Electron micrograph of cathode oxides (4400 diameters)

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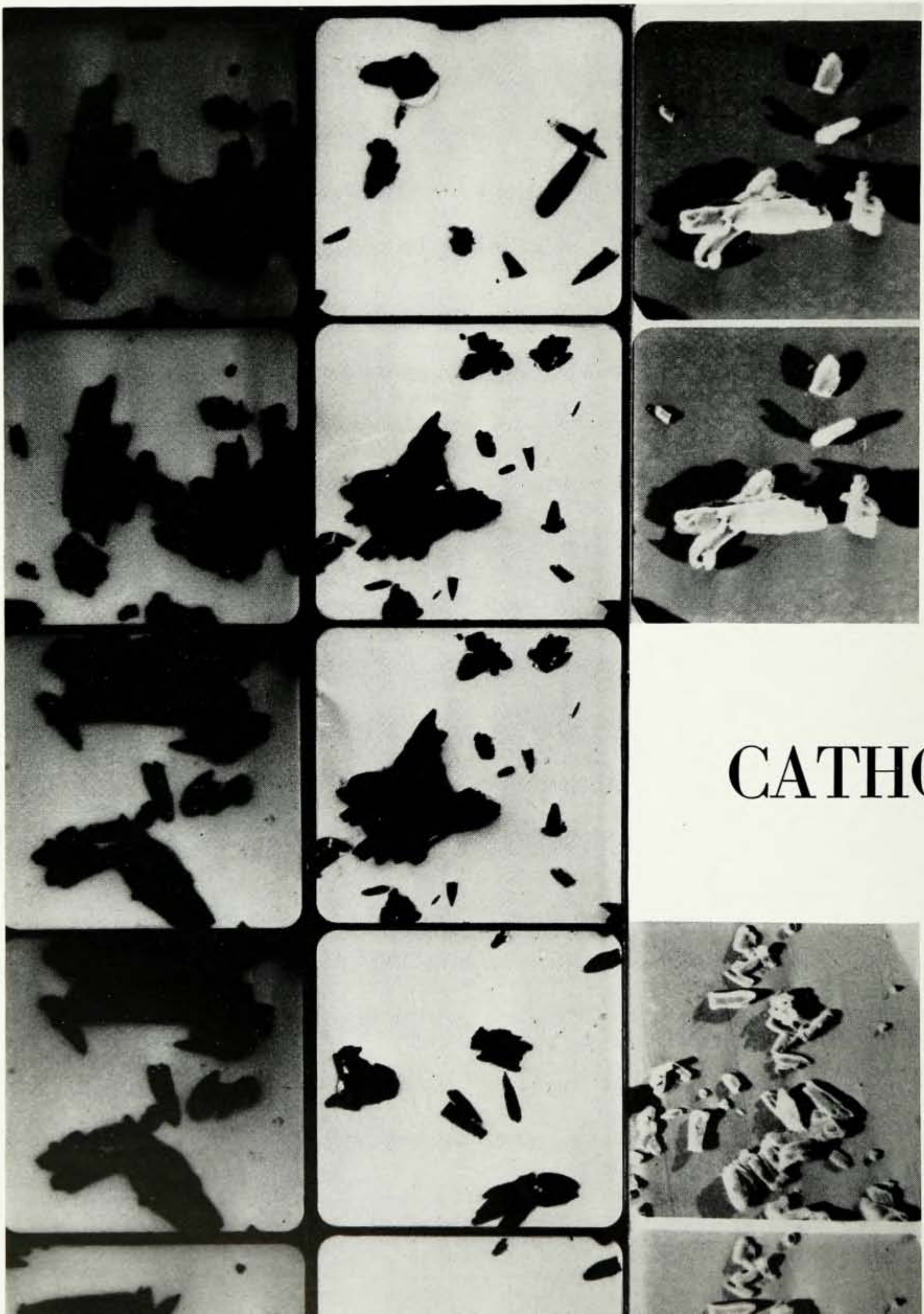
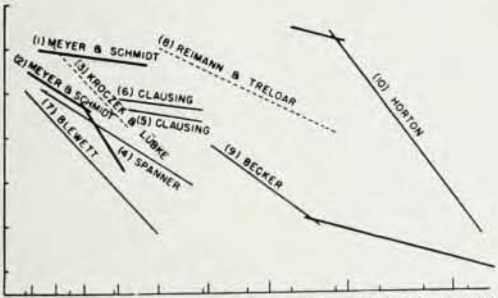


