

The CPC: A Medium Current Density, High Reliability Cathode

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The coated powder cathode is an inexpensive, reproducible emitter which combines the virtues of various conventional cathode types, and is suited to use in modern high-power, high-reliability electron tubes. It is best considered as a modification of the classic oxide cathode in which each particle of the emissive coating is covered with a thin layer of nickel. Inherent advantages of this cathode over the oxide cathode include the ability to sustain current densities up to 1 amp/cm² over long, calculable lifetimes, increased flexibility in time and temperature during processing, and improved coating adhesion. This paper describes the concept, fabrication and mechanism of the cathode and presents data obtained from a diode evaluation program.

I. INTRODUCTION

Modern requirements for high-power microwave tubes having very high reliability have accentuated the demand for cathodes capable of dc or long pulse emission in the range 0.5 to 1.0 amps/cm² over lifetimes up to 50,000 hours. The best oxide cathodes available function only at the lower end of this range over relatively short lifetimes, and in consequence metal matrix types are normally used. The most widely used of these is the tungsten matrix, but this demands operating temperatures of the order of 1000°C,* and the reliability of the tube then begins to depend on factors such as the integrity of the cathode heater and its radiation shielding. Nickel matrix cathodes, prepared from powder compacts of nickel and active oxides, and

*Throughout the remainder of this paper, °C will be used to mean degrees Centigrade true temperature. The abbreviation °B will be used to mean degrees Centigrade brightness on nickel as measured by optical pyrometer on the side of the cathode button.

capable of operating at temperatures between the tungsten matrix and oxide cathodes, are limited in high-reliability applications by their shrinkage, residual gas context, and local inhomogeneities. The conventional oxide cathode, with its low operating temperature and "clean" structure, would normally be the best choice if it were possible to modify it in such a manner as to permit emission of the order of 1 amp/cm² over lifetimes in excess of 20,000 hours.

The coated powder cathode (CPC) can be regarded as a modified oxide cathode in which the active coating is prepared from particles of conventional electron tube grade carbonates, each lightly coated with nickel. The nickel normally constitutes only 1 to 3 percent by weight of the carbonate. Its primary effects are to change the electrical resistance, sintering behavior, and emissivity of the coating. The improved performance of the coated powder cathode can be interpreted in terms of these primary effects.

If an oxide cathode coating is permeated by metal forming electrical contacts between the base and the vacuum interface, the field lines along which electron donors drift during high current density operation are modified. The major component of the field will become transverse when the distance between metal "electrodes" in the coating becomes substantially less than the coating thickness. The donors will then remain in the surface layers of the cathode coating, keeping the work function low. This situation exists in metal matrix cathodes, where relatively small particles of oxide are embedded in nickel or tungsten, an analogy being one of metal tubes filled with oxide extending to the surface. The donors in such systems would be expected to move toward the metal-oxide boundary at the surface as current density is increased, giving an oxide-vacuum surface having a nonuniform but essentially constant concentration of donors. Despite the nonuniformity, the average or effective work function remains low.

The CPC is constructed with a novel distribution of nickel in the active coating, which achieves the surface donor retention mentioned above with only 0.5-3.0 wt percent of metal.* This should be compared to 70-80 wt percent metal normally required to provide a conducting path through a conventional matrix cathode. In reducing the amount of metal involved in the surface one approaches the lowest

* Normal oxide cathodes have resistances of the order of 1-10 Ω/cm^2 . Assuming the bulk resistivity of nickel, the nickel coating of a CPC particle could in theory be of the order of 10^{-13} cm thick to have a resistance comparable to the activated oxide. Therefore, films of the order used (0.01 μ) should have substantial effects even if the resistivity of the film is substantially greater than the bulk resistivity.

practical work function—that of the classic oxide cathode. Thus, the operating temperature of the CPC (700-800°C) is comparable to that of the oxide cathode, and is essentially unaffected by the emission level in the region studied. Operating temperature is, however, influenced by the vehicle employed, in proportion to the rate of poisoning reactions. Thus, a close-spaced diode normally requires a cathode temperature of the order of 800°C, while a travelling-wave tube with a slow wave structure and remote collector will operate in the 700-750°C region.

The nickel film around each particle also inhibits the growth of relatively inactive, large single crystals of (Ba, Sr)O during high temperature outgassing. In this respect, note that Eisenstein¹ has shown (Ba, Sr)O crystallite growth in oxide cathodes to be relatively rapid above 900°C and many workers have observed the degraded high current density characteristics of oxide cathodes that experienced appreciable time at temperatures above 900°C. This is consistent with the suggestion² that donor movement in single crystal material is very fast, leading to deep donor depletion layers.

CP cathodes can be processed at temperatures as high as 1150°C without detectable degradation in subsequent emission. This has practical advantages in the reduction of time on the tube processing station, and in the thorough degassing afforded the heater-cathode assembly.

The inhibition of crystallite growth extends to the reprocessing of an activated CPC which has been exposed to room atmospheres. Although X-ray diffraction photographs taken before and after exposure show that water and carbon dioxide are indeed reabsorbed, the coating does not lift or "bloom," and if reprocessed by a conventional schedule will normally reactivate. This implies that the mixture of barium and strontium hydroxides and carbonates formed within each nickel shell is largely retained within the shell during reprocessing, reducing the tendency to form a glassy phase.

When sprayed onto a nickel base with a conventional nitrocellulose binder, the CPC coating shows excellent adhesion, resisting a Scotch Tape test. This appears to be related to the slight roughness of the particle surface. This is visible in Fig. 1, which shows representative photomicrographs of coated and uncoated powders. During breakdown of the carbonate to oxide, the nickel film is split to allow the escape of carbon dioxide, and at the same time, nickel-to-nickel sintering begins. The latter is effective in increasing the adhesion to the base and

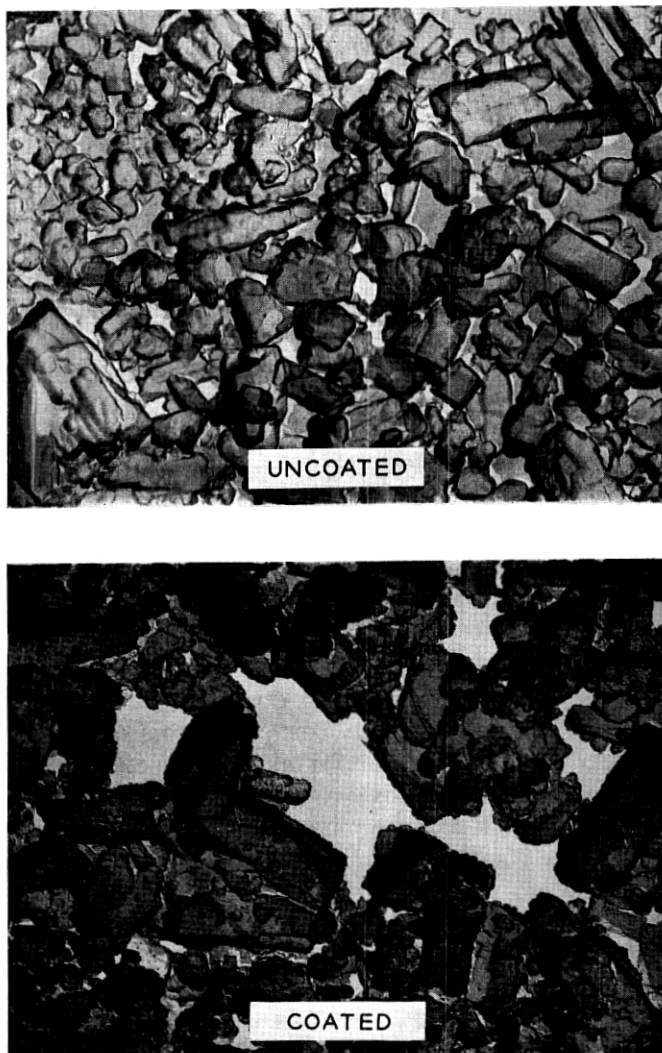


Fig. 1—Electron micrographs of nickel coated and uncoated double carbonate particles.

the cohesion of the coating still further. The oxidation of the nickel shell during carbonate breakdown is found to be very slight. In tubes requiring ultra-smooth coatings (ultrafine powder), excessive cohesion between particles can give rise to surface cracking known as "mud-flattening" unless care is exercised during the processing. However, through the particle size range normally used in oxide cathode technology, the integrity and adhesion of the processed coating is excellent.

