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Czuha, Jr.

[11] **3,926,745**

[45] **Dec. 16, 1975**

[54] **DEPOSITION OF P_2O_5 IN AN ELECTROLYTIC MOISTURE CELL**

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[21] Appl. No.: **459,324**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 281,859, Aug. 18, 1972, abandoned.

[52] **U.S. Cl.** ..... **204/1 T**; 204/195 W; 136/86 E

[51] **Int. Cl.**[2] **H01M 4/86**

[58] **Field of Search** ..... 204/1 T, 20, 56 R, 57, 204/195 W; 136/86 E

[56] **References Cited**

UNITED STATES PATENTS

3,001,918	9/1961	Czuha	204/1 T
3,188,283	6/1965	Cole	204/1 T
3,696,007	10/1972	Bennett et al.	204/1 T

Primary Examiner—John H. Mack
Assistant Examiner—H. A. Feeley

[57] **ABSTRACT**

Deposition of P_2O_5 on an electrically nonconductive substrate disposed between two electrodes, particularly in the formation of an electrolytic cell, is accomplished by passing gaseous phosphorus over a substrate, in the presence of water, while maintaining a potential between the electrodes sufficient to electrolyze the water and form P_2O_5 on the surface of the substrate in the region between the electrodes.

16 Claims, 6 Drawing Figures

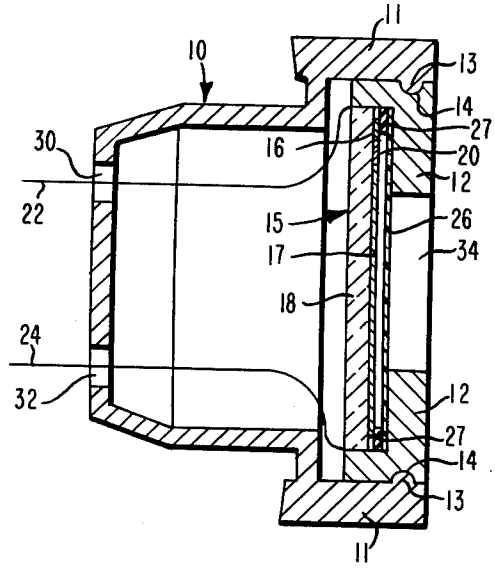


FIG. 1

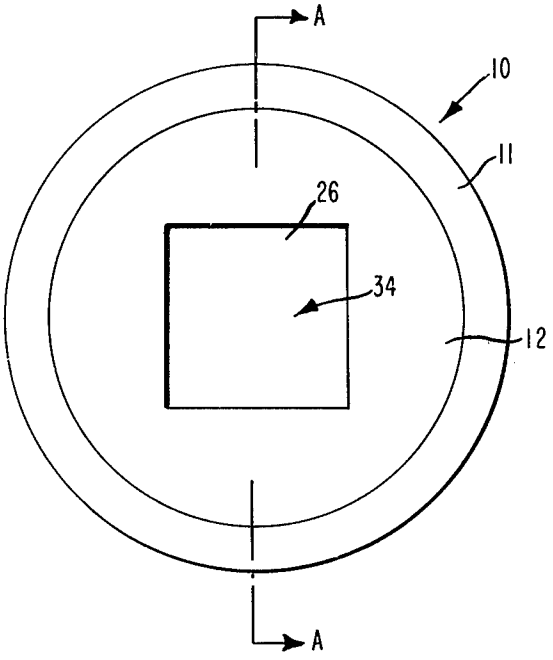


FIG. 1A

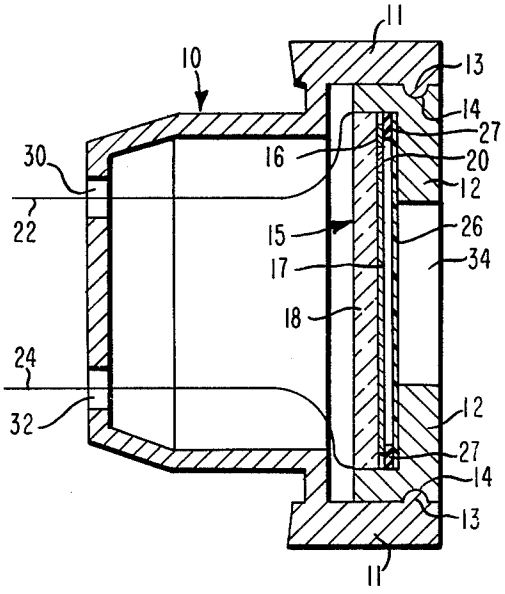


FIG. 2

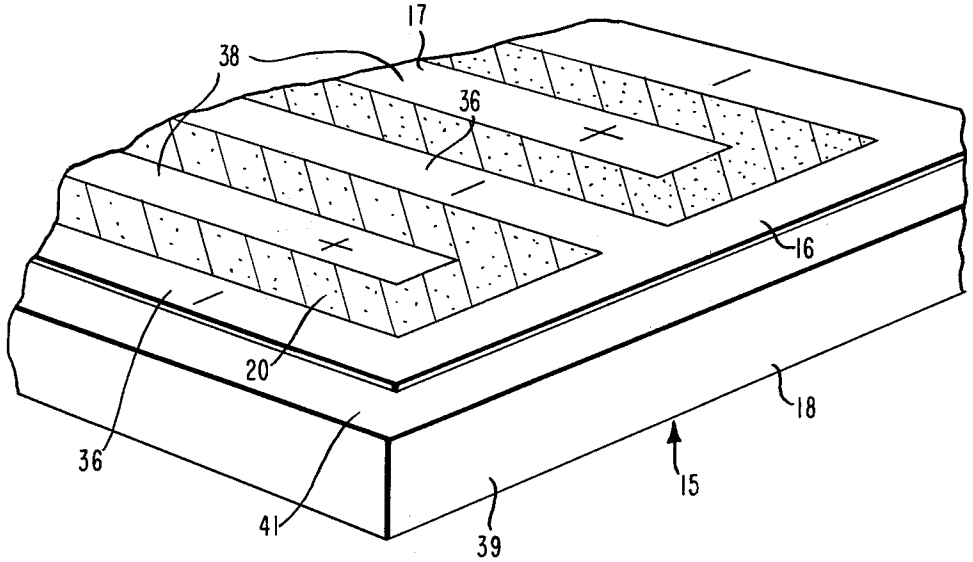


FIG. 3

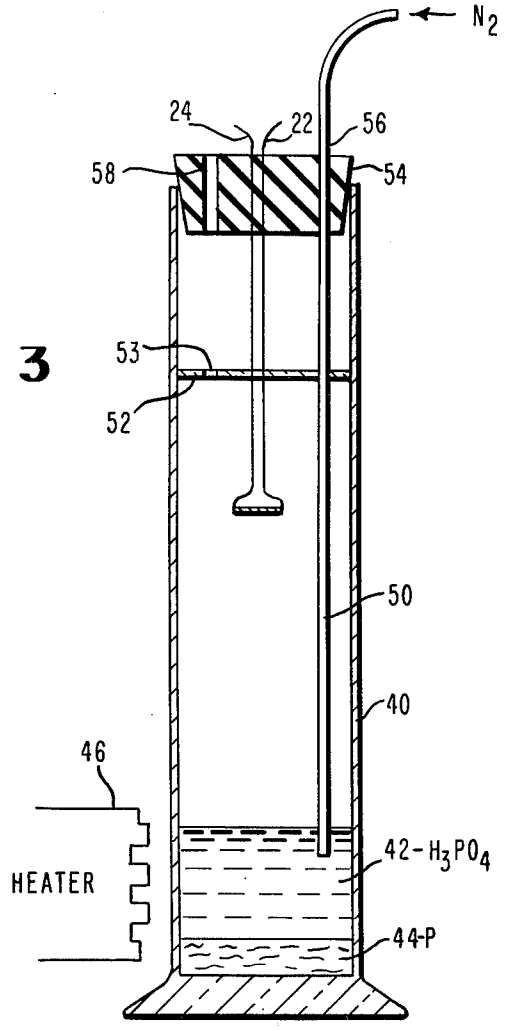

N_2
24
22
56
58
54
53
52
50
40
46
HEATER
42-H_3PO_4
44-P

FIG. 4

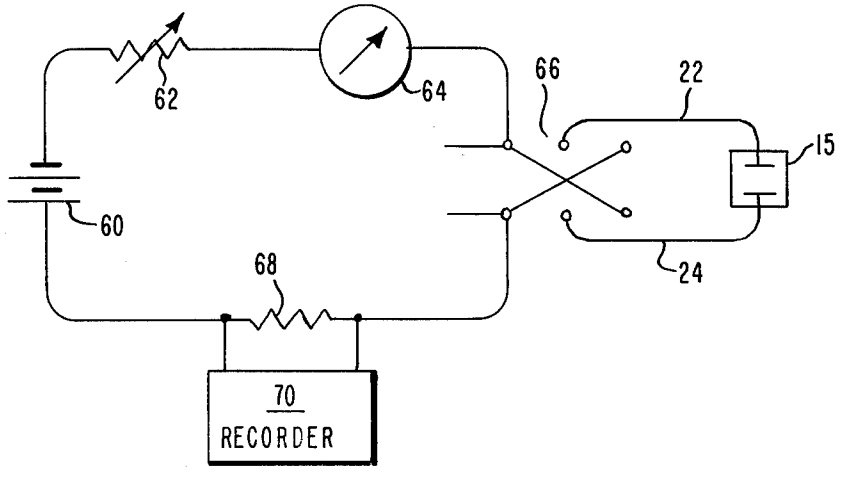

62
64
66
22
15
60
68
24
70
RECORDER

FIG. 5

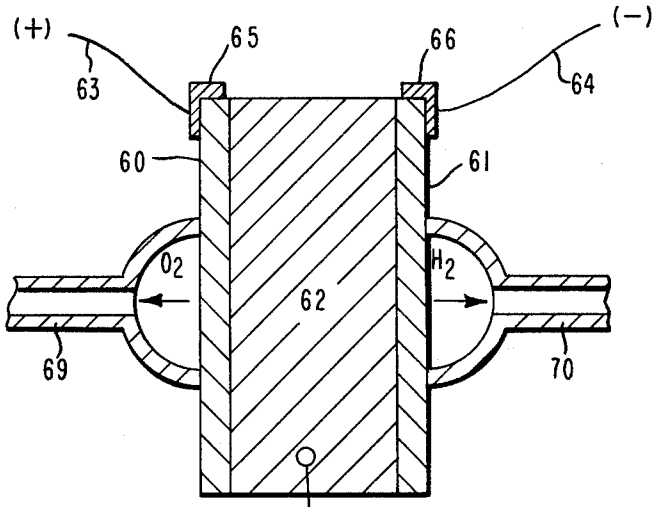
