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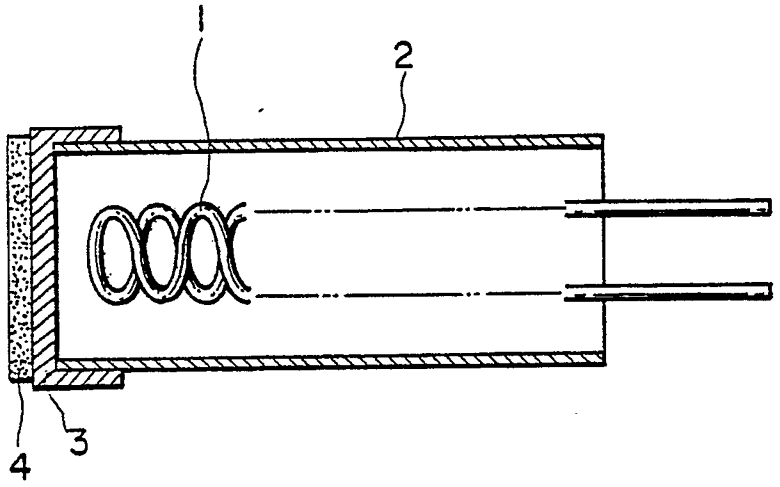
㊹ **Cathode for electron tubes.**

㊼ A cathode for electron tubes is described, which comprises a substrate metal mainly composed of nickel and a reducing agent such as tungsten and a coating layer formed on the substrate metal and made of oxides obtained from alkaline earth metal carbonates which contain at least one of zinc (Zn) and aluminium (Al). A method for fabricating the cathode is also described, in which the additive element such as Zn and/or Al is removed by immersion of the alkaline earth metal carbonates containing the at least one of Al and Zn when existing in excess. By this, the cathode has high capability of electron radiation and a prolonged life.

FIG. 1



CATHODE FOR ELECTRON TUBES

BACKGROUND OF THE INVENTION

Field of The Invention

This invention relates to a cathode for electron tube employed in image receiving tubes and image pickup tubes more particularly, to a so-called oxide coated cathode for electron tubes. The invention also relates to a method for fabricating a cathode of the type mentioned above.

Description of The Prior Art

Ordinarily employed oxide coated cathodes (hereinafter referred to simply as cathode or cathodes) mostly include metal substrate mainly composed of nickel (Ni) and several percent of tungsten (W) and the like used as a reducing agent and a coating formed on the substrate and made of a ternary alkaline earth metal oxide consisting of barium (Ba), strontium (Sr) and calcium (Ca).

With regard to the working temperature of the cathode. a lower working temperature is more advantageous not only saving the consumption power for heaters for the cathode, but also in the improvement of the life characteristic of the cathode. More particularly, it is known that the life characteristic is greatly influenced by the intermediate layer formed owing to the thermal reaction between the oxide and the coated metal substrate during operation. The lowering of the working temperature of the cathode brings about a prolonged life by suppressing the formation of the intermediate layer.

The addition of indium (In) in the form of indium oxide (In_2O_3) to the ternary oxide material for the cathode is adapted for improving the capability of electron radiation with a working temperature for the same level of radiation current being reduced. This is disclosed in Japanese Patent Publication No. 38-2334.

According to the Meoruganichekie Materiali Vol. 12, No. 5, 1979, pp. 859 - 862, the reduction of the temperature is stated to be in the range of from 120 to 150° C. However, with the cathode to which In has been added, it is difficult to obtain the stable electron radiation capability.

The reason for this is considered as follows. In_2O_3 has a sublimation temperature of about 850° C which is lower than the thermal decomposition temperature of alkaline earth metal carbonates. Accordingly, most In_2O_3 which has been added to the alkaline earth metal carbonates will be lost from the cathode layer during a step where the carbonates are heated at 1000 to 1100° C and decomposed into oxides during evacuation under vacuum or during the so-called thermal decomposition activation step for the cathode. Actually, the results of the analysis on the composition of the oxide cathode prior to and after the thermal decomposition and activation reveal, as shown in Tables 1 and 2, that the oxide cathode layer prior to the thermal decomposition and activation contains 2 to 3 atomic percent of In^{3+} whereas the oxide cathode layer after the thermal decomposition and activation has a considerably reduced content of In^{3+} of not larger than 0.005 atomic percent. The small amount of remaining In contributes to good electron radiation characteistics of the cathode. Too large particles of In or In compounds existing prior to the activation step may cause their neighboring regions to be molten depending on the thermal decomposition and activation conditions, resulting in bad influences on the electron radiation characteristics.

