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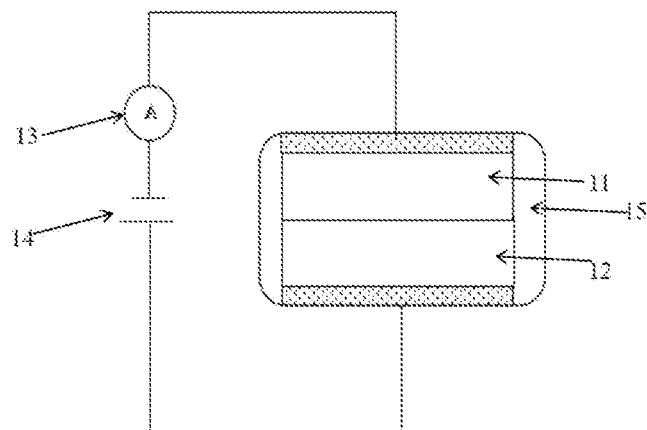
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(54)

PREPARATION METHOD OF LIMITING CURRENT TYPE OXYGEN SENSOR WITH DENSE DIFFUSION LAYER.

(57)

The present invention relates to a preparation method of a limiting current type oxygen sensor with a dense diffusion layer, which has the advantages of simple process, easy operation, low cost, short time and high success rate.



PREPARATION METHOD OF LIMITING CURRENT TYPE OXYGEN SENSOR WITH DENSE DIFFUSION LAYER

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TECHNICAL FIELD

[01] The present invention relates to the technical field of oxygen sensors, in particular to a method for preparing a limiting current type oxygen sensor with a dense diffusion layer.

BACKGROUND ART

[02] At present, the materials used as the dense diffusion layer are mainly mixed conductor materials, and their high ionic conductivity and electronic conductivity can ensure that the oxygen sensor has excellent performance such as high sensitivity. However, the mixed conductor material and solid electrolyte material belong to the materials with large differences in physical and chemical properties, which are prone to cracks in production and application due to the difference in expansion rates of the two materials, and even cause the glass glaze that acts as a seal on the outside to crack, leading the sensor to failing.

SUMMARY

[03] (I) Technical problem to be solved

[04] In view of the above-mentioned disadvantages and deficiencies of the prior art, the present invention provides a method for preparing a limiting current type oxygen sensor with a dense diffusion layer.

[05] (II) Technical scheme

[06] In order to achieve the above object, the present invention adopts the following technical scheme:

[07] In a first aspect, the present invention provides a preparation method of a limiting current type oxygen sensor with a dense diffusion layer, the method comprising: preparing a solid electrolyte layer and a dense diffusion layer separately;

[08] applying a Pt slurry film on a lower surface of the solid electrolyte layer to form an anode, applying the Pt slurry film on an upper surface of the dense diffusion layer to form a cathode, and at the same time, applying a Pt slurry strip on a side of the dense diffusion layer in a thickness direction to be electrically connected with the cathode on the upper surface of the dense diffusion layer; and

[09] laminating and combining the solid electrolyte layer and the dense diffusion layer, bonding by using a Pt slurry, co-firing to obtain a double-layer structure, and sealing the peripheral side of the double-layer structure by using a high-temperature-resistant material.

[10] (III) Beneficial effects:

[11] The present invention has the following technical effects:

[12] (1) By applying the Pt slurry strip on the side in the thickness direction of the dense diffusion layer, the selection range of the materials of the dense diffusion layer is widened.

[13] (2) The dense diffusion layer made of the solid electrolyte is high in matching

degree with a homogeneous solid electrolyte layer material, solving the problems of cracks, breakage of the seal structure and the like caused by unmatched linear coefficient and sintering shrinkage rate in a high-temperature application environment and a preparation process of the existing oxygen sensor; and the dense diffusion layer and the solid electrolyte layer have high bonding tightness, improving the performance and the performance stability of the oxygen sensor. Moreover, the width and the thickness of the Pt connecting portion can be accurately controlled, and the preparation process is very simple. The Pt connecting portion is suitable for large-scale production.

