Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2455480 A1 2003/02/27

(21) 2 455 480

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2002/08/02
(87) Date publication PCT/PCT Publication Date: 2003/02/27
(85) Entrée phase nationale/National Entry: 2004/01/27
(86) N° demande PCT/PCT Application No.: US 2002/024557
(87) N° publication PCT/PCT Publication No.: 2003/016893
(30) Priorités/Priorities: 2001/08/13 (60/311,909) US;
2002/06/06 (10/164,539) US

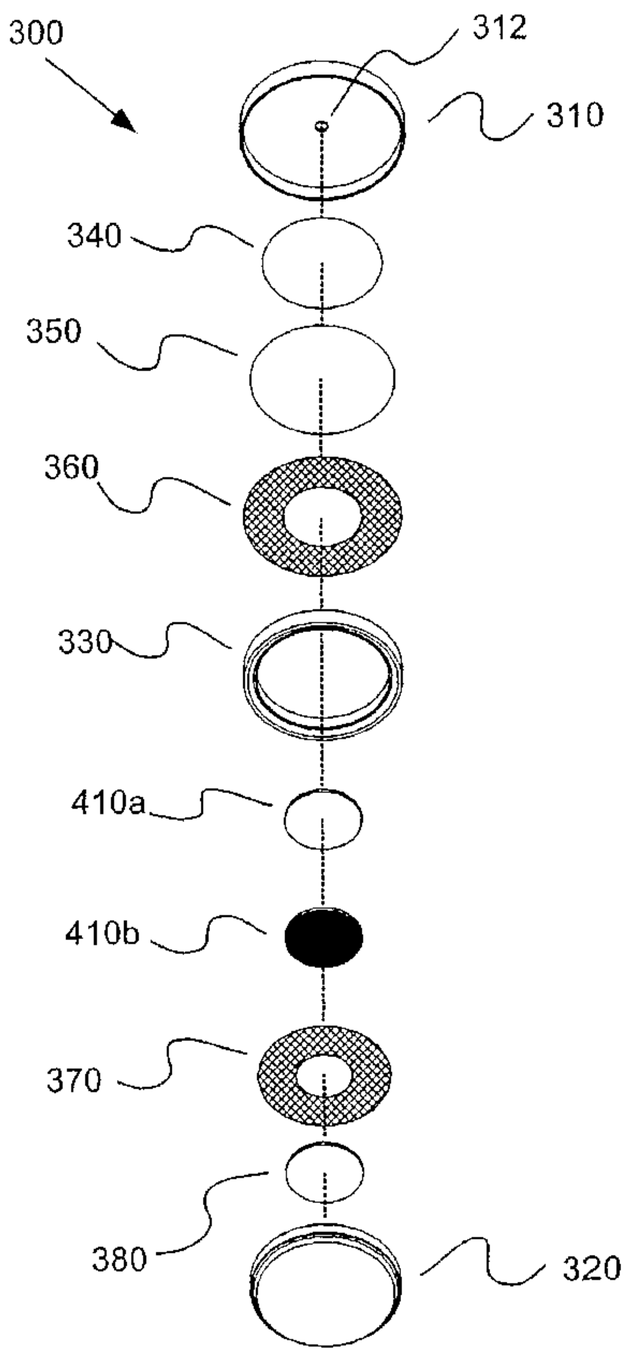
(51) Cl.Int.^{7}/Int.Cl.^{7} G01N 27/49

(71) Demandeur/Applicant:
MINE SAFETY APPLIANCES COMPANY, US

(72) Inventeurs/Inventors:
DAVIS, BRIAN K., US;
SCHEFFLER, TOWNER B., US;
BUSBY, LOUIS J., JR., US;
NEIGHOFF, JOHN F., JR., US

(74) Agent: OGILVY RENAULT

(54) Titre : CAPTEUR ELECTROCHIMIQUE
(54) Title: ELECTROCHEMICAL SENSOR



(57) Abrégé/Abstract:
An electrode for use in an electrochemical sensor includes a catalyst dispersed within an electrolyte. Preferably, the catalyst is immobilized within a matrix of the electrolyte. In one embodiment, the electrode of the present invention includes at least one catalyst/electrolyte layer having a mixture of a powdered catalyst, a powdered, quasi-solid electrolyte and a binder material compressed together. The quasi-solid electrolyte can include a liquid electrolyte immobilized by a high-surface-area, high-pore-volume solid.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 February 2003 (27.02.2003)

PCT

(10) International Publication Number
WO 03/016893 A3

(51) International Patent Classification[7]: G01N 27/49

(21) International Application Number: PCT/US02/24557

(22) International Filing Date: 2 August 2002 (02.08.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/311,909 13 August 2001 (13.08.2001) US
10/164,539 6 June 2002 (06.06.2002) US

(71) Applicant: **MINE SAFETY APPLIANCES COMPANY** [US/US]; 121 Gamma Drive, Pittsburgh, PA 15238 (US).

(72) Inventors: **DAVIS, Brian, K.**; 438 Dutchtown Road, Butler, PA 16002 (US). **SCHEFFLER, Towner, B.**; 221 Beech Road, Butler, PA 16001 (US). **BUSBY, Louis, J., Jr.**; 404 Monmouth Drive, Cranberry, PA 16006 (US). **NEIGHOFF, John, F., Jr.**; 162 Scott Ridge Road, Harmony, PA 16037 (US).

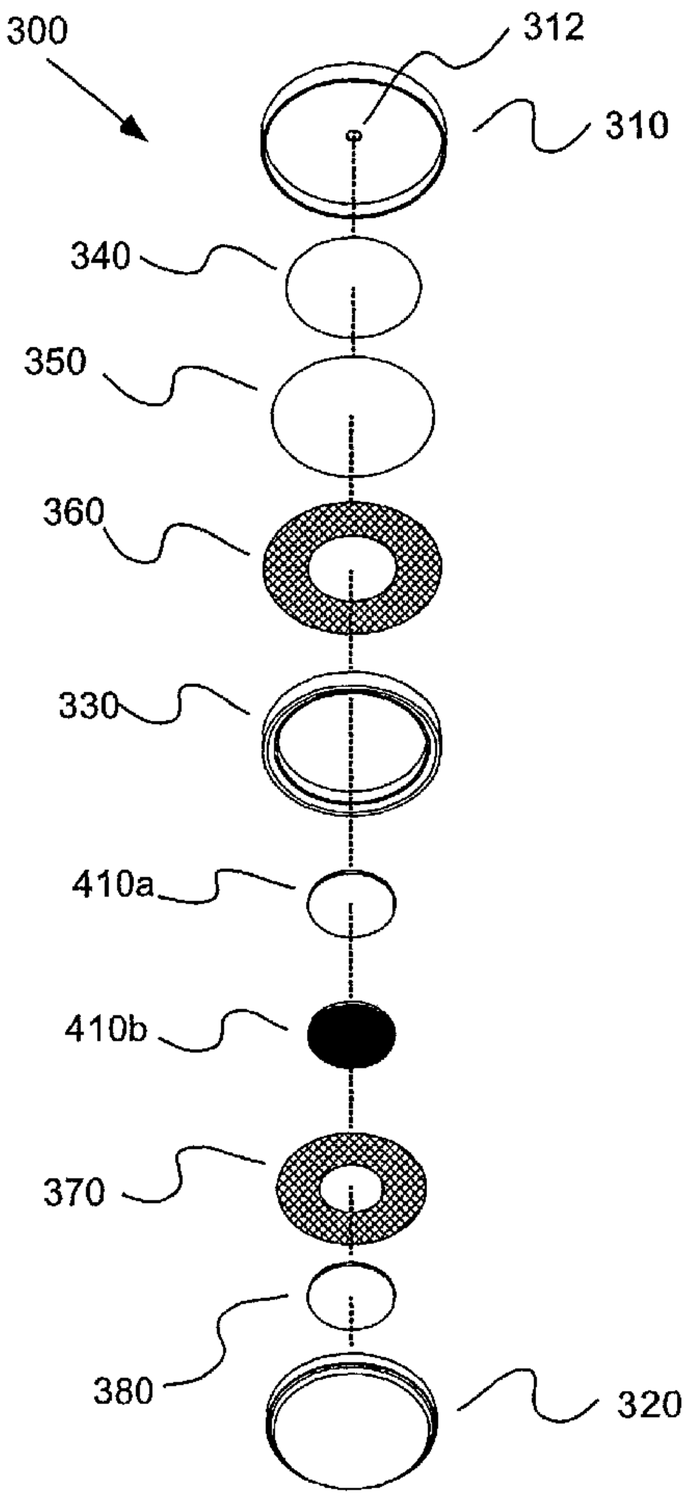
(74) Agent: **UBER, James, G.**; Mine Safety Appliances Company, P.O. Box 426, Pittsburgh, PA 15230-0426 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: ELECTROCHEMICAL SENSOR



(57) Abstract: An electrode for use in an electrochemical sensor includes a catalyst dispersed within an electrolyte. Preferably, the catalyst is immobilized within a matrix of the electrolyte. In one embodiment, the electrode of the present invention includes at least one catalyst/electrolyte layer having a mixture of a powdered catalyst, a powdered, quasi-solid electrolyte and a binder material compressed together. The quasi-solid electrolyte can include a liquid electrolyte immobilized by a high-surface-area, high-pore-volume solid.

A3

WO 03/016893

WO 03/016893 A3

European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations*

Published:

— *with international search report*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(88) Date of publication of the international search report:
26 June 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

TITLE

ELECTROCHEMICAL SENSOR

Cross-Reference to Related Application

This application claims benefit of U.S. Provisional Patent Application 60/311,309 filed August 13, 2001, the contents of which is incorporated herein by reference.

Background of the Invention

The present invention relates to an electrochemical sensor, and particularly, to an electrochemical sensor having improved response time.

In a typical electrochemical gas sensor, the gas to be measured typically passes from the atmosphere into the sensor housing through a gas porous or gas permeable membrane to a working electrode (sometimes called a sensing electrode) where a chemical reaction occurs. A complementary chemical reaction occurs at a second electrode known as a counter electrode (or an auxiliary electrode). The electrochemical sensor produces an analytical signal via the generation of a current arising directly from the oxidation or reduction of the analyte gas (that is, the gas to be detected) at the working and counter electrodes. A comprehensive discussion of electrochemical gas sensors is also provided in Cao, Z. and Stetter, J.R., "The Properties and Applications of Amperometric Gas Sensors," Electroanalysis, 4(3), 253 (1992), the disclosure of which is incorporated herein by reference.

To be useful as an electrochemical sensor, a working and counter electrode combination must be capable of producing an electrical signal that is (1) related to the concentration of the analyte and (2) sufficiently strong to provide a signal-to-noise ratio suitable to distinguish between concentration levels of the analyte over the entire range of interest. In other words, the current flow between the working electrode and the counter electrode must be measurably proportional to the concentration of the analyte gas over the concentration range of interest.

In addition to a working electrode and a counter electrode, an electrochemical sensor can include a third electrode, commonly referred to as a reference electrode. A reference electrode is used to maintain the working electrode at a known voltage or potential. The reference electrode should be physically and chemically stable in the electrolyte and carry the lowest possible current to maintain a constant potential.

Electrical connection between the working electrode and the counter electrode is maintained through an electrolyte. The primary functions of the electrolyte are: (1) to efficiently carry the ionic current; (2) to solubilize the analyte gas; (3) to support both the counter and the working electrode reactions; and (4) to form a stable reference potential with the reference electrode. The primary criteria for an electrolyte include the following: (1) electrochemical inertness; (2) ionic conductivity; (3) chemical inertness; (4) temperature stability; (5) low cost; (6) low toxicity; (7) low flammability; and (8) appropriate viscosity.

In general, the electrodes of an electrochemical cell provide a surface at which an oxidation or a reduction reaction occurs to provide a pathway whereby the ionic conduction of the electrolyte is coupled with the electron conduction of the electrode to provide a complete circuit for a current.

