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# The BaO-Ni Matrix Cathode Formed by the Nickelate Technique

T. J. Szczech and D. E. Anderson

Physical Electronics Laboratory, University of Minnesota
Minneapolis, Minnesota

## Abstract:

The properties of an indirectly-heated cathode produced by reacting barium carbonate and nickel oxide on nickel are described. A eutectic melt of nickel oxide and barium nickelate occurs as a necessary step in the preparation of the cathode. Reduction of the nickel oxide and barium nickelate into nickel and barium oxide by using hydrogen at an elevated temperature is also necessary. Studies using X-ray diffraction techniques and an electron beam microprobe indicate that the cathode consists of a uniform mixture of nickel and barium oxide. Thermionic emission data taken after vacuum lifing of various cathodes including carbon-activated cathodes, and after sputtering of the surfaces will be presented. A discussion of some of the theoretical aspects of the formation techniques and of the operation of the cathode in various environments will be presented.

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In 1934 Edwards and Smith[1] patented a cathode which they named the "nickelate" cathode. This cathode was reported to have desirable thermionic emission properties but physical properties resembling metallic Ni. as opposed to the fragile, powder-like composition of an oxide cathode. The cathode was said to consist of barium nickelate dissolved in a Ni core. Harwood, Herzfeld and Martin[2] and Lander[3] have studied $BaNiO_2$ and find that it may be formed by reacting BaO and NiO. Lander reports a melting point for $BaNiO_2$ at 1240°C with a eutectic melt of $BaNiO_2$ and NiO occurring at 1190°C. Harwood and associates, report that there was no appreciable emission from $BaNiO_2$ until it had been heated in vacuum for several hours. Subsequent examination revealed that the $BaNiO_2$ had been reduced to Ni and BaO.

The nickelate cathode has been used commercially in gas tubes since its discovery. Strecker[4] reports that the nickelate cathode is superior to the oxide cathode in regard to low-grid emission and high-sputter resistance and that its properties are somewhat dependent on the processing schedule employed during fabrication. Very little work has been done to determine the thermionic emission capabilities of a nickelate cathode under vacuum conditions. This is probably because the cathode has had a reputation for being somewhat gassy. Composition studies by Pohl and Tooper[5] using X-ray and electron diffraction techniques, indicate that cathodes.

which have been processed so as to obtain high-sputter voltages and high-thermionic emission, consist of BaO uniformly distributed in a Ni matrix. It has been the purpose of these studies to fabricate suitable cathodes and study their composition as an extension of previous studies. Also, the determination of thermionic emission under vacuum lifing of cathodes was carried out.

Initially, a technique for construction was developed which consistently produced cathodes with suitable properties. The method finally devised is the following: Three parts by weight of NiO is mixed with one part by weight of $BaCO_3$ using a mortar and pestle. Amyl acetate and a nitrocellulose binder is added to the mixture. The cathode assembly consists of an indirectly heated Ni disk welded to a Ni sleeve which is mounted in a heat shield. A ruling pen is used to coat the disk with the mixture. After drying, the coating is shaved to a 3 mil thickness. The resulting coating weighs approximately 28 $mg/cm^2$.

The cathode assembly is mounted in a tube structure and processed under vacuum using an ion pump. The tube is baked following a standard schedule of ten hours at 350 °C with a resulting pressure after bakeout of about $10^{-9}$ Torr. The metal parts are outgassed by RF heating at about 800 °C holding the pressure below $10^{-5}$ Torr and heating the part until the pressure drops below $10^{-7}$ Torr. Each tube has several movable Ti anodes which are changed for conversion, reduction and lifing of the cathode.

After the tube has been processed, the cathode is heated to 1250 °C momentarily, after which it is cooled to 1200 °C and held at this temperature for ten minutes. By the time 1250 °C has been reached, the coating has melted. Upon cooling, it sinters to the Ni base. This process of reducing the carbonate to the oxide and of melting the $BaNiO_2$ and NiO mixture is referred to as the "conversion" process. After the conversion process, the cathode consists of uniform mixture of $BaNiO_2$ and NiO. In addition, there is a small amount of vacuum reduced Ni.

Following conversion, the cathode is heated to about 800 °C in a stream of flowing $H_2$ at one atmosphere, and held at this temperature for ten minutes. The process of $H_2$ firing is referred to as the "reduction" process. At this stage, the cathode consists of a uniform mixture of porous Ni and BaO. To complete the processing, the cathode is outgassed by heating to 1000 °C in vacuum, the temperature is lowered to 800 °C and current is drawn until the emission stabilizes.