[14] (3) By adopting the method provided by the present invention, the solid electrolyte (oxygen ion conductor material) can be used for manufacturing the dense diffusion layer, without causing problems of cracking of the oxygen sensor or chemical reaction of the two materials.

BRIEF DESCRIPTION OF THE DRAWINGS

[15] FIG. 1 is a schematic structural diagram of a limiting current type oxygen sensor with a dense diffusion layer in prior art.

[16] FIG. 2 is a schematic structural diagram of the limiting current type oxygen sensor with a dense diffusion layer of Example 1 of the present invention.

[17] FIG. 3 is an oxygen measurement performance comparison of the limiting current type oxygen sensor with a dense diffusion layer of Example 1 of the present invention with that of the prior art.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[18] EXAMPLE 1

[19] FIG. 2 is a schematic structural diagram of a limiting current type oxygen sensor with a dense diffusion layer according to the present invention. The figure includes an oxygen sensor 20, an external power supply 30 and an ammeter. Wherein the sensor 20 comprises a dense diffusion layer 21 on an upper layer and a solid electrolyte layer 22 on a lower layer, and a high-temperature glass sealant 23 applied on the peripheral surfaces of the dense diffusion layer 21 and the solid electrolyte layer 22 on the lower layer. A cathode 211 formed of a Pt slurry is provided on an upper surface of the dense diffusion layer 21, and a Pt slurry strip 212, which is electrically connected to the cathode 211, is provided on a side in the thickness direction of the dense diffusion layer 21. An anode 221 formed of the Pt slurry is provided on a lower surface of the solid electrolyte layer 22. Wherein, the anode 221 is connected to a positive pole of the external power supply 30 by a Pt wire, and the cathode 211 is connected to a negative pole of the external power supply 30 by the Pt wire. The ends of the two Pt wires are bonded to the cathode 211 and the anode 221 by the Pt slurry. A lower surface of the dense diffusion layer 21 and an upper surface of the solid electrolyte layer 22 is applied with the Pt slurry therebetween, and bonded by the Pt slurry. Wherein, the Pt slurry strip 212 on the side in the thickness direction of the dense diffusion layer 21 is also electrically connected to the Pt slurry on the lower surface of the dense diffusion layer 21. Wherein, the number of Pt slurry strips 212 may be multiple, which are dispersedly applied on the peripheral side of the dense diffusion layer 21.

[20] The preparation method of the oxygen sensor 20 with the above structure was as follows:

[21] (1) Preparation of solid electrolyte layer

[22] The material of the solid electrolyte is 8YSZ (8% yttrium oxide stabilized zirconium dioxide), and the preparation method comprised: yttrium nitrate and zirconium nitrate were prepared into a salt solution according to a certain proportion, which was stirred vigorously until the solution was completely dissolved; ammonia water was added dropwise under stirring, and a precipitate was formed when the pH value was 9; the precipitate was then filtered, washed with absolute ethyl alcohol for several times, and dried in a drying oven of 70°C; and then, the precipitate was calcined at 800°C for 2 hours to obtain 8YSZ solid electrolyte powder. The solid electrolyte powder was pressed into 10 mm diameter tablets at 100 MPa and sintered at 1500°C for 10 h.

[23] (2) Preparation of dense diffusion layer

[24] The 8YSZ solid electrolyte powder prepared by the method is pressed into 10 mm diameter tablets at 100 MPa and sintered at 1500°C for 10 h.

[25] (3) The solid electrolyte layer obtained in step (1) were applied with Pt slurry on both the upper and the lower surfaces, applied with a narrow strip of Pt slurry on the side to connect the Pt slurry on both the upper and the lower surfaces, and subjected to high-temperature treatment at 850°C for 10 minutes.