Table 1

Results of Chemical Analysis On Cathode Oxide Layer Prior To Activation		
	No In Added (atomic %)	In Added (Atomic %)
Ba^{2+}	49.0	46.0
Sr^{2+}	43.7	44.3
Ca^{2+}	7.3	7.2
In^{3+}	-	2.4

Table 2

Results of Chemical Analysis On Cathode Oxide Layer After Activation		
	No In Added (atomic %)	In Added (Atomic %)
Ba^{2+}	45.6	43.0
Sr^{2+}	46.2	48.2
Ca^{2+}	8.3	8.8
In^{3+}	-	0.0042

From the above, it is considered that the amount of an additive element necessary for improving the electron radiation capability should be small sufficient to have it incorporated in the crystals of alkaline earth metal carbonates and that particles of an additional element or its compound not incorporated in the crystals should be preliminarily removed from the carbonate composition prior to the activation, which is important for obtaining the stable capability of electron radiation.

SUMMARY OF THE INVENTION

An object of the invention is to provide a cathode for electron tubes which has high capability of electron radiation and is stable by removing an additional additive element or its compound from carbonate crystals.

Another object of the invention to provide a cathode for electron tubes wherein an element capable of producing an amphoteric compound is used as an additive element.

A further object of the invention is to provide a method for fabricating the cathode mentioned above.

We have studied additive elements which can be removable when the additive element or its compounds are not incorporated in the crystals of alkaline earth metal carbonates and remain in excess. As a result, it has been found that an element capable of forming an amphoteric compound soluble in both an acid solution and an alkaline solution can meet the above requirement.

In accordance with one embodiment of the invention, there is provided a cathode for electron tubes which comprises a substrate metal mainly composed of nickel and a reducing agent and a coating layer of a composition comprising alkaline earth metal carbonates and formed on the substrate metal, the alkaline earth metal carbonates in the coating layer being converted into corresponding metal oxides, characterized in that the alkaline earth metal carbonates contain at least one of zinc (Zn) and aluminium (Al).

In accordance with another embodiment of the invention. there is provided a method for fabricating a cathode for electron tubes which comprises the steps of:

adding at least one element of Zn and Al or its compound to a solution of water-soluble salts of alkaline earth metals;

adding a carbonate precipitant to the solution thereby causing co-precipitation to obtain a powder mainly composed of a multi-component alkaline earth metal carbonate;

immersing the powder in an alkaline aqueous solution and subjecting the resulting mixture to filtration to obtain an alkaline earth metal carbonate containing Al and/or Zn from which the element in excess is removed by dissolution;

applying, onto a substrate metal, a cathodic material composition obtained by mixing the alkaline earth metal carbonate and a binder therefor to form a layer of the cathodic material composition; and

heating the thus formed layer in an evacuated closed system to convert the layer into an oxide layer.

The cathode obtained above has not only high capability of electron radiation as in the case where In is added, but also more stable characteristics than in the case of adding In. This is considered for the reason that the addition of Zn or Al in small amounts has the effect of enhancing the capability of electron radiation as in the case where In is added and that the additive element is incorporated in the crystals of the alkaline earth metal carbonate prior to activation of the cathode. An additional additive element or its compound which is not incorporated in the crystals and which is amphoteric in nature is dissolved by the use of an alkaline solution and removed sufficiently. Moreover, since the sublimation temperature (about 1270 ° C) of zinc oxide (ZnO) and the boiling point (about 850 ° C) of aluminium oxide (Al_2O_3) are higher than the sublimation temperature (about 850 ° C) of In_2O_3, the addition of Zn and Al is more advantageous from the standpoint of the stability of the characteristics over the addition of In.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an enlarged sectional view of an essential part showing an arrangement of an ordinary cathode for an electron tube;

Fig. 2 is a flow chart showing a fabrication procedure of a cathode according to the invention;

Fig. 3 is a schematic view of a typical surface configuration of crystals of a quaternary carbonate of Ba. Sr, Ca and Zn obtained according to the invention;

Fig. 4 is a schematic view of a typical surface configuration of crystals of a ternary carbonate of Ba, Sr and Ca;

Fig. 5 is a graph showing the pulse emission characteristic of cathodes of the invention and for comparison;

Fig. 6 is a frequency distribution chart of the pulse emission current obtained with respect to the cathodes of the invention;

Fig. 7 is a flow chart showing a fabrication procedures of cathodes for comparison; and

Fig. 8 is a frequency distribution chart of the pulse emission characteristic obtained with respect to cathodes for comparison.