The measurable current arising from the cell reactions of the electrochemical cell is directly proportional to the rate of reaction. Preferably, therefore, a high reaction rate is maintained in the electrochemical cell. For this reason, the counter electrode and/or the working electrode of the electrochemical cell generally comprise an appropriate electrocatalyst on the surface thereof to enhance the reaction rate. If the reaction rate of either half cell reaction is impeded, resulting in a low exchange current density, the equilibrium current of the electrochemical cell may be changed or perturbed during measurement. Such change can result in undesirable side reactions and/or nonlinear behavior over the range of analyte concentrations desired to be detected.

The type, rate, and efficiency of the chemical reactions within an electrochemical gas sensor are controlled, in significant part, by the material(s) used to make the working electrode and counter electrode. Indeed, extensive research efforts are expended to develop improved working electrodes, counter electrodes and electrochemical systems generally. See Cao, supra.

As illustrated in Figure 1, electrodes 110 in electrochemical gas sensors 100 typically include a hydrophobic catalyst layer 120 adhered to a micro-porous, hydrophobic membrane 130 such as a Gore-tex® membrane. Membrane 130 is porous to gases from the exterior of sensor 100 but is not porous to the electrolyte 140 contained within the interior of sensor 100. Catalyst layer 120 is three-dimensional and hydrophobic. Catalyst layer 120 thus resists ingress of electrolyte 140 into its internal structure, especially if a quasi-solid state electrolyte is used. However, to be detected, the analyte gas (represented by arrows in Figure 1) must reach a point where catalyst 120 and electrolyte 140 are in very close proximity with one another. The gas must first diffuse through membrane 130, then into catalyst layer 120 and then through catalyst layer 120 until it reaches a catalyst/electrolyte interface 150. At interface 150, the gas is oxidized or reduced as described above. The time required for the gas to diffuse from the outside environment to such an interface 150 has a substantial effect upon the sensor response time.

It is desirable, therefore, to develop new electrochemical sensors and electrodes for use in such electrochemical sensors for the detection of analyte gases exhibiting improved response time.

Summary of the Invention

In one aspect, the present invention provides an electrode for use in an electrochemical sensor including a catalyst dispersed within an electrolyte. Preferably, the catalyst is immobilized within a matrix of the electrolyte.

In current electrochemical sensors in which a liquid electrolyte is used, the liquid electrolyte can penetrate a solid catalyst layer formed on an electrode of the sensor to provide conductive contact. In a number of electrochemical sensors (for example, electrochemical sensors with metallic housings) it is desirable, however, to immobilize the electrolyte. In current sensors with immobilized electrolytes, there is generally no penetration of a catalyst layer of an electrode thereof by the immobilized electrolyte. Interfacial contact between the electrolyte and the catalyst can thus be diminished as compared to sensors in which a liquid electrolyte is used. The present inventors have discovered that good contact between a catalyst and an immobilized electrolyte can be achieved, while maintaining catalyst activity, by dispersing/immobilizing the catalyst within the electrolyte.

In one embodiment, the electrode of the present invention includes at least one catalyst/electrolyte layer having a mixture of a powdered catalyst, a powdered, quasi-solid electrolyte and a binder material compressed together. The quasi-solid electrolyte can include a liquid electrolyte immobilized by a high-surface-area, high-pore-volume solid. The solid can, for example, be SiO_2. The liquid electrolyte can, for example, be H_2SO_4. An example of a suitable binder material is polytetrafluoroethylene.

The electrode can further include at least one electrolyte layer adjacent to the catalyst/electrolyte layer. The electrolyte layer can include a mixture of a powdered, quasi-solid electrolyte and a binder material compressed together. The electrolyte layer can be bound to the catalyst/electrolyte layer. As described above, the quasi-solid electrolyte of the

electrolyte layer can include a liquid electrolyte immobilized by a high-surface area, high-pore volume solid.

In another aspect, the present invention provides an electrochemical sensor for the detection of an analyte gas including a housing with at least one working electrode and at least one counter electrode disposed therein. The working electrode includes a catalyst dispersed within an electrolyte as described above. The catalyst is preferably immobilized within a matrix of the electrolyte.

In one embodiment, the working electrode includes at least one catalyst/electrolyte layer having a mixture of powdered catalyst, powdered, quasi-solid electrolyte and binder material compressed together as described above. The working electrode can further include at least one electrolyte layer adjacent to the catalyst/electrolyte layer. The electrolyte layer preferably includes a mixture of a powdered, quasi-solid electrolyte and a binder material compressed together.

The counter electrode can also include at least one catalyst/electrolyte layer having a mixture of powdered catalyst, powdered, quasi-solid electrolyte and binder material compressed together. The catalysts of the working electrode and/or the counter electrode can, for example, independently be iridium, platinum, carbon, silver or gold. In one embodiment, the catalyst of the working electrode is iridium and the catalyst of the counter electrode is iridium. Such a sensor is, for example, operable to sense hydrogen sulfide.

The sensor can further include a reference electrode having at least one catalyst/electrolyte layer including a mixture of a powdered catalyst, a powdered, quasi-solid electrolyte and a binder material compressed together.

In still another aspect, the present invention provides a method of fabricating an electrode for use in an electrochemical sensor comprising the step of dispersing a catalyst

within an electrolyte. The catalyst is preferably immobilized within a matrix of the electrolyte.

The step of dispersing a catalyst within an electrolyte can include the step of forming a catalyst/electrolyte layer by mixing a powdered catalyst, a powdered, quasi-solid electrolyte and a binder material and compressing the mixture. The method can further include the steps of: forming an electrolyte layer by mixing a powdered, quasi-solid electrolyte and a binder material; and compressing the mixture together. The step of compressing the mixture of a powdered, quasi-solid electrolyte and a binder material of the electrolyte layer can, for example, be done over the compressed mixture of powdered catalyst, powdered, quasi-solid electrolyte and binder material of the catalyst/electrolyte layer to form an electrolyte layer bound to the catalyst/electrolyte layer.

The electrodes, sensors and methods of the present invention improve catalyst electrolyte contact and improve sensor response time as compared to sensors incorporating electrodes in which a hydrophobic catalyst layer is deposited upon a porous membrane. Moreover, the electrodes of the present invention are relatively easy and inexpensive to manufacture in various sizes and, particularly, in reduced size as compared to currently available electrodes. The reduced size of the electrodes of the present invention facilitate the manufacture of compact sensors. Additionally, the electrodes of the present invention are easily formed as, for example, stacks of multiple electrodes or multiple-layer electrodes for manufacture of compact sensors suitable for detection of multiple analytes. The electrodes of the present invention are also suitable for use with generally any electrolyte, including aqueous, inorganic and/or organic electrolytes. The electrolytes used with the electrodes of the present invention can also be acidic, basic or neutral. Still further, the electrodes of the present invention have been found to provide improved response signals, particularly with catalyst materials of intrinsically low surface area (for example, gold).

Brief Description of the Drawings

Figure 1 illustrates a side cross-sectional view of a portion of a sensor incorporating an electrode in which a catalyst is deposited upon a porous membrane.

Figure 2A illustrates a side cross-sectional view of a sensor incorporating a bi-layer, composite electrode of the present invention.

Figure 2B illustrates a top plan view of the electrode of Figure 2A.

Figure 3A illustrates a disassembled or exploded view of a two-electrode sensor including two bi-layer electrodes of the present invention.

Figure 3B illustrates a side view of the sensor of Figure 3A in an assembled state.

Figure 4A illustrates a side, cross sectional view of a portion of a sensor including a plurality of bi-layer electrodes of the present invention.

Figure 4B illustrates a top perspective view of the sensor portion of Figure 4A.

Figure 4C illustrates a top perspective view of another sensor including a plurality of bi-layer electrodes of the present invention.

Figure 5 illustrates an embodiment of a tri-layer composite electrode of the present invention.

Figure 6 illustrates a graph of the output of several two-electrode H_2S sensors of the present invention.

Figure 7 illustrates a graph of the output of several two-electrode CO sensors of the present invention.

Figure 8 illustrates a graph of the output of several two-electrode NO_2 sensors of the present invention.

Figure 9 illustrates a graph of the output of several two-electrode SO_2 sensors of the present invention.

Figure 10 illustrates a graph of the output of several two-electrode NO sensors of the present invention.

Figure 11 illustrates a graph of a comparison of the output of a two-electrode NO sensor of the present invention and two three-electrode NO sensors of the present invention.

Detailed Description of the Invention

It is believed that the electrodes of the present invention improve response time of sensors incorporating the electrodes by making regions where catalyst and electrolyte form an interface favorable to reaction more available to the analyte gas. The electrodes of the present invention can be formed as multi-layer pellets. The pellet has at least one layer including a mixture of catalyst powder and a powdered quasi-solid state electrolyte. Mixing the catalyst and the electrolyte together results in intimate contact between the catalyst and the electrolyte. The relatively thick, hydrophobic catalyst layer characteristic of currently available electrodes is eliminated. The analyte gas has direct access to catalyst/electrolyte interfaces immediately, for example, after passing through a membrane, resulting in faster response times.

Figures 2A and 2B illustrate a bi-layer pellet electrode 210 of the present invention. As illustrated in Figure 2B, bi-layer pellet electrode 210 is of generally circular shape. Bi-layer pellet electrode 210 includes an electrolyte layer 220 and a catalyst/electrolyte layer 230. Electrolyte layer 220 is made from a composite powder containing a mixture an electrolyte material, a powder having a relatively high surface area and a relatively high pore volume and a binder material. In general, the powder is a porous powder such as a porous ceramic or a porous polymer.

Binder materials used in the present invention can be polymeric materials that are suitable to form a three-dimensional matrix around and thus bind together the electrolyte material. The binder material is preferably generally inert to the electrolyte material, to the catalyst and to substances to which the sensor will be exposed during use. An example of a suitable binder material is a polymer such as TEFLON (polyfluorotetraethylene or PTFE) and like materials that are generally inert and have glass transitions temperature above which the polymer softens and can flow (for example, during pressing) to form a three-dimensional matrix or support, binding the electrolyte material together. A binder material for use in the present invention can also be a powder having a particle size different from the particle size of the electrolyte material that is suitable to form an interlocking matrix with the electrolyte material.

In several electrodes studied in the present invention, the electrolyte was H_2SO_4, the high-surface-area, high-pore-volume powder was SiO_2 and the binder was PTFE (TEFLON). An example of a suitable SiO_2 powder is SIPERNAT® 22 (a synthetic amorphous precipitated silica powder) available from Degussa AG of Frankfurt, Germany. That silica powder was indicated by the manufacturer to have a BET surface area of approximately 190 m^2/g. Catalyst/electrolyte layer 230 was made from the same mixture of materials used in the electrolyte layer 220 with the addition of an appropriate catalyst powder.

In several studies of the present invention, electrolyte layer 220 was first made by compressing a volumetrically measured sample of the above-described mixture in a die cavity. A second volumetrically measured sample of catalyst/electrolyte layer mixture is then pressed on top of electrolyte layer 220 to produce one, bi-layer pellet electrode 210. Of course, the order of formation of the layers can be reversed.

To produce a two-electrode sensor, two bi-layer pellets 210 can, for example, be placed back to back in the sensor assembly with their electrolyte layers 220 touching. This assembly provides ionic contact for sensor operation. The bi-layer pellet that is placed closest to the inlet hole in the sensor can function as the sensing (working) electrode. The bi-layer pellet that is placed farthest away from the inlet hole can function as the counter/reference electrode. Selectivity for a specific target gas is obtained by choosing the appropriate catalyst combination for the sensing pellet electrode and the counter/reference pellet electrode. Three-electrode sensors can be made by adding an additional bi-layer pellet electrode to serve exclusively as a reference electrode, as opposed to a counter/reference electrode. The reference pellet electrode can, for example, be placed between the sensing and counter pellet electrodes.

Figures 3A and 3B illustrate an assembly of one embodiment of a two-electrode sensor 300 of the present invention. Sensor 300 is housed within a metallic cell or case as described, for example, in U.S. Patent No. 5,906,726 and U.S. Patent No. 5,667,653, the contents of which are incorporated herein by reference. In that regard, sensor 300 includes a first case member 310 in which an inlet 312 is formed to allow analyte gas to enter sensor 300 from the surrounding environment. Sensor 300 also includes a second case member 320 which can be crimped under first case member 310 to form the outer housing of sensor 300 as illustrated in Figure 3B.