[26] (4) The dense diffusion layer obtained in step (2) were applied with Pt slurry on both the upper and the lower surfaces, and subjected to high-temperature treatment at 850°C for 10 minutes.

[27] (5) The solid electrolyte layer in step (3) was placed below, and the dense diffusion layer in the step (4) was placed above; the two were bonded together by using the Pt slurry, and subjected to high-temperature treatment at 850°C for 10 minutes.

[28] Wherein, in step (5), ends of two wires (Pt wires) connected with the external power supply can also be bonded to the cathode (Pt slurry) above the dense diffusion layer and the anode (Pt slurry) below the solid electrolyte layer by using the Pt slurry at the same time, which was collectively subjected to high-temperature treatment at 850°C for 10 minutes to complete connection of the Pt wires finally. However, in the solution of the present invention, the connection of the lead wire (Pt wire) to both poles of the oxygen sensor is not important, and thus is briefly described.

[29] (6) The entire peripheral side was sealed with a high temperature glass sealant to obtain the oxygen sensor shown in FIG. 2.

[30] The oxygen sensor prepared by the present invention can be used at 500-900°C and oxygen concentration of 0-100 vol%.

[31] According to the structure of the oxygen sensor 20 shown in FIG. 2 and the above-described preparation method, an oxygen sensor without the Pt slurry strip 212 was fabricated at the same time, and the oxygen measurement performance was compared.

[32] Wherein, the thickness and size of each layer of the oxygen sensor 20 containing the Pt slurry strip 212 and the oxygen sensor without the Pt slurry strip 212 are shown in the following table:

	T1	D1	T2	D2	Pt thickness on T1	Pt thickness below T1	Pt thickness on T2	Pt thickness below T2	Pt strip thickness on side	Pt strip total width on side
No Pt strip	1.36 mm	9.25 mm	1.35 mm	9.11 mm	0.01 mm	0.01 mm	0.01 mm	0.01 mm	0	0
with Pt strip	1.35 mm	9.24 mm	1.36 mm	9.07 mm	0.01 mm	0.01 mm	0.01 mm	0.01 mm	0.01 mm	1 mm

[33] wherein:

[34] T1 represents the thickness of the dense diffusion layer 21, and D1 represents the diameter of the dense diffusion layer 21;

[35] T2 represents the thickness of the solid electrolyte layer 22, and D1 represents the diameter of the solid electrolyte layer 22;

[36] "Pt thickness on T1" is the thickness of the Pt film on the upper surface of the dense diffusion layer 21;

[37] "Pt thickness below T1" is the thickness of the Pt film on the lower surface of the dense diffusion layer 21;

[38] "Pt thickness on T2" is the thickness of the Pt film on the upper surface of the solid electrolyte layer 22;

[39] The "Pt thickness below T2" is the thickness of the Pt film on the lower surface of the solid electrolyte layer 22.

[40] The above-described two kinds of oxygen sensors with the Pt strip and without Pt strip on the side were subjected to an oxygen measurement experiment at a temperature of 800°C and an oxygen concentration of 0-10 vol%. Experimental results were as shown in FIG. 4, with the oxygen concentration being 2 vol%, 4 vol%, 6 vol%, 8 vol%, 10 vol% in order from bottom to top.

[41] The results showed that, when the side of the dense diffusion layer 21 was not provided with the Pt stripe (the dense diffusion layer 21 was made of the same material as the solid electrolyte), no limiting current plateau was generated and the sensor cannot perform oxygen measurement. However, when the Pt strip was provided on the side of the dense diffusion layer 21 and connected to the cathode Pt film, significant limiting current plateaus (2 vol%, 4 vol%, 6 vol%, 8 vol%, 10 vol%, respectively) were produced by the oxygen sensor 21, indicating that the oxygen sensor 20 can perform oxygen measurement and is very effective.