DETAILED DESCRIPTION AND EMBODIMENTS OF THE INVENTION

Embodiments of the invention are described with reference to the accompanying drawings.

One embodiment of a cathode to which the present invention is directed is shown in Fig. 1. The cathode has a heater 1 for heating the cathode to a working temperature and a cathode sleeve 2 in which the heater is built, and a substrate metal 3 provided at one end of the sleeve 2 and made primarily of nickel. On the substrate metal 2 is further formed an oxide layer 4 mainly compose of alkaline earth metal oxides and serving to emit electrons. Such a cathode is used as an electron gun according to an ordinary arrangement and is built in an electron tube. The fabrication procedures of the cathode of the type set forth above and the results of measurement of electron emission characteristics of the fabricated cathodes are described by way of example of the invention and comparative example according to prior art.

Example

Fig. 2 is a flow chart showing a fabrication procedure of a cathode according to the invention. This fabrication procedure is illustrated in more detail.

Barium carbonate ($BaCO_3$), strontium carbonate ($SrCO_3$) and calcium carbonate ($CaCO_3$) are weighed at ratios by weight of 62:35.5:2.5 and dissolved in and mixed with a dilute nitric acid aqueous solution, to which ZnO is added for dissolution in amounts of from 1 to 3 wt% based on the total amount of the alkaline earth metal carbonates. To the thus obtained four-component nitrate aqueous solution (about 0.4 mols/l) is gradually added an ammonium carbonate ($(NH_4)_2CO_3$) aqueous solution (about 1.5 mols/l) while sufficiently agitating, thereby causing a precipitate mainly composed of a quaternary carbonate of Ba, Sr, C and Zn and containing Zn or a Zn compound, followed by filtration. Thereafter, the thus obtained precipitate is immersed in an ammonium hydroxide ((NH_4OH) aqueous solution (about 3 mols/l) or ammonium carbonate ($(NH_4)_2CO_3$) aqueous solution (about 3 mols/l), sufficiently agitated and filtered. After repetition of the immersion and filtration several times, the precipitate is well washed with hot pure water and dried to obtain a quaternary carbonate powder of Ba, Sr, Ca and Zn.

The thus obtained quaternary carbonate crystals have such an irregular structure on the surface thereof as is schematically shown in Fig. 3, which is considered to result from the incorporation of Zn in the alkaline earth metal carbonate crystals.

The crystals of a ternary carbonate of Ba. Sr and Ca obtained without addition of any Zn for comparison have a smooth surface as is schematically shown in Fig. 4.

Thereafter, the thus obtained quaternary carbonate powder and nitro cellulose used as a binder are added to and mixed with a mixed organic solvent of ethyl acetate and isoamyl acetate to prepare a paste composition for cathode material. Subsequently,. the above cathode material composition is spray coated, n a thickness of 100 μ m at a density of 0.8 g/cm^3, on a substrate metal; which consists of nickel containing 4 wt% of tungsten as a reducing agent and which is provided at one end of the cathode sleeve to form a coating layer of the cathode material.

Moreover, according to an ordinary fabrication procedure, an electron gun is assembled using the cathode and built in an electron tube. The electron tube is evacuated and subjected to thermal decomposition and activation treatment at a temperature of 1000 to 1100°C. By the thermal decomposition and activation treatment, the quaternary carbonate contained in the cathode material coated layer is converted into oxides, thereby producing an oxide layer having good capability of electron emission. Thirty cathodes are fabricated in this manner and are subjected to measurement of a pulse emission characteristic. At a constant voltage for the heater, a single pulse with a pulse width of 45 microseconds and a voltage of EpV is passed between the cathode and an electrode at the high voltage side, after which the voltage Ep is changed to measure a current density at the cathode. Fig. 5 shows a typical pulse emission characteristic curve among the results of the measurement. Fig. 6 is a frequency distribution of a pulse emission current at Ep = 400 V obtained with respect to the thirty cathodes.

The case where ZnO is added has been described above, and similar results are obtained when using aluminium hydroxide, which is an amphoteric compound, instead of ZnO.

Comparative Example

A cathode to which In is added according to a known technique is fabricated according to the flow chart shown Fig. 7. The fabrication procedure is described in detail.

$BaCO_3$, $SrCO_3$ and $CaCO_3$ are weighed at ratios of 62:35.5:2.5 and dissolved in and mixed with a dilute nitric acid aqueous solution. To the resultant ternary nitrate aqueous solution (about 0.4 mols/l) is gradually added an $(NH_4)_2CO_3$ aqueous solution (about 1.5 mols/l) while sufficiently agitating, thereby causing a precipitate of a ternary carbonate of Ba, Sr and Ca, followed by filtration. This ternary carbonate is washed with hot pure water and dried.