A gasket 330 can be placed within sensor 300 to assist in forming an adequate connection/seal between case members 310 and 320, to provide electrical insulation between

case members 310 and 320, and to assist in positioning the other components of sensor 300 within the sensor housing. One or more filters 340 and 350 can be placed adjacent first case member 310 within sensor 300. Filter 340 can, for example be a spun mat glass filter suitable, for example, to diffuse gas entering sensor 300 and/or to remove interferants. Filter 350 can, for example, be a porous GORE-TEX® membrane available from W.L. Gore & Associates and suitable to filter solids and liquids, but porous to gases. In the embodiment of Figures 3A and 3B, a screen contact member 360 is placed in electrical contact with the electrolyte/catalyst layer of bi-layer pellet working electrode 410a and with first case member 310. A second screen contact member 370 is placed in electrical contact with the electrolyte/catalyst layer of bi-layer pellet counter electrode 410b and with second case member 320. A buffer or spacer 380 is placed between pellet counter electrode 410b and second case member 320.

As illustrated in Figures 4A and 4B, several pellet electrodes 510a, 510b, 510c ••• can be incorporated into a sensor 500 for the detection of multiple analyte gases. Each of bi-layer pellet electrodes 510a, 510b, 510c ••• can, for example, be fabricated as described above. However, each of electrolyte/catalyst layers 520a, 520b, 520c ••• can include a different catalyst (for example, platinum (Pt), iridium (Ir), gold (Au) etc.) as desired to catalyze a reaction of and thereby sense the presence of different analyte gases. Electrical contact members 540a, 540b, 540c ••• are placed in contact with electrolyte/catalyst layers 520a, 520b, 520c ••• to carry a signal to, for example, a measurement circuit as known in the art. In the embodiment of Figures 4A and 4B, electrodes 510a, 510b, 510c ••• are, for example, formed in the shape of a cylindrical rings with passages 550a, 550b, 550c ••• formed generally centrally therein. Passages 550a, 550b, 550c ••• form a composite passage generally through the center of sensor 500 when electrodes 510a, 510b, 510c ••• are stacked in general alignment through which analyte gasses can pass to contact catalyst/electrolyte layers 520a, 520b, 520c •••.

Figure 4C illustrates another embodiment of a sensor 600 in which several pellet electrodes 610a, 610b, 610c ••• can be incorporated into a sensor 600 for the detection of multiple analyte gases. Each of bi-layer pellet electrodes 610a, 610b, 610c ••• can, for example, be fabricated as described above. Each of electrolyte/catalyst layers 620a, 620b, 620c ••• can include a different catalyst as described above. In the embodiment of Figure 4C, sensor 600 can be formed by first forming a generally circular or generally oval composite sensor, which is subsequently sliced/bisected to form two generally semicircular sensors 600 in which electrodes 610a, 610b, 610c ••• are stacked in general alignment and wherein analyte gasses can contact catalyst/electrolyte layers 620a, 620b, 620c ••• at the open face of electrode 600 created during bisection.

Moreover, the electrodes of the present invention can also be formed as multi-layer pellets other than bi-layer electrode. For example, Figure 5 illustrates a tri-layer pellet electrode 710 including a first electrolyte/catalyst layer 720a, an intermediate electrolyte layer 730 and a second electrolyte/catalyst layer 720b. The catalysts of first electrolyte/catalyst layer 720a and second electrolyte/catalyst layer 720b can be different. Electrolyte/catalyst layers 720a and 720b, electrolyte layer 730 and any other electrolyte or electrolyte/catalyst layers can be formed generally as described above.

EXPERIMENTAL EXAMPLES

A number of electrodes as illustrated in Figures 3A and 3B were tested for various analyte gases using various electrode catalysts in a two-electrode sensor configuration as summarized in Table 1. The catalysts used in the studies of the present invention are further characterized in Table 2.

Table 1

Analyte Gas	Active Catalyst Working Electrode	Active Catalyst Counter Electrode	Bias Potential
H_2S	Iridium	Iridium	0 mV
CO	Platinum	Platinum	0 mV
NO_2	Activated Carbon	Activated Carbon	0 mV
SO_2	Gold	Platinum	0 mV
NO	Carbon	Platinum	+300 mV
NH_3	Iridium	Iridium	+235 mV

Table 2

Catalyst	Manufacturer	Surface Area, m^2/g	Sensor
Iridium	Englehard	15.5-21.5	H_2S
Platinum	Englehard	>25	CO, SO_2, NO
Activated Carbon	Johnson Matthey	Not Available	NO_2 (75%)
Carbon Black (Regal 330R)	Cabot	94	NO_2 (25%)
Gold	Technic Inc.	0.4-1.0	SO_2
Graphite (EG-31)	Sigri Great Lakes Carbon Co.	Not Available	NO

Each of the sensors studied included a working and counter electrode as described above. In forming the bi-layer electrodes, the electrolyte was H_2SO_4, the high-surface-area, high-pore-volume powder was SiO_2 and the binder was PTFE (TEFLON). As set forth in Table 1, in the case of H_2S (hydrogen sulfide), CO (carbon monoxide) and NO_2 (nitrogen dioxide) analyte gases, the catalyst on the working and counter electrodes was the same. In the case of SO_2 (sulfur dioxide) and NO (nitric oxide) analyte gases , the catalyst on the working and counter electrodes was different. The NO sensor was operated at a positive bias potential (approximately +300mV), whereas the other sensors were operated at a zero bias potential.

Studies were also performed upon NO sensors having a three-electrode configuration (working electrode, counter electrode and reference electrode). As with the two-electrode NO sensors, the three-electrode NO sensors were operated at a positive bias potential of approximately +300mV.

In general, the present studies were performed under computer control in which twenty (20) sensors could be tested simultaneously. A baseline current reading for each sensor was established as the sensor output after an exposure to air (0 ppm analyte gas). In testing for analyte gas concentration, air was first applied to the sensors for a period of time followed by application of air having a known concentration of analyte gas for a period of time. A purge with air followed exposure to analyte gas in some experiments.

In general, the response time of the sensors of the present invention are substantially improved as compared to sensors in which currently available electrodes are used. Response time is a measure of the speed of response of a sensor and can be dependent on the manner in which the test is performed (for example, the length of time the experiment lasts and/or the time at which the sensor reaches 100% of its final output). In the present studies, response times were based on exposure to test gas for a known amount of time. Response time was generally tabulated as the 90% response time (t_{90}) unless otherwise indicated. The t_{90} response time is the time, in seconds, required for the sensor to reach 90% of a generally stable response or output. The sensitivity (in units of μA/ppm analyte) was established as the sensor output after exposure to analyte gas for a sufficient period of time to reach a stable output.

Hydrogen Sulfide Sensors

As described in Table 1, H_2S sensors of the present invention included a bi-layer working electrode having an iridium catalyst and a bi-layer counter electrode having an iridium catalyst. The electrodes and the sensors were formed generally as described above in

connection with Figures 2A through 3B and as further described below. Figure 6 illustrates the measured output for several such sensors over time during operation with a potentiostat at 0 mV bias potential. The experiments of Figure 6 included 2 minutes of baseline in which the sensor was exposed to air without analyte gas, followed by 5 minutes of analyte gas exposure (50 ppm H_2S), followed by 2 minutes of air purge.

Table 2 summarizes results for 200 sensors using bi-layer electrodes of the present invention and 200 sensors using currently available electrodes in which catalyst is deposited upon a porous membrane. Errors reported in Table 3 represent one standard deviation.

Table 3.

Electrode Type	**Sensitivity (Microamps/ppm)**	**Response Time, T_{90} (Seconds)**
Catalyst deposited on membrane	0.194 ± 0.023	149 ± 36
Bi-layer composite electrode	0.189 ± 0.034	15 ± 4

Carbon Monoxide Sensors

As described in Table 1, CO sensors of the present invention included a bi-layer working electrode having an platinum catalyst and a bi-layer counter electrode having an platinum catalyst. The electrodes and the sensors were formed generally as described above in connection with Figures 2A through 3B. Figure 7 illustrates the measured output for several such sensors over time during galvanic operation using a 500 ohm resistor. The experiments of Figure 7 included 1 minute of baseline in which the sensor was exposed to air without analyte gas (100 ppm CO), followed by 15 minutes of analyte gas exposure.

Nitrogen Dioxide Sensors

As described in Table 1, NO_2 sensors of the present invention included a bi-layer working electrode having an activated carbon catalyst and a bi-layer counter electrode having an activated carbon catalyst. The activated carbon in each electrode was 75% activated carbon and 25% carbon black. The electrodes and the sensors were formed generally as described above in connection with Figures 2A through 3B. Figure 8 illustrates the measured output for several such sensors over time during operation with a potentiostat at 0 mV bias potential. The experiments of Figure 8 included 2 minutes of baseline in which the sensor was exposed to air without analyte gas, followed by 10 minutes of analyte gas exposure (44 ppm NO_2), followed by 2 minutes of air purge.

Sulfur Dioxide Sensors

As described in Table 1, SO_2 sensors of the present invention included a bi-layer working electrode having a gold catalyst and a bi-layer counter electrode having a platinum catalyst. The electrodes and the sensors were formed generally as described above in connection with Figures 2A through 3B. Figure 9 illustrates the measured output for several such sensors over time during operation with a potentiostat at 0 mV bias potential. The experiments of Figure 9 included 2 minutes of baseline in which the sensor was exposed to air without analyte gas, followed by 10 minutes of analyte gas exposure (12 ppm SO_2), followed by 2 minutes of air purge.

Nitric Oxide Sensors (two electrode configuration)

As described in Table 1, NO sensors of the present invention included bi-layer working electrode having a carbon catalyst and a bi-layer counter electrode having a platinum catalyst. The electrodes and the sensors were formed generally as described above in connection with Figures 2A through 3B. Figure 10 illustrates the measured output for several

such sensors over time during operation with a potentiostat at +300 mV bias potential. The experiments of Figure 9 included 2 minutes of baseline in which the sensor was exposed to air without analyte gas, followed by 5 minutes of analyte gas exposure (49 ppm NO), followed by 2 minutes of air purge. Data including response times for several NO sensors are also set forth in Table 4.

Table 4.

Sensor	Base Current (uAmps)	Output Response (uA/PPM)	Response Time (Secs)
1	3.326	0.870	45
2	2.338	0.763	14
3	3.920	0.836	45
4	2.360	0.781	17

Often, electrochemical sensors are subjected to a "cook-down" or "equilibration" period before use thereof to provide an adequately stable and low baseline current. During the cook-down or equilibration period, the electrochemical sensor is stored at ambient conditions and maintained at operating potential for a defined period of time. A cook-down period of approximately 4 hours was used in the studies of Figure 9 and Table 4.

Nitric Oxide Sensors (three electrode configuration)

Three-electrode NO sensors of the present invention included a bi-layer working electrode having a carbon catalyst, a bi-layer counter electrode having a platinum catalyst and a bi-layer reference electrode having a platinum catalyst. The electrodes and the sensors were formed generally as described above in connection with Figures 2A through 3B. However, a reference electrode was included in sensor 2 and 3 of Figure 11 and Table 5. The three-electrode sensor was prepared generally in the manner described in U.S. Patent No. 5,906,726 and U.S. Patent No. 5,667,653. Sensor 1 included only a working electrode and a counter electrode as described above. Figure 11 illustrates the measured output for

several such sensors over time during operation with a potentiostat at +300 mV bias potential. The experiments of Figure 11 included 2 minutes of baseline in which the sensor was exposed to air without analyte gas, followed by 5 minutes of analyte gas exposure (49 ppm NO), followed by 2 minutes of air purge. An overnight cook-down period was use in the studies. Data including response times for the two-electrode NO sensor and the two three-electrode NO sensors are set forth in Table 5.

Table 5.

