(12) UK Patent Application (19) GB (11) 2 429 066 (13) A

(43) Date of A Publication 14.02.2007

(21) Application No: 0613155.1

(22) Date of Filing: 03.07.2006

(30) Priority Data:
(31) 0513631 (32) 01.07.2005 (33) GB

(71) Applicant(s):
Alphasense Ltd
(Incorporated in the United Kingdom)
3 Oak Industrial Park, Chelmsford Road,
GREAT DUNMOW, Essex, CM6 1XN,
United Kingdom

(72) Inventor(s):
Darryl Hirst Dawson
William Joseph Yost III
Christopher William Ogilvie Thompson

(74) Agent and/or Address for Service:
Hindle Lowther
28 Rutland Square, EDINBURGH,
EH1 2BW, United Kingdom

(51) INT CL:
G01N 27/30 (2006.01) ***C23C 16/30*** (2006.01)

(52) UK CL (Edition X):
G1N NBEC N25A1 N25C4C1 N25DX

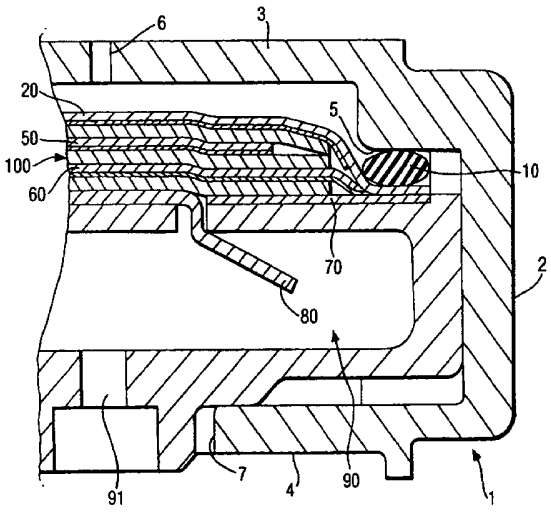
(56) Documents Cited:
WO 2005/090954 A1 **WO 2003/066930 A1**

(58) Field of Search:
INT CL **G01N**
Other:

(54) Abstract Title: **A gas permeable electrode comprising an electrocatalyst**

(57) A gas permeable electrode 21 comprises an electrocatalyst which is permeable to a reactant or reactant product. The said electrocatalyst comprises particulate boron-doped diamond. The electrode may be provided with a gas diffusion means, permeable to the gas but not to an electrolyte. The boron-doped diamond may be mixed with a hydrophobic material such that it is permeable to a gas but impermeable to an electrolyte. The electrode may be doped with between 10^{19} or 10^{21} boron atoms per cubic centimeter of solid. The boron-doped diamond particles may be between 0.1 and 50 microns in diameter. Also disclosed is a method of making an electrode comprising an electrocatalyst, and a method of making the electrocatalyst via a chemical vapor deposition technique (CVD).

Fig.1.



GB 2 429 066 A

Fig.1.

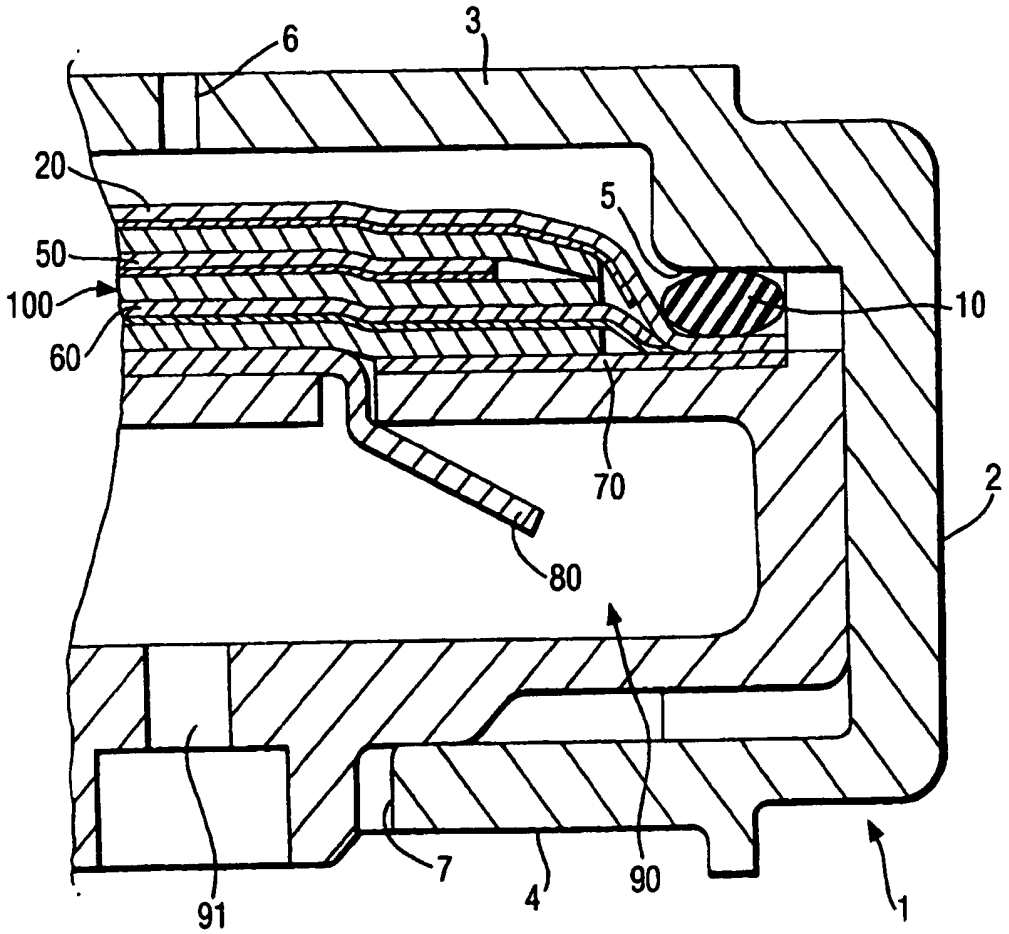


Fig.2.