Thereafter, commercially available finely divided indium hydroxide (with a size of not larger than 10 μ ml) is added to the ternary carbonate in an amount of 3 wt%. After sufficient agitation, the procedure of example including the passing is repeated to fabricate a cathode. In this manner, thirty cathodes are fabricated and subjected to measurement of th pulse emission characteristic in the same manner as in the example. A typical characteristic curve is shown as curve II in Fig. 5 for easy comparison with the results of the example. The frequency distribution of the pulse emission current at Ep = 400 V with respect to the thirty cathodes is shown in Fig. 8.

For comparison, with respect to the cathodes fabricated without use of any In, the results of the measurements of a typical pulse emission characteristic curve are shown as curve III in Fig. 5.

The results of the measurement shown in Figs. 5, 6 and 8 reveal that the cathodes obtained in the example have significantly better capability of electron radiation than the additive element-free cathodes and ensure better stability with respect to the capability of electron radiation which is as high as that of the cathodes to which In is added by the known procedure.

As will be apparent from the above, the addition of Zn and/or Al is effective in improving he electron radiation capability to an extent equal to that conventionally attained by the addition of In. Moreover, in the fabrication process of the cathode, the best use is made of characteristic features of Zn and Al which are elements capable of producing amphoteric compounds, i.e. additive elements or compounds thereof, which are considered as harmful and have not been incorporated in alkaline earth metal carbonates, can be sufficiently removed, ensuring the characteristics to be readily stabilized. The improvement in the electron radiation capability will bring about a reduced working temperature of the cathode and a prolonged life of the cathode.

Claims

1. A cathode for electron tubes which comprises a substrate metal mainly composed of nickel and a reducing agent and a coating layer of a composition comprising alkaline earth metal carbonates and formed on the substrate metal, the alkaline earth metal carbonates in the coating layer being converted into corresponding metal oxides, characterized in that the alkaline earth metal carbonates contain at least one of zinc (Zn) and aluminium (Al).

2. A cathode according to Claim 1, wherein said alkaline earth metal carbonates contain Ba, Sr and Ca at the same time.

3. A method for fabricating a cathode for electron tubes which comprises the steps of:
adding at least one element of Zn and Al or its compound to a solution of water-soluble salts of alkaline earth metals;
adding a carbonate precipitant to the solution thereby causing co-precipitation to obtain a powder mainly composed of a multi-component alkaline earth metal carbonate;
immersing the powder in an alkaline aqueous solution and subjecting the resulting mixture to filtration to obtain an alkaline earth metal carbonate containing Al and/or Zn from which the element in excess is removed by dissolution;
applying, onto a substrate metal, a cathodic material composition obtained by mixing the alkaline earth metal carbonate and a binder therefor to form a layer of the cathodic material composition; and
heating the thus formed layer in an evacuated closed system to convert the layer into an oxide layer.

4. A method according to Claim 3, wherein the water-soluble salts of the alkaline earth metals are $BaCO_3$, $SrCO_3$ and $CaCO_3$.

5. A method according to Claim 3, wherein said carbonate precipitant is $(NH_4)_2CO_3$ or Na_2CO_3.

6. A method according to Claim 3, wherein the Zn and/or Al compound is ZnO and/or $Al(OH)_3$.

7. A method according to Claim 3, wherein the Zn and/or Al compound is added in an amount of from 1 to 3 wt% of the total amount of the alkaline earth metal carbonates.