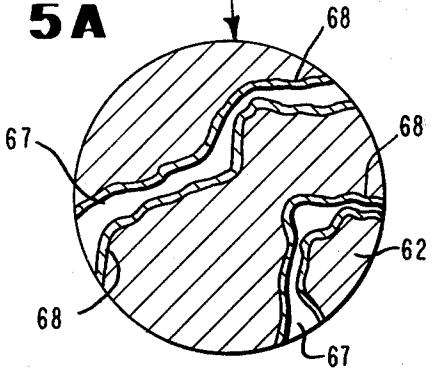


FIG. 5A



DEPOSITION OF P_2O_5 IN AN ELECTROLYTIC MOISTURE CELL

CROSS REFERENCE TO RELATES APPLICATIONS

This application is a continuation-in-part of U.S. Pat. application Ser. No. 281,859, which was filed on Aug. 18, 1972.

BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention relates to the deposition of phosphorus pentoxide on an electrically nonconductive substrate disposed between two electrodes and to the structure produced by this process. In particular, it relates to the formation of an electrolytic cell, such as a moisture cell or a fuel cell, of the type employing phosphorus pentoxide as a solid, regenerable hydroscopic electrolyte.

2. Discussion of the Prior Art

There are a number of known devices comprising a pair of spaced apart electrodes deposited on, or in contact with, one or more surfaces of an electrically nonconductive substrate in which a film of hydroscopic electrolyte covers the surface of the substrate between the electrodes. Examples of such devices are electrolytic moisture cells and fuel cells.

One of the most used hygroscopic materials used in the construction of such devices is a material referred to as phosphorus pentoxide (P_2O_5). Actually, phosphorus pentoxide is a highly hygroscopic material with an overwhelming tendency to hydrolyze to phosphoric acid. Certainly as it functions in an electrolytic cell and probably even in its so-called initial or active state, the material referred to as phosphorus pentoxide contains a mixture of compounds including at the very least phosphorus pentoxide, and phosphoric acid. The material might more properly be