The nickel network responsible for the improved performance of the CPC is maintained during life by sublimation of nickel from the base alloy into the coating. An equilibrium is attained, wherein nickel is lost by evaporation from the surface of the coating, and replenished from the base. Thus, a CPC coating, applied to a low vapor pressure metal such as platinum, would slowly lose its metal network during life, and transform into a simple oxide cathode. This transformation has been observed, but has not been studied quantitatively. However, many of the advantages of the CPC are gained by establishing nickel-to-nickel contact between each particle prior to breakdown and activation, and use on substrates other than nickel to gain processing advantages is not unreasonable. Notice that the overall rate of nickel sublimation from a CPC is identical to that of an oxide cathode operating at the same temperature.

II. PREPARATION OF THE NICKEL COATED POWDER

A useful technique for the preparation of metal coated powders involves the decomposition of a thermally unstable metal compound in a "fluid bed." In conventional nickel coating, the powder is normally maintained "fluidized" by the passage of hydrogen through a sintered disc at the foot of a vertical tube containing the powder. Nickel carbonyl, $\text{Ni}(\text{CO})_4$, is introduced to the hydrogen stream and thermally decomposed to nickel on contact with the heated powder. This method is excellent for use with metal powders or insulating materials of particle size $>50 \mu$. However, in the range $50 \mu \rightarrow 5 \mu$ the agglomeration of insulating particles as a result of the accumulation of static charge becomes increasingly serious, and it has previously been considered impractical to coat each individual particle of an insulating powder of particle size $<5 \mu$.³ Since most cathode powders are substantially $<5 \mu$, and the coating of individual particles was most desirable, a new technique was required. This was found in a method we choose to call "wet" fluid-bed coating. The powder is maintained suspended in a suitable inert liquid and $\text{Ni}(\text{CO})_4$ introduced through

a bubbler. This eliminates agglomeration, at the expense of an additional processing step—the removal of the liquid.

Since we are dealing with a cathode material where trace contamination may poison the emission and cause tube failure, extreme care in handling under ultraclean conditions is imperative. All vessels and handling devices must be cleaned according to normal oxide cathode preparation specifications, and all materials used must pass oxide cathode specifications for impurity content. Once cleaned, vessels must be protected from contamination prior to use.

The powders used in these experiments were coprecipitated from nitrate solutions with ammonium carbonate and have been extensively used for conventional cathode coatings. For the present study the "as received" powders were reduced in particle size by ball milling to give very smooth "high density" cathode coatings.* This procedure does not improve emission, and is, therefore, only required where electrode spacings require tight tolerances on coating uniformity and smoothness. Where the particle size of commercially available carbonate is appropriate for the tube requirement, "as received" powder may be nickel-coated without any preconditioning.

Fig. 2 is a schematic of the nickel coating apparatus. The apparatus is composed of a reaction vessel and a flow system. Hydrogen is the carrier gas used during the reaction. Nitrogen is used for flushing to keep the system free of contamination while on standby and to purge the hydrogen at the termination of the reaction.

A modified 500 cc gas wash bottle is used as the reaction vessel. It is modified to bring a gas entry tube down the wall inside the vessel to within 1 inch of the bottom. The center of the vessel is then free for a nickel stirring rod adapted to the vessel through a nickel taper fitting in the ground glass joint at the top. The nickel taper is, in turn, fitted to a rotary vacuum feed-through coupled to an electric motor. All of the joints are vacuum tight and only nickel faces the inside of the vessel, thus avoiding foreign contamination. The entire vessel is immersed to just below the gas inlet tube in an oil bath and the contents of the vessel brought to the reaction temperature of 110°C with a hotplate. A suspension of the carbonate in amyl acetate is added to the reaction vessel before sealing the system. A condenser is installed at the exhaust end of the reaction vessel to allow reflux of the amyl acetate that vaporizes at 110°C, thus keeping the solution level constant.

* Particle size: 90 percent $< 1.6 \mu$; coating density: approximately 2 g/cc.

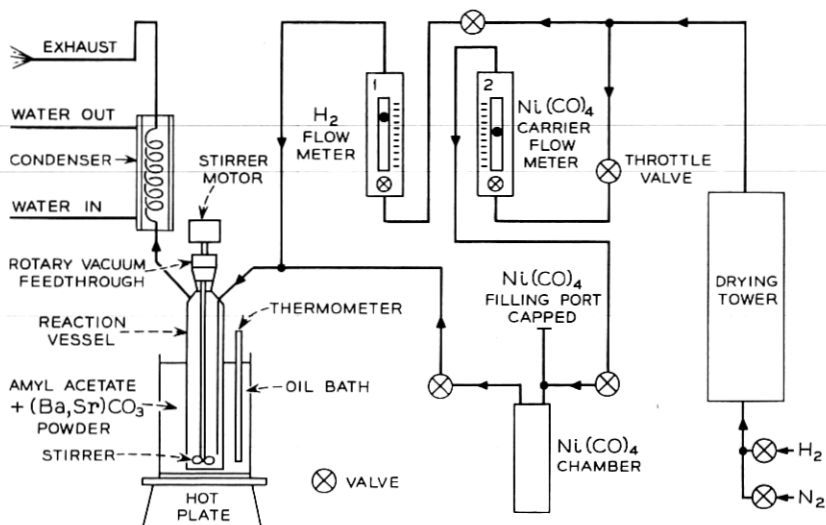


Fig. 2 — Nickel coating apparatus.

The Ni(CO)₄ chamber is made of metal, with a gas inlet tube running to within ½ inch of the bottom, and an inlet port that can be opened for filling and sealed during the reaction. A measured excess of carbonyl is added before every reaction and the chamber emptied and flushed with nitrogen at the completion of every run.

After the system is sealed and purged with nitrogen, a flow of hydrogen is established, bypassing the carbonyl chamber, such that vigorous bubbling occurs in the reaction chamber, and a hydrogen flame is established at the exhaust. Some hydrogen is then diverted through the carbonyl chamber and this proportion increased until the hydrogen flame at the exhaust become luminous with green fringes, indicating that excess carbonyl is being burned. Under these conditions of excess carbonyl and constant bath temperatures, with a given system and powder particle size distribution, the percent nickel deposited depends on the reaction time. For our system and particle size distribution, we achieved 2.5 ± 0.3 weight percent nickel in $3\frac{1}{2}$ hours, although this is not a linear function of time (the reaction is autocatalytic).

The thickness of nickel on each particle will be constant under the above conditions regardless of the particle size distribution. The percent nickel in the lot, however, will vary with the particle size. Thus, the operating parameters of a given system must be determined em-

pirically. Note that since the powder used in the study described here was very fine, values of approximately 1.0 wt percent Ni would correspond to comparable Ni thickness on coarser, conventional powder.

During the coating reaction there is essentially no agglomeration of the coated powder; however, pure nickel is deposited on some parts of the reaction vessel and flakes off into the mix. To remove these flakes the coated suspension is sieved, first through a 37μ sieve and then through a 20μ sieve. Concentrated nitrocellulose solution is then added to bring the suspension to a condition suitable for spraying. Spray mix prepared from nickel-coated powder has similar settling characteristics to conventional oxide cathode mixes. If long shelf-life precedes use, ultrasonic agitation should be used to resuspend prior to transferring to spray equipment.

Fig. 3 shows the effect of nickel coating on the particle size of the carbonate crystallites and indicates the change to be of the order of 10 to 15 percent of the initial size. This may be accounted for by slight agglomeration rather than particle size growth. This conclusion is supported by the many photomicrographic comparisons made between coated and uncoated double carbonates. (Fig. 1) It can be seen that the coated powder has a rougher surface than the uncoated powder. This roughness may account for the superior adhesion characteristic of the coated powder.

