

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 December 2007 (27.12.2007)

PCT

(10) International Publication Number
WO 2007/148085 A2

(51) International Patent Classification:
C25B 1/13 (2006.01) **C25B 11/04** (2006.01)

(21) International Application Number:
PCT/GB2007/002299

(22) International Filing Date: 19 June 2007 (19.06.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0612094.3 19 June 2006 (19.06.2006) GB

(71) Applicant (for all designated States except US): **CLARIZON LIMITED** [GB/GB]; Adaptive House, Quarrywood Court, Livingston, West Lothian, EH54 6AQ (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CHRISTENSEN, Paul, Andrew** [GB/GB]; 11 Copper Chare, Morpeth, Northumberland NE61 1BS (GB). **LIN, Wen, Feng** [GB/GB]; 141 Holystone Crescent, Newcastle-Upon-Tyne, NE7 7HA (GB).

(74) Agent: **KENNEDYS PATENT AGENCY LIMITED**; 185 St. Vincent Street, Glasgow G2 5QD (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

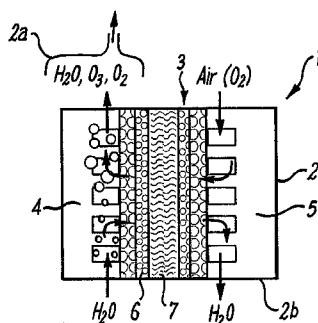
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

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.

(54) Title: ELECTRODE, METHOD OF MANUFACTURE AND USE THEREOF



(57) Abstract: An electrode for effective ozone production in an electrochemical cell by a modified electrode design which adopts a novel catalytic component. The catalytic component has a number of elements selected from various metals and metalloids, and is applied to a substrate in multiple coatings or layers. The catalytic component forms a catalytic surface which is at least partially disrupted by the presence of an element which is relatively inactive with respect to oxygen evolution.

WO 2007/148085 A2

1 Electrode, method of manufacture and use thereof

2
3 Technical Field

4
5 This invention relates to production of ozone at a higher
6 efficiency, and hence predictably at a lower cost, than
7 current technologies. The invention to be more
8 particularly described hereinafter involves use of a
9 catalyst in an electrochemical cell.

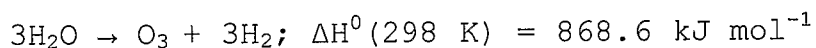
10
11 Background Art

12
13 The fact that ozone can be manufactured has been known
14 for a long time (c.f. Werner Von Siemens "Ozonizer" circa
15 1857-1858). The Siemens apparatus operated to produce an
16 electrical discharge as a "corona" or silent discharge.
17 Ozone has been commercially generated in air or oxygen by
18 means of such a corona discharge at a very high voltage
19 ever since then. However, there are concerns that this
20 technology is somewhat inefficient and rather costly in
21 today's market. It has been reported in US2003/209447 A1
22 that yields in the corona discharge process generally are
23 in the vicinity of 2% ozone, i.e. the exit gas may be

CONFIRMATION COPY

1 about 2% O₃ by weight. Obtaining this concentration
2 requires that the input gas is cold and dry and that the
3 system is cooled, typically with large quantities of cold
4 water. The concentration of O₃ in the exit gas can be
5 increased by using cold, dry, pure oxygen as the input
6 gas and O₃ concentrations in the exit gas of up to 12%
7 have been reported. However, this requires the supply or
8 production of the pure oxygen at extra cost and requiring
9 additional energy. Such O₃ concentrations, while quite
10 poor in an absolute sense, are still sufficiently high to
11 furnish usable quantities of O₃ for many commercial
12 purposes, which explains why the corona discharge
13 methodology has persisted commercially. Using pure
14 oxygen also overcomes another disadvantage of the corona
15 discharge process, which is that it oxidises any nitrogen
16 in the input gas to produce harmful nitrogen oxides (NO_x).
17 Thus, other than the aforementioned electric discharge
18 process, there is no other commercially exploited process
19 for producing large quantities of O₃.

20
21 Ozone may also be produced by an electrolytic process,
22 wherein an electric current (normally D.C.) is applied
23 across electrodes immersed in an electrolyte. The
24 electrolyte includes water, which in the process
25 dissociates into its respective elemental species, O₂ and
26 H₂. Under the proper conditions, the oxygen is also
27 evolved as the O₃ species. The evolution of O₃ may be
28 represented as:



31
32 Therefore, from a commercial standpoint, the known
33 electrolytic process may be viewed as thermodynamically

1 unfavourable in comparison with the established corona
2 discharge process.