referred to as phosphoric anhydride (see the definition of phosphoric anhydride in the Condensed Chemical Dictionary, Seventh Edition). The overwhelming tendency among those skilled in the art, however, is to refer to this material as phosphorus pentoxide, and that terminology will be retained here. It is to be understood, however, that, as used in this specification, the term phosphorus pentoxide shall refer broadly to compositions, such as phosphoric anhydride, which contains phosphorus pentoxide.

In the formation of electrolytic cells, a variety of substrates and electrode configurations have been used. One particularly useful electrolytic cell comprises a pair of thin ribbon electrodes, often interdigitated electrodes, deposited on one surface of a non-porous, electrically nonconductive substrate such as glass or a ceramic. In this embodiment, the film of hygroscopic material generally fills all of the available space between the electrodes and also covers the electrodes as well.

Upon the application of an electric potential, between the electrodes, the electrolyte, in the absence of any moisture, does not permit current to flow between the electrodes. However, with water present, the electrolyte absorbs the moisture; becomes conductive; and a current will flow through the space between adjacent portions of the electrodes. As a current flows between the electrodes, the water electrolyzes to hydrogen and oxygen. The electrolyte, thus, continuously regenerates itself. Furthermore, the electrical energy consumed in the electrolysis represents an accurate measure of the moisture absorption, in accordance with Faraday's law.