Data shown in Table I indicate an analysis representative of a CPC surface ready for activation compared with an analysis of the as-received powder. No pick-up of undesirable elements should occur

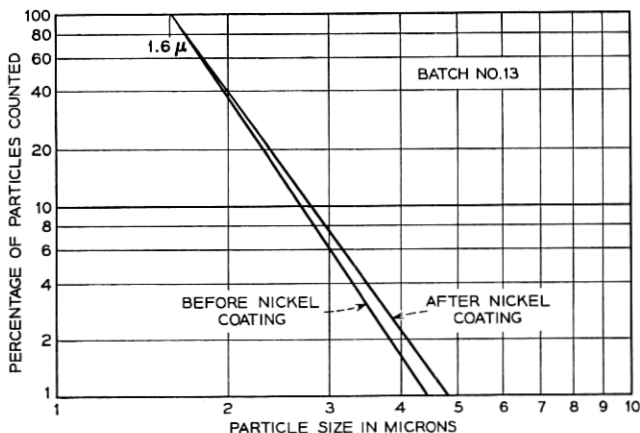


Fig. 3 — Effect of nickel coating on particle size.

TABLE I—SPECTROGRAPHIC ANALYSIS OF BARIUM-STRONTIUM CARBONATE BEFORE AND AFTER NICKEL COATING

Element	Before (as received)	After (Ni coating)
Barium	Major	Major
Strontium	Major	Major
Nickel	0.00X	Major low
Calcium	0. X high	0. X high
Sodium	0. 0X	0. 0X
Copper	0. 00X	0. 0X low
Silicon	Not found	Not found
Magnesium	0. 00X	0. 00X
Iron	0. 00X low	0. 00X
Lead	0. 00X low	0. 00X
Potassium	0. 00X low	0. 00X
Manganese	0. 000X	0. 000X
Silver	0. 000X low	0. 000X low

Elements checked but not found: zinc, cadmium, indium, bismuth, antimony, arsenic, tin, thallium, gallium, germanium, zirconium, cobalt, chromium, molybdenum, vanadium, tungsten, lithium.

Note: Major = >5% Estimated

0. X, 0. 0X, 0. 00X, etc. = Concentration of Elements estimated to nearest decimal place, e.g., 0. 0X = 0. 01 – 0. 09% estimated.

as a consequence of the coating operation. Infrared spectrographic analyses were made of the amyl acetate before and after the coating process. No contamination or change in the amyl acetate absorption spectrum was observed.

It is important to determine carbon introduced by the coating process, since carbon activation of the cathode would result in premature loss of oxide. Control analyses performed on nickel coated MgO of similar particle size shows that the carbon introduced (corrected for intrinsic carbon and absorbed amyl acetate) is of the order of 0.1–0.2 percent by weight of powder. This carbon appears to be completely removed during the breakdown of the carbonate to the oxide, probably through the high temperature oxidation-reduction reaction $C + CO_2 \rightleftharpoons 2CO$ which favors the production of CO at temperatures above 800°C. This view is supported by the fact that there is no immediate activation in diodes, and that mass spectrometer analyses of platinum-based cathodes show no CO tail after breakdown.

III. EMISSION AND LIFE TESTING

3.1 Cathode Preparation, Vehicle, Processing and Testing

The application of the coated powders to cathode bases used in the study described was carried out by conventional spray techniques.

Binder burnout⁴ was used throughout diode testing. However, this has been found undesirable in processing large area cathodes coated with powder of a conventional particle size, since the coating coherence after binder burnout was minimal and did not allow good yields in assembly. Cathode bases were preconditioned by a rigorous method based on volatile acid cleaning⁵ and including a liquid honing of the surface by calcium oxide. The base metal was high purity 0.1 weight percent zirconium/nickel alloy (see Table II) unless otherwise stated. This alloy is used to obtain long life, and is relatively inactive by comparison to standard alloys such as 220 grade nickel.

The test diode is illustrated in Fig. 4. It features a 0.085-inch cathode in a ceramic insulator, mounted on a massive anode heat sink, which includes a nickel button anode. The diode contained conventional tube materials including Kovar, steel, molybdenum, copper, nickel and ceramic. The final closure of the tube was done by heliarc welding. Pieceparts and subassemblies were cleaned by rigorous processing techniques and were atomizer clean.^{5,6} Minimum grade: 3. These techniques were designed to eliminate activation or deactivation by extraneous variables and permit the study of deliberate changes in processing or material variables with a minimum of samples. The success of this can be estimated from the narrow spread in activity of "identical" diodes (Section 3.2.5) and the fact that the yield of tubes in the entire program was approximately 98 percent seal-in.

Tubes were processed in groups of six on individual getter-ion pump stations. Bakeout was for 16 hours at 425°C, at which point, the pressure was normally in the 10⁻⁹ torr range. All tubes then passed through

TABLE II—IMPURITY SPECIFICATION FOR HIGH PURITY ZIRCONIUM-NICKEL CATHODE ALLOY

Element	Percent max.	Element	Percent max.
Copper	0.005	Iron	0.005
Manganese	0.005	Carbon	0.003
Silicon	0.005	Sulphur	0.001
Titanium	0.005	Magnesium	0.005
Tungsten	0.005	Oxygen	0.001
Hydrogen	0.001	Nitrogen	0.001
Cobalt	0.005	Each Other Metal	0.005

All other impurities than those listed shall not exceed a total of 20 ppm and no individual impurity shall exceed 1 ppm.

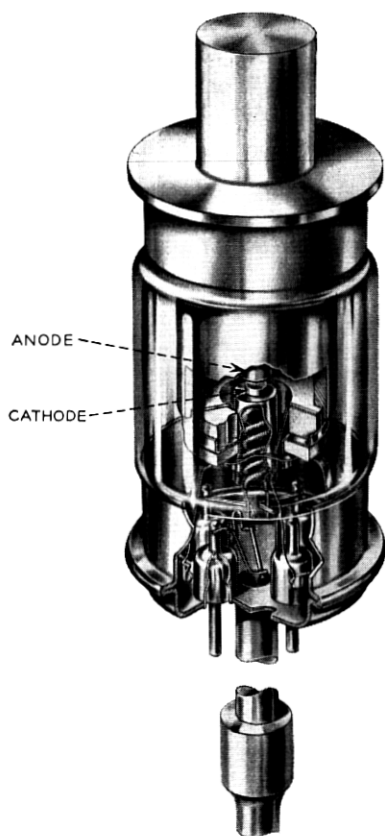


Fig. 4 — M-4059 diode.

a standard processing cycle which is described in Appendix A. They were then placed on aging racks with the cathodes at 900°C and with dc voltage applied. After 16 hours at this condition, the cathode temperature was lowered to 810°C and emission current adjusted to 0.3 amps/cm^2 . This was the predominant current density throughout the diode program, and was based on past experience of adverse "diode effects" observed in the diode used at higher loadings. In addition, it represented a cathode design objective at the time.

The test method used for all of these tubes was the IR dip.⁷ This is a modification of the dip test in which the cathode current-tempera-

ture transient is plotted on an $X-Y$ recorder when the heater power is turned off. Cathode activity is given by the temperature of the transition from space charge limited emission to temperature limited emission. Unless otherwise noted, all measurements were made at 125 mA/cm² rather than the operating level, to be assured of an activity measurement in extreme cases where the emission is not space charge limited at the operating level. With this analysis, high temperature indicates low activity, and low temperature high activity.

3.2 Results of Diode Program

Except where noted, each of the curves of diode activity shown in this section represent the average of six identical diodes. Since the significance of the difference between two such curves is difficult to assess without a knowledge of the spread in the data, the values of the probability that there is a difference between two curves are shown at significant points on the plots. The probability, P , is based on Student's t -test.

3.2.1 Reproducibility

Fig. 5 shows the individual "IR dip" temperatures on a batch of six diodes processed according to the standard technique (Appendix A). The spread is rather wide early in life, and becomes much smaller after about 1000 hours as the tubes "age in." This allows an estimate of the spread inherent in the data to be illustrated in subsequent figures.