FIG. 1

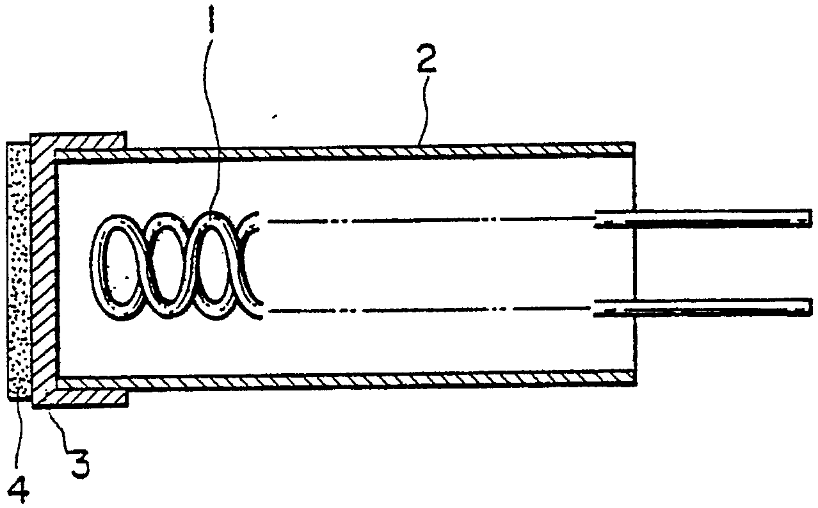


FIG. 2

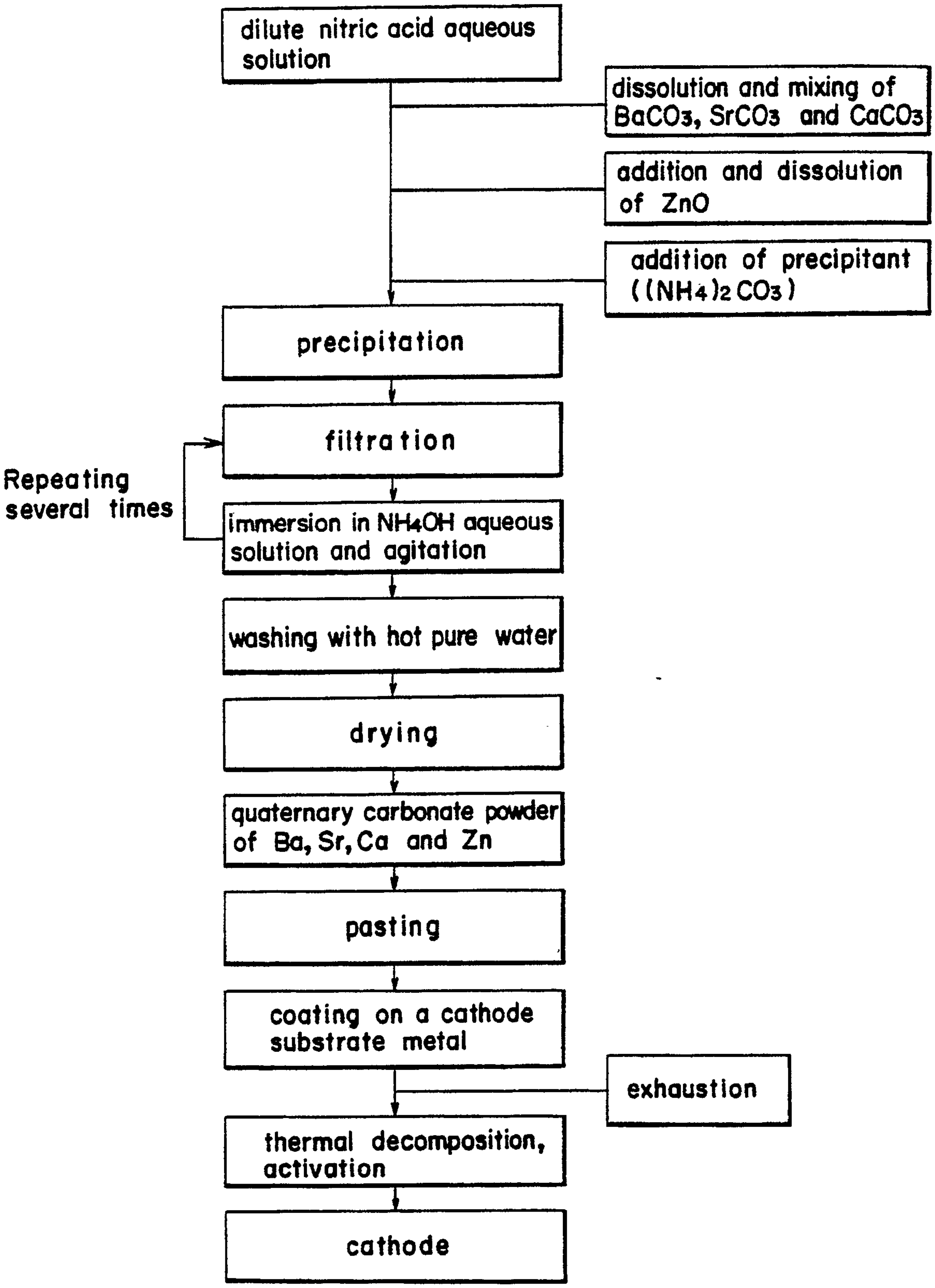

dilute nitric acid aqueous solution
dissolution and mixing of $BaCO_3$, $SrCO_3$ and $CaCO_3$
addition and dissolution of ZnO
addition of precipitant ($(NH_4)_2CO_3$)
precipitation
filtration
Repeating several times
immersion in NH_4OH aqueous solution and agitation
washing with hot pure water
drying
quaternary carbonate powder of Ba, Sr, Ca and Zn
pasting
coating on a cathode substrate metal
exhaustion
thermal decomposition, activation
cathode