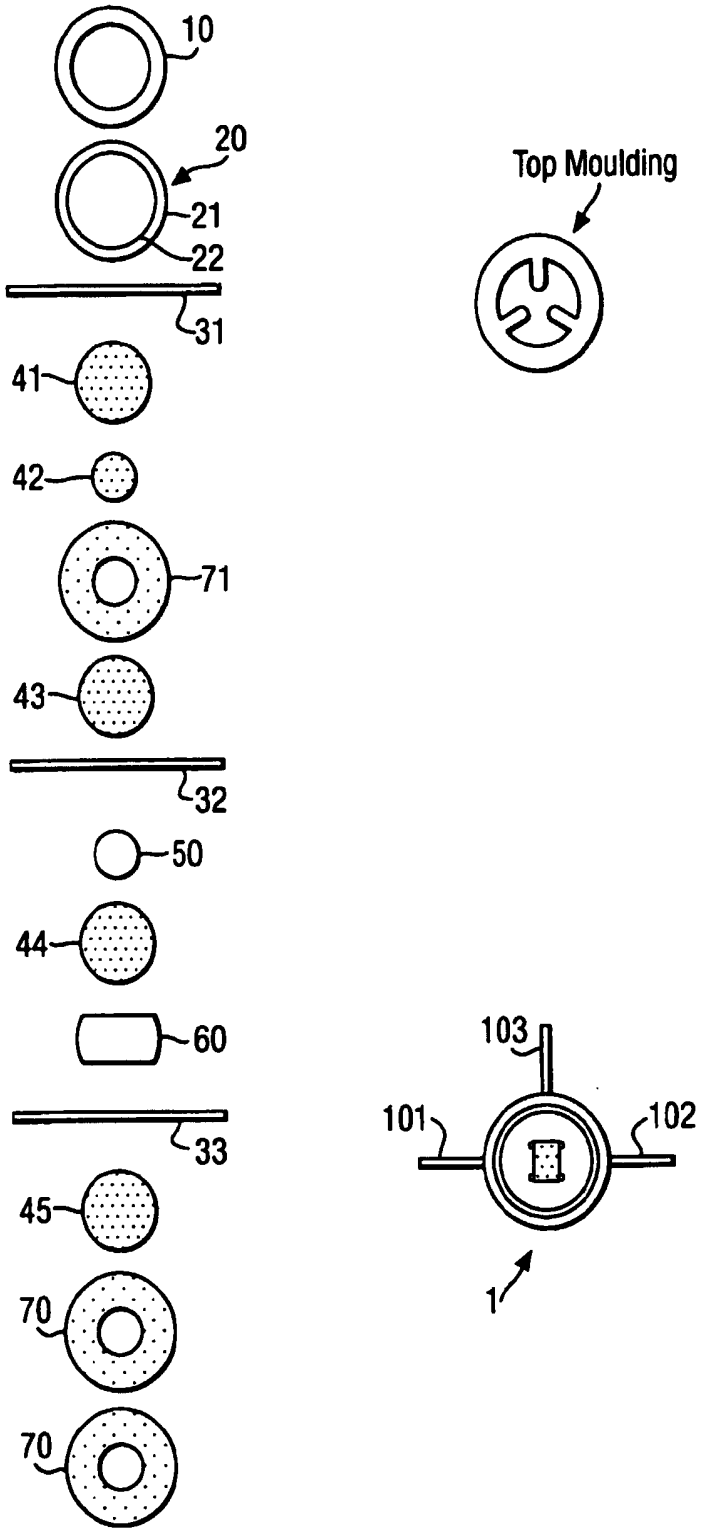

10
20
21
22
31
41
42
71
43
32
50
44
60
33
45
70
70
Top Moulding
103
101
102
1

Fig.3.