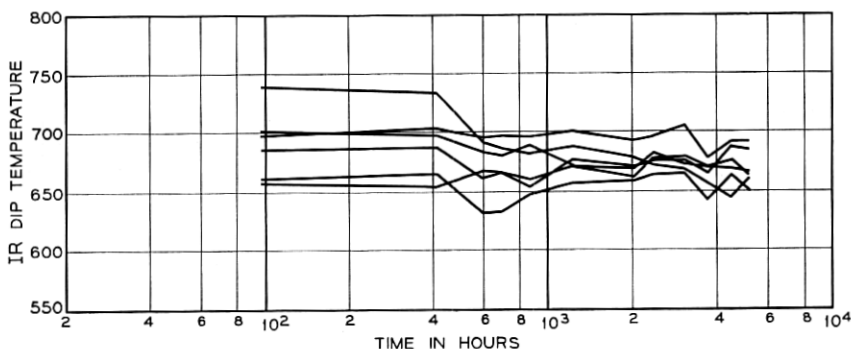


Fig. 5— Typical spread in the data for six "identical" diodes.

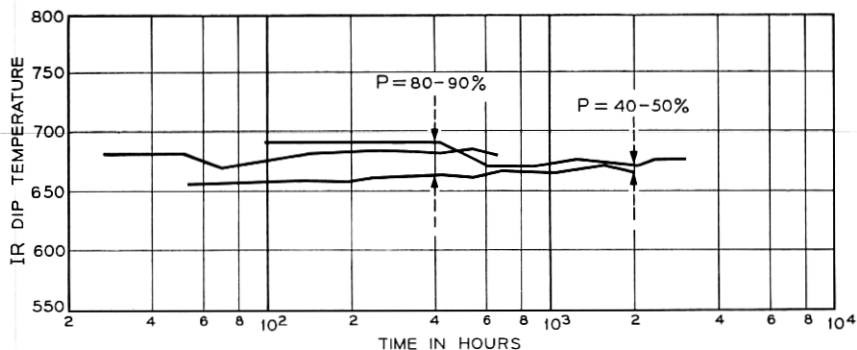


Fig. 6 — Reproducibility of the coating batches.

3.2.2 Reproducibility of Coating Batches

Fig. 6 shows the results of three groups each containing six diodes processed by standard technique, sprayed from three independent coating batches which were prepared in an "identical" manner. There is approximately 35°C spread in temperature initially, but by 1000 hours this spread is completely insignificant. This indicates that while there are some differences, perhaps in the small details of the processing cycle, or in the trace amounts of impurities within the system, these are lost after approximately 1000 hours.

3.2.3 Percent Nickel in the Coating

Fig. 7 shows the average dip temperatures for two groups of six diodes each made from the same coating batch which had been divided into two parts to permit different exposure times to nickel carbonyl. Batch 15b has 7.26 percent by weight of nickel,* and batch 15a 2.58 percent. As nickel content is reduced, we approach the oxide cathode which represents the lowest attainable work function in the system, useful as such when the required current density causes no appreciable donor depletion. Note that these measurements were carried out at a life condition of $0.3\text{A}/\text{cm}^2$, where the detrimental effect of excessive nickel coating is accentuated. At higher current densities where donor depletion in the uncoated oxide is more significant, the beneficial effect of nickel coating tends to dominate even if nickel is applied in thicknesses substantially greater than the optimum.

* This cannot be considered a representative batch since it was deliberately created with an excessive nickel content to produce a pronounced effect.

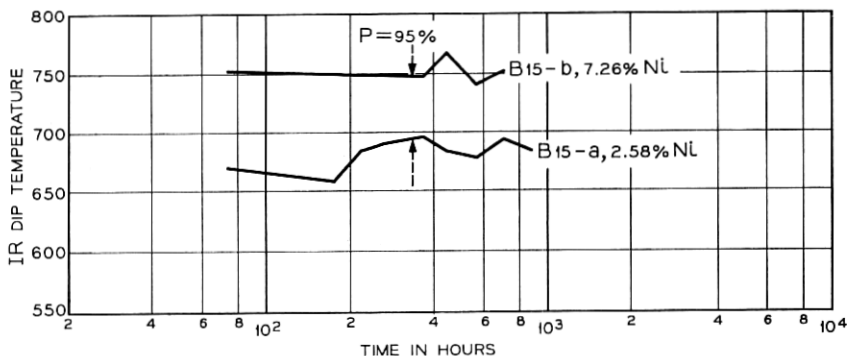


Fig. 7 — The effect of the percent nickel in the coating batch.

3.2.4 *The Effect of Cathode Coating Thickness*

This effect is shown in Fig. 8 in which we have plotted the data from cathodes coated with batch 15b which was discussed above. One group is sprayed 2-mils thick, the other 0.65-mils thick. The thicker spray coating yields a higher activity level. These effects may be explained as follows. The thin coating would be of the order of five particle diameters thick. The likelihood of a barium atom produced at the coating-base interface simply evaporating from a pore-end is relatively high. However, in the thicker coating there is a larger cross section for adsorption of the barium atom into the oxide lattice. Hence, the donor concentration in the surface of the thicker coating is likely to be higher than the concentration in the thinner

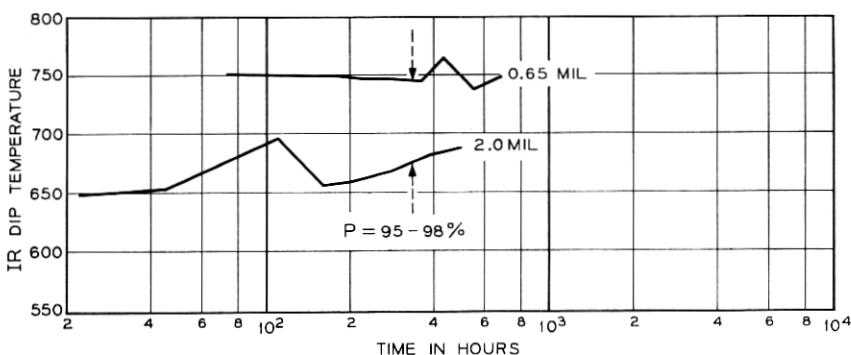


Fig. 8— The effect of the sprayed coating thickness.

coating, and the activity level higher in the former. One would expect this effect to be less pronounced with coatings which have a lower percentage nickel since there would be a higher probability of barium adsorption in the latter case.

3.2.5 Coatings Applied by Electrophoresis

A technique for applying the nickel-coated carbonate to cathode bases by electrophoresis was developed by M. Hanes⁸ using a nickel nitrate activator. Diodes were made from six cathodes coated by this technique. These were processed by the standard technique and the results are shown in Fig. 9. These results are essentially the same as those obtained by other coating techniques and demonstrate that the nickel nitrate used as an activator in the electrophoresis process does not have an appreciable deleterious effect on the emission. This approach could prove useful in cases in which spray coating proved difficult, such as on very large radiused cathodes or filaments.

3.2.6 Dependence on the Base Alloy

Fig. 10 shows the results of two batches of six diodes based on two different cathode alloys. One group is on the alloy, used throughout the program, 0.1 percent zirconium/nickel the other is on a commercial alloy called "RM No. 8" which is essentially a magnesium/nickel alloy. The latter alloy is quite active. As expected, the "RM No. 8" activity is higher than the zirconium/nickel activity early in life since the former produces large initial amounts of reducing agent. Eventually, after approximately 1000 hours, the tubes are completely activated and give essentially the same result. Choice of base alloy

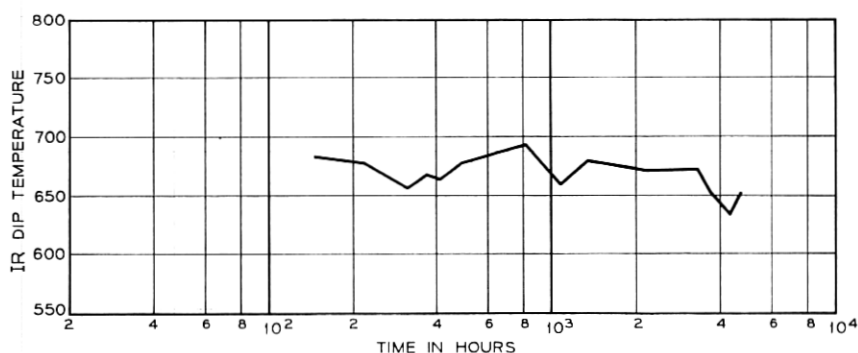


Fig. 9 — Cathode coatings applied by electrophoresis.