FIG. 3

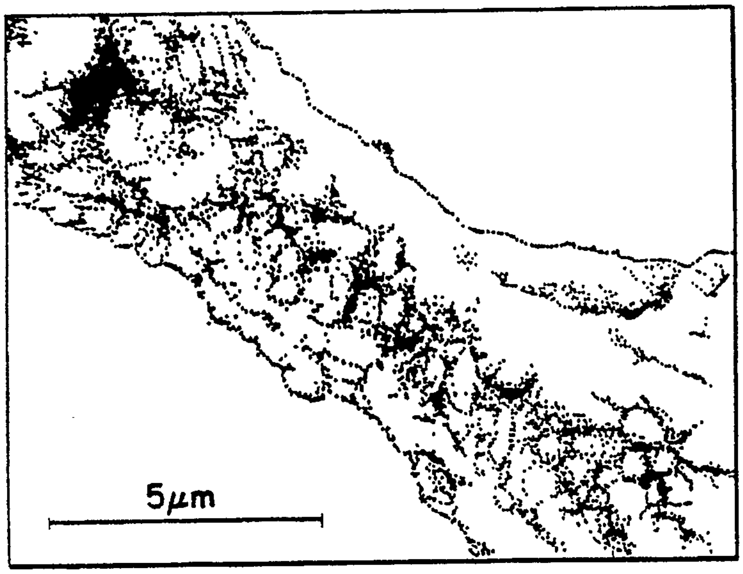


FIG. 4

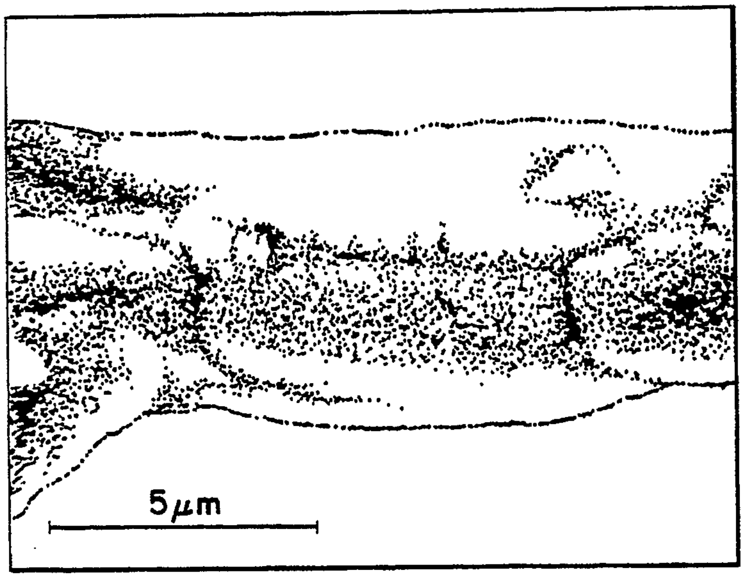


FIG.5

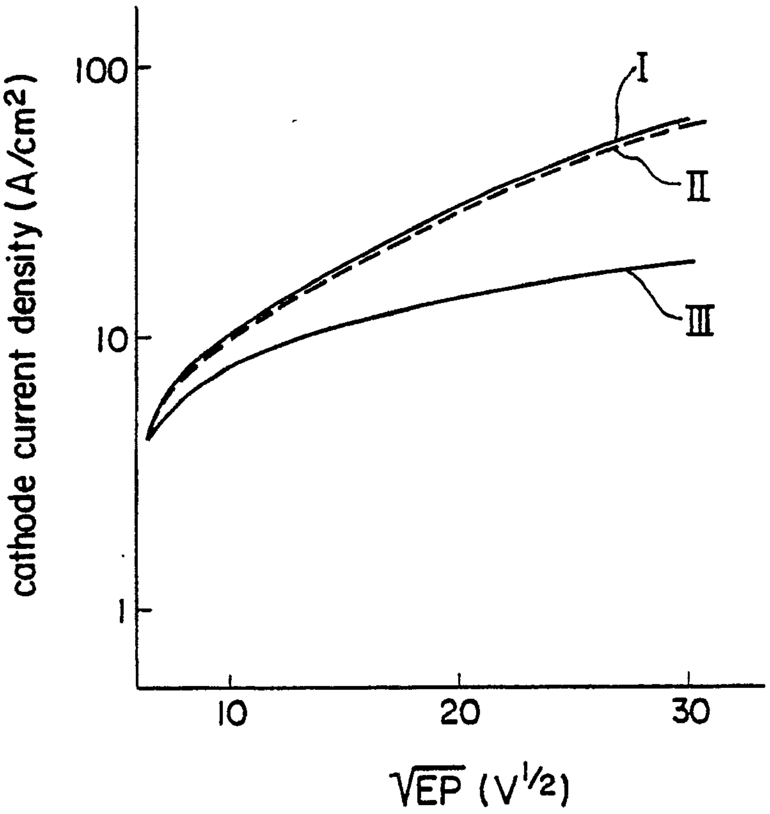


FIG.6