Deposition of the P_2O_5 between the electrodes represents an important facet in the making of an electrolytic moisture cell. Reducing the thickness of the electrolytic film generally provides shorter response times since otherwise, the moisture must diffuse through greater amounts of electrolyte to reach the electrodes. At some point, however, further decreasing the thickness of the electrolyte film apparently causes discontinuities in the film and produces an increase in the cell response time. Furthermore, deposition of the P_2O_5 on areas of the cell which do not take part in the electrolysis reaction results in the absorption of moisture in nonactive portions of the cell. At such nonactive locations, the absorbed water cannot undergo the usual electrolysis to hydrogen and oxygen. This represents a further increase in the cell response time since this moisture must then diffuse to active portions of the cell.

One way in which phosphorus pentoxide can be deposited on the cell is by passing an aqueous solution of the electrolyte through the cell and subsequently subjecting the cell to an air stream to remove excess moisture. When a voltage is applied to the electrodes, complete electrolytic drying of the electrolyte is effected, leaving a solid film deposit on the electrodes and the substrate. However, this procedure requires a relatively long drying time to prepare the film. It also will often produce a relatively thick and nonuniform deposition which results in an instrument having long response times.

U.S. Pat. No. 3,072,556 disclosed a significantly improved method of depositing the hygroscopic electrolyte onto the cell. The cell housing with the electrodes is filled with an aqueous solution of the hygroscopic electrolyte mixed with a water-miscible organic liquid, which should have a higher vapor pressure than water. After placing the solution in the housing, a stream of gas is passed through the housing to dry the electrodes. The high vapor pressure of the organic liquid, such as acetone, permits speedy removable of most of the solvent. Removal of whatever residual water remained within the electrolyte is accomplished by applying a voltage to the electrodes for a short time. Not only does the use of a miscible organic liquid result in a more rapid production of electrolytic cells, it also provides a thinner film of electrolyte with accompanying shorter response times. Films having a thickness as small as 30 microinches gave satisfactorily fast response times from the cells.

L. G. Hall et al. in U.S. Pat. No. 3,081,250 discuss the deposition of vaporous P_2O_5 directly onto the cell. This technique allowed better control over the thickness of the film, but it resulted in a coating of P_2O_5 over everything, including the electrodes. Furthermore, this technique requires temperatures above the sublimation point of 347°C. of P_2O_5, and it also requires a high vacuum.

Fuel cells represent another area in which phosphorus pentoxide coatings are useful. At present, such devices comprise a hygroscopic medium disposed between two electrodes. The type of hygroscopic material available for such use, however, is fairly limited. Nonhygroscopic substrates, particularly porous substrates could be used to support the electrodes if a way could be found to impregnate them with a hygroscopic material, such as phosphorus pentoxide. One such device

would consist of a porous substrate separating two electrodes, either deposited on or in contact with opposite surfaces of the substrate. The pores of the structure would be coated with phosphorus pentoxide. When water is introduced into the pores, a potential is generated between the electrodes as the water dissociates to hydrogen and oxygen, which can be collected at the electrodes. As can be imagined, the problem of depositing phosphorus pentoxide in the pores of such a structure is considerable.

The search continues for improved methods of depositing electrolyte films on the surfaces of substrates to produce completely new and different structures which will result in electrolytic cells with faster response times. The electrolyte, phosphorus pentoxide, however, has shown itself amendable to an entirely new method of deposition upon the cell substrate.

SUMMARY OF THE INVENTION

This new method of depositing phosphorus pentoxide on an electrically nonconductive substrate disposed between two electrodes comprises the steps of:

a. contacting the electrode and the substrate, in the presence of water, with gaseous phosphorus; and

b. applying an electrical potential between the electrodes of sufficient strength to electrolyze the water and form phosphorus pentoxide on the substrate in the region between the electrodes.

The method is applicable to the situation where the substrate is a porous substrate and the step of contacting the electrodes and the substrate with gaseous phosphorus is accomplished by flowing gaseous phosphorus through the pores in the substrate. The method is also applicable to the situation where the substrate is a non-porous substrate, and the step of contacting the electrodes and the substrate with gaseous phosphorus is accomplished by flowing gaseous phosphorus over the substrate.

More specifically, to deposit the phosphorus pentoxide on the substrate between the electrodes, the substrate and the electrodes are contacted with gaseous phosphorus in the presence of water usually in the form of vapor. While contacting the phosphorus, an electric potential applied to the electrodes causes the production of oxygen and the subsequent reaction between phosphorus and oxygen to produce phosphorus pentoxide.

After the application of the electric potential but prior to the deposition of any P_2O_5, a film of moisture, generally adsorbed from water vapor in the surroundings, electrolyzes between the electrodes according to the reaction:

$$2H_2O \xrightarrow{\text{electrolysis}} 2H_2 + O_2 \quad (1)$$

This reaction produces a very low current within the cell of about 1 to 5 microamps. The reaction liberates oxygen at the anode and hydrogen at the cathode.