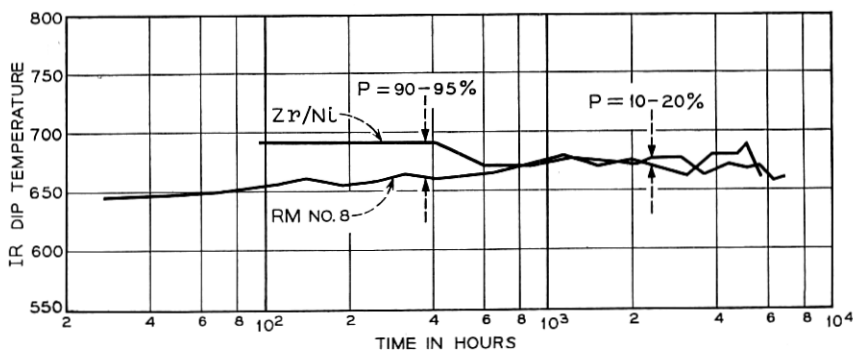


Fig. 10 — The effect of the base alloy.

would, therefore, normally be made on the basis of desired life, since high initial activity is reflected in shortened lifetimes.

3.2.7 The Effect of Processing

Fig. 11 shows the results of three groups of six diodes each, processed by different techniques. One set is processed by the standard technique already described. Another group marked "matrix," was processed according to a schedule originally developed for a nickel matrix cathode which features activation at 1050°B for 20 minutes. The detailed schedule is given in Appendix B. The third group marked "standard and bake" used the standard processing up to the point at which dc voltage had been applied. The dc voltage was turned off after about one hour and the cathode temperature reduced to approximately

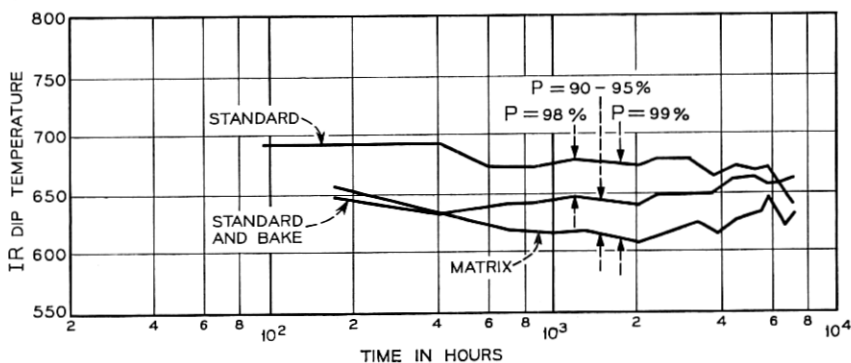


Fig. 11 — The effect of processing.

750°B. The tubes were then replaced in the oven and baked at 425°C for an additional 16 hours. The filaments were then turned off, the getters flashed, and the tubes pinched off.

The matrix processing results in tubes of much higher activity than either of the other processes; however, the rebake results in tubes of higher activity than the standard processing. In the case of standard plus bake, the substantial improvement in activity is attributed to reduction in "diode effects" such as gas on the anode. A rebake after the standard processing technique drives off a large amount of this gas and results in cathodes of higher activity, though this effect would not be so pronounced in an open structure. Matrix processing also achieves this by heating the anode to much higher temperatures than are encountered during the standard processing technique. Whether the cathodes processed by the matrix technique are inherently better than those processed by the standard technique other than because of diode effects is not clear. It is certainly evident that the matrix technique has no great detrimental effect on the cathode activity (as would be the case for an oxide cathode) and this confirms the function of the nickel network in inhibiting sintering. This property is of considerable practical importance. The fact that high temperatures are not detrimental means that temperature control during processing is no longer critical. More importantly, high temperature processing means more rapid outgassing of the cathode and its environment and more rapid activation. Together, these advantages can lead to greatly reduced processing and aging time.

3.2.8 Anode Power and Current Density

Fig. 12 shows the results of three groups of six diodes each at different anode powers and current densities. All diodes were processed by standard technique and placed on life at 800°B. One group was set at 0.3 amp/cm² with 0.9 watts anode dissipation. A second group was at 0.3 amp/cm² and 1.8 watts anode dissipation. A third group was set at 0.6 amp/cm² and three watts anode dissipation. These anode powers and current densities were achieved by varying the voltage and the cathode-anode spacing. In the two groups operating at 0.3 amp/cm², the higher the anode power, the lower the activity. This is due to outgassing of the anode and represents a "diode effect," as mentioned in the previous section. The third group, operating at twice the current density and at higher anode power has the highest activity level of all. This indicates that high current density per se is bene-

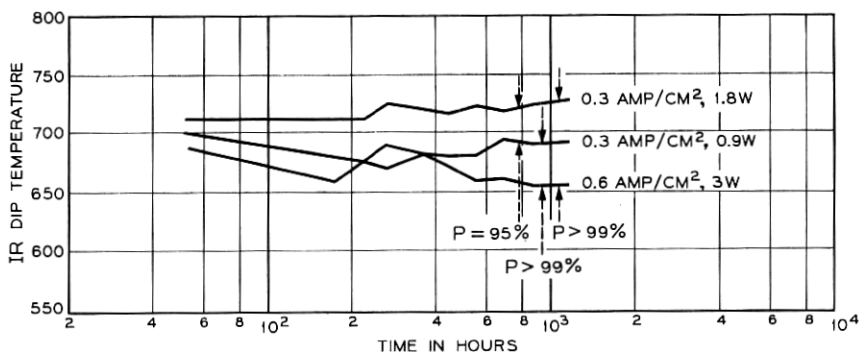


Fig. 12 — The effect of anode power and current density.

ficial to CPC activity and in this case was apparently sufficient to overcome even the effects of a higher power level on the anode. This activity enhancement by higher current density is probably a result of electrolytic activation. This effect will be discussed further in Section 4.3.

3.2.9 The Effect of Breaking the Coated Carbonates

As discussed above, we postulate that a large proportion of the barium atoms in the top layer of the cathode coating arrive there by a process of diffusion through the pores of the intervening coating. Upon arrival, they must contact an oxide particle to be useful as donor precursors. A continuous nickel film surrounding these particles would obstruct entry of the barium atoms into the oxide lattice and make the effective donor production rate low. It is reasonable to suppose that during the breakdown, ($\text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2$) numerous fractures occur in the nickel film originally placed on the carbonate particles. These would be sites through which donor precursors could enter the surface particles.

If the coated particles are fractured by milling, the area of exposed oxide would be substantially larger and the number of Ba atoms absorbed might be expected to be higher. At low current densities, where donor depletion effects are insignificant, one would prefer the extreme configuration—the classic oxide cathode. At intermediate current densities, an optimum degree of fracture should be observed. We have shown this at 0.3 amp/cm² by ball milling the coated carbonate particles for 20 to 40 hours to fracture them and increase the exposed carbonate area. The results of these experiments are shown in

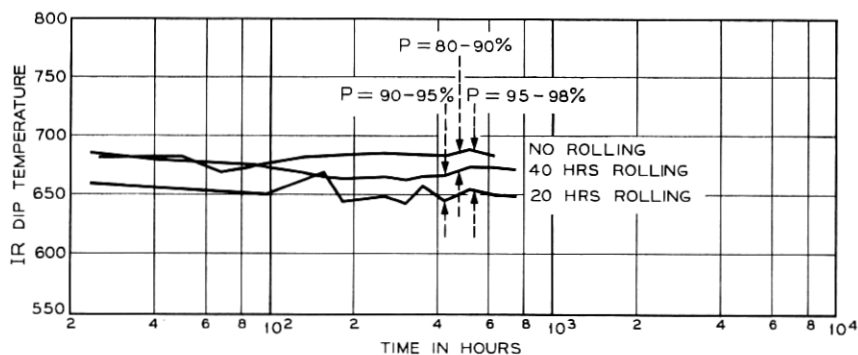


Fig. 13 — The effect of breaking the coated carbonates.