[42] Although the preparation method of the above steps (1)-(6) is feasible, it is somewhat cumbersome. Therefore, the present invention further combines and simplifies the process steps on the premise of guaranteeing the quality and the operability. Since that the steps of applying Pt slurry and subjecting to high-temperature treatment at 850°C for 10 minutes were present in preparing both the solid electrolyte

layer and the dense diffusion layer, the final two layers of the solid electrolyte layer and the dense diffusion layer also need to be bonded by the Pt slurry and subjected to high-temperature treatment at 850°C for 10 minutes again, the combination treatment can be carried out for the purpose of simplifying the process steps. For example, high-temperature treatment at 850°C can be collectively performed after applying the Pt slurry in each step is completed. In addition, since Pt slurry is required to be used for bonding connection when the two layers, the solid electrolyte layer and the dense diffusion layer are bonded finally, the lower surface of the dense diffusion layer may not be applied with the Pt slurry at first. The dense diffusion layer may be applied with the Pt slurry film only on the upper surface and applied with the Pt slurry strip on the side in the thickness direction diffusion layer, then bonded with the solid electrolyte layer applied with the Pt slurry on both the upper and the lower surface or only the lower surface, and finally collectively subjected to high-temperature treatment at 850°C. Or, the Pt slurry strips may be applied on both the upper surface and the lower surface/only the upper surface and the side in the thickness direction of the dense diffusion layer; then bonded with the solid electrolyte layer applied with the Pt slurry on the only lower surface by using the Pt slurry, and finally collectively subjected to high-temperature treatment at 850°C.

[43] Based on the above ideas, after the solid electrolyte layer and the dense diffusion layer are separately prepared, the oxygen sensor of the present example can be prepared by any one of the following modes:

[44] Mode B: the solid electrolyte layer was applied with the Pt slurry film on one surface and subjected to the treatment at 850°C for 10 min. The dense diffusion layer were applied with Pt slurry films on both the upper and lower surfaces, and applied with the Pt slurry strip on the side in the thickness direction to be connected with the Pt slurry layers applied on both the upper and lower surfaces, and subjected to the treatment at 850°C for 10 min. The surface of the solid electrolyte layer which was not applied with the Pt slurry film and one surface of the dense diffusion layer were fitted correspondingly, bonded together with the Pt slurry, and subjected to the treatment at 820-850°C for 10 min to obtain the double-layer structure, which was sealed by the high-temperature-resistant glass sealant on the peripheral side.

[45] Mode C: the solid electrolyte layer was applied with the Pt slurry film on both the upper and the lower surfaces, and subjected to the treatment at 850°C for 10 min; the dense diffusion layer was applied with the Pt slurry film on one surface, and applied with the Pt slurry strip on the side in the thickness direction at the same time to be connected with the Pt slurry layer applied on the surface, and subjected to the treatment at 850°C for 10 min; the solid electrolyte layer and one surface of the dense diffusion layer which was not applied with the Pt slurry film were fitted correspondingly, bonded together with the Pt slurry, and subjected to the treatment at 820-850°C for 10 min to obtain the double-layer structure, which was sealed by the high-temperature-resistant glass sealant on the peripheral side.

[46] Mode D: the solid electrolyte layer was applied with the Pt slurry film on one surface, and subjected to the treatment at 850°C for 10 min; the dense diffusion layer was applied with the Pt slurry film on one surface, and applied with the Pt slurry strip

on the side in the thickness direction at the same time to be connected with the Pt slurry layer applied on the surface, and subjected to the treatment at 850°C for 10 min; the surface of solid electrolyte layer which was not applied with the Pt slurry and the surface of the dense diffusion layer which was not applied with the Pt slurry film were fitted correspondingly, bonded together with the Pt slurry, and subjected to the treatment at 820-850°C for 10 min to obtain the double-layer structure, which was sealed by the high-temperature-resistant glass sealant on the peripheral side.