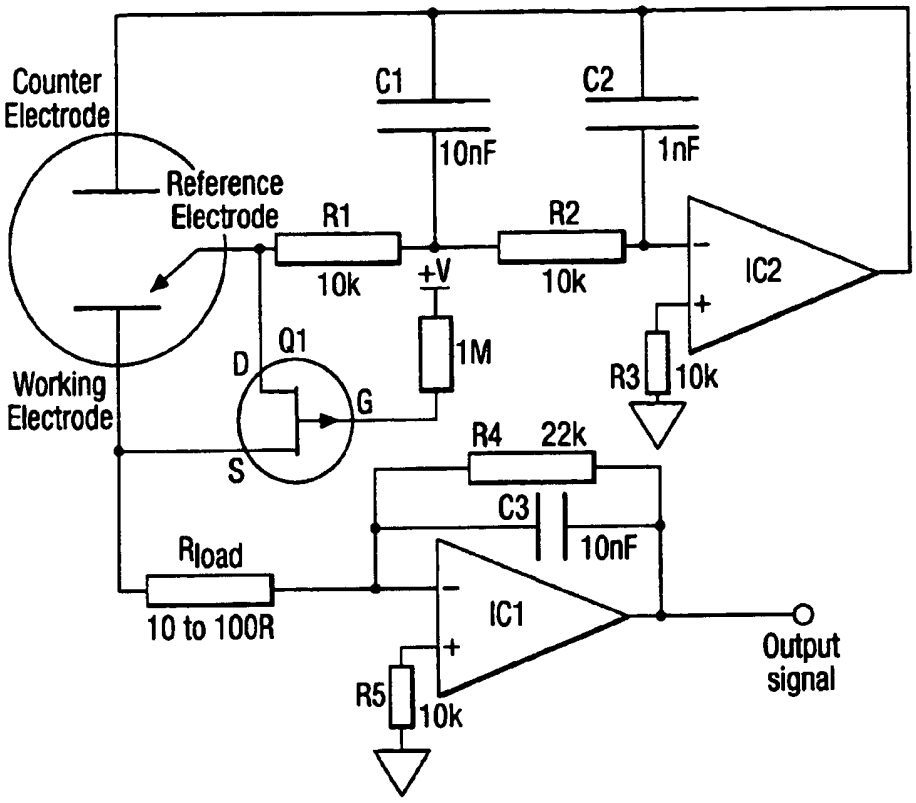

Counter Electrode
C1
10nF
C2
1nF
Reference Electrode
R1
10k
R2
10k
+V
IC2
1M
Q1
D
G
S
R3
10k
Working Electrode
R4
22k
C3
10nF
Rload
10 to 100R
IC1
Output signal
R5
10k

Fig.4.

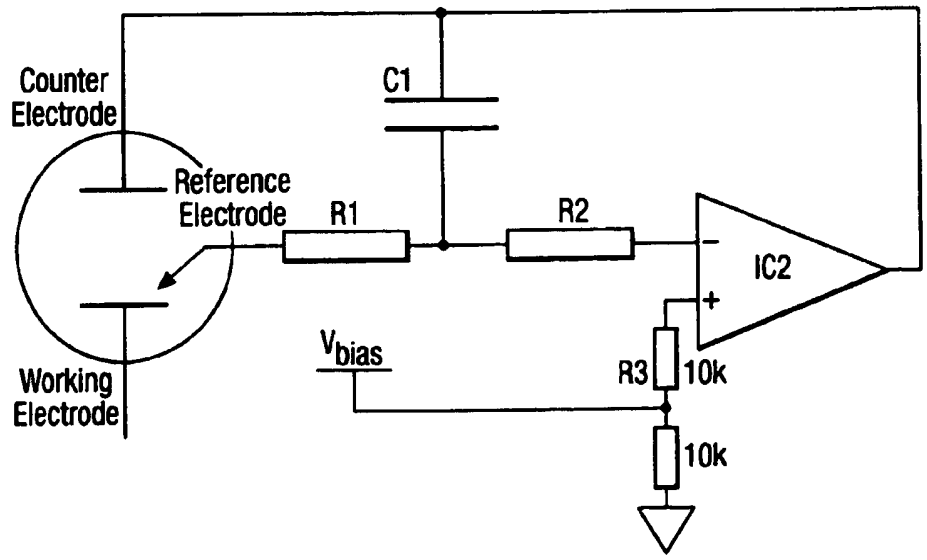

Counter Electrode
C1
Reference Electrode
R1
R2
IC2
Vbias
R3
10k
Working Electrode
10k

Fig. 5.