Fig. 13. The 20-hour rolling yields the highest activity level; the 40-hour rolling has caused some degradation. These rolled particles would not be expected to have as good high current density properties since the nickel network will be less complete.

3.2.10 The Effect of Using Double or Triple Carbonates

Fig. 14 shows the curves for two groups of six diodes prepared from nickel-coated double and nickel-coated triple carbonates, respectively, and processed by the standard technique. Both have the same amount of nickel in the coating. Obviously, the triple carbonates give much higher activity levels. Since one would expect the advantages due to the presence of nickel films to be common to any active oxide configuration, further experiments have been initiated.

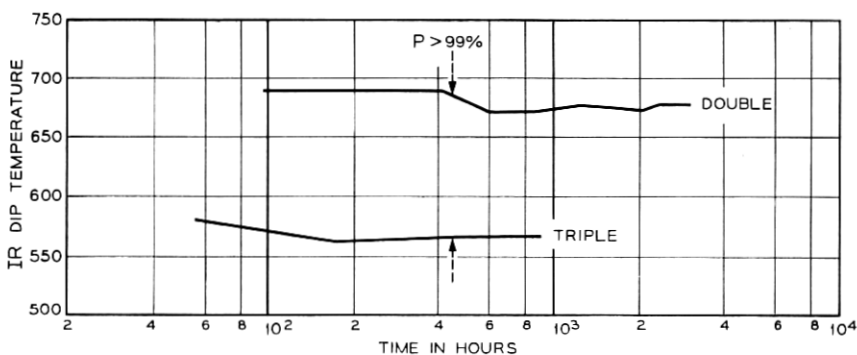


Fig. 14 — Comparison between double and triple carbonates.

3.2.11 High Current Density Behavior

The test diode used showed significant "diode effects" at current densities above approximately 0.5 amps/cm², and these were pronounced around 1 amp/cm². These effects are difficult to analyze and assign, and in proving the ability of the cathode to withstand current drain up to 1 amp/cm² it was necessary to rely on the IR dip characterization previously described.⁷ The validity of this approach can be illustrated by the following example. When cathodes were operated at 810°C and 0.6 amps/cm² in the diode, classic $I^{2/3}$ vs V activity plots entered the "knee" into temperature limited emission below the operating voltage. However, IR dip temperatures remained constant with time, and <700°C, implying that space-charge limited operation at 0.6 amps/cm² should be attained near 700°C in a "clean" structure. When the cathode was used in a traveling-wave tube operating at 0.6 amps/cm², the absence of anode effects allowed space-charge limited operation at temperatures as low as 700°C, and life is currently beyond 7000 hrs. with no sign of deterioration.

Fig. 15 illustrates the variation in IR dip temperature with time for a group of six diodes operated at 810°C, all at identical anode voltages, but with diode effects causing variations in available current between 0.7 and 1.0 amps/cm². Stability out to 25,000 hrs. is demonstrated, with a 100°C margin between the operating temperature and the maximum IR dip temperature observed.

IV. LIFE EXPECTANCY

This section describes evidence that the mechanism of operation and the life limiting factors of the CPC are similar to those of an oxide

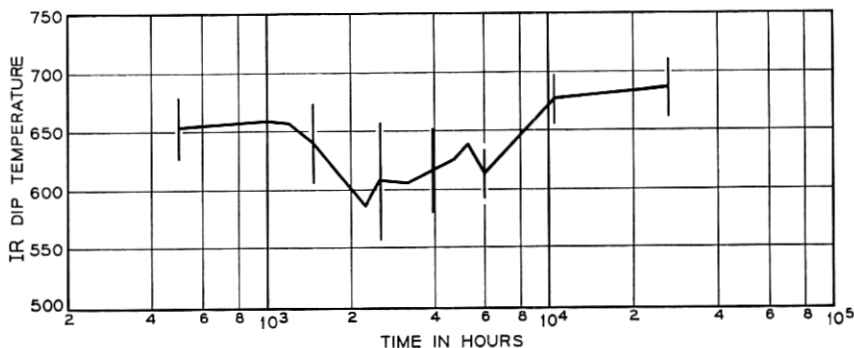


Fig. 15 — The effect of current densities up to 1 amp/cm².

cathode operated in a low current density regime where donor depletion effects are insignificant. Coating depletion and reducing agent arrival rate are demonstrated to be life determining processes. The theoretical basis for life prediction and its experimental verification are also included.

4.1 Activation Mechanism

In the studies described here, the zirconium/nickel base alloy was given an extensive wet hydrogen firing to reduce the initial zirconium arrival rate at the coating base interface and to reduce the total carbon content and hence its coating depletion effects (cf. Section 4.2). It is presumed that the cathode activation, defined as the increase in donors in the coating to a maximum level of cathode activity, involves an equilibrium between (i) the production of donors by zirconium at a relatively low and constant rate over the activation time, (ii) the production of donors by carbon at a relatively high initial rate which then falls off exponentially over a few hundred hours, and (iii) the loss of donors or reducing agent by oxidation in the initially poor environment which will improve with the arrival of reducing agents and the consequent irreversible consumption of oxidizing agents.

To demonstrate this and to show that zirconium is the ultimate activator during the life of the cathode, two cathodes were processed, one on 0.1 percent zirconium nickel and the other on a "pure" nickel similar in all impurity levels other than the omission of zirconium. These were set to operate at 850°B to accentuate the effect. Both alloys had 0.002 percent carbon. The results are shown in Fig. 16. The "pure" nickel alloy was quite active initially but declined very rapidly.

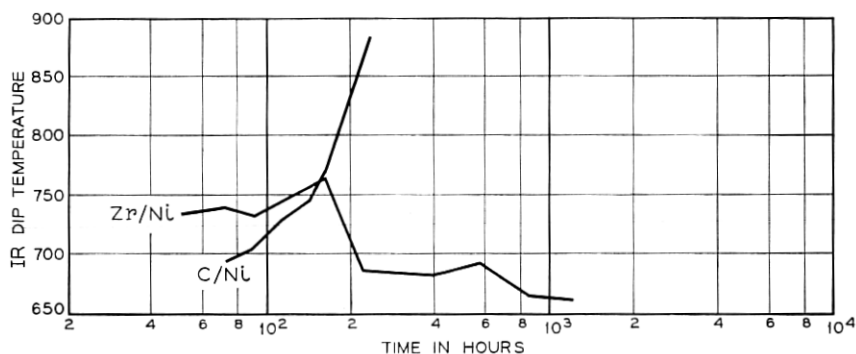


Fig. 16—The activation profile on zirconium nickel and "pure" nickel.

It reached end-of-life at about the same point as the maximum in the zirconium nickel curve. It is reasonable to assume that the particular balance of the three factors mentioned above made carbon the dominant activator initially; as this was exhausted the cathode began to show signs of deactivation in both cases. During this period, oxidizing agents were scavenged to a sufficient degree to allow the relatively low zirconium arrival rate to build up the donor concentration beyond 200 hours—eventually completing the activation.

It should be emphasized that much faster activation can readily be obtained by such techniques as reducing or omitting the wet hydrogen prefiring of the cathode base. However, for maximum life in a system limited by eventual coating depletion, excessive initial donor production is undesirable. In such a case, the minimum donor production rate consistent with the tube meeting operating specifications as it leaves the processing station would normally be preferred.

4.2 Coating Depletion

If the arrival rate of reducing agent at the base remains above the emission cut off rate⁹ for the operating current density for a sufficient time, the life of the cathode will be limited by coating depletion. Coating depletion is the result of several effects, some of which we can only estimate:

(i) Reaction of the coating with the reducing agent in the base. This can be calculated from the well-known diffusion equations. Included here must be the effect of prefiring on the zirconium and carbon profiles and the depletion during the activation cycle.