3

4 Nevertheless, generation of ozone in aqueous media by
5 direct electrolysis is still a technically attractive
6 goal, particularly if dissolved ozone is needed (ozone is
7 poorly soluble in water).

8

9 There have been some proposals to develop the evolution
10 of ozone by electrolysis of various electrolytes
11 utilizing very low electrolyte temperatures, but a
12 discouragement to commercial exploitation of these
13 proposals is the need to maintain the necessary low
14 temperatures, requiring costly cooling equipment as well
15 as the attendant additional energy cost of operation.

16

17 There remain many commercial drivers towards successful
18 exploitation of electrolysis-based ozone production. The
19 efficient, electrochemical generation of ozone is
20 attractive due to the many uses of such a 'clean' and
21 powerful oxidant. Interest in this field increased
22 significantly in the 1980's, with increased focus on
23 water disinfection and detoxification.

24

25 The following patent publications are generally
26 indicative of background art describing prior proposals
27 to utilise electrolytic processes for ozone generation or
28 which produce ozone as a by-product.

29

30 US-A-3,256,164 (June 14, 1966), Donohue, John A., et al.
31 *Electrolytic Production of Ozone*. In this method of
32 producing ozone, an electric current is passed through a
33 liquid electrolyte, hydrogen fluoride containing not more

1 than 10 weight percent of water, to produce a mixture of
2 gases which contains ozone in large amounts. The
3 procedure is carried out at a temperature of not more
4 than 50 °C but preferably between -20 °C and +20 °C. At
5 least one weight percent of water must be present so that
6 the electric current may pass through the liquid hydrogen
7 fluoride and so that oxygen is present which may be
8 converted to ozone. However, hydrofluoric acid is avoided
9 in commercial systems due to the dangers it presents to
10 health.

11
12 US-A-4,316,782 (February 23, 1982) Foller, Peter C., et
13 al. *Electrolytic Process for the Production of Ozone*,
14 discusses an electrolytic cell for production of ozone
15 with current efficiencies of up to 52%. The cell uses a
16 solution of highly electronegative anions, preferably
17 hexafluoro-anions of phosphorus, arsenic, or silicon.
18 The anode is made of either platinum or lead dioxide, and
19 the cathode is made of platinum, nickel, or carbon. When
20 a direct current is applied using the electrodes, ozone
21 and oxygen are produced at the anode, and hydrogen gas is
22 produced at the cathode.

23
24 US-A-4,375,395 (March 1, 1983) Foller, Peter C., et al.
25 *Process for Producing Ozone*, describes an electrolytic
26 cell for production of ozone at high current efficiencies
27 which uses glassy carbon electrodes in an electrolytic
28 solution containing highly electronegative BF_4^- or BF_6^-
29 anions. These electrodes are resistant to corrosion by
30 the electrolytic fluorine-anion-containing solution used
31 to produce ozone at the anode. A disadvantage to this
32 method of production of ozone is that glassy carbon
33 electrodes are costly.

1
2 US-A-4,416,747 (November 22, 1983) Menth, Anton, et al.
3 *Process for the Synthetic Production of Ozone by*
4 *Electrolysis and Use Thereof*, outlines a process for
5 production of ozone by electrolysis in which the produced
6 ozone is used in water treatment. The anode and cathode
7 are made of stainless steel, and between the anode and
8 cathode is a solid electrolyte made of a plastic polymer
9 based on perfluorinated sulphonic acids. The solid
10 electrolyte serves as a thin ion-exchange membrane which
11 is coated on the cathode side with a layer of a mixture
12 of 85% by weight carbon powder and 15% by weight platinum
13 powder. The anode side of the membrane is coated with
14 PbO_2 powder. A solution of oxygen-saturated water is fed
15 into the cell, and ozone is produced in the solution on
16 the anode side of the solid electrolyte ion-exchange
17 membrane while water is formed on the cathode side. The
18 H^+ which is produced on the anode side by the
19 decomposition of water to form oxygen and ozone migrates
20 through the ion-exchange membrane and reacts with oxygen
21 in the water on the cathode side to form water. The
22 evolution of hydrogen at the cathode is thereby
23 suppressed.