[47] Mode E: the solid electrolyte layer was applied with the Pt slurry film on both the upper and the lower surfaces; the dense diffusion layer was applied with the Pt slurry film on both the upper and lower surfaces, and applied with the Pt slurry strip on the side in the thickness direction at the same time to be connected with the Pt slurry layers applied on both the upper and lower surfaces; the solid electrolyte layer and the dense diffusion layer were fitted correspondingly, and subjected to the treatment at 820-850°C for 10 min to obtain the double-layer structure, which was sealed by the high-temperature-resistant glass sealant on the peripheral side.

[48] Mode F: the solid electrolyte layer was applied with the Pt slurry film on one surface; the dense diffusion layer was applied with the Pt slurry film on both the upper and lower surfaces, and applied with the Pt slurry strip on the side in the thickness direction at the same time to be connected with the Pt slurry layers applied on the upper and lower surfaces. The surface of the solid electrolyte layer which was not applied with the Pt slurry film and the dense diffusion layer were fitted correspondingly, and subjected to the treatment at 820-850°C for 10 min to obtain the double-layer structure, which was sealed by the high-temperature-resistant glass sealant on the peripheral side.

[49] Mode G: the solid electrolyte layer was applied with the Pt slurry film on both the upper and the lower surfaces; the dense diffusion layer was applied with the Pt slurry film on one surface, and applied with the Pt slurry strip on the side in the thickness direction at the same time to be connected with the Pt slurry layer applied on the surface. The surface of the solid electrolyte layer and the surface of the dense diffusion layer which was not applied with the Pt slurry were fitted correspondingly, and subjected to the treatment at 820-850°C for 10 min to obtain the double-layer structure, which was sealed by the high-temperature-resistant glass sealant on the peripheral side.

[50] Finally, ends of two wires (Pt wires) connected with the external power supply can also be bonded to the cathode (Pt slurry) above the dense diffusion layer and the anode (Pt slurry) below the solid electrolyte layer by using the Pt slurry, which was collectively subjected to high-temperature treatment at 850°C for 10 minutes to complete connection of the lead wires. The Pt wires were connected to the external power supply and the current meter, and the oxygen concentration test can be performed under the working conditions of 500-900°C and 0-100 vol% of oxygen concentration.

WHAT IS CLAIMED IS:

1. A preparation method of a limiting current type oxygen sensor with a dense diffusion layer, characterized by comprising: preparing a solid electrolyte layer and a dense diffusion layer separately;

applying a Pt slurry film on a lower surface of the solid electrolyte layer to form an anode, applying the Pt slurry film on an upper surface of the dense diffusion layer to form a cathode, and at the same time, applying a Pt slurry strip on a side of the dense diffusion layer in a thickness direction to be electrically connected with the cathode on the upper surface of the dense diffusion layer; and

laminating and combining the solid electrolyte layer and the dense diffusion layer, bonding by using a Pt slurry, co-firing to obtain a double-layer structure, and sealing the peripheral side of the double-layer structure by using a high-temperature-resistant material.

2. The preparation method according to claim 1, characterized in that, the solid electrolyte layer and the dense diffusion layer are separately prepared and then treated in one of the following modes:

Mode A:

applying the Pt slurry films on both an upper surface and the lower surface of the solid electrolyte layer, and treating for 5-15 minutes under 820-850°C; applying the Pt slurry films on both the upper surface and a lower surface of the dense diffusion layer, at the same time, applying the Pt slurry strip on the side of the dense diffusion layer in the thickness direction to be connected with the Pt slurry layers applied on both the upper surface and the lower surface, and then treating for 5-15 minutes under 820-850°C; and

bonding the solid electrolyte layer and the dense diffusion layer with the Pt slurry treated by the above steps, treating for 5-15 minutes under 820-850°C to obtain the double-layer structure, and sealing the peripheral side of the double-layer structure with the high-temperature-resistant material;