Sensor	Base Current (uAmps)	Output Response (uA/PPM)	Response Time (Secs)
1	1.528	0.709	113
2	3.013	0.754	172
3	1.450	0.918	45

Ammonia Sensors (neutral or basic electrolyte)

Ammonia sensors were fabricated similarly to other bi-layer sensors described above. The electrolyte used was 5 M LiCl solution, absorbed onto an SiO_2 support in a 0.75:1 weight ratio ($LiCl:SiO_2$). The catalyst was Ir powder. The electrodes and the sensors were formed generally as described above in connection with Figures 2A through 3B. The ammonia sensors were operated in the electrolytic mode at approximately +235 mV in sensing ammonia gas.

Preparation of Electrolyte Powder

In preparation of typical preparation, approximately 190 grams of precipitated silica (DeGussa SIPERNAT 22) was placed into a round, 1/2 gal. Nalgene mixing container under a ventilated hood. Approximately 165 grams of PTFE powder (Dupont Teflon 850A) was then added to the mixing container. The mixing container was then closed and lightly shaken to pre-mix the components.

Approximately 145 grams of 6.7N sulfuric acid was then poured into the pre-mixed powder. The cap was then closed and the container gently shaken for a few seconds to disperse the liquid. The mixing container was then tumbled for 15-20 minutes at approximately 40 rpm using a LorTone rock tumbler.

Preparation of Electrolyte/Catalyst Powder

In a typical case of an iridium catalyst as described above, each pellet of a sensor included approximately 0.06 grams of electrolyte/catalyst powder per pellet. The electrolyte/catalyst powder was approximately 50 % electrolyte powder as described above and approximately 50 % catalyst blend powder as described below.

In one example, 2.4 grams PTFE (DuPont Teflon 850A), 0.8 grams graphite, 0.8 grams precipitated silica (DeGussa SIPERNAT were added to a mixing container. After addition of these components, the container was lightly shaken for about 5 minutes. Then the electrolyte powder was added. Approximately, 8 grams of Iridium powder were added to the mixing container. The mixing container was then place in a rubber sleeve and tumbled using a LorTone rock tumbler for about 15 minutes at approximately 40 rpm.

Preparation of Pellets

In forming a bilayer pellet, the cavity of a die having a fill depth of approximately 0.117 inches and a diameter of approximately 0.5 in. was first filled with electrolyte powder as descried above flush with the top of the die. A metal rod was used to gently tamp the powder down. A first stop was then slid over the die; causing a small depression. This depression defined the fill depth for the electrolyte/catalyst powder as describe above. The resulting cavity or depression was then filled with a small amount of catalyst/electrolyte powder. Excess powder was scraped off so that the powder was flush with the top of the die. The top platen was place on the top of the cavity, and the die was slid

under a ram. The pellet was then pressed with a dwell time at the bottom of the stroke of approximately 3-5 seconds. The ram was in operative connection to a 6 inch air cylinder to which compressed air was supplied at a pressure of approximately 90 to approximately 110 psi. After retraction of the die, the pellet was removed. In general, the bilayer pellet electrodes used in the studies of the present invention had a thickness in the range of approximately .044 to approximately .047 inches. The electrolyte layer of the bilayer pellet electrodes was in the range of approximately 0.037 to approximately .040 inches thick.

Although the present invention has been described in detail in connection with the above examples, it is to be understood that such detail is solely for that purpose and that variations can be made by those skilled in the art without departing from the spirit of the invention except as it may be limited by the following claims.

WHAT IS CLAIMED IS:

1. An electrode for use in an electrochemical sensor comprising: a catalyst dispersed within an electrolyte.

2. The electrode of Claim 1 wherein the catalyst is immobilized within a matrix of the electrolyte.

3. The electrode of Claim 2 wherein the electrode comprises at least one catalyst/electrolyte layer including a mixture of a powdered catalyst, a powdered, quasi-solid electrolyte and a binder material compressed together.

4. The electrode of Claim 3 wherein the quasi-solid electrolyte comprises a liquid electrolyte immobilized by a high-surface-area, high-pore-volume solid.

5. The electrode of Claim 4 wherein the solid is SiO_2.

6. The electrode of Claim 5 wherein the liquid electrolyte is H_2SO_4

7. The electrode of Claim 3 wherein the binder material is polytetrafluoroethylene.

8. The electrode of Claim 3 wherein the electrode further comprises at least one electrolyte layer adjacent to the catalyst/electrolyte layer, the electrolyte layer including a mixture of a powdered, quasi-solid electrolyte and a binder material compressed together.

9. The electrode of Claim 8 wherein the electrolyte layer is bound to the catalyst/electrolyte layer.

10. The electrode of Claim 9 wherein the quasi-solid electrolyte of the electrolyte layer comprises a liquid electrolyte immobilized by a high-surface area, high-pore volume solid.

11. The electrode of Claim 10 wherein the solid of the electrolyte layer is SiO_2.

12. The electrode of Claim 11 wherein the liquid electrolyte of the electrolyte layer is H_2SO_4

13. The electrode of Claim 9 wherein the binder material of the electrolyte layer is polytetrafluoroethylene.

14. An electrochemical sensor for the detection of an analyte gas, comprising: a housing, the housing having disposed therein at least one working electrode and at least one counter electrode, the working electrode including a catalyst dispersed within an electrolyte.

15. The electrochemical sensor of Claim 14 wherein the catalyst is immobilized within a matrix of the electrolyte.

16. The electrode of Claim 15 wherein the working electrode comprises at least one catalyst/electrolyte layer including a mixture of powdered catalyst, powdered, quasi-solid electrolyte and binder material compressed together.

17. The sensor of Claim 16 wherein the quasi-solid electrolyte comprises a liquid electrolyte immobilized by a high-surface-area, high-pore-volume solid.

18. The sensor of Claim 17 wherein the solid is SiO_2.

19. The sensor of Claim 18 wherein the liquid electrolyte is H_2SO_4

20. The sensor of Claim 16 wherein the binder material is polytetrafluoroethylene.

21. The sensor of Claim 16 wherein the working electrode further comprises at least one electrolyte layer adjacent to the catalyst/electrolyte layer, the electrolyte layer including a mixture of a powdered, quasi-solid electrolyte and a binder material compressed together.

22. The sensor of Claim 21 wherein the electrolyte layer is bound to the catalyst/electrolyte layer.

23. The sensor of Claim 21 wherein the quasi-solid electrolyte of the electrolyte layer comprises a liquid electrolyte adsorbed into a high-surface-area, high-pore-volume solid.

24. The sensor of Claim 23 wherein the solid of the electrolyte layer is SiO_2.

25. The sensor of Claim 24 wherein the liquid electrolyte of the electrolyte layer is H_2SO_4

26. The sensor of Claim 25 wherein the binder material of the electrolyte layer is polytetrafluoroethylene.

27. The sensor of Claim 26 wherein the catalyst of the working electrode includes iridium, platinum, carbon, silver or gold.

28. The sensor of Claim 27 wherein the counter electrode includes at least one catalyst/electrolyte layer having a mixture of powdered catalyst, powdered, quasi-solid electrolyte and binder material compressed together.

29. The sensor of Claim 28 wherein the catalyst of the counter electrode includes iridium, platinum, carbon, silver or gold.

30. The sensor of Claim 29 wherein the catalyst of the working electrode is iridium and the catalyst of the counter electrode is iridium, the sensor being operable to sense hydrogen sulfide.

31. The sensor of Claim 28 further including a reference electrode having at least one catalyst/electrolyte layer including a mixture of a powdered catalyst, a powdered, quasi-solid electrolyte and a binder material compressed together.

32. A method of fabricating an electrode for use in an electrochemical sensor comprising the step:

dispersing a catalyst within an electrolyte.

33. The method of Claim 32 wherein the catalyst is immobilized within a matrix of the electrolyte.

34. The method of Claim 33 wherein the step of dispersing a catalyst within an electrolyte includes the step of forming a catalyst/electrolyte layer by mixing a powdered catalyst, a powdered, quasi-solid electrolyte and a binder material and compressing the mixture.

35. The method of Claim 34 further including the steps:

forming an electrolyte layer by mixing a powdered, quasi-solid electrolyte and a binder material; and

compressing the mixture together.

36. The method of Claim 35 wherein the step of compressing the mixture of a powdered, quasi-solid electrolyte and a binder material of the electrolyte layer is done over the compressed mixture of powdered catalyst, powdered, quasi-solid electrolyte and binder material of the catalyst/electrolyte layer to form an electrolyte layer bound to the catalyst/electrolyte layer.