In order to determine the composition of a cathode after conversion or after reduction, X-ray diffraction studies were made of various cathodes. This study differed from that of Pohl and Tooper in that the cathodes studied were protected from the atmosphere using microscope immersion oil. The comparisons are based on the intensity of the primary peak of each substance. Two results of the study are important. First, the $BaNiO_2$ appearing during the conversion is necessary in forming the melt and subsequent sintering of the cathode to the Ni base. Second, the reduced or finished cathode is found to consist of BaO and Ni. The results of the X-ray diffraction studies are shown in Fig. 1.

The X-ray diffraction results were incomplete in that they gave no indication of the BaO distribution in the Ni matrix. In particular, the distribution of BaO as a function of depth is important. In order to get this type of information, an electron microprobe was employed.

This device focuses an electron beam one micron in diameter and larger on a specimen. The beam energy is on the order of 25 KeV. The high-energy electrons cause transitions in the K and L bands of elements present in the specimen. The X-radiation produced is detected according to wavelength and intensity. In this study, the Ba atom distribution was determined and equated to the BaO distribution. Percentages shown are weight percentages.

The penetration of the electron beam into the specimen is only about one micron. Thus, the specimen is prepared so that its surface is representative of the bulk. This is done by cutting the cathode at an angle to expose its interior from base to surface. A scan of the electron beam across the surface then covers the composition from the cathode base to its surface. Several points where taken at a particular distance from the base and averaged. The average values along with the root mean square deviations are plotted vs. the distance from the base in Fig. 2. The cathodes are prepared with a weight percentage of about twenty-four. The important thing to notice here is the presence of BaO from cathode surface to base.

In addition to data taken with the 100 micron diameter beam, cathodes which had been lifed from 3000 to 6000 hrs at 1073°K in vacuum were examined with a 1 micron diameter beam. There was more scatter in the data as shown by the larger RMS deviations. The important results of the study are that the BaO particles appear to be only about one micron in diameter because none of the spots examined contained 100% BaO. Also, there does not appear to be appreciable dispenser action as evidenced by the presence of BaO in the bulk in cathodes which show depletion of their surface. The results of these studies are shown in Fig. 3.

To determine a cathode's performance and possible usefulness thermionic pulse emission measurements were made on various cathodes. The voltage applied to the cathode reached a maximum of 5000 volts in 3 microseconds. The corresponding current was measured and Schottky plots were made. A typical series of Schottky plots for various cathode temperatures are shown in Fig. 4. The emission is extrapolated to zero field; these points are used to prepare Richardson plots. It should be mentioned that for ordinary oxide cathodes, the slope in the straight line or high field region is typically high so that the apparent temperature of the cathode necessary to obtain a fit of the data to the Schottky equation, is only about 1/3 of the actual temperature. In this figure, the Schottky equation fits the data quite well with a Schottky temperature very close to the actual temperature. This behavior was typical for these cathodes.

The cathodes studied were lifed at 1073°K between measurements and Richardson data are presented for various periods of life at this temperature. Pressures attained were below $10^{-6}$ Torr. Typical pressures at 1073°K were about $5 \times 10^{-9}$ Torr. Shown in Fig. 5 is behavior typical of the four cathodes examined. That is, a decline of thermionic emission with life. Since BaO was present in the bulk of the cathode, the decay of emission seems to indicate lack of dispenser action.

In addition to cathodes prepared on a pure nickel base, some cathodes were carbon activated. The carbon activated cathodes differ from ordinary cathodes in that carbon is placed on the back side of the cathode disk after the conversion process. The carbon diffuses through the disk during cathode life to reduce the BaO forming excess Ba in the BaO. This increases the thermionic emission as can be seen from the Richardson data in Fig. 6 in which the initial current levels are somewhat higher than for pure nickel based cathodes. However, a rapid decay of emission with time occurs.

It has been pointed out that a decay of emission with time occurs for all cathodes examined and particularly in carbon activated cathodes. The microprobe data in Fig. 7 show a corresponding decrease of BaO at the surface of these cathodes. In all cases, however, there does not appear to be a depletion of BaO in the bulk. To confirm this idea, two cathodes were sputtered with argon.

To sputter the cathodes a dc technique, similar to that used by Wehner's group,[6] was employed. This allowed a somewhat quantitative calculation of the Ni removed. The Ar was leaked into the tube using a vacuum valve after gettering for impurities with Ti. Each cathode was sputtered at room temperature. After each sputtering period the Ar was pumped from the tube with a triode ion pump. Thermionic pulse emission measurements were taken each time after the material had been removed. In the data shown, the emission from the cathode was monitored while the other cathode was sputtered.

The emission from both cathodes was somewhat low initially. After sputtering, there was an increase of emission which remained constant with sputtering until the base was reached as shown in Fig. 8. The other cathode studied showed similar behavior but was not sputtered to the base. An examination of the two cathodes using the electron microprobe showed almost no BaO in the former cathode and BaO composition percentage in the latter cathode.