Mode B:

applying the Pt slurry film on one surface of the solid electrolyte layer, and treating for 5-15 minutes under 820-850°C; applying the Pt slurry films on both the upper surface and the lower surface of the dense diffusion layer, at the same time, applying the Pt slurry strip on the side of the dense diffusion layer in the thickness direction to be connected with the Pt slurry layers applied on both the upper surface and the lower surface, and then treating for 5-15 minutes under 820-850°C; and

fitting the surface of the solid electrolyte layer treated by the above steps which is not applied with the Pt slurry film and one surface of the dense diffusion layer correspondingly and bonding together with the Pt slurry, treating for 5-15 minutes under 820-850°C to obtain the double-layer structure, and sealing the peripheral side of the double-layer structure by using the high-temperature-resistant material.

Ansprüche

1. Herstellungsverfahren eines Sauerstoffsensors vom Grenzstromtyp mit einer dichten Diffusionsschicht, dadurch gekennzeichnet, dass es separates Herstellen einer Festelektrolytschicht und einer dichten Diffusionsschicht umfasst;
Aufbringen eines Pt-Aufschlammungsfilms auf eine untere Oberfläche der Festelektrolytschicht, um eine Anode zu bilden, Aufbringen des Pt-Aufschlammungsfilms auf eine obere Oberfläche der dichten Diffusionsschicht, um eine Kathode zu bilden, und gleichzeitig Aufbringen eines Pt-Aufschlammungsstreifens auf eine Seite der dichten Diffusionsschicht in einer Dickenrichtung, die elektrisch mit der Kathode auf der oberen Oberfläche der dichten Diffusionsschicht verbunden ist; und Laminieren und Kombinieren der Festelektrolytschicht und der dichten Diffusionsschicht, Verbinden unter Verwendung einer Pt-Aufschlammung, gemeinsames Brennen, um eine Doppelschichtstruktur zu erhalten, und Versiegeln der Umfangsseite der Doppelschichtstruktur unter Verwendung eines hochtemperaturbeständigen Materials.
2. Herstellungsverfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Festelektrolytschicht und die dichte Diffusionsschicht getrennt hergestellt und dann in einem der folgenden Modi behandelt werden:
Modus A:
Aufbringen der Pt-Aufschlammungsfilme sowohl auf eine obere Oberfläche als auch auf die untere Oberfläche der Festelektrolytschicht und Behandeln für 5-15 Minuten bei 820-850°C; Auftragen der Pt-Aufschlammungsfilme auf sowohl die obere Oberfläche als auch eine untere Oberfläche der dichten Diffusionsschicht, gleichzeitiges Aufbringen des Pt-Aufschlammungsstreifens auf der Seite der dichten Diffusionsschicht in der Dickenrichtung, die mit den aufgetragenen Pt-Aufschlammungsschichten sowohl auf der oberen Oberfläche als auch auf der unteren Oberfläche verbunden werden soll, und dann 5-15 Minuten bei 820-850 °C behandeln; und Verbinden der Festelektrolytschicht und der dichten Diffusionsschicht mit der durch die

obigen Schritte behandelten Pt-Aufschlammung, Behandeln für 5-15 Minuten bei 820-850 °C, um die Doppelschichtstruktur zu erhalten, und Versiegeln der Umfangsseite der Doppelschicht Struktur mit dem hochtemperaturbeständigen Material;

Modus B:

- 5 Aufbringen des Pt-Aufschlammungsfilms auf eine Oberfläche der Festelektrolytschicht und Behandeln für 5–15 Minuten bei 820–850 °C; Auftragen der Pt-Aufschlammungsfilme sowohl auf die obere Oberfläche als auch auf die untere Oberfläche der dichten Diffusionsschicht, gleichzeitiges Aufbringen des Pt-Aufschlammungsstreifens auf der Seite der dichten Diffusionsschicht in der
- 10 Dickenrichtung, die mit den aufgetragenen Pt-Aufschlammungsschichten sowohl auf der oberen Oberfläche als auch auf der untere Oberfläche verbunden werden soll, und dann 5-15 Minuten bei 820-850 °C behandeln; und
- entsprechendes Passen der Oberfläche der durch die obigen Schritte behandelten Festelektrolytschicht, die nicht mit dem Pt-Aufschlammungsfilm aufgetragen wurde, und
- 15 einer Oberfläche der dichten Diffusionsschicht und Verbinden mit der Pt-Aufschlammung, Behandeln für 5-15 Minuten unter 820-850° C, um die Doppelschichtstruktur zu erhalten, und Abdichten der Umfangsseite der Doppelschichtstruktur unter Verwendung des hochtemperaturbeständigen Materials.