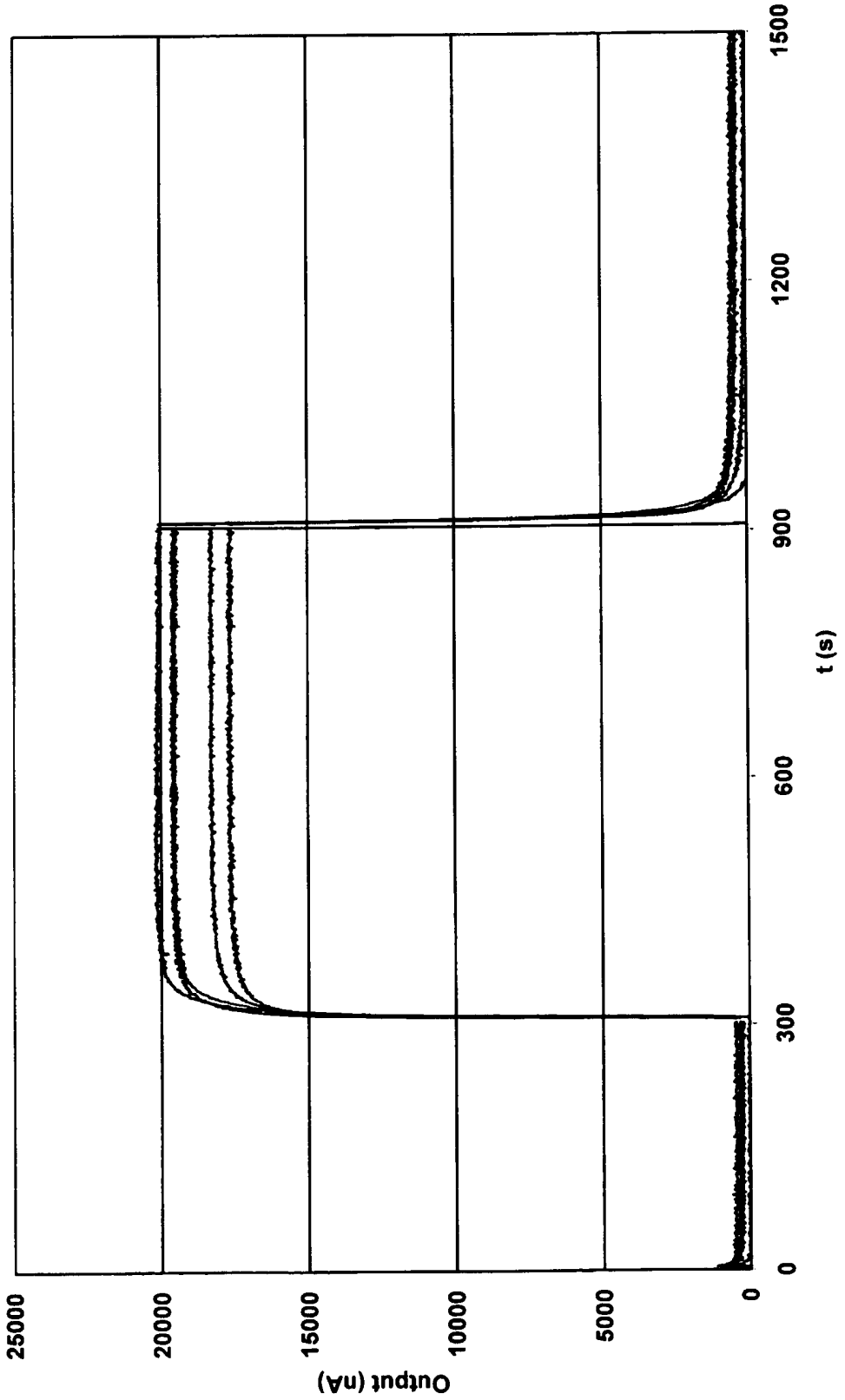
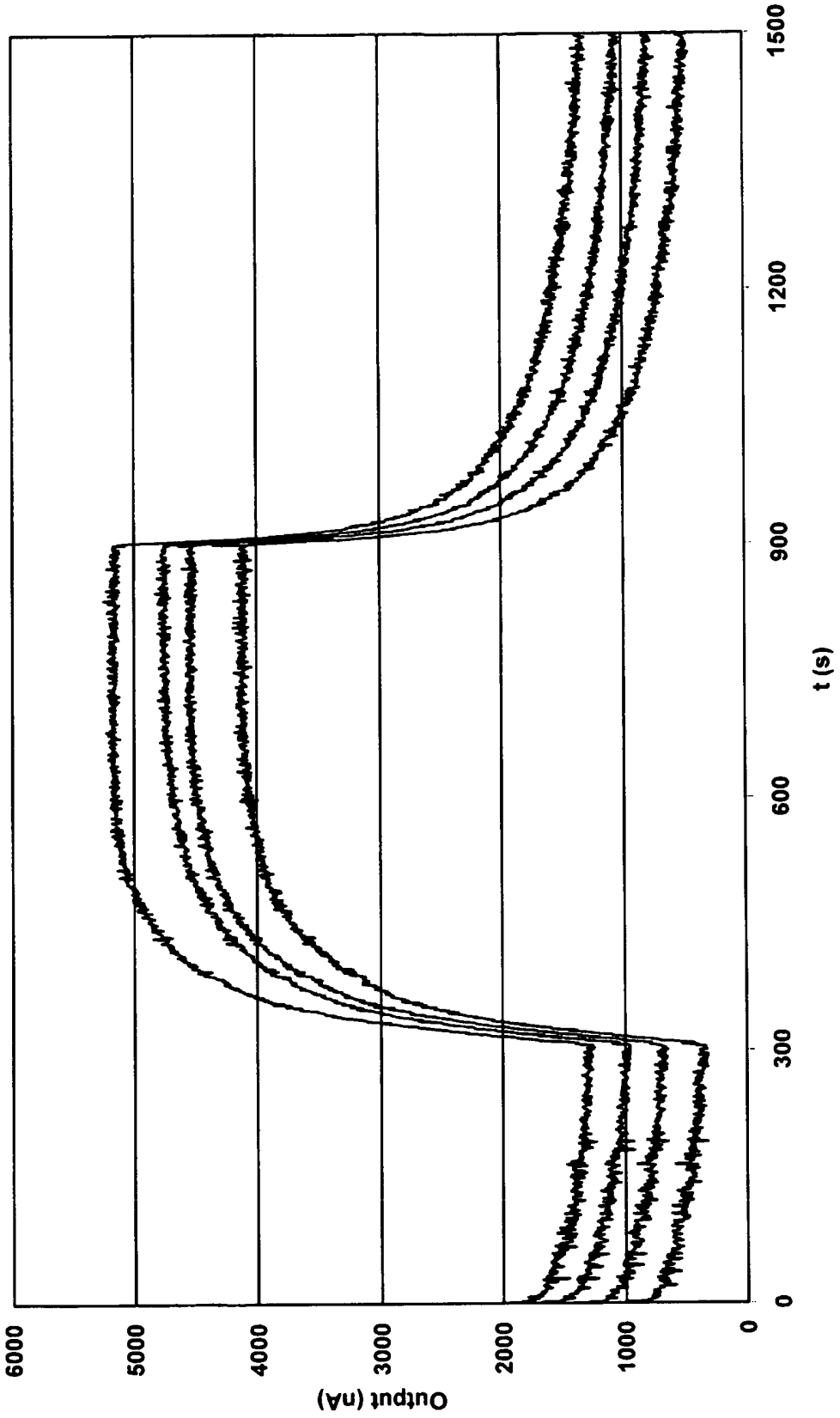

Output (nA)
25000
20000
15000
10000
5000
0
0
300
600
900
1200
1500
t (s)

Fig. 6.


