photochemical Processes", 64 (Chemical Catalog Co., 1928).

⁴ Pauling, L., *Phys. Rev.*, **34**, 954 (1929).

⁵ Kallmann, H., and Pope, M., *Nature*, [185, 753 (1960)].

⁶ Silver, M., Ph.D. thesis, New York University (1959).

⁷ Kallmann, H., and Pope, M. (unpublished results).

CRYSTALLOGRAPHY

Growth of Single Crystals of Copper

DURING experiments on the effects of alternating deformation on the hardening of single crystals of spectrographically pure copper¹, difficulties were experienced in obtaining reproducible hardening behaviour under the same conditions of alternating straining from 2-cm. long specimens taken from opposite ends of longer crystals. A brief discussion of experiments made to investigate this disparity follows.

The method of crystal growth described by Andrade and Roscoe² did not yield a long coherent length of crystal, and growth experiments were therefore confined to a Bridgman-type apparatus³ inclined about 25° from the vertical. Moulds were prepared from spectrographically pure graphite rod by drilling a 1.6-mm. diameter hole, which was then reamed to a slight taper (1:3,000); the reaming also provided a smoother bore. Moulds were baked *in vacuo* before use.

Crystals 25 cm. long could be readily grown using a rate of furnace travel of 3.8 cm./hr., but they were firmly stuck in the moulds at the lower end, due to impregnation of the graphite with copper to a depth of about 0.5 mm. Shorter crystals 14 cm. long were then grown, and these could be removed from the moulds by tapping. However, the yield stress and the initial rate of hardening of a specimen taken from the lower end of a crystal orientated for easy glide were both about three times larger than for a specimen from the top end; the yield stress for the upper specimen was usually about 27 gm./mm.².

The orientation difference between upper and lower specimens was not obviously greater than the error of orientation determination by the Laue method used⁴. Moreover, spectrographic analysis showed that there was no significant difference in analysis between the two ends of the crystal.

Crystals 10 cm. long were then prepared, and were perfectly free in the moulds. Specimens taken from each end of a crystal gave yield stresses and hardening curves which agreed to within 10 per cent between themselves and with those of the upper specimens of 14 cm. crystals. Further reduction in crystal length did not improve this variability, which was attributed to minor variations in lineage structure (cf. Diehl⁵).

The disparity in results obtained from longer crystals appears to be due to impregnation by molten copper of the porous graphite moulds, resulting in deformation during removal of crystals from the moulds. The extent of impregnation decreases as crystal length decreases, and becomes insignificant in crystals 10 cm. long or less. The effect of the accidental deformation on hardening behaviour is more apparent in alternating straining than in unidirectional testing, since the length of the easy glide region is greater and the rate of hardening is lower^{1,6}.

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¹ Kemsley, D. S., and Paterson, M. S., *Acta Met.* (in the press).

² Andrade, E. N. da C., and Roscoe, R., *Proc. Phys. Soc.*, **49**, 152 (1937).

³ Bridgman, P. W., *Proc. Amer. Acad. Arts Sci.*, **58**, 165 (1923).

⁴ Greninger, A. B., *Trans. Amer. Inst. Min. Met. Eng.*, **117**, 61 (1935).

⁵ Diehl, J., *Z. Metallkunde*, **47**, 411 (1956).

⁶ Paterson, M. S., *Acta Met.*, **3**, 491 (1955).

GEOPHYSICS

Motion of Geomagnetic Field Lines

PRIMARY auroral particles, from the Van Allen radiation belt or interplanetary space, travel down to the upper atmosphere along lines of force of the geomagnetic field. Hence they strike the atmosphere in regions which move with the field lines when these are distorted. The purpose of this communication is to show that this motion of the impact regions can only be very slow, because the high conductivity of the Earth's interior limits the field distortion. This throws serious doubt on the hypothesis of Rees and Reid¹ that a diurnal motion of auroral hydrogen emission through many degrees of latitude may be explained by distortions of the Earth's field. Rees and Reid's theory considers particles from the radiation belt, the orbits of which drift in longitude. Using Alfvén's perturbation method², it may be shown that the drifting orbits of this model pass through the same magnetic field lines on each circuit of the Earth and so follow the motion of these lines.

The distortion involved is the horizontal displacement of a force-line at auroral altitudes, say 100 km. For, however distorted the lines at greater heights, this is the displacement of the primary particles where they are observed. The Earth's conductivity may be taken³ as negligible to 700 km. depth, and as more than 10⁻¹¹ e.m.u. below 800 km. For a period of one day, this latter conductivity gives a skin-depth of 150 km. Thus the displacement of the field lines may be approximated by that for an Earth non-conducting to about 900 km. depth, with an infinitely conducting core below. The lines are immobile in the core, and their displacement in the first 1,000 km. height above that is required.