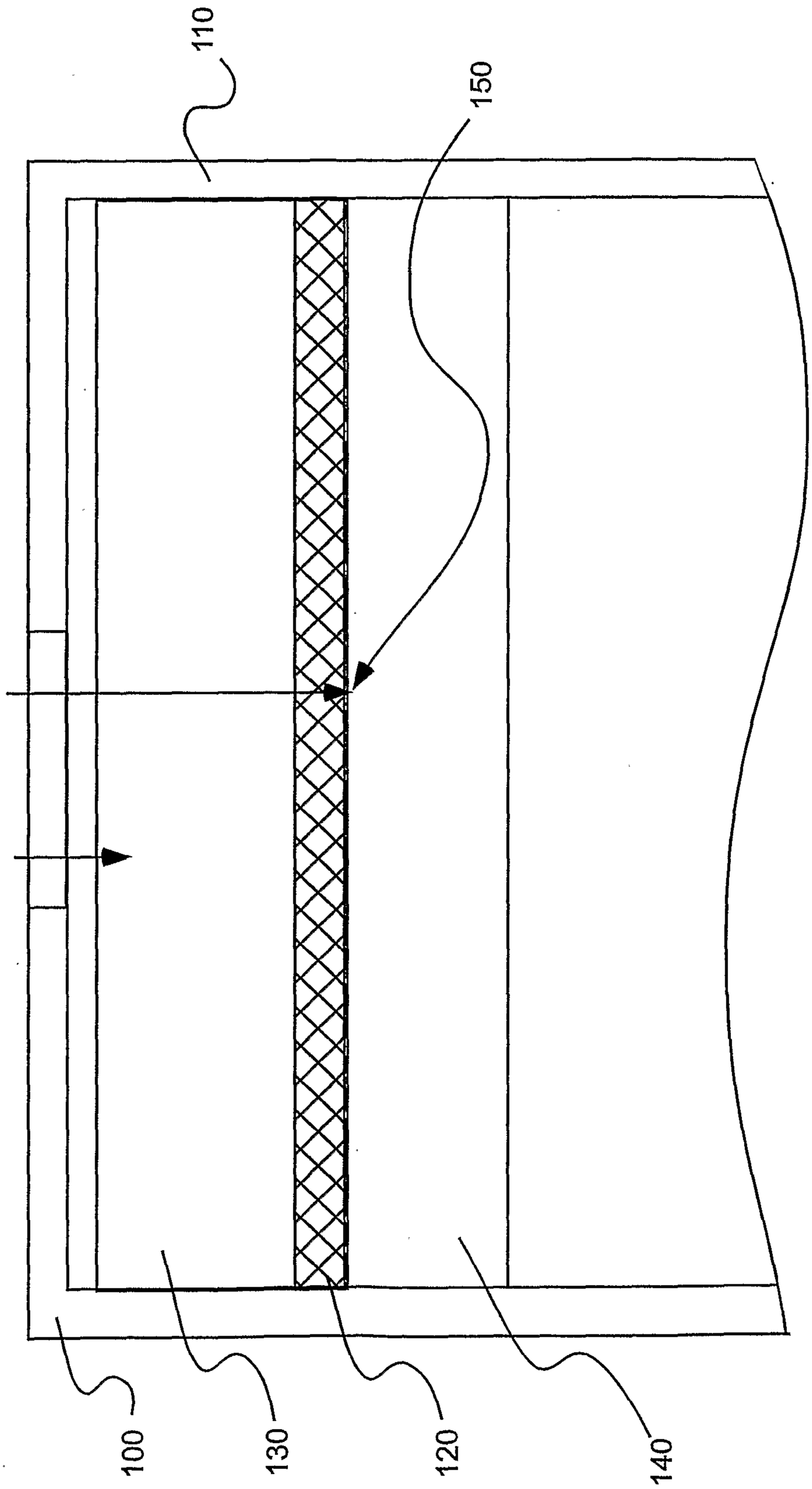


Figure 1

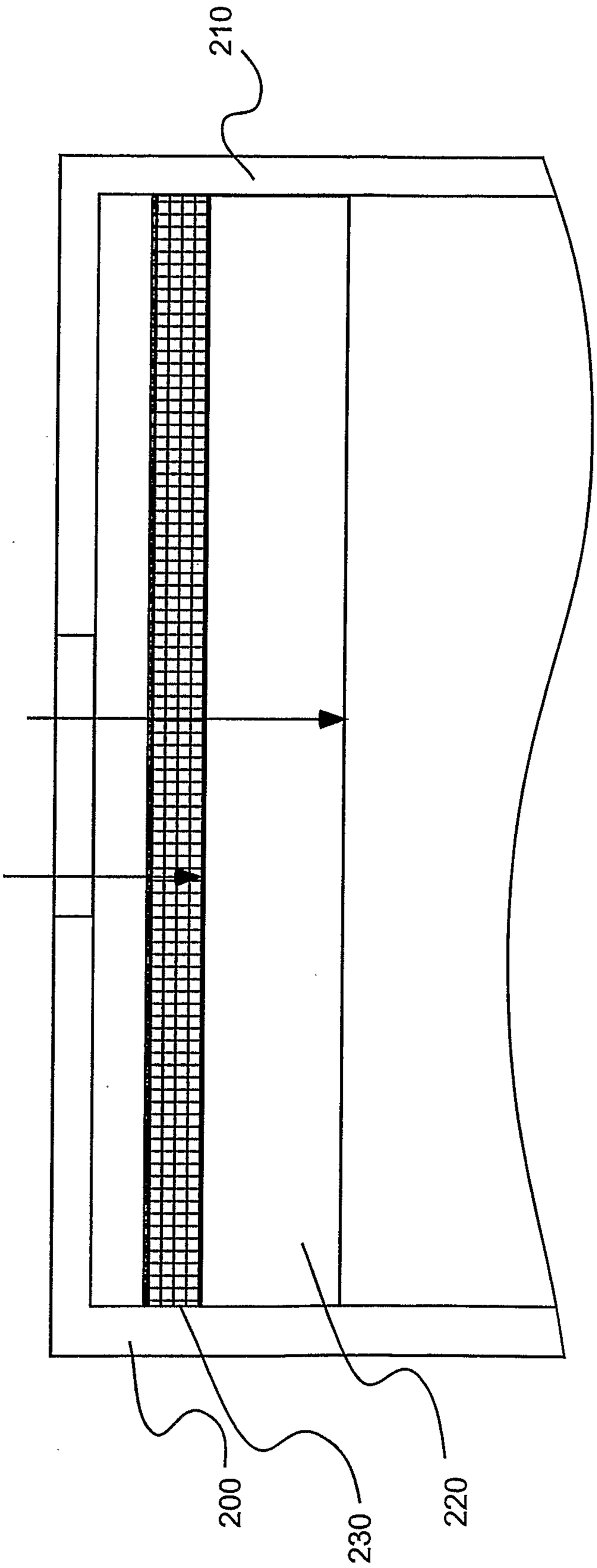


Figure 2A

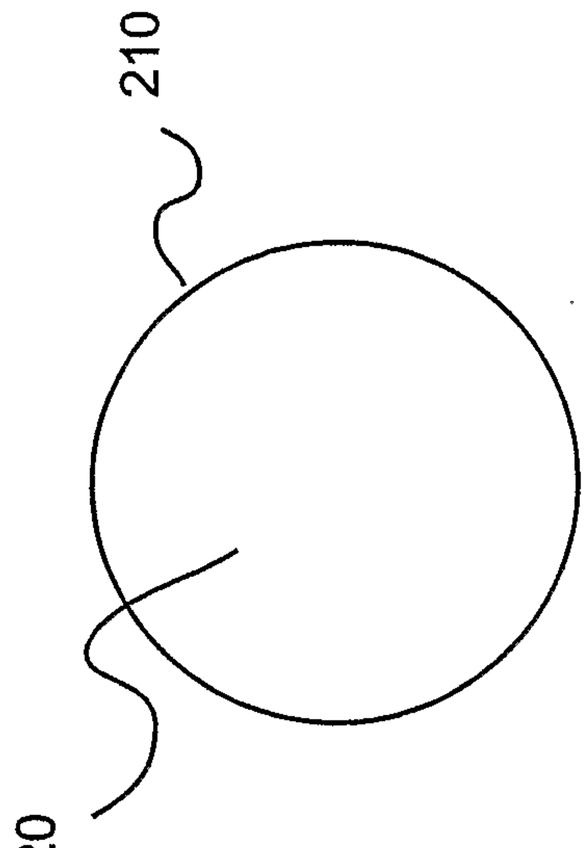


Figure 2B

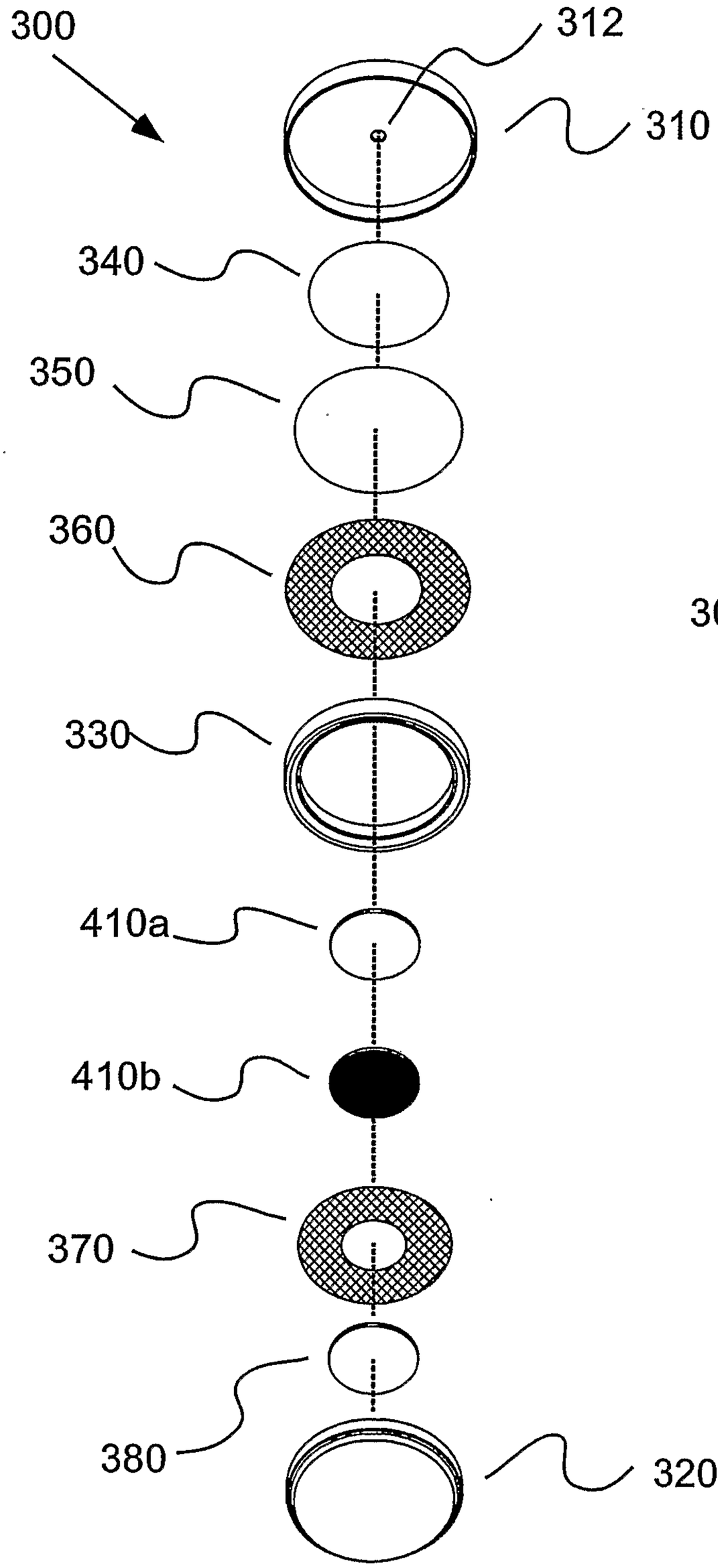


Figure 3A