Phosphorus vapor diffuses to the anode and reacts with the oxygen according to the reaction:

$$P_4 + 5O_2 \longrightarrow 2P_2O_5 \quad (2)$$

The phosphorus pentoxide formed from reaction (2) hydrolyzes to phosphoric acid by the reaction:

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \quad (3)$$

This increases the conductance in the cell and also results in the electrolysis of the acid, according to the reaction:

$$4H_3PO_4 \xrightarrow{\text{electrolysis}} 6H_2 + 3O_2 + 2P_2O_5 \quad (4)$$

The generation of more oxygen increases the current flow in the cell and allows the coating to rapidly build up between the electrodes until the inter-electrode space becomes completely covered. Reversing the polarity of the applied voltage maintains an even film growth at both electrodes.

The current between the electrodes levels off at approximately 5 to 10 milliamps. This leveling off of the current appears to result in a reduction in the growth rate of the P_2O_5 film. Stopping the coating process at this point produces the preferred electrolyte film. Formation of additional phosphoric acid does not contribute to the electrolyzing capacity of the sensor in the cell, and further causes an increased drying time of the cell and a slower response to changing humidity.

The reaction can be stimulated by supplying additional oxygen from an oxygen-containing gas, such as pure oxygen or air, after the step of contacting the electrodes and the substrate with gaseous phosphorus.

The electrochemical coating of phosphorus pentoxide produces thinner and more uniform films than previously achieved by the manual application of dilute solutions. Furthermore, it lends itself to the automatic and simultaneous coating of a large number of sensors.

Due to the necessity of the driving electric potential, the P_2O_5 deposition can occur only in active portions of the cell experiencing the potential. In regions of the cell where the electrode configuration can produce no current under actual analysis conditions, no phosphorus pentoxide can deposit during the coating process. This avoids "dead" volumes of electrolyte that will absorb moisture and increase cell response times because of the necessity for this moisture to diffuse into "active" portions of the cell. The avoidance of inactive volumes of electrolyte represents a particular advantage in cells having sensors with thin ribbon electrodes attached in an interdigitized grid array. These sensors, and hence, the electrochemical deposition of P_2O_5, find particular use in diffusion cells in which only a portion of the moisture actually in the sample reaches the electrodes. The electrochemical deposition of P_2O_5 also minimizes the formation of puddles or "bubbles" of phosphorus pentoxide which absorb larger amounts of moisture than the thinner portions and cause a slower cell response under changing conditions.

Further, the electrochemical deposition of P_2O_5 permits the application of a very smooth and thin film on the sensor. As a result, phosphorus pentoxide films which are less than 0.5 micron thick display good response times in actual moisture analyses.

BRIEF DESCRIPTION OF FIGURES

FIG. **1** is a frontal view of one embodiment of a diffusion electrolytic moisture cell;

FIG. **1A** is a cross-sectional view of the diffusion cell of FIG. **1** taken along the line A—A;

FIG. **2** is an elevated view of the sensor of FIG. **1A**, with grid electrodes attached to a substrate;

FIG. **3** is an illustration of one apparatus that can be used for the electrochemical deposition of phosphorus pentoxide on a moisture cell sensor;

FIG. **4** is a circuit diagram of an apparatus that can be used for the electrochemical deposition of P_2O_5;

FIG. **5** is a schematic cross-sectional view of one embodiment of a fuel cell made according to the present invention; and

FIG. 5A is an enlargement of a portion of the substrate used in the fuel cell of FIG. 5 showing schematically its porous nature.

DESCRIPTION OF THE PREFERRED EMBODIMENT OF THE INVENTION

Referring to FIGS. 1 and 1A, the diffusion type electrolytic moisture cell along with its uses and advantages receive a general description in M. Czuha, Jr.'s U.S. Pat. No. 3,001,918 of Sept. 26, 1961. The cell **10** enclosed by the polyethylene wall **11** and the tetrafluoroethylene ring **12**, contains a sensor, indicated generally at **15**, which includes a first electrode **16** and a second electrode **17**, in contact with the hygroscopic substance, phosphorus pentoxide, **20** on the substrate or support **18**. A diffusion barrier **26** along with the spacer ring **27** and the support **18** form an enclosure about the electrodes, **16** and **17**, and the P_2O_5, **20**. The stainless steel ribbon leads **22** and **24** make contact with the electrodes **16** and **17**, respectively; pass through openings **30** and **32** in the cell wall **11**; and thus, provide electrical connection between these electrodes and the outside. The diffusion barrier **26** may simply have pores extending through it, or alternately can use a thin permeable membrane. A controlled porosity polycarbonate film represents a preferred choice. The retaining ring **12** also provides an opening **34** to allow a sample to contact the diffusion barrier **26**.