Output (nA)
6000
5000
4000
3000
2000
1000
0
0
300
600
900
1200
1500
t (s)

Electrode and method for making electrode

Field of the invention

The present invention relates to electrodes for electrochemical uses, and methods of making electrodes. The electrodes are particularly useful for applications where it is desirable for a chemical species, such as an analyte, a reactant or a reaction product, to be able to penetrate or leave the electrode.

Background to the invention

Within this description and the attached claims, the term catalyst includes any substance which, when added to a reaction mixture, changes the rate of attainment of equilibrium in the system without itself undergoing a permanent chemical change. The term catalyst includes substances which might be changed physically during the reaction they catalyse but which could in theory be recovered chemically unchanged at the end of the reaction. The term electrocatalyst refers to an electrochemically active catalyst.

There are some applications where it is desirable for a chemical species to be able to penetrate or leave an electrode. For example, electrochemical gas sensors are well known. In one configuration, working, counter and reference electrodes are connected through a potentiostatic circuit which maintains a bias potential between the working and reference electrodes. A gas to be measured penetrates the working electrode and undergoes a catalytic reaction. For example, in the case of oxidation of NO,

$$NO + H_2O \rightleftharpoons NO_2 + 2H^+ + 2e^-$$

A reduction occurs on the counter electrode:

$$1/2\,O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$$

Similar principles apply to electrochemical sensors for measuring liquid analytes.

It is also well known to use an electrode in an electrochemical cell to generate a gas, such as chlorine, or to carry out an electrochemical reaction which consumes a gas. The necessary high reaction rates can be obtained where an electrode is permeable and a higher catalytic surface area is made available. For example, the following working electrode reaction can be used to generate chlorine:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

On the other electrode:

$$2H^+ + 2e^- \rightarrow H_2$$

It has been known for some time to form an electrode for electrochemical uses by coating a conductive metal with boron-doped diamond. For example, US Patent 6,267,866 discloses an electrode for electrochemical uses made of a conductive metal mesh coated with boron-doped diamond. Boron-doped diamond has desirable electrochemical properties, such as a wide potential window. That is to say, boron-doped diamond can be used as a catalyst at high anodic or cathodic potentials without itself undergoing degradation and without electrochemically oxidising or reducing common solvents such as water. Although boron-doped diamond is an acceptable electrocatalyst for gases such as nitric oxide and ammonia, it is a very poor electrocatalyst for water oxidation or reduction. This advantage allows selective oxidation or reduction of a gas at electrochemical potentials where competing reactions are not favoured. However, known boron-doped diamond coated electrodes include an impervious layer of boron-doped diamond overlaying a conductive metal electrode.

An aim of the present invention is to provide an electrode comprising boron-doped diamond which is permeable to a reactant or reaction product.

Summary of the invention

According to a first aspect of the present invention there is provided a gas permeable electrode comprising an electrocatalyst which is permeable to a reactant or reaction product, the electrocatalyst comprising particulate boron-doped diamond.

By using an electrocatalyst comprising particulate boron-doped diamond, we have obtained an electrode which is permeable to a reactant or reaction product.

Preferably, the electrode is for catalysing a reaction in which either or both of a reactant or a reaction product is a gas, and the electrode further comprises gas diffusion means to enable a gas to penetrate or leave (as appropriate) the electrocatalyst.

Preferably, the gas diffusion means comprises a material which is permeable to gas but impermeable to electrolyte.

Preferably, the gas diffusion means comprises a hydrophobic material, intimately mixed with the boron-doped diamond, such that the resulting mixture of boron-doped diamond and hydrophobic material is permeable to gas but impermeable to electrolyte. A suitable hydrophobic material is microporous PTFE (e.g. ICI Fluon). The hydrophobic material is preferably particulate, such as particulate microporous PTFE. The gas diffusion means may also comprise a sheet or strand of material which supports the boron-doped diamond and hydrophobic material and is also permeable to gas but impermeable to electrolyte.

The gas diffusion means may comprise a sheet or strand of material which is permeable to gas and impermeable to electrolyte, to which the particulate boron-doped diamond is bonded.

Preferably, the boron-doped diamond particles comprise diamond doped with between 10^{19} and 10^{21} boron atoms per cubic centimetre. More preferably, the boron-doped diamond particles comprise diamond doped with the order of 10^{20} boron atoms per cubic centimetre.

The boron-doped diamond particles are preferably between 0.1 and 50 microns in diameter, more preferably 1 to 10 microns in diameter. Most preferably, the particles have a diameter of

approximately 2 microns. This size range is suitable for use with the electrode manufacturing process described below. The particles do not need to be homogenous in size.

The invention also extends to an electrochemical cell comprising a working electrode, the working electrode being an electrode according to the first aspect. The electrochemical cell may be an electrochemical gas sensor for sensing a gaseous analyte and the electrocatalyst may be permeable to the analyte.

According to a second aspect of the present invention there is provided a method of making an electrocatalyst which is permeable to a reactant or reaction product, the method comprising the step of forming an electrocatalyst comprising particulate boron-doped diamond.

The particular boron-doped diamond is preferably obtainable by (preferably obtained by) chemical vapour deposition. The particulate boron-doped diamond may be obtainable by (preferably obtained by) forming boron doped diamond using chemical vapour deposition in a reactor under conditions where particles of the above dimensions are formed in the gas phase.

The particulate boron-doped diamond may be obtainable by (preferably obtained by) using chemical vapour deposition to deposit a boron-doped diamond layer onto a substrate, releasing the layer which is formed, and then grinding the resulting boron-doped diamond.

Chemical vapour deposition is preferably metal-organic chemical vapour deposition.