CATHODE

by a well established process, activity trouble has been encountered erratically and to a serious degree. For the research worker, who makes complicated and expensive tubes with many untried features, activity troubles have been more frequent and even more serious. Lack of activity has been attributed to almost everything: to the cathode coating, to the underlying nickel, to dirt, to the perspiration from workers' hands, and to salt or gases in the air. A standard way of treating activity trouble has been to wash the assembled tube parts in boiling distilled water. One company is even said to make a practice of *stopping* its washing of tubes during periods of activity trouble.

Further, not only activity but all other matters concerning oxide-coated cathodes have been a matter of art and lore. When during the war I was privileged to learn something about the making of cathodes in another country, I was bewildered rather than enlightened. One company attributed its success to the use of a light, fluffy coating. Another manufacturer used a dense coating of almost enamel-like texture. In one place, almost any nickel was accepted as a core material, while another company lamented its inability to get from Austria a special nickel, which had been used in making soup kettles and was apparently just the thing for oxide-coated cathodes.

Such experiences, true as they are, tend of course to create an exaggerated impression of confusion. Certainly, the users of cathodes have worked cooperatively together, and much valuable empirical knowledge has been obtained concerning nickel, coatings, and techniques. The fact remains, however, that there is still a considerable amount of disagreement and confusion about very practical matters concerning oxide-coated cathodes.



(*J. P. Blewett, J. App. Phys., Vol. 10, p. 676*)

One aspect of much early work on oxide-coated cathodes is typified by these data on the conductivity of barium oxide. The conductivity is plotted vs the reciprocal of the absolute temperature. The agreement between the measurements by different workers is scarcely striking.

Three Theories

One wonders what the physicists have been doing through all these long years. It cannot be said that they have neglected the problem, but for a very long time no general agreement was reached. The oxide-coated cathode proved a difficult thing to deal with. In the realm of experiment, its seeming simplicity was offset by its delicacy. For instance, there was for a long time extreme disagreement in the measurement of emission. This has proved to be not a matter of differences in cathodes only, but of differences in measuring techniques. New measuring techniques using short pulses have shown that the electron emission of an oxide-coated cathode may under some circumstances rise or decline rapidly with time after a voltage is applied to cause the electron flow.

Physical measurements made to determine the properties of barium oxide itself have shown a variation comparable to that in measurements of emission. Chemical analysis of the most refined nature did indicate that some active cathodes contained less free barium than would be necessary to form a monatomic layer on the surface, but they failed to establish whether or not the presence or quantity of free barium in the coating was related to the cathode activity. It is not surprising that in these circumstances many workers in thermionics turned to the study of emission from pure tungsten. When a man working with tungsten used reasonable care, he could expect his results to be determined more by the physical properties of tungsten than by his experimental technique. If emission from oxide coatings was of more technological importance, that was just too bad for technology.

In the absence of decisive experimental results, theories flourished, and the theories did not differ in fine points alone. The chief schools were three. One of these held that the barrier to emission of electrons was at the surface of the oxide coating, and that in an active cathode a layer of barium atoms covering the surface of the oxide lowered the potential barrier and thus increased the thermionic emission. A second school believed that the barrier to emission was at the surface of the nickel, and that once out of the nickel, the electrons diffused readily through the pores of the oxide and out of the coating. In a modi-

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fied form of this doctrine, the electrons were supposed to pass through the oxide by thermionic emission from particle to particle. The third school held that there is only a small and relatively constant potential barrier at the oxide surface, and that differences in cathode activity are to be attributed chiefly to differences in the number of free electrons in the oxide which are available for emission.