The sensor **15** forms a tight press-fit in the retaining ring **12**. This not only retains the sensor in place, but also rigidly entraps the membrane **26** and the tetrafluoropolyethylene spacer ring **27**. The tight fit of the sensor **15** in the retaining ring **12** also positions the electrical leads **22** and **24** and insures their electrical contact with the electrodes **16** and **17**, respectively.

The retaining ring **12** in turn fits into position in the wall **11**. The protruding ring **13** on the wall **11** aligns with the indented ring **14** in the retaining ring **12** and insures a close and tight fit between the two components.

The time required for moisture to diffuse through the barrier **26** increases the response time of the cell to changing moisture conditions. Having an excessively thick electrolyte layer or placing electrolyte in portions of the cell through which no current passes between the electrodes **16** and **17** would further increase the cell response time. Accordingly, the electrochemical deposition of phosphorus pentoxide, which avoids both of these problems, finds particular use in the diffusion type electrolytic moisture cell.

FIG. 2 shows the sensor **15** in greater detail, looking at a corner of the sensor. The electrodes **16** and **17** contact and adhere to the support or substrate **18**. Phosphorus pentoxide **20** also adheres to the substrate **18** and fills the spaces between the electrodes **16** and **17**. The substate **18** itself should not conduct appreciable amounts of electricity between the electrodes. Suitable substrates include glass or alumina with the former representing a preferred choice.

The thin ribbon electrodes **16** and **17** generally have a thickness in the range of about 0.1 to 1 micron. They generally have a width in the order of approximately 25 microns, and are usually spaced about 12 to 25 microns apart. While platinum has seen frequent use as the electrodes in electrolytic moisture cells, iridium and rhodium appear to possess important advantages over platinum, especially in diffusion cells. The processes of metal sputtering and ion beam plating allow the achievement of the thin metals on the substrates as well as their narrow widths and the close spacing between them.

The sputtering or ion beam plating techniques also allow the use of a mask during the plating or sputtering in order to achieve a desired electrode pattern on the substrate. The pattern shown in FIG. 2 represents a particularly useful design. Each of the two electrodes **16** and **17** have fingerlike extensions **36** and **38**, respectively, which interdigitate with the extensions of the other electrode in the fashion of a grid. This pattern represents a particularly large area of phosphorus pentoxide **20** between closely spaced electrodes and, thus, permits rapid electrolysis of any moisture passing through the diffusion barrier **26** of FIGS. **1** and **1A**. To aid in visualizing the electrode pattern of FIG. **2**, the extensions **36** on the first electrode **16** carry a negative sign, while the extensions **38** of the other electrode **17** bear a positive sign.

FIG. **2** also shows the particular advantages of depositing the P_2O_5 only in the active areas of the cell. Since the electric potential exists primarily between the electrodes, no phosphorus pentoxide deposits on the edge of the sensor **39** or on top of the sensor **41** peripherally to the electrodes. Further, only minimal phosphorus pentoxide deposits upon the top of electrodes **16** and **17**. This clearly obviates the hygroscopic substance **20** absorbing moisture in areas where the moisture cannot undergo electrolysis.

The cell's performance exhibits some dependence upon the nature of the interface between the electrodes and the substrate. Possible problems include the loss of electrode contact with substrate; poor contact between the electrode and the substrate; and overetching in sensor agreas not covered by the electrodes, resulting from longer sputtering than required to produce the clear areas on the substrate. This extended sputtering creates an undercut at the electrode edge detectable with a fine pointed scribe.

These poor interface conditions between the electrode and the substrate produce cells which saturate at low current levels, for example, 5 milliamps, or take inordinately long times to reach their saturation level. Such poor results represent the primary indicators of defective sensors.

The apparatus of FIG. **3** provides one way to electrolytically deposit phosphorus pentoxide. A container **40**, conveniently a 250 ml. cylinder, and a stopper **54** provide a controlled atmosphere of water and phosphorus vapors around the sensor **15**. The leads **22** and **24** suspend the sensor **15** within the container **40** and electrically connect the sensr to the electric potential discussed in connection with FIG. **4**. At the bottom of the container **40** rests molten phosphorus **44** immersed within a phosphoric acid solution **42** containing approximately 50% by weight of H_3PO_4. A heater **46** maintains the temperature of the phosphoric acid solution and the molten phosphorus generally above the melting point of phosphorus.

Some of the molten phosphorus dissolves into the phosphoric acid solution. A stream of nitrogen introduced into the phosphoric acid solution **42** through tube **56** carries the phosphorus and also water vapor over the sensor **15**, through the hole **53** in the baffle **52**, and out the hole **58** in the rubber stopper **54**.

The initiation of the P_2O_5 deposition depends upon an absorbed film of water on the substrate between the electrodes. The absorption of such a film of water re-

quires strict cleanliness of the substrate surface. Accordingly, a thorough cleaning of the sensor should proceed its attempted coating with P_2O_5. The usual dichromate-sulfuric acid cleaning solution does an effective job after which the wafer should be rinsed with distilled water and dried.