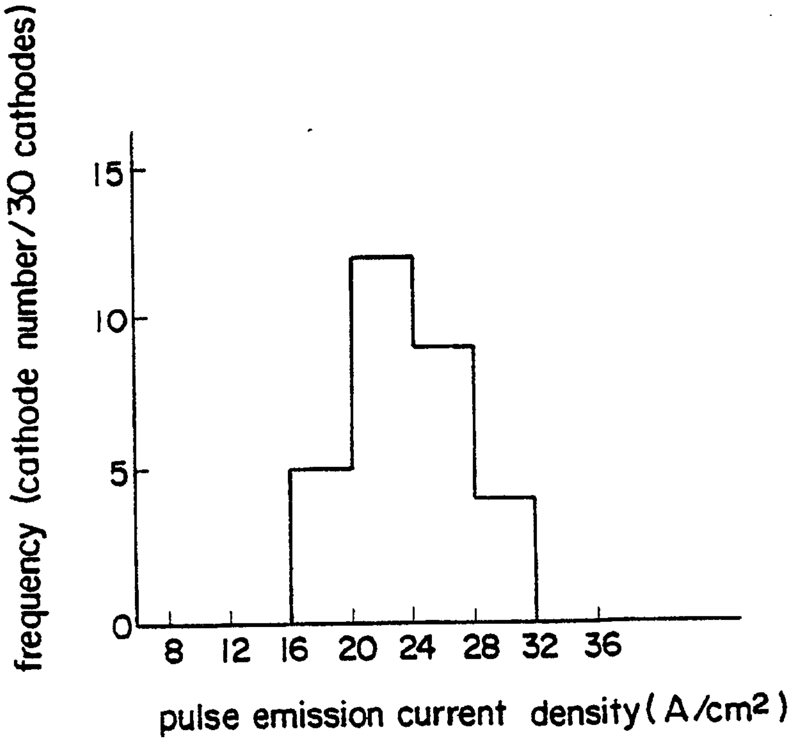

frequency (cathode number/30 cathodes)
15
10
5
0
8
12
16
20
24
28
32
36
pulse emission current density(A/cm2)