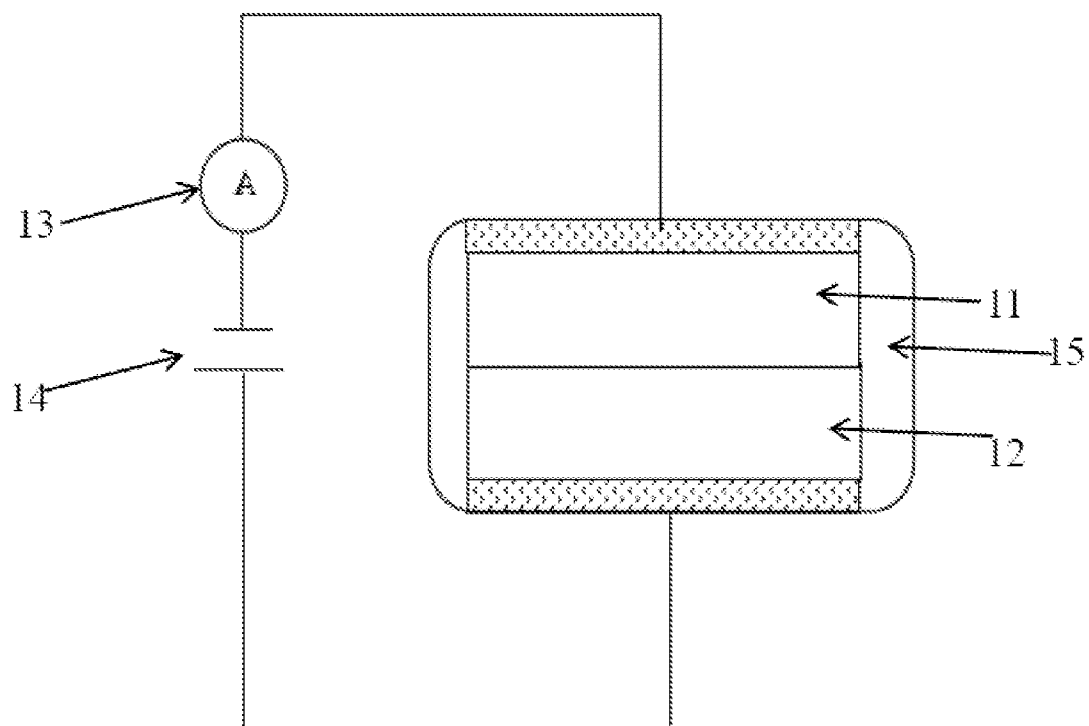


FIG. 1

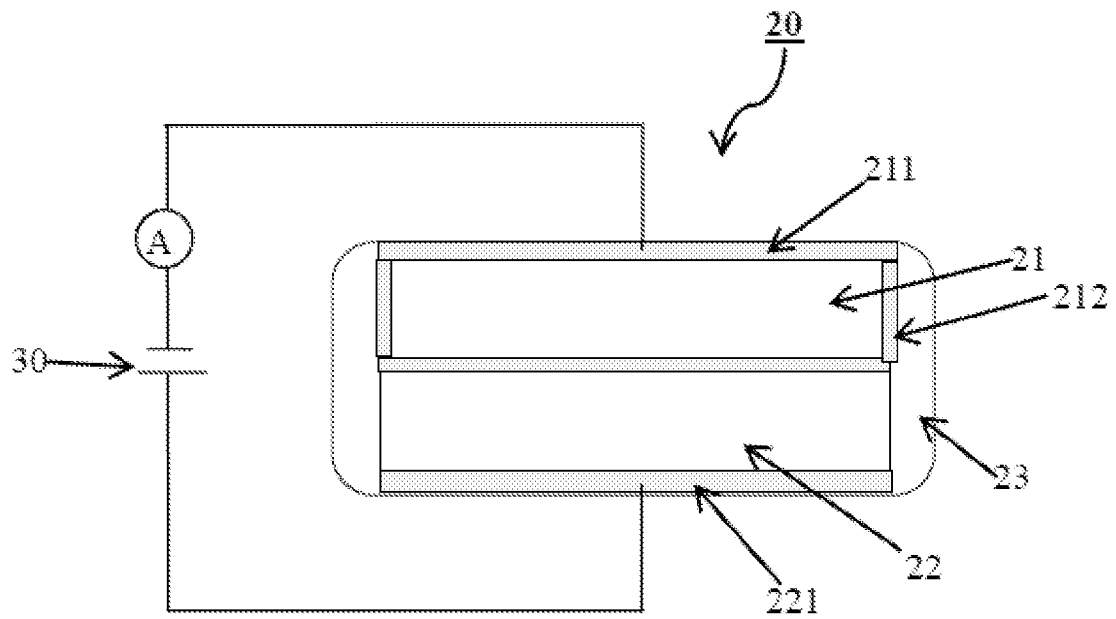