During the actual deposition, the velocity of the nitrogen or other inert gas can vary within a wide range, with 100 to 1000 cc. per minute providing satisfactory results. Two hundred cubic centimeters per minute represents a preferred velocity.

The heater **46** generally maintains the temperature of the phosphoric acid solution **42** and the molten phosphorus **44** above the melting point of the phosphorus, which for yellow phosphorus lies at 44°C.; 50°C. represents a convenient temperature. While the P_2O_5 deposition will proceed with the temperature slightly below the melting point of the phosphorus, it will produce a lower concentration of gaseous phosphorus in the vicinity of the sensor **15** and will require a necessarily longer period of time. Thus, maintaining the temperature of the phosphorus above its melting point insures a sufficiently high concentration of its vapor to allow a reasonably rapid process.

The phosphoric acid within the solution **42** above the phosphorus **44** serves to reduce the vapor pressure of water in the vicinity of the sensor **15.** Too much moisture will cause condensation and droplets with a resulting uneven film of P_2O_5 on the substrate. Maintaining about 50% by weight of H_3PO_4 in the solution **42** obviates this problem.

The orientation of the wafer **15** above the phosphorus **44** and the phosphoric acid solution **42** does not appear critical. However, maintaining the surface with the electrodes horizontally over the solution **42** and phosphorus **44** promotes an even coating over the substrate. Tilting the surface can produce a coating that is thicker at the lower end than at the higher end.

The deposition of the phosphorus pentoxide begins slowly. After the initiation, however, the propogation increases in speed and proceeds exponentially. At some point, however, the current through the cell approaches a constant level, generally within the range of about 5 to 10 milliamps. This approach to a constant current level represents a suitable point for terminating the deposition. Carrying it further only produces thicker film with longer response times, although not deleterious in other regards.

Introducing oxygen into the vicinity of the sensor **15** quickens the initiation of the deposition. Apparently, the oxygen reacts with phosphorus in the vicinity of the sensor to form P_2O_5 which then deposits upon the sensor itself. Continuing this beyond the initiation period, however, tends to produce an uneven film of electrolyte upon the substrate and, thus, should usually be avoided. Any oxygen containing gas, such as pure oxygen or air, can be used.

A suitable circuit for applying the electric potential to the sensor electrodes appears in FIG. **4.** A potential source **60** applies a d.c. electric potential across resistors **62** and **68,** through the reversing switch **66** to the leads **22** and **24** and the sensor **15.** The variable resistor **62** allows the adjustment of the potential applied to the sensor leads to a desirable level. Actually, a potential as low as two volts can be used, but at this level, electrolysis takes place very slowly, so generally a potential within the range of 40 to 100 volts is used. Seventy volts represents a convenient level.

The ammeter **64** allows monitoring the progress of the electrolyte deposition. As discussed above, when the current through the ammeter **64** approaches a constant level, the deposition should generally continue no further. A recorder **70** across the resistor **68** will provide a permanent record of the electrolyte deposition.

The reversing switch **66** reverses the polarity of electric potential applied to the leads **22** and **24** of the sensor **15.** By reversing the potential, phosphorus pentoxide will grow from both electrodes towards the other. Otherwise, the film appears to grow from the anode electrode only. Furthermore, reversing the polarity also appears to suppress the development of a runaway or hot spot film growth between the electrodes. A reversal rate within the range of 4 to 15 times per minute will generally accomplish these results.

Cell sensors prepared in this fashion have displayed very short response times to changing moisture conditions. Thus, sensors **15** of FIG. **2,** experiencing a change in the humidity of its immediate environment from 1000 parts per million to 10 p.p.m., can show a 90% change in its reading between these levels in no more than five seconds, and generally in less than about two seconds. These response times represent the behavior of the cell in FIG. **1A** to moisture changes occurring in the area **34** behind the diffusion barrier **26.** As suggested above, these short times for the cell to respond to changing conditions in the immediate vicinity of its electrodes and electrolytes becomes a particularly important advantage in diffusion cells. For, in such cells, this period adds to the times required for the moisture to penetrate the diffusion barrier to obtain the overall time that the cell requires to reflect changes in external humidity conditions.

A fuel cell is illustrated schematically in FIG. **5.** Two electrodes **60** and **61** are deposited on a substrate **62** which can be made from any suitable electrically nonconductive material. In the embodiment illustrated, it is a porous substrate as can be seen from FIG. **5A** which shows, schematically and in enlarged form, a portion of the substrate **62.** Electrodes **60** and **61** are connected to wires **63** and **64** through connectors **65** and **66.**

The pores **67** in substrate **62** are coated with a thin layer **68** of phosphorus pentoxide, formed as described above, by flowing phosphorus gas and water vapor through the pores while applying an electrical potential to the electrodes. The pores can be of any shape and configuration, but they should form a continuous, if tortuous, path for the gases to pass from one electrode to another. While the substrate can be made from any suitable material, such as glass or ceramic, the heat generated in the conversion process has been found to create stresses in such a system so that the substrate will crack or craze. It is preferred, therefore, to use a more flexible material, such as a plastic as the substrate.