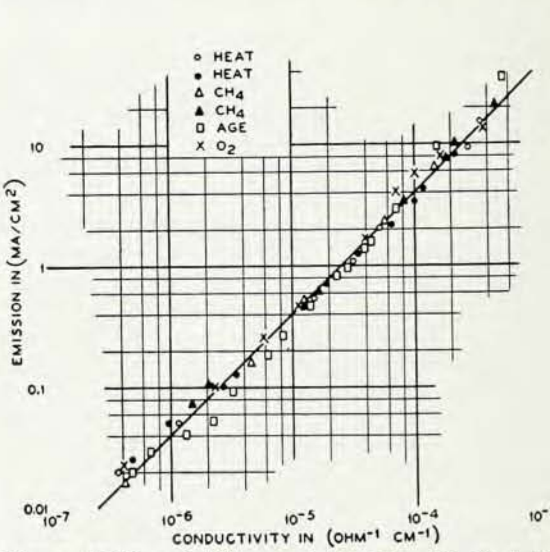
Experimental evidence has been adduced in support of all of these theories. Evaporation of barium into the surface of an oxide-coated cathode sometimes enhances the emission, and this was interpreted as favoring the surface layer theory. During the war studies were made of the cathodes used in magnetrons, from which currents of thirty to ninety amperes per square centimeter were drawn in pulses of a microsecond and less duration. Some measurements indicated a voltage drop between the body of the coating and the nickel core. This led to an extensive study and a considerable literature concerning conditions at the oxide-nickel interface. It now seems somewhat doubtful, however, whether this has any direct bearing on emission from typical oxide-coated cathodes.

Free Electrons

The third theory, that the emission is nearly proportional to the density of free electrons in the oxide coating, is subject to a rather direct experimental check. The conductivity of the coating should also be proportional to the number of free electrons. Thus, when the activity changes, the conductivity should change also. The presence of free electrons in the oxide is presumed to be due to the presence of excess barium atoms as impurities. Now means for changing the activity of an oxide-coated cathode in a reversible fashion have long been known. Exposure of a cathode to oxygen reduces its activity; it is assumed that this is because the free barium is oxidized. Prolonged heating, with or without the drawing of emission, or the exposure of the hot cathode to a strong reducing agent such as methane, increases the activity. It is assumed that this increase is due to the reduction of some of the barium oxide to form free barium.

Thus, a simple test would be to measure simultaneously the electron emission and the conductivity of an oxide coating as it is activated and deactivated. The difficulty is that the test is simple in conception only. In a cracked or inhomogeneous oxide coating, the conductivity and the resistance between test electrodes would not be simply related. Further, the most scrupulous cleanliness is needed in order to obtain an uncontaminated oxide coating whose properties are reproducible. Finally, great care must be taken in measuring the emission in order to obtain a meaningful and reproducible result, without changing or damaging the coating.

Nishibori and Kawamura, Albricht, and others have tackled this tricky problem. Finally, results published in July of this year by Hannay, MacNair, and White seem such as to establish a linear relation between conductivity and emission almost beyond doubt. The test was simple. Two fine platinum wires were wound side by side in a spiral about a long thin core of magnesium oxide. Standard cathode coating was sprayed over the core and the wires.



(Hannay, McNair, and White; J. of App. Phys., Vol. 20, p. 673)

The conductivity of thermionic emission of a barium-strontium oxide coating at a fixed temperature was repeatedly increased by heating above test temperature, by heating and drawing emission, and by heating in methane, and repeatedly decreased by exposure to oxygen. The thermionic emission was always closely proportional to the electrical conductivity. This supports the theory that both are proportional to the density of free electrons in the oxides. At a fixed temperature, the number of free electrons is supposed to be determined by the number of atoms of free barium.

The whole assembly could be heated by a tungsten coil passing through longitudinal holes in the magnesia core. The conductivity could be obtained by measuring the resistance between the two platinum spirals. The emission to an anode surrounding the assembly could be measured.