(ii) Evaporation of the coating at the operating temperature. BaO is the only major active component of the coating which evaporates at an appreciable rate. Since coprecipitated carbonates were used, the oxides form mixed crystals, and the vapor pressure of the BaO will be reduced. As an approximation we have assumed that the vapor pressure of BaO will be proportional to the mole fraction of BaO in the mixed crystal. Furthermore, to be conservative, we have not assumed that the vapor pressure decreases because of the decreasing net mole fraction of BaO as it evaporates. This is partially valid because many individual crystallites are involved (i.e., a large surface area) but the vapor pressure must decrease to some extent later in life. Therefore, the results of these calculations must be considered somewhat pessimistic as life considerations. Fig. 17 shows the results of a coating depletion calculation for cathodes given standard processing

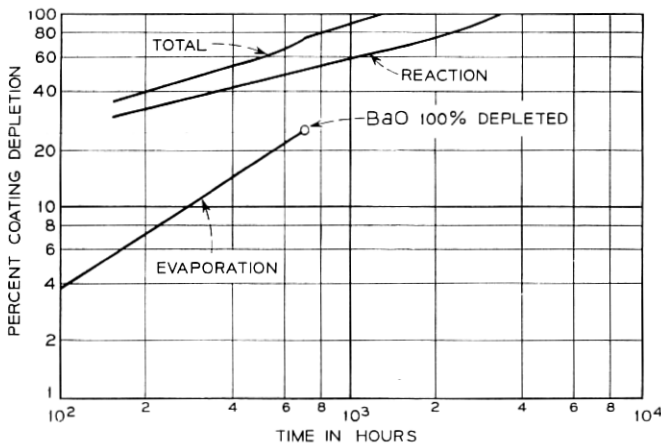


Fig. 17 — Calculation of coating depletion at 850°B on alloy CA703. Coating: 1.0g/cc, 0.6 mil thick.

and accelerated through life at 850°B. They were sprayed 1.0 g/cc, 0.6-mil thick on cathodes based on an alloy which had 0.1 percent Zr and 0.002 percent carbon. The curve marked "reaction" is the percent depletion due to carbon and zirconium. The curve marked "evaporation" is the corresponding percent depletion by evaporation. The latter curve has a point marked "100 percent BaO depletion." This assumes that the "reaction" proceeds at an equal rate for BaO and SrO and the "100 percent BaO depletion" point is reached when the sum of $\frac{1}{2}$ the "reaction" curve plus the evaporation curve equals the total amount of BaO. From this point on, the cathode is assumed to be pure SrO. Fig. 18 shows the IR dip temperatures for these six diodes. It can be seen that the agreement between theory and experiment is good.

Fig. 19 shows similar results on a set of diodes lifed at 800°B. The uncertainty shown results from assuming the thickness to be 0.6 ± 0.1 mils. This gives some indication of the expected errors. As mentioned above, the calculation is somewhat pessimistic; therefore, the fact that the diodes run somewhat longer than the calculation predicts is not unexpected.

4.3 Electrolytic Donor Production

If the surface donor depletion under the influence of current induced emf is inhibited by a nickel network in the coating, the effect

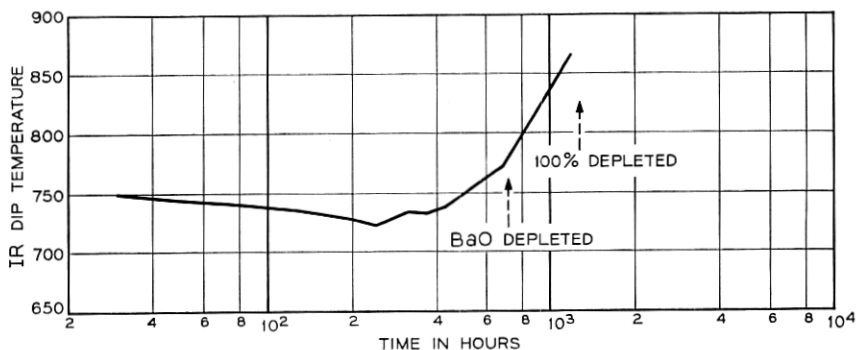


Fig. 18—Coating depletion—comparison between theory and experiment at 850°B.

of electrolytic activation should be enhanced because donors will be trapped in the surface layers. We have observed the effect of electrolytic activation several ways:

(i) By activity measurement on a set of eight diodes using the IR dip technique with 5, 50, and 500 μ sec pulses at 0.5 amp/cm². The duty cycle was maintained the same for each pulse length by varying the pulse frequency. In this way, the anode power level remained constant. The results are shown in Table III. The enhancement in activity with longer pulses is caused by the increasing concentration of donors induced in the coating by electrolysis.

(ii) With the IR dip technique, the work function, ϕ , may be deter-

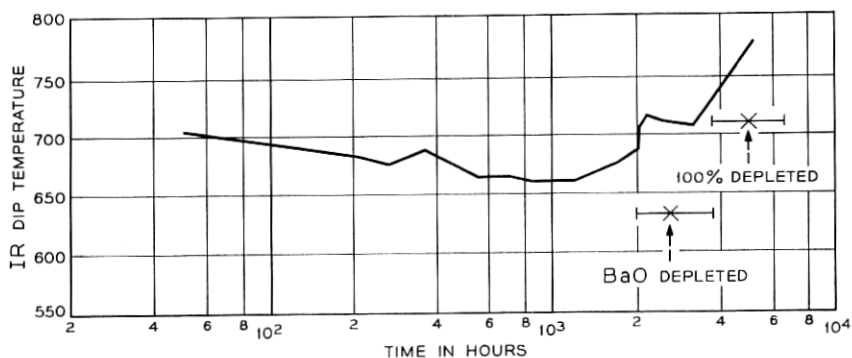


Fig. 19—Coating depletion—comparison between theory and experiment at 800°B.

TABLE III—AVERAGE ACTIVITY MEASUREMENT ON EIGHT DIODES AS A FUNCTION OF PULSE LENGTH FOR CONSTANT DUTY CYCLE

Pulse Length (μsec)	5	50	500
IR dip Temperature, $^{\circ}\text{C}$	725	681	672

mined as a function of temperature independent of the Richardson constant A .⁷ When this is done for dc operation and for 500-micro-second pulse operation on a CPC cathode at 0.3 amp/cm², the result shown in Fig. 20 was obtained. As the temperature increases, the donor concentration decreases because evaporation loss increases faster than the production rate. Since electrolysis augments production more in dc operation than in pulse operation, ϕ remains constant over this temperature range for dc operation whereas it increases for the pulse operation.

(iii) By the apparent lowering of the emission cut-off rate as will be discussed in the next section.

4.4 Emission Cut-Off Rate, ECOR

ECOR is defined as the minimum donor production rate from the reactions of reducing agents in the base which is necessary to sustain emission at a given level. This rate varies with current density because: (i) the number of donors required in the cathode surface is a function of current density and temperature, and (ii) at current densities above about 0.2 amp/cm², electrolysis of the coating adds to the donor concentration. Data shown by Kern⁹ for the ECOR of

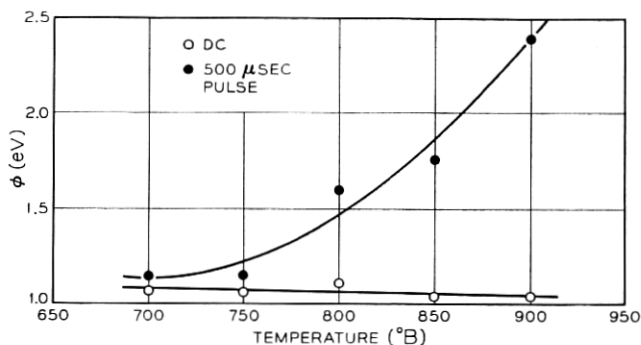


Fig. 20 — $\phi(T)$ for CPC.

oxide cathodes indicates that it varies rapidly with current density. His highest value is 1×10^{-8} $\mu\text{moles}/\text{cm}^2/\text{sec}$ at $200 \text{ ma}/\text{cm}^2$.