The operation of fuel cells is well known to those skilled in the art. Generally, water is supplied to the system, generally in the direction indicated by the arrow, and a potential is generated between the electrodes. Hydrogen and oxygen are then collected at the electrodes. In FIG. **5,** electrodes **60** and **61** are shown connected to collector cups **69** and **70.** In the region where these cups contact the electrodes, the electrodes themselves must be porous or at least permeable by hydrogen and oxygen.

As is well known to those skilled in the art, the system can be operated in reverse.

The above description has been given for the purpose of illustrating the invention and is not intended to limit the scope of the invention set forth in the appended claims.

What is claimed is:

1. A method of depositing phosphorus pentoxide on an electrically nonconductive substrate disposed between two electrodes comprising the steps of:

a. contacting said electrodes and said substrate, in the presence of water vapor, with gaseous phosphorus; and

b. applying an electric potential between said electrodes of sufficient strength to electrolyze the water vapor and form phosphorus pentoxide on said substrate only in the region between said electrodes.

2. The method of claim **1** wherein said substrate is a porous substrate and the step of contacting said electrodes and said substrate with gaseous phosphorus is accomplished by flowing gaseous phosphorus through the pores in said substrate.

3. The method of claim **1** wherein said substrate is a non-porous substrate, and the step of contacting said electrodes and said substrate with gaseous phosphorus is accomplished by flowing gaseous phophorus over said substrate.

4. The method of claim **1** wherein said substrate is a non-porous substrate and said electrodes are thin interdigitated ribbon electrodes deposited on one surface of said substrate, and wherein the step of contacting said electrodes and said substrate with gaseous phosphorus is accomplished by flowing gaseous phosphorus over said substrate and said electrodes.

5. The method of claim **4** wherein said water vapor and said gaseous phosphorus are brought into contact with said electrodes and substrate by passing an inert gas through an aqueous phosphoric acid solution in contact with molten phosphorus.

6. The method of claim **5** wherein said aqueous phosphoric acid solution contains at least about 50% by weight of phosphoric acid.

7. The method of claim **5** wherein said aqueous phosphoric acid solution is maintained at a temperature of at least about 50°C.

8. The method of claim **4** wherein the electric potential applied between said electrodes is within the range of about 40 to about 100 volts.

9. The method of claim **8** further comprising the step of reversing the polarity of the electric potential applied to said electrodes.

10. The method of claim **8** wherein the polarity of the electric potential is reversed at a rate of about **4** to about **15** times a minute.

11. The method of claim **8** wherein the electric potential is removed from said electrodes when the current between said electrodes reaches a level of about 5 to about 10 milliamps.

12. A method of depositing phosphorus pentoxide on the surface of an electrically nonconductive substrate disposed between thin ribbon electrodes attached to and supported by said substrate to form an electrolytic moisture cell, comprising the steps of:

a. passing an inert gas through an aqueous phosphoric acid solution containing at least about 50% by weight of phosphoric acid and maintained at a temperature of at least about 50°C. to produce water vapor and gaseous phosphorus, sad aqueous phosphoric acid solution being in contact with molten phosphorus;

b. contacting said electrodes and substrate with said water vapor and gaseous phosphorus; and

c. applying an electric potential of about 40 to about 100 volts between said electrodes, when in contact with said water vapor and gaseous phosphorus to form phosphorus pentoxide on said substrate only in the region between said electrode.

13. The method of claim **12** wherein:

a. the electric potential applied between said electrodes is in the range of about 40 to about 70 volts;

b. the polarity of the electric potential applied to said electrodes is reversed at a rate of about 4 to 15 times a minute; and

c. the electric potential is removed from said electrodes when the current between said electrodes reaches a level of about 5 to about 10 milliamps.

14. The method of claim **13** wherein said electrodes and substrate are contacted with a gas containing molecular oxygen after initiation of the step of contacting said electrodes and substrate with gaseous phosphorus.

15. An electrolytic cell comprising a substrate, at least two spaced-apart thin ribbon electrodes deposited on the surface of said substrate, and a thin layer of phosphorus pentoxide deposited on said substrate and filling only the space between said electrodes, said phosphorus pentoxide contacting only the edge of said electrodes adjacent to said substrate and having a thickness less than about 0.5 micron.

16. A fuel cell comprising a porous, electrically nonconductive substrate, at least two electrodes in contact with opposite sides of said substrate, electrical circuit means connected to said electrodes, and a thin coating of phosphorus pentoxide on the surface of the pores in said substrate.

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