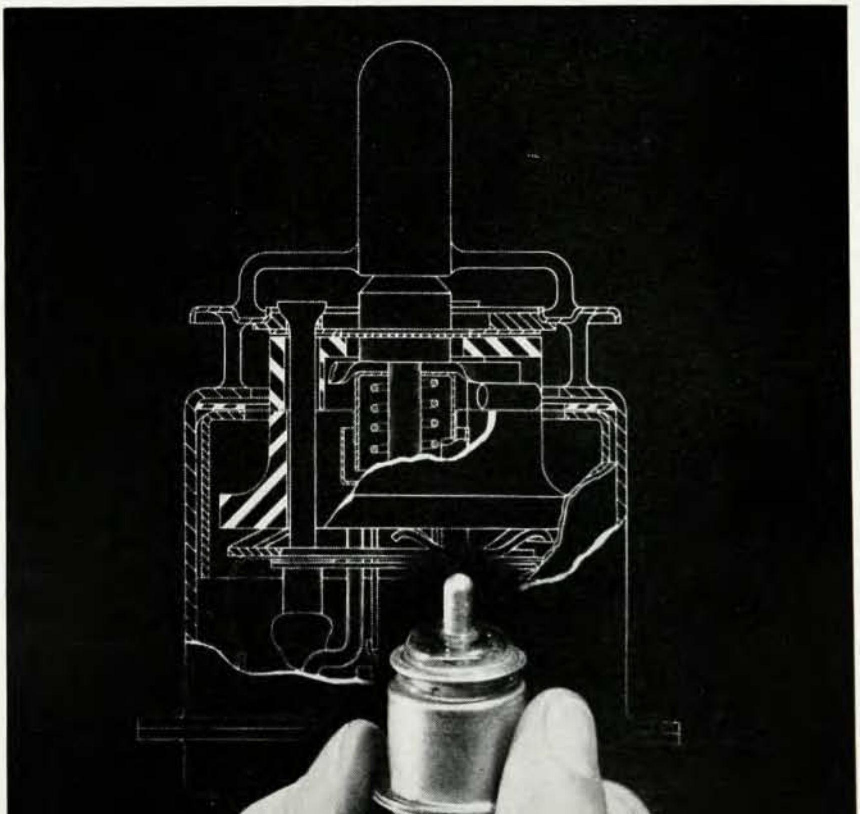
Repeated measurements made at a fixed temperature on each of a number of tubes established the same constant proportionality between electron emission and electrical conductivity. This is shown in the figure. When activity was increased, whether by heating and drawing emission (aging), or by exposure to methane, the conductivity was increased proportionately. When activity was reduced by exposure to oxygen, the conductivity was proportionately reduced.

Careful auxiliary tests indicated that the conductivity measurement was reliable. No evidence of polarization at the electrodes was found. Admission of helium did not change the conductivity, indicating that the electron flow was actually through the solid oxide and not through the interstices of the coating or around the surface. The third theory therefore is the likely one: differences in cathode activity are to be attributed chiefly to differences in the number of free electrons in the oxide.

If there is a moral to this story, it is perhaps that the issue is always in doubt until sufficiently careful measurements have been made, and that it is never too late to make careful measurements as long as the issue is in doubt.

In the practical business of making oxide-coated cathodes, no sudden change has taken place. Knowing that activity is due to a minute trace of an impurity does not tell one how the impurity can be controlled. In an analogous case, the semiconducting property of silicon and germanium is due to the presence of impurities. Contrasted with oxide coatings, these materials are nonporous and can be worked with at room temperature and in air. Yet, it has taken decades to control their properties.

Making one good experiment, however, leads to another. No longer so bedeviled by contradictory theories, physicists and chemists may make progress which will ultimately change the art of making good cathodes into a science. Too, the artists themselves should make better progress, once given sound guidance concerning basic principles. A clear understanding of the nature of thermionic emission should prove an invaluable guide in unifying and directing studies of particular materials and particular processes.



This tube, which uses an oxide coated cathode, has been developed for radio relay systems

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