The particular boron-doped diamond may be obtainable by (preferably obtained by) a high-pressure, high-temperature diamond formation technique and then ground.

Preferably, the particulate boron-doped diamond is brought into contact with gas diffusion means which is permeable to gas but impermeable to electrolyte.

The step of bringing the particulate boron-doped diamond into contact with gas diffusion means may comprise forming a layer comprising the particulate boron-doped diamond on a sheet or strand of material which is permeable to gas but impermeable to electrolyte.

The step of bringing the particulate boron-doped diamond into contact with gas diffusion means may comprise the step of intimately mixing the particulate boron-doped diamond with a

hydrophobic material. The step of bringing the particulate boron-doped diamond into contact with gas diffusion means may comprise the step of mixing the particulate boron-doped diamond with a particulate material which is permeable to gas but impermeable to electrolyte. The resulting electrocatalyst may be formed as a layer on a sheet or strand of material which is permeable to gas but impermeable to electrolyte.

According to a third aspect of the present invention, there is provided a process for making a gas permeable electrode comprising the steps of making an electrocatalyst according to the second aspect of the present invention and forming a gas permeable electrode comprising the electrocatalyst.

According to a fourth aspect of the present invention, there is provided a method of making an electrochemical cell comprising the step of making a gas permeable electrode according to the method of the second aspect. There is also provided a method of making an electrochemical gas sensor, comprising the step of making a gas permeable working electrode according the method of the second aspect.

Brief Description of the Drawings

The invention will be further described, by way of illustration, with reference to the accompanying drawings, in which:

Figure 1 is a sectional view of one embodiment of an assembled nitric oxide sensor in accordance with the invention;

Figure 2 is an exploded view of an electrode stack assembly for the electrochemical sensor of Figure 1;

Figure 3 is a circuit diagram of a standard potentiostatic circuit, suitable for use with the electrochemical sensor of the present invention;

Figure 4 is a variant of part of the circuit diagram of Figure 3, for applying a bias potential between the working and reference electrode of a nitric oxide or ammonia sensor;

Figure 5 is a graph showing the working electrode current with time of an electrochemical gas sensor in response to 20ppm of nitric oxide; and

Figure 6 is a graph showing the working electrode current with time of an electrochemical gas sensor, with a bias of 900mV, in response to 25ppm ammonia.

Detailed Description of an Example Embodiment

An electrocatalyst comprising particulate boron-doped diamond which is permeable to a reactant or reaction product can be made as follows:

Boron-doped diamond grit with a typical particle size of 2 microns diameter and a level of doping of at least 10^{20} boron atoms per cubic centimetre can be made by high pressure, high temperature growth in a press and then ground to 2 microns particle size. The concentration of boron atoms is not critical and is not tightly controlled. Boron-doped diamond grit with these properties is available from Element Six (UK) Ltd. of Maidenhead, United Kingdom.

Firstly, 1.0g of boron-doped diamond is added to a 1.8ml solution of 1.4% isooctylphenoxypolyethoxyenthanol (Triton X) solution in water. Thereafter, 0.15ml of PTFE in aqueous dispersion (Fluon GP1 brand) is added thereto and the components are mixed by sonication (10 minutes) and stirred with a magnetic stirrer bar. Triton X is available from BDH (Poole, United Kingdom) and Fluon GPI is distributed by Whitford Plastics Ltd., Runcorn, United Kingdom (Triton X and Fluon are Trade Marks).

The resulting slurry is then drawn up into a pipette, and 50 microlitres is dispensed in to a circular depression on an electrode forming mould. The mould comprises disc shaped depressions of 13rnm diameter over a pressable member. The electrocatalyst is spread throughout the disc with the pipette, as evenly as possible.

The resulting cakes of electrocatalyst are then dried for 60 minutes at 60 C, followed by a further 30 minutes at 150 C9 then 15 minutes at 280 C. A membrane disc, of gas porous hydrophobic PTFE, such as Zytex, Goretex or Mupor (Zytex, Goretex and Mupor are Trade Marks) is placed on top of the press A baked electrocatalyst disc from the previous step is then placed on top of the membrane, with the cake side facing down, and the electrocatalyst cake and electrode disc

being lined up coaxially. Next, a mechanical press applies pressure to the pressable member, thereby pressing the electrocatalyst into the PTFE membrane.

Thereafter, the press and mould can be removed revealing the electrocatalyst cake.

One preferred embodiment of a sensor in accordance with the invention, for measuring nitric oxide or ammonia in a gas sample, is illustrated in Figures 1 and 2. Figure 1 is slightly simplified, with some of the components shown in Figure 2 omitted from Figure 1 for clarity. The physical structure, construction and operation of the sensor are generally known, the novelty lies in the working electrode, discussed above, and the resulting sensor properties.

As shown in Figure 1, the sensor comprises a generally cylindrical sensor housing or casing 1, made of a corrosion resistant engineering plastic material such as polycarbonate or polysulfone, approximately 25mm in diameter in which is housed an electrolyte reservoir 90 made of polysulfone or polycarbonate, an electrode stack assembly 100 and a wick 80 of unbound glass fibre, a hydrophilic non-conductive electrolyte transporting material which functions as a wick, extending into the reservoir 90 for contact with electrolyte therein.

Sensor casing 1 has a cylindrical side wall 2 and generally planar circular top and bottom walls, 3 and 4, respectively. The top wall 3 has a stepped configuration and includes an annular shoulder portion S around the periphery. A central circular opening 6 passes through the top wall 3 which functions to permit gas passage to the interior of the casing whilst acting as a means to restrict the diffusion of the gas sample to the working electrode, discussed below. The circular opening 6 is referred to as the capillary. In the present example, the capillary is 4mrn diameter. The bottom wall 4 includes a larger central circular opening 7 through which protrudes part of the reservoir 90, this part including a suitable opening 91 to enable supply of electrolyte to the reservoir, during manufacture.