In summary, a cathode produced by reacting $BaCO_3$ and NiO at elevated temperatures is found to consist of BaO uniformly distributed in a Ni matrix. Barium nickelate is found to occur after the conversion process and is necessary in forming a melt and subsequent sintering of the cathode material to the Ni base. The cathode has the mechanical strength and conductivity of metallic nickel. It may be exposed to the atmosphere for short periods of time and subsequently reactivated. Such cathodes have been used in our laboratories in low energy electron diffraction guns. There does not appear to be any appreciable dispenser action in spite of the fact that microphotographs of cathode cross sections indicate that the cathode is criss-crossed with 1 - 10 micron pores. However, the cathode seems ideally suited to applications where surface sputtering by inert gases occurs. The cathode has been used as an electron source for low pressure Ar sputtering systems with promising results. This research was supported in part by a NASA grant (NGR-24-005-063) to the Space Science Center of the University of Minnesota and by the Air Force Avionic Laboratory Contract No. AF 33(657)-10475.

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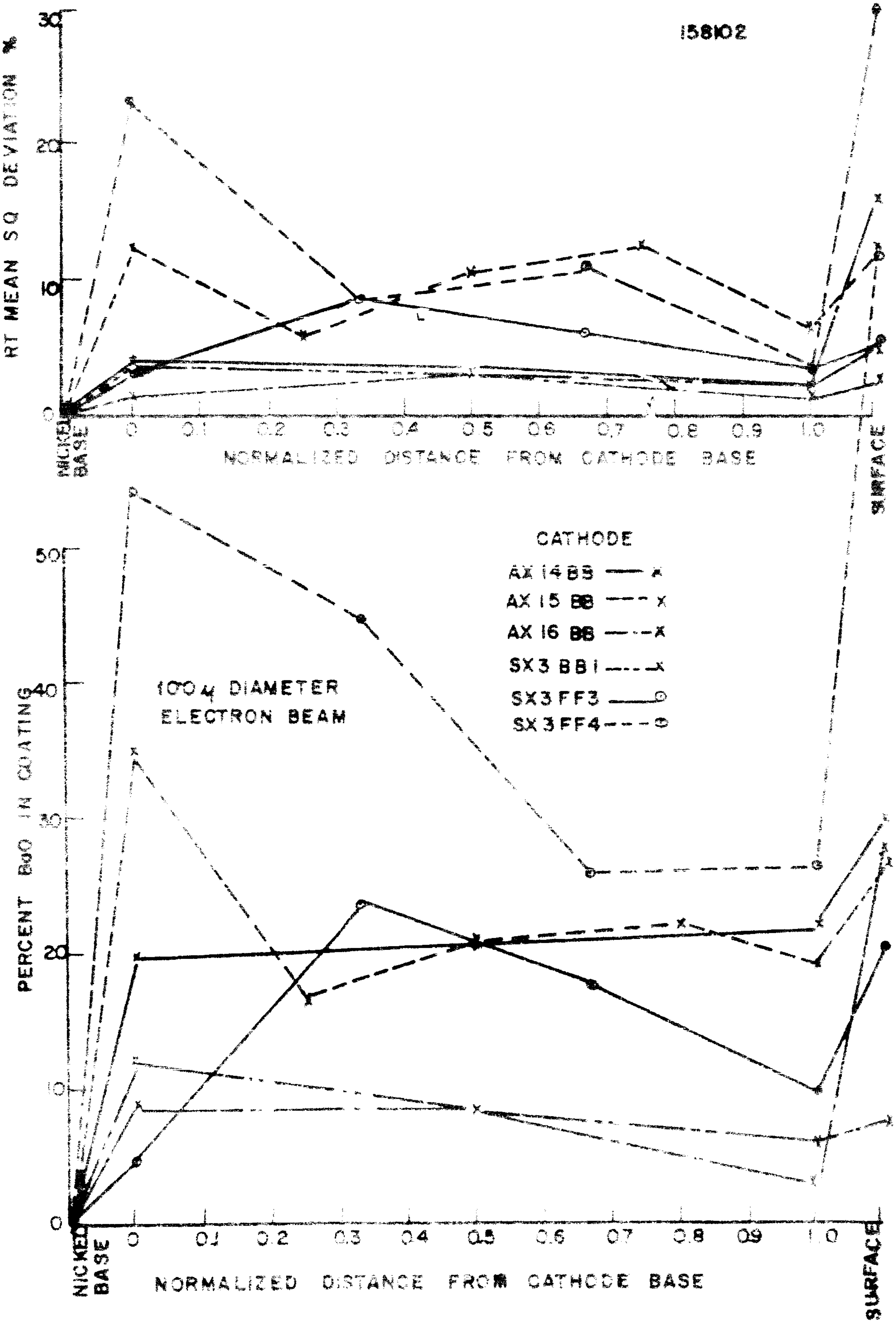
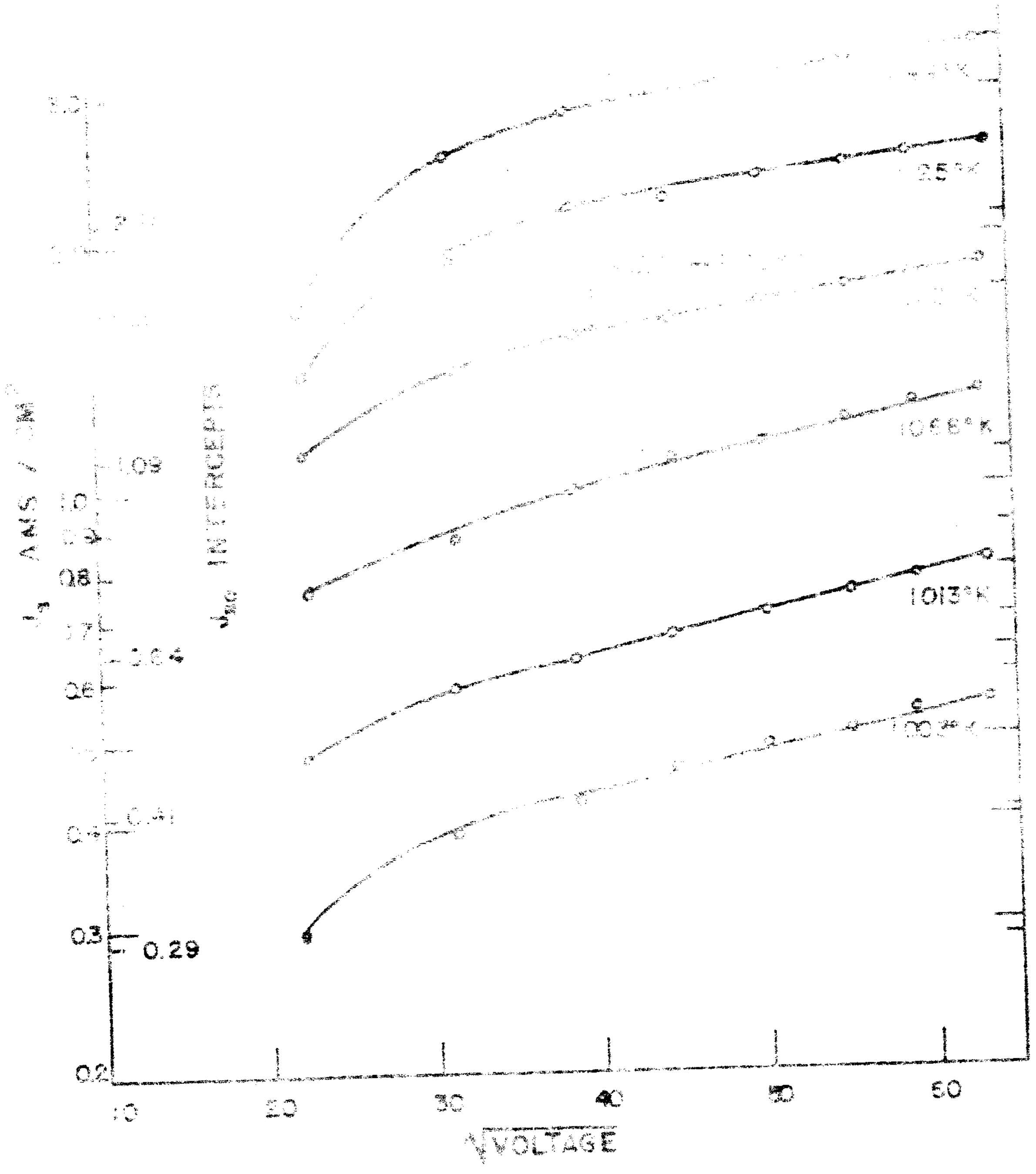

158102
RT MEAN SQ DEVIATION %
30
20
10
0
NICKEL BASE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
SURFACE
NORMALIZED DISTANCE FROM CATHODE BASE
CATHODE
AX 14 BB
AX 15 BB
AX 16 BB
SX 3 BB 1
SX 3 FF 3
SX 3 FF 4
100 μ DIAMETER
ELECTRON BEAM
PERCENT BaO IN COATING
50
40
30
20
10
0
NICKEL BASE
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
SURFACE
NORMALIZED DISTANCE FROM CATHODE BASE

Fig. 2



Cathode AX4B4, Lifed 40 Hrs. [illegible]