FIG. 7

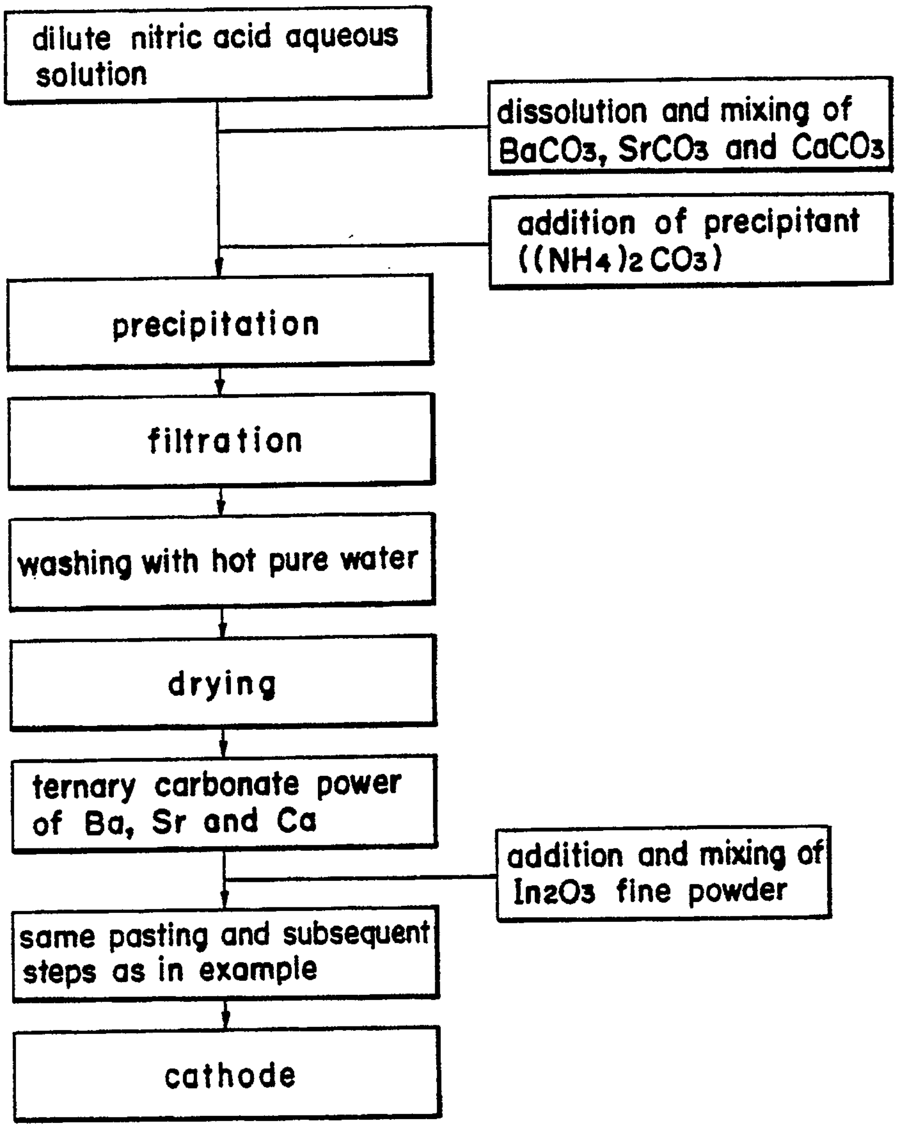
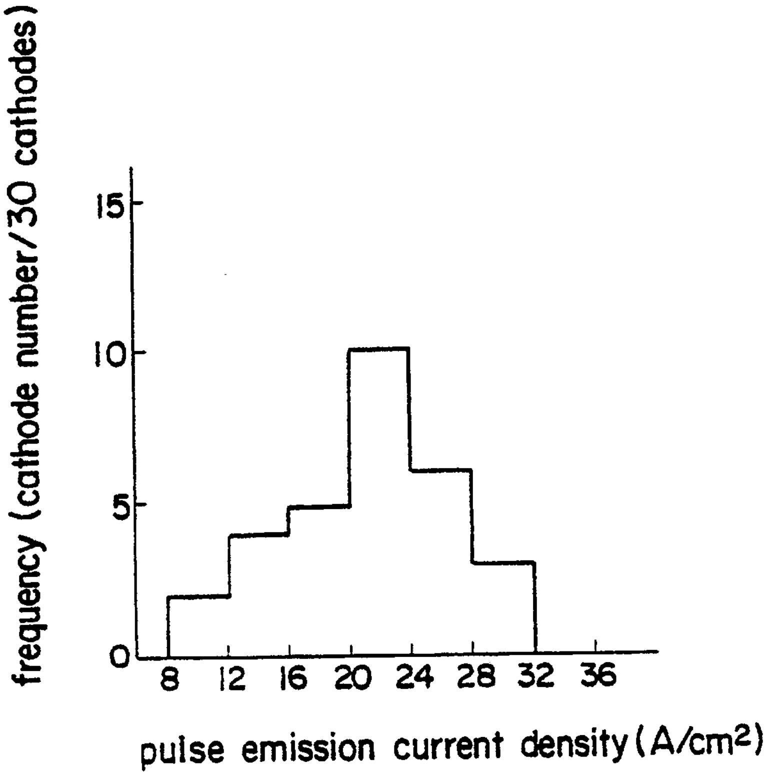

dilute nitric acid aqueous solution
dissolution and mixing of $BaCO_3$, $SrCO_3$ and $CaCO_3$
addition of precipitant $((NH_4)_2CO_3)$
precipitation
filtration
washing with hot pure water
drying
ternary carbonate power of Ba, Sr and Ca
addition and mixing of In_2O_3 fine powder
same pasting and subsequent steps as in example
cathode

FIG. 8


frequency (cathode number/30 cathodes)
15
10
5
0
8
12
16
20
24
28
32
36
pulse emission current density (A/cm²)