The casing 1 is conveniently of two-part construction (not shown) for assembly purposes The electrode stack 100 is further illustrated in Figure 2. In Figure 2, the relative dimensions of the various components are as shown. The components of the electrode stack are generally of planar or sheet-like form, generally being of circular or annular configuration as shown in Figure 2.

Working from the bottom up as shown in Figure 2, electrode stack 100 comprises two annular

stack bases 70 of gas porous hydrophobic PTFE polymer material in the form of Zytex, Goretex or Mupor (Zytex, Goretex and Mupor are Trade Marks). (Only one stack base is shown in Figure 1). These are followed by a circular separator disc 45 made of unbound glass fibre which is a hydrophilic, non-conductive material permeable to the electrolyte which functions to wick electrolyte. Then follows a platinum strip or rod 33 (not shown in Figure 1) that functions as an electrical conductor for connection to a first terminal pin 101 on the sensor housing. The assembly then includes a counter electrode 60 that is generally rectangular in plan.

Counter electrode 60 comprises an electocatalytic layer covering the full extent of the downward facing side of a hydrophobic microporous PTFE support (e.g. of Zytex, Goretex or Mupor). The electrocatalytic layer is formed from a mixture of Platinum oxide (Johnson Matthey) and PTFE binder sintered at elevated temperature to give a porous binder/catalyst material that can be bonded to the support.

The stack then includes a further separator disc 44 similar to separator disc 45. Next in the assembly is circular reference electrode 50 of similar materials and construction as the counter electrode 60 and comprising a Platinum oxide (Johnson Matthey)/PTFE electrocatalytic layer covering the downward facing side of a hydrophobic microporous PTFE support. Then follows a second platinum strip 32 similar to strip 33 and leading to a second terminal pin 102. A third separator disc 43 similar to discs 45 and 44 is then provided, followed by a further gas porous PTFE ring 71, similar to stack base 70 and having a smaller separator disc 42, which is similar to discs 43, 44 and 45 in all but size. Thereafter, a further separator disc 41, similar to disc 45 is provided followed by a third platinum strip 31, similar in construction and function to strips 33 and 32 and leading to a third terminal pin 103.

(Items 71, 42 and 41 and platinum strips 31 are not shown in Figure 1).

Finally, the electrode assembly includes a circular working electrode 20. The working electrode 20 includes a boron-doped diamond/PTFE electrocatalytic layer on the circular central portion only of the downward facing surface of a hydrophobic microporous PTFE support. The manufacturing of the boron-doped diamond/PTFE electrocatalytic layer is discussed above. In the present example, the electrocatalytic portion of the working electrode 20 is 13mm in diameter.

The components of the electrode stack assembly are assembled in order on the reservoir 90

and wick 80 with the electrocatalytic layers on the undersides of the associated supports, facing downwardly towards the reservoir as shown in Figure 1. An "O" ring 10 is located on top of the assembly, being sized to contact the outer periphery of the working electrode support 21. On insertion of the assembly into the casing 1, as shown in Figure 1, the casing shoulder 5 contacts the "O" ring 10 which urges the working electrode support 21 into contact with the outer periphery of the stack base 70 and forms a seal, also bringing the various electrode stack components into close contact as shown. During this assembly some of the electrode stack components deform from their initially planar condition, but such components are still to be considered as of planar configuration.

5 Molar sulfuric acid electrolyte is located in the chamber within reservoir 90 for contact with wick 80. The reservoir is not filled completely with electrolyte, leaving a free volume in the reservoir to allow for the possibility of water absorption resulting in an increase in the electrolyte volume, or for water loss through evaporation past the working electrode 20, reducing electrolyte volume. The reservoir may include hydrophilic non-conductive wicking or wetting material to provide a continuous electrolyte path from the reservoir to the separator discs.

The electrode supports are all made from hydrophobic microporous PTFE. The stack base 70 is made from PTFE. The hydrophobic properties of the material mean it is impermeable to the electrolyte so that electrolyte is effectively sealed within the housing by virtue of the seal between stack base 70 and the working electrode support 21 produced by "O" ring 10.

Before use, the sensor is assembled, and then the sensor is tested and calibrated. In each of these steps, the casing terminal pins are connected to an external potentiostat, which is used in known manner to set the potential difference of the working electrode with respect to the potential of the reference electrode. An example potentiostat circuit which can be used to operate the electrochemical sensor of the present invention is shown in Figure 3. The reference electrode provides a standard voltage which, in a potentiostatic circuit, sets the working electrode operating potential. An important benefit of the invention is that this potentiostat circuit is a well-known standard, which can readily be optimised by one skilled in the art. Figure 4 illustrates a conventional modification which enables a bias potential to be applied between the working and reference electrodes. In Figures 3 and 4, IC1 and IC2 are Operational Amplifiers and Q1 is a depletion mode JFET. Application note AAN 105, available from Alphasense Limited (Great Dunmow, United Kingdom) discusses such circuitry in more depth.

In use, a potentiostat shown in figure 4 applies a potential difference (typically 300 mV) between the reference and working electrodes, with the resulting working electrode current being proportional to the concentration of nitric oxide up to over 2000ppm.