FIG. 2

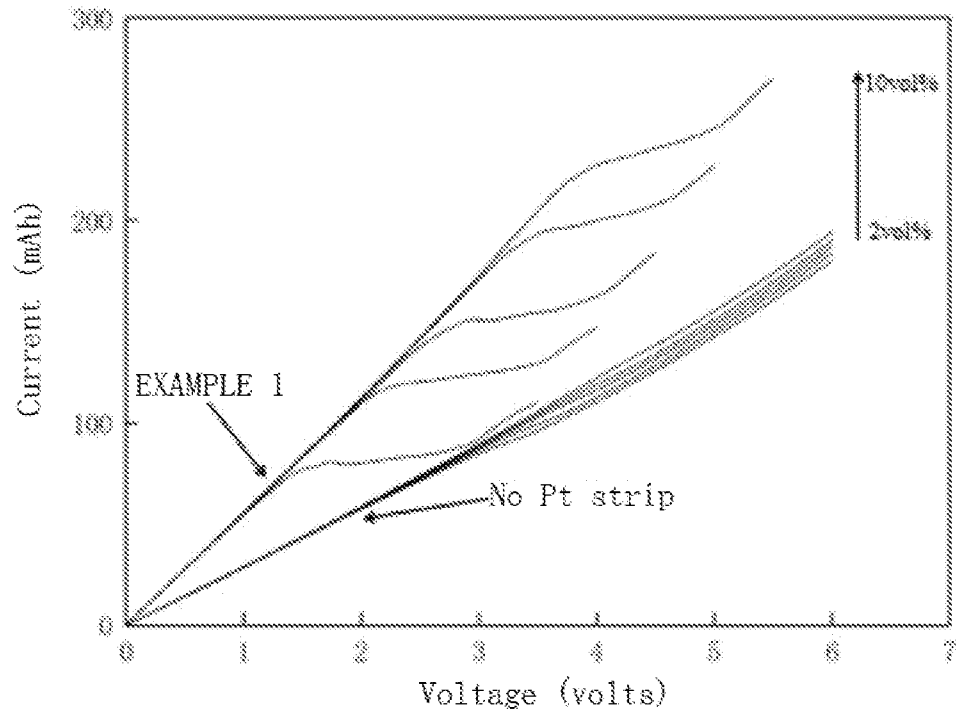


FIG. 3