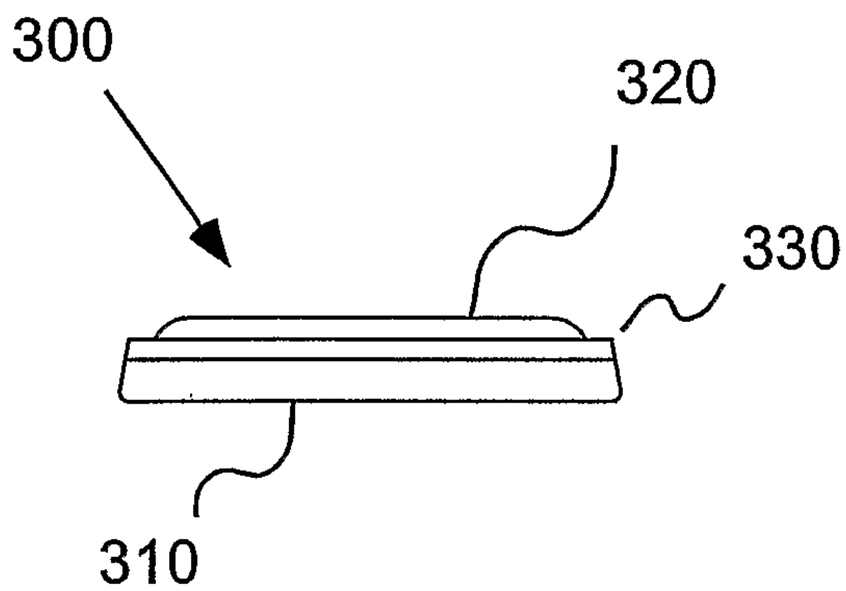


Figure 3B

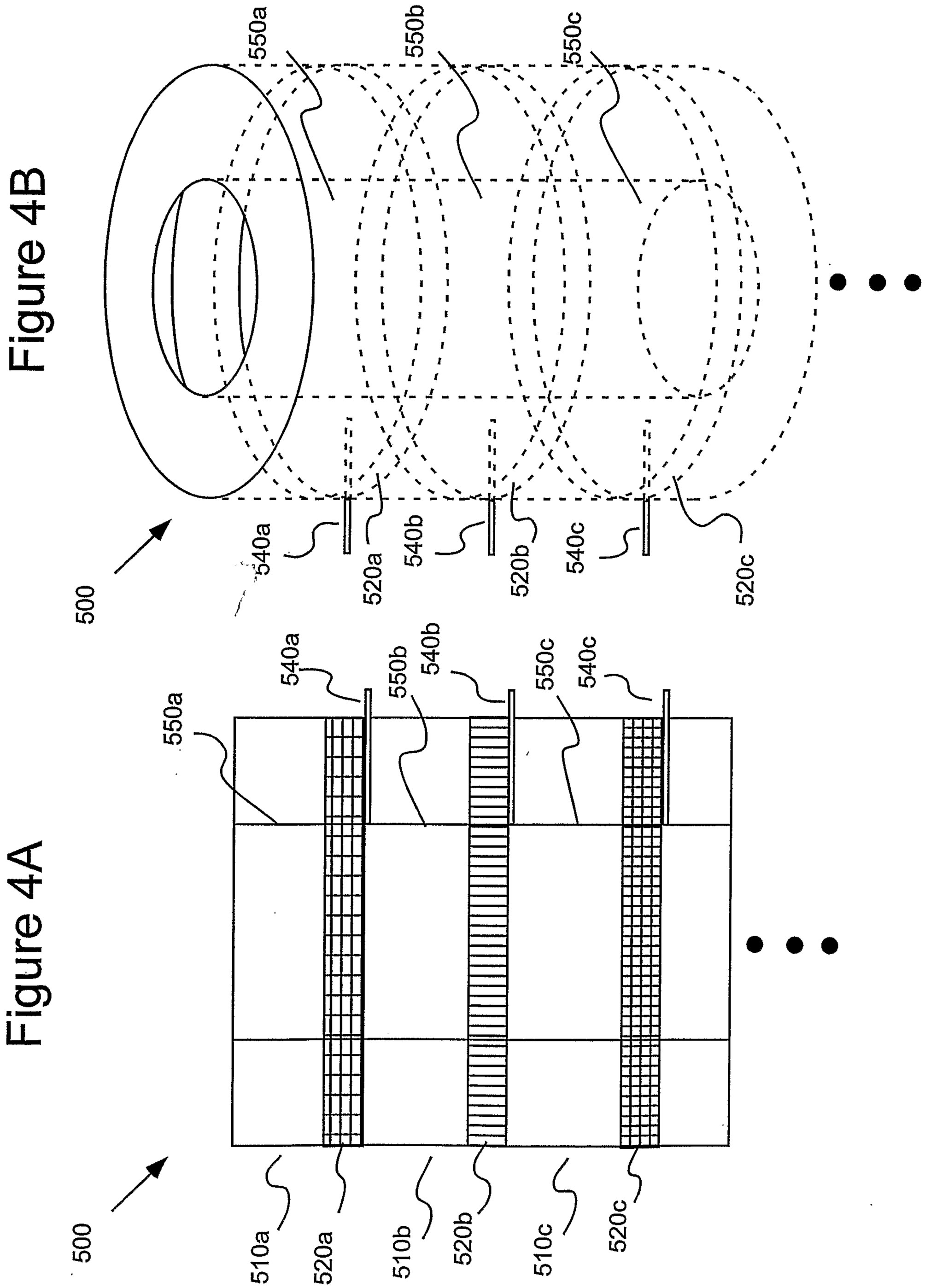


Figure 4A

Figure 4B

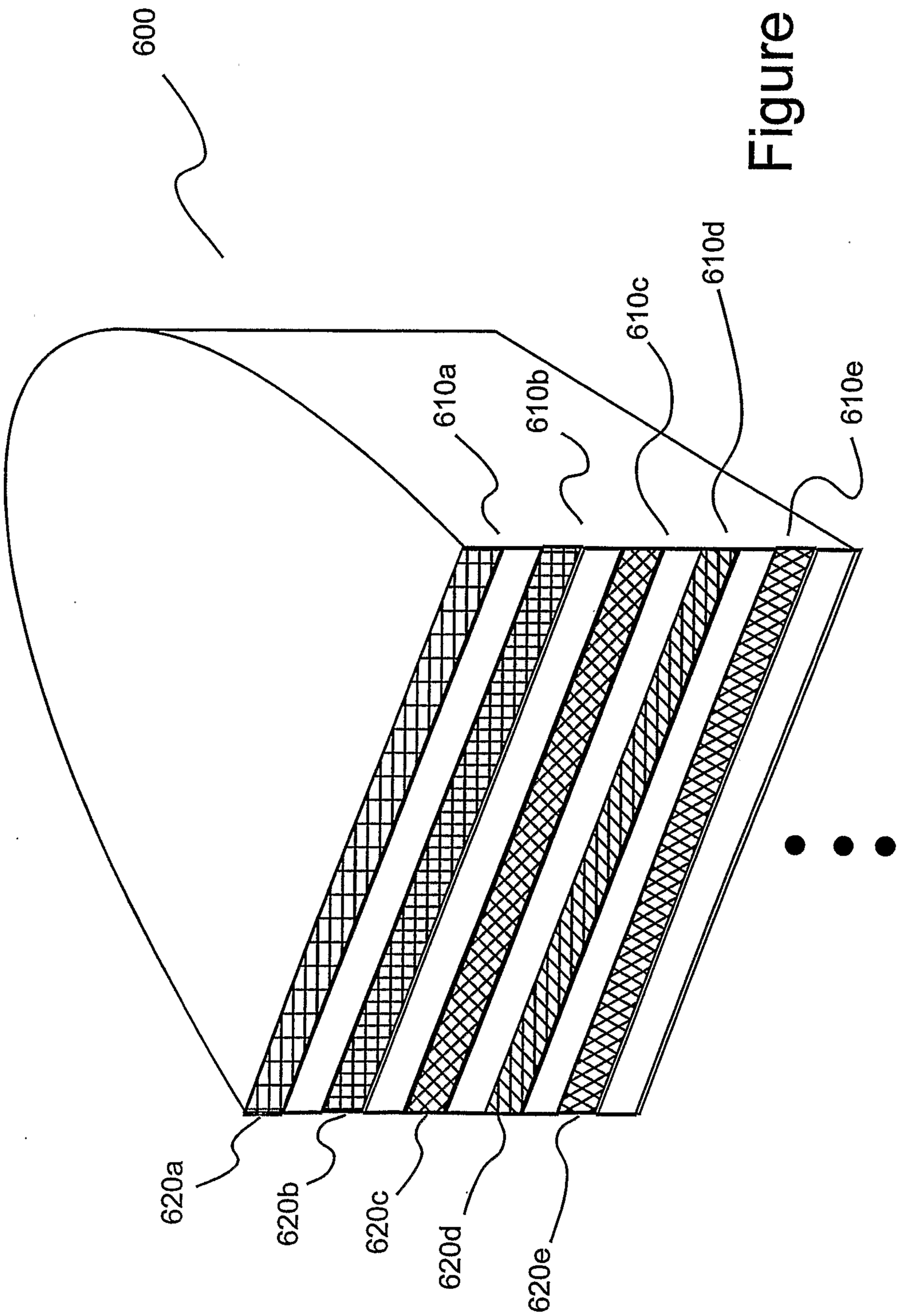


Figure 4C

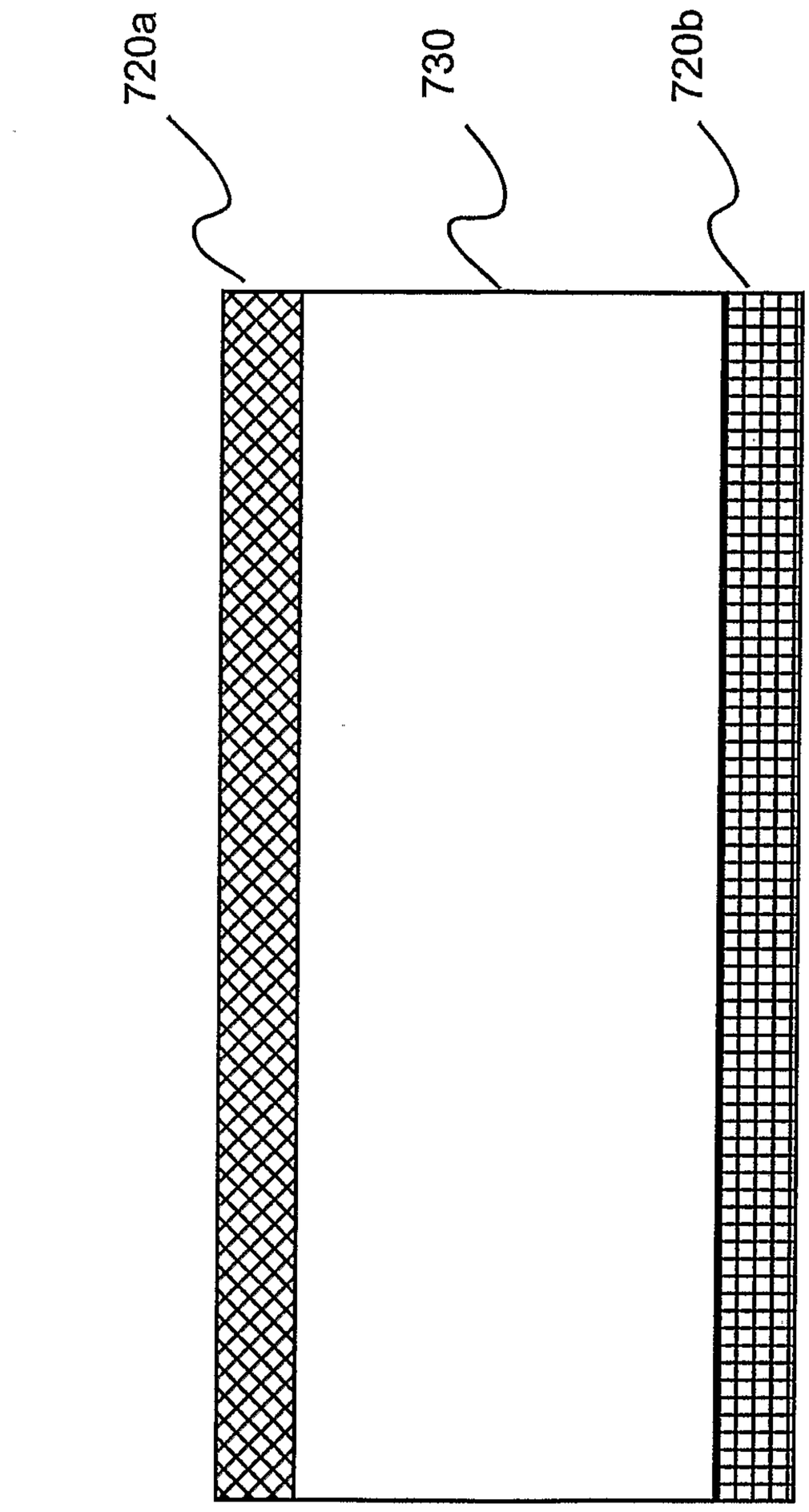