Figure 5 is a graph showing the resulting working electrode current response with time when the electrochemical gas sensor, with a bias voltage of 300mV, is brought into contact with 20ppm of nitric oxide. Clean air without nitric oxide is first passed over the sensor at 0.5 litre/minute flow rate for 5 minutes. Then a gas mixture of 20 ppm nitric oxide and balance nitrogen is passed over the sensor for 5 minutes, also at 0.5 litre/minute. Finally, clean air without nitric oxide is passed over the sensor at the same flow rate. The current generated by the working electrode is measured continuously.

Figure 6 is a graph showing the resulting working electrode current response with time when the electrochemical gas sensor, with a bias voltage of 900mV, is brought into contact with 25ppm ammonia. Clean air without ammonia is first passed over the sensor at 0.5 litre/minute flow rate for 5 minutes. Then a gas mixture of 25 ppm ammonia and balance air is passed over the sensor for 5 minutes, also at 0.5 litre/minute. Finally, clean air without ammonia is passed over the sensor at the same flow rate. The current generated by the working electrode is measured continuously.

Further alterations and modifications may be made within the scope of the invention herein disclosed.

Claims

1. A gas permeable electrode comprising an electrocatalyst which is permeable to a reactant or reaction product, the electrocatalyst comprising particulate boron-doped diamond.

2. An electrode according to claim 1 for catalysing a reaction in which either or both of a reactant or a reaction product is a gas, and the electrode further comprises gas diffusion means to enable a gas to penetrate or leave the electrode catalyst.

3. An electrode according to claim 1 or claim 2, wherein the gas diffusion means comprises a material which is permeable to gas but impermeable to electrolyte.

4. An electrode according to claim 3, wherein the gas diffusion means comprises a hydrophobic material, intimately mixed with the particulate boron-doped diamond, such that the resulting mixture of particulate boron-doped diamond and hydrophobic material is permeable to gas but impermeable to electrolyte.

5. An electrode according to claim 3 or claim 4, wherein the gas diffusion means comprises a particulate material which is permeable to gas but impermeable to electrolyte and which is mixed with the particulate boron-doped diamond.

6. An electrode according to any one of claims 3 to 5, wherein the gas diffusion means comprises a sheet or strand of material which supports the catalyst and hydrophobic material and is also permeable to gas but impermeable to electrolyte.

7. An electrode according to claim 3 wherein the gas diffusion means comprises a sheet or strand of material which is permeable to gas and impermeable to electrolyte, to which the particulate boron-doped diamond is bonded.

8. An electrode according to any one preceding claim, wherein the boron-doped diamond particles comprise diamond doped with between 10^{19} and 10^{21} boron atoms per cubic centimetre of solid.

9. An electrode according to claim 8, wherein the boron-doped diamond particles comprise diamond doped with the order of 10^{20} boron atoms per cubic centimetre.

10. An electrode according to any one preceding claim, wherein the boron-doped diamond particles are between 0.1 and 50 microns in diameter.

11. An electrochemical cell comprising a working electrode according to any one of claims 1 to 10.

12. An electrochemical gas sensor for sensing a gaseous analyte, comprising a working electrode according to any one of claims 1 to 10, wherein the electrocatalyst is permeable to the analyte.

13. A method of making an electrocatalyst which is permeable to a reactant or reaction product, the method comprising the step of forming an electrocatalyst comprising particulate boron-doped diamond.

14. A method according to claim 13, wherein particulate boron-doped diamond is obtainable by forming boron-doped diamond using chemical vapour deposition.

15. A method according to claim 14, wherein particulate boron-doped diamond is obtainable by using chemical vapour deposition to deposit a boron-doped diamond layer onto a substrate, releasing the later which is formed, and then grinding the resulting boron-doped diamond.

16. A method according to any one of claims 11 to 15, wherein the particulate boron-doped diamond is obtained by a high-pressure, high-temperature diamond formation technique and then ground.

17. A method according to any one of claims 11 to 16, wherein the particulate boron-doped diamond is brought into contact with gas diffusion means which is permeable to gas but impermeable to electrolyte.

18. A method according to claim 17 wherein the step of bringing the particulate boron-doped diamond into contact with gas diffusion means comprises the step of forming a layer

comprising the particulate boron-doped diamond on a sheet or strand of material which is permeable to gas but impermeable to electrolyte.

19. A method according to claim 17 or claim 18, wherein the step of bringing the particulate boron-doped diamond into contact with gas diffusion means comprises the step of intimately mixing the particulate boron-doped diamond with a hydrophobic material.

20. A method according to any one of claims 17 to 19, wherein the step of bringing the particulate boron-doped diamond into contact with gas diffusion means comprises the step of mixing the particulate boron-doped diamond with a particulate material which is permeable to gas but impermeable to electrolyte.

21. A method for making a gas permeable electrode comprising the steps of making an electrocatalyst according to any one of claims 13 to 18 and forming a gas permeable electrode comprising the electrocatalyst.

22. A method of making an electrochemical cell comprising the step of making a gas permeable electrode according to claim 21.

23. A method of making an electrochemical gas sensor, comprising the step of making a gas permeable working electrode according to claim 21.

Application No: GB0613155.1 **Examiner:** Mr Peter Mason

Claims searched: 1-12 and 21-23 **Date of search:** 29 November 2006

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X,E	1, 8-10, 12, and 21-23	WO 2005/090954 A1 (ELEMENT SIX B.V) See whole document, particularly note summary of the invention bridging pages 2 and 3.
X	1, 8-10, 12, and 21-23	WO 03/066930 A1 (ELEMENT SIX (PTY) LTD.) See whole document, particularly note composition of Example 1 on page 9.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

G01N

The following online and other databases have been used in the preparation of this search report

Online: EPODOC, WPI, selected English language full text patent databases.