ECOR for the CPC at medium current densities would be expected to be lower than for the oxide cathode because electrolysis will contribute to the net concentration of donors in the surface. Experimental results to date have established an upper limit on ECOR for coated powder cathodes at current densities up to $1 \text{ amp}/\text{cm}^2$ as 1.5×10^{-8} $\mu\text{moles}/\text{cm}^2/\text{sec}$ confirming the stability of the CPC in this operating range.

4.5 Typical Life Calculation

In Fig. 21 we have plotted, for a typical cathode configuration, the barium production rate at 800°C as a result of zirconium diffusion in micromoles/ cm^2/sec vs time in hours for a cathode alloy of 0.07 ± 0.01 percent zirconium, and for two different thicknesses of base metal. The higher percent zirconium results in a higher barium production rate. Thicker base metals yield the same barium production rates except that the "knee" occurs further out in time. For the 0.1-inch thick base the knee does not occur in the time interval shown. Since the ECOR is less than 1.5×10^{-8} $\mu\text{moles}/\text{cm}^2/\text{sec}$ a lower limit on the lifetime set by this mechanism is of the order 100,000 hours for the 0.06-inch thickness, and will increase with base thickness.

Coating depletion calculations have already been discussed. Fig. 22 shows the results of such a calculation on a typical cathode. The cathode considered is based on a 100 mil thick 0.08 percent zirconium,

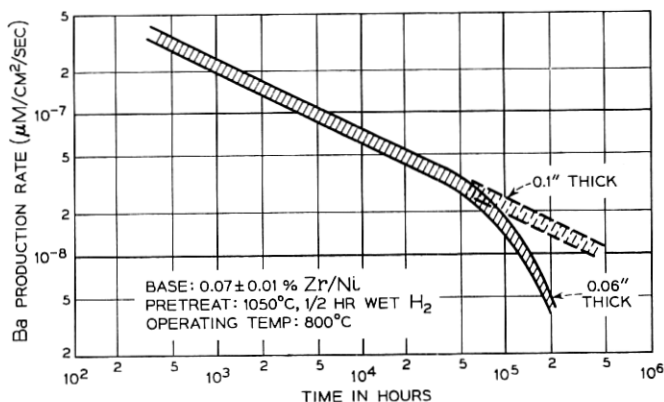


Fig. 21 — Ba production rate.

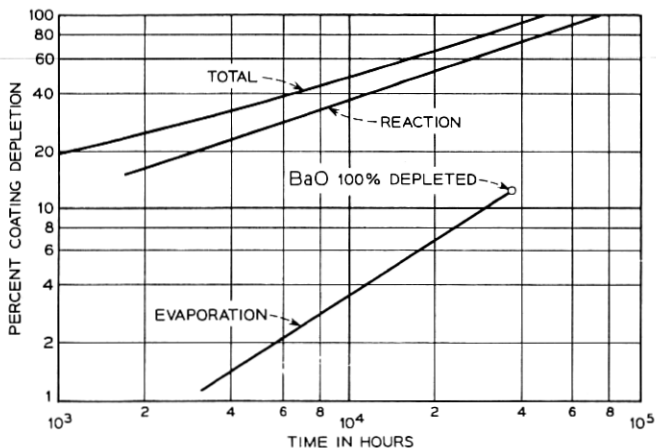


Fig. 22 — Calculation of coating depletion at 800°C on 0.08% Zr, 0.001% C/Ni 0.1 inch thick, coating: 1.1g/cc, 1.5 mil thick.

0.001 percent C alloy, sprayed with coated double carbonate at 1.1 g/cc, 1.5 mil thick. The base alloy has been pretreated in wet H₂ at 1050°C for ½ hour. The cathode is activated by the schedule; 800°B, 1 hour; 950°B, 6 minutes; 850°B, 17 hours, and operated at 800°C. Following the analysis described in Section 4.2, BaO is 100 percent depleted after 40,000 hours. It should be emphasized that while operation at 800°C is reasonable for diodes, tubes such as TWT's with more open structures can normally run at substantially lower temperatures, thus improving life expectancy still further.

4.6 Life Prediction

The lifetime of a typical CP cathode operating at less than 1 amp/cm² on a 0.10 inch thick 0.07 ± 0.01 percent zirconium/Ni at 800°C is therefore limited not by ECOR but by coating depletion, and in the typical examples described, BaO would be 100 percent depleted in >40,000 hours. The assumptions made in this prediction are supported by: (i) The failure of groups of diodes, on schedule, (Figs. 18 and 19) and (ii) 28 diodes currently on life, beyond 25,000 hours.

V. SUMMARY

Examination of the theory of operation of the oxide cathode suggests that in order to improve the high current density properties of oxide cathodes, the movement of donors under the influence of cur-

rent-induced emf's should be inhibited. To do this a method of coating each individual particle of carbonate powder with a thin nickel film has been successfully developed. Carbonates coated in this manner have been used to prepare cathodes by conventional techniques.

Extensive diode experiments made mainly at 0.3 amps/cm² have outlined the general character of such cathodes and the major factors affecting their performance. Definitive comparisons of maximum performance with other cathode types were in general not attempted because diode effects were shown to obscure the interpretation of deliberate variations in cathode parameters at high current densities.

It has been shown that the new coating can be prepared reproducibly. The nickel film around each particle inhibits sintering of the oxide, enhances the beneficial effects of electrolytic activation, and allows operation of the cathode at temperatures in the range 700-800°C over lifetimes which are essentially independent of the current density up to 1 amp/cm². The cathode has been demonstrated to activate quickly and efficiently through high temperature processing schedules. Faster outgassing of the structure is therefore possible, and faster activation can be achieved. Direct substitution of CPC for oxide cathodes in production sequences is practical, since conventional activation schedules may also be used. In this case, the tolerance of the cathode to accidental overheating is helpful.

Activation and life determining mechanisms operative in the CPC have been defined as reducing agent diffusion and coating depletion, with the latter determining end-of-life in most practical configurations. Good agreement was obtained between theory and experiment for coating depletion, and a lower limit on reducing agent arrival rate of 1.5×10^{-8} μ moles/cm²/sec has been established for current densities up to 1 amp/cm². On this basis lifetimes of 40,000 to 50,000 hours are entirely feasible for CPC operating up to 1 amp/cm².

The coated powder cathode, therefore, appears to combine many of the advantages of the standard oxide cathode with those of the matrix type. The system variables have been thoroughly explored, indicating its utility, particularly in the operating range 0.2 to 1.0 amps/cm², where diode life tests have presently reached 25,000 hours.

VI. ACKNOWLEDGMENTS

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APPENDIX A

Standard Cathode Breakdown and Activation Schedule

(°B Represents Optical Pyrometer Measurement on Cathode Base)

1. Bake out 16 hours at 425°C.
2. Outgas the getter.
3. Outgas the heater by slowly raising the cathode temperature to ca. 500°C keeping the pressure below 5×10^{-5} torr on the getter ion pump.
4. Raise the cathode temperature as rapidly as possible to 800°B keeping the pressure $< 5 \times 10^{-5}$ torr.
5. Hold until $P \leq 10^{-7}$ torr.
6. Raise the cathode temperature rapidly to 950°B and hold for five minutes then lower the temperature to 850°B.
7. Apply 25 Vdc and age ca. one hour.
8. Turn off anode voltage and heater voltage and flash getter. Pinch off tube within 30 seconds after getter flash.

APPENDIX B

High Temperature Processing Schedule

(°B Represents Optical Pyrometer Measurement on Cathode Base)

1. Follow the standard schedule (Appendix A) through step 3.
2. Raise the cathode temperature as rapidly as possible to 850°B keeping the pressure $< 5 \times 10^{-5}$ torr on the getter ion pump.
3. Hold until $P \leq 10^{-7}$ torr.
4. Rise the cathode temperature rapidly to 1050°B and hold for 20 minutes.
5. Apply dc voltage to the anode to draw 1 amp/cm² (40 mA).
6. When the activity reaches 1 amp/cm² (usually immediately) lower the cathode temperature in 50° steps holding at each step until 1 amp/cm² is attained. Continue until 850°B is reached.

7. Turn off anode and heater voltage and flash getters. Pinch off the tube within 30 seconds after the getter flash.

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