Figure 5

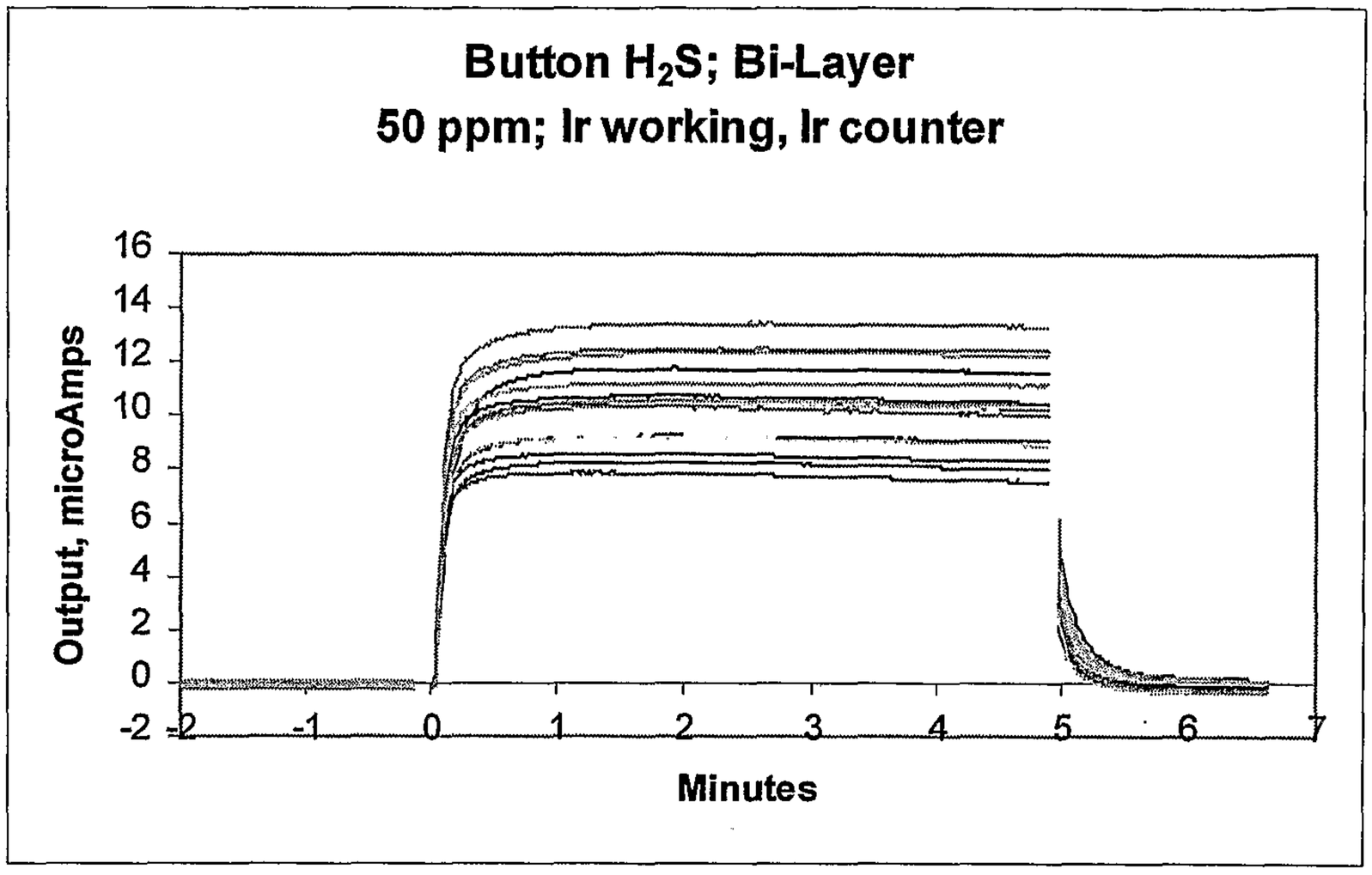


Figure 6

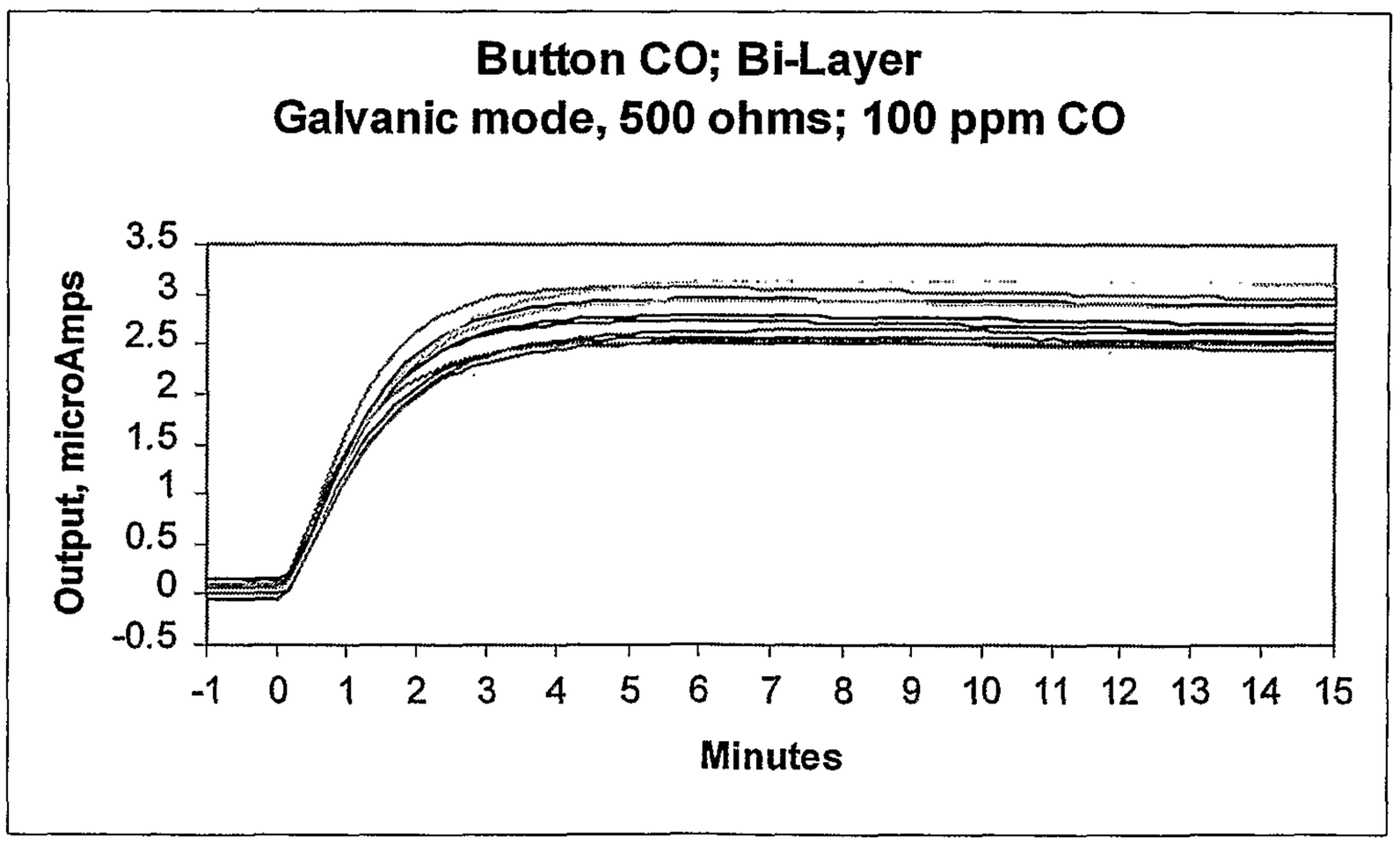


Figure 7

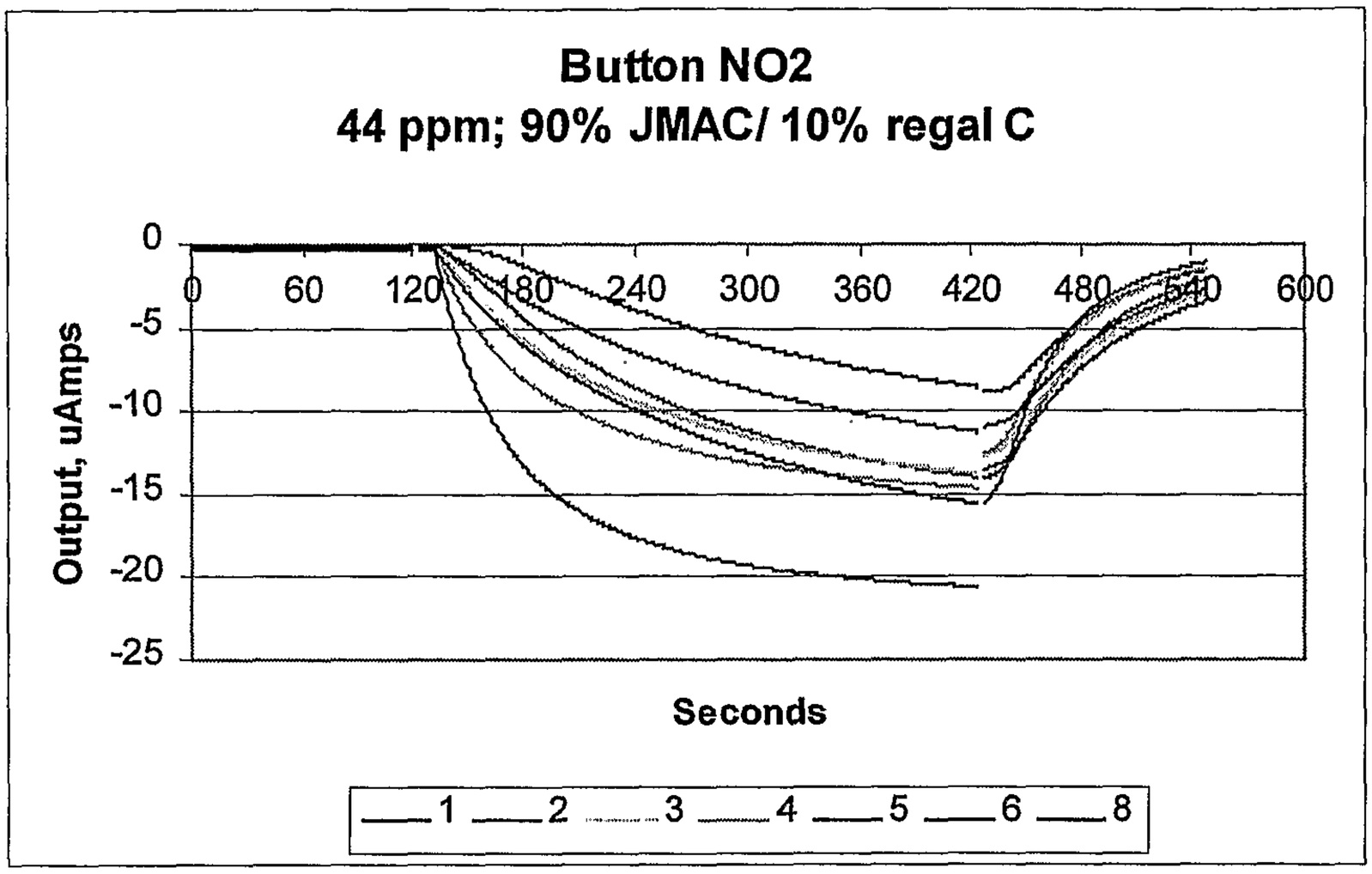


Figure 8

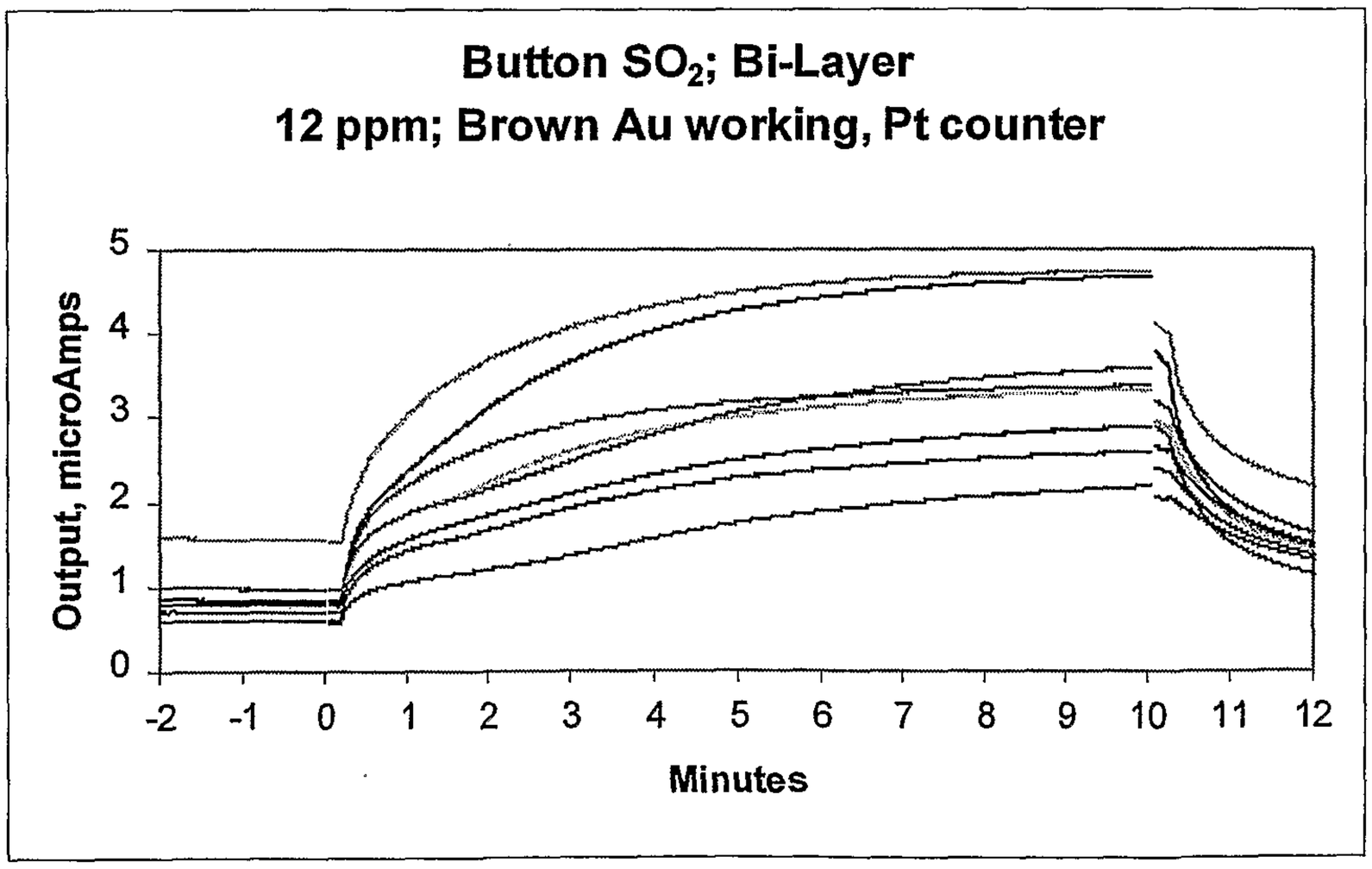


Figure 9

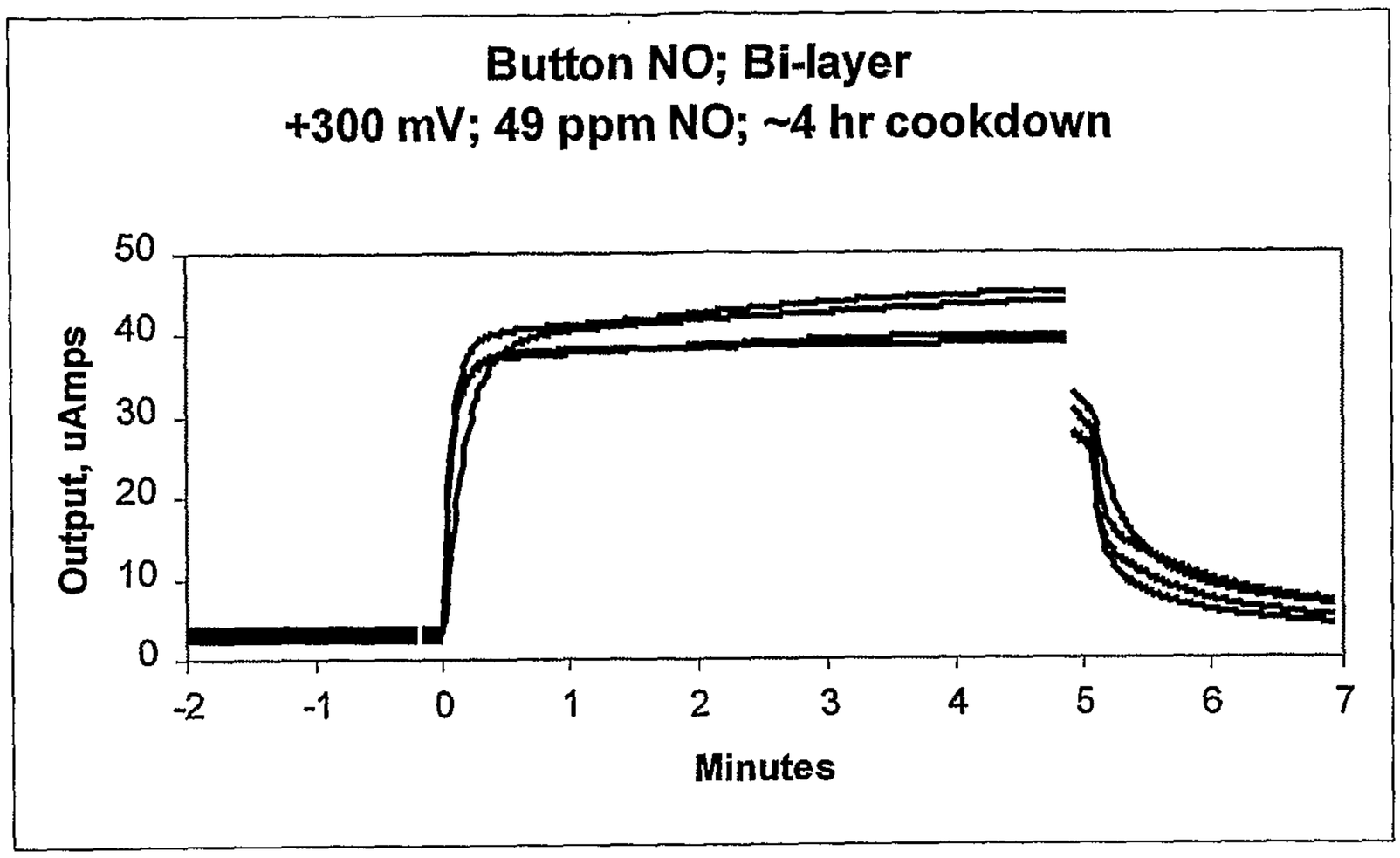


Figure 10

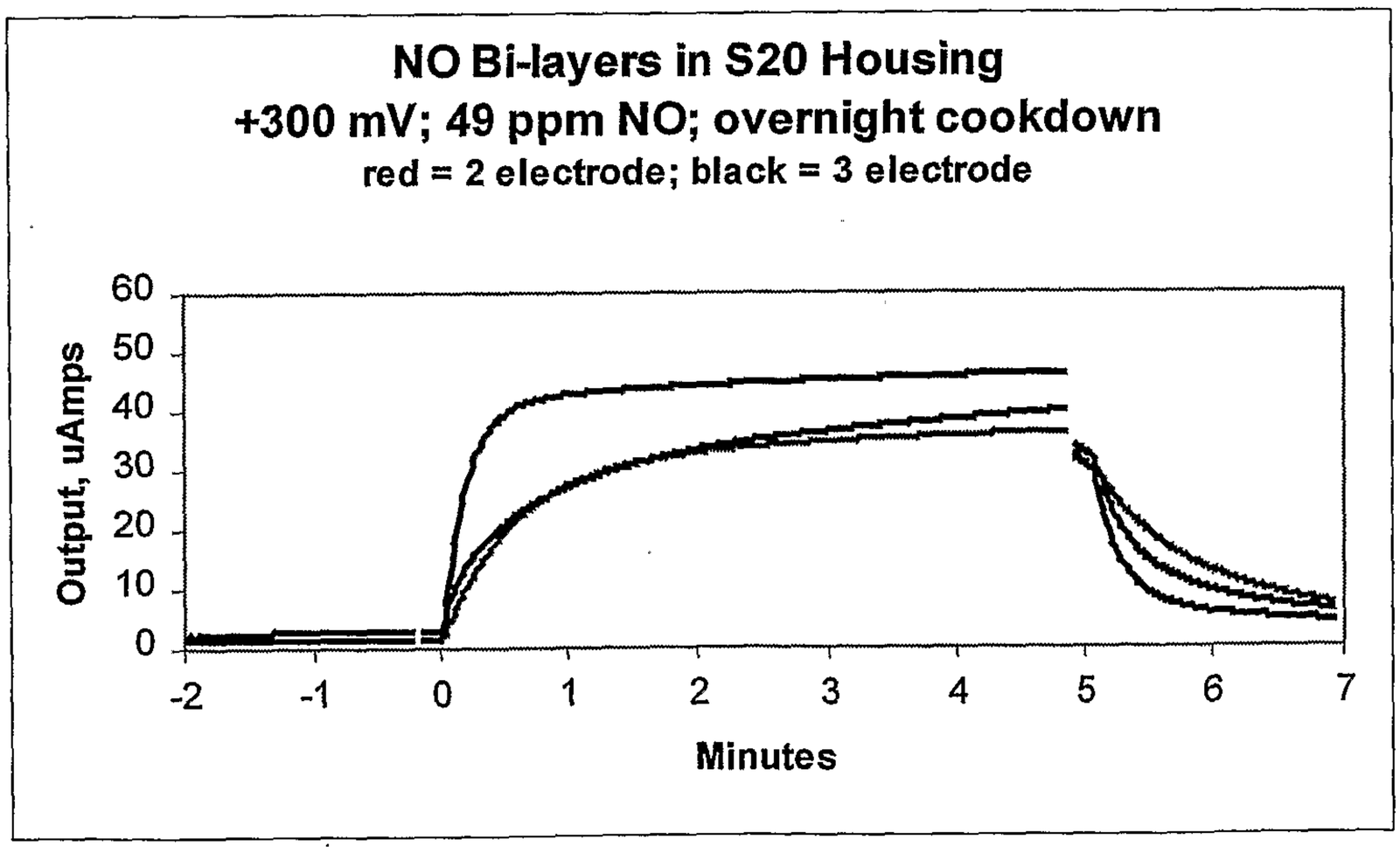
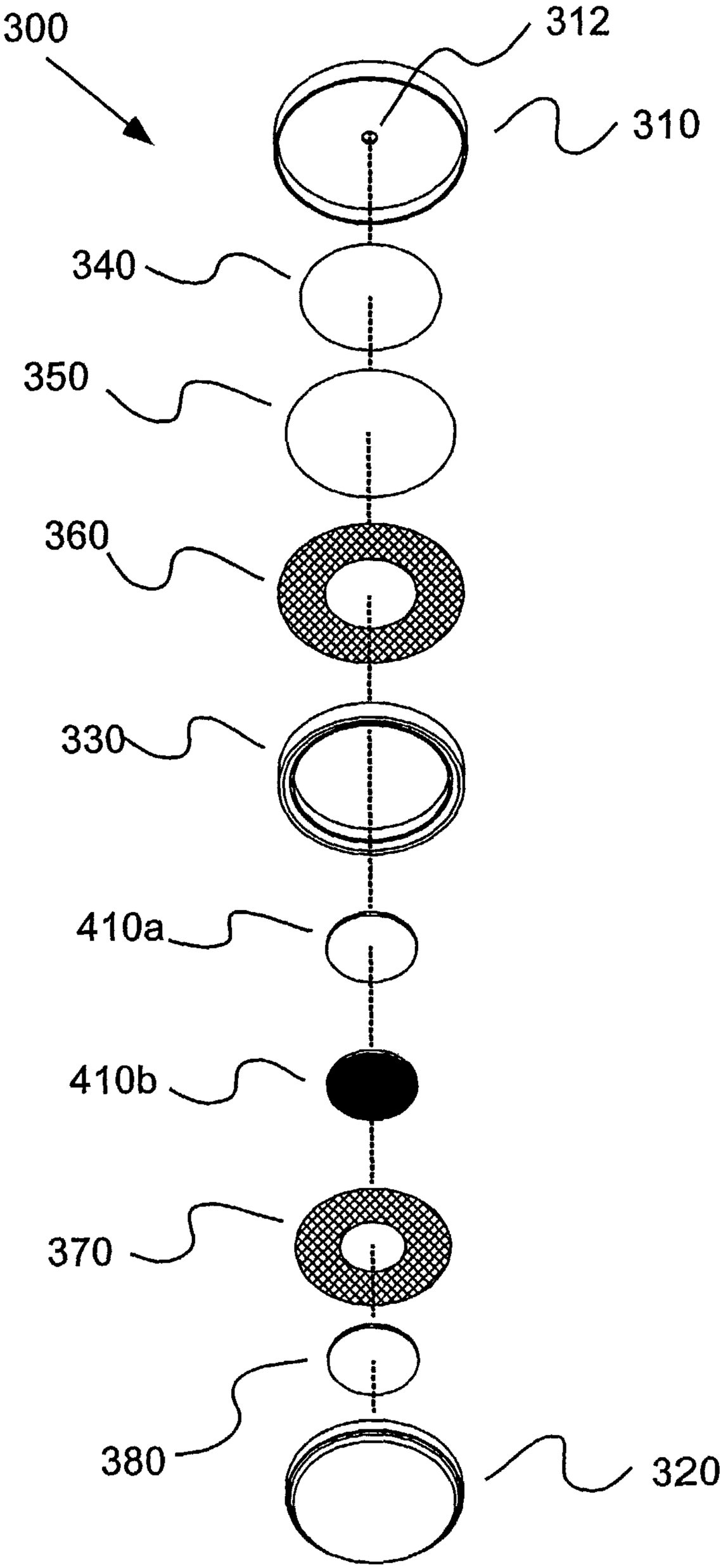


Figure 11


300
312
310
340
350
360
330
410a
410b
370
380
320