24
25 US-A-4,541,989 (September 17, 1985) Foller, Peter C.
26 *Process and Device for the Generation of Ozone via the*
27 *Anodic Oxidation of Water* describes using an electrolytic
28 cell in which an air cathode reduces the oxygen in air to
29 water, and an inert anode decomposes the water to ozone
30 at claimed levels of ten pounds per day by electrolysis
31 using DC current.
32

1 US-A-5,154,895 (October 13, 1992) Moon, Jae-Duk. *Ozone*
2 *Generator in Liquids* suggests an ozone generator
3 consisting of one or more pairs of strip electrodes made
4 of an oxidation resistant metal such as Pt, PbO₂, or SnO₂
5 mounted on a substrate inside an ozonizing chamber with
6 outer terminals extending outside the ozonizing chamber.
7 The chamber has an inlet for a liquid such as water or
8 solutions of H₂SO₄, HClO₄, HBF₄, or H₃PO₄. An electric
9 current is supplied to the electrodes through the
10 terminals outside the chamber, and water molecules are
11 dissociated at the electrodes producing ozone gas in the
12 liquid without use of the conventional blower to supply
13 carrier air to the ozone generator.

14
15 US-A-5,203,972 (April 20, 1993) Shimamune, Takayuki, et
16 *al. Method for Electrolytic Ozone Generation and*
17 *Apparatus Therefor* describes an electrolytic cell wherein
18 the electrolyte separating the anode and cathode is a
19 solid electrolyte, preferably a perfluorocarbon sulfonic
20 acid-based ion-exchange membrane. The anode is made by
21 covering a titanium substrate first with a coat of
22 platinum, gold, or like metal, and then with an
23 electrodeposited layer of lead dioxide. When an electric
24 current is passed through the cell ozone is formed at the
25 anode in an ozone resistant chamber made of Teflon® or
26 titanium.

27
28 US-A-5,332,563 (July 26, 1994) Chang, Shih-Ger. *Yellow*
29 *Phosphorus Process to Convert Toxic Chemicals to Non-*
30 *Toxic Products* outlines a process which involves passing
31 air or oxygen over aqueous emulsions of yellow
32 phosphorus, P₄, which results in the formation of P₄O₁₀ or
33 P₂O₅, and an abundance of reactive species such as atomic

1 oxygen and ozone. This process is a development from the
2 disclosure of US-A-5,106,601 (April 21, 1992) which
3 outlines a method for removing acid-forming gases such as
4 NO and NO₂ from exhaust gases. Ozone is produced in the
5 process. In both cases production of P₄O₁₀ or P₂O₅ results
6 when the phosphorus combines with oxygen molecules and a
7 large amount of atomic oxygen is detected in area of the
8 reaction. The atomic oxygen may combine with oxygen
9 molecules to form ozone.

10
11 US-A-5,460,705 (October 24, 1995) Murphy, Oliver J., et
12 *al. Method and Apparatus for Electrochemical Production*
13 *of Ozone* describes an electrochemical method and
14 apparatus for production of ozone which uses an anode
15 made up of a substrate made from porous titanium,
16 titanium sub-oxides, platinum, tungsten, tantalum,
17 hafnium, niobium, or similar material, and a catalyst
18 coating selected from lead dioxide, platinum-tungsten
19 alloys, glassy carbon or platinum. The cathode is a gas
20 diffusion cathode consisting of a
21 polytetrafluoroethylene-bonded, semi-hydrophobic catalyst
22 layer supported by a hydrophobic gas diffusion layer.
23 The catalyst layer consists of a proton exchange polymer,
24 polytetrafluoroethylene polymer, and a metal such as
25 platinum, palladium, gold, iridium, or nickel. The anode
26 and cathode are separated by an ion-conducting
27 electrolyte which is a proton exchange membrane (PEM)
28 with one side bonded to the catalyst layer of the gas
29 diffusion cathode and a second side touching the anode.
30 An electric current is passed through the anode and the
31 gas diffusion cathode, and ozone is formed at the anode.

32

An international patent application, WO 2004/072329 (26 August 2004) Cheng, S., et al, *Device for and Method of Generating Ozone* describes an electrode made from a substrate selected from titanium, gold-coated titanium, and other inert conducting materials, with a coating of tin dioxide modified by antimony. The coating may also include nickel. The coating may comprise particles of from 3 nm to 5 nm in size and in a ratio of Sn:Sb in the range of from about 6:1 to 10:1. Multiple coatings may be applied to the substrate, e.g. by dip-coating and heat treatment steps. The electrode is suitable for direct generation of ozone in water or through water into a gaseous state.

The use of the electrode is described in a cell containing an electrolyte which may comprise $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and SbCl_3 in an ethanol-HCl mixture, or which may simply utilize pure water without any dissolved ions. An optional alternative system comprises a solid polymer electrolyte, such as Nafion®.

Whilst this system represents a significant improvement over previous proposals, there remains room for improvement in certain aspects. In particular, the lifetime of the catalyst in prototype systems developed following this patent has been found to be limited to a few days to weeks at best and the innovations presented in this patent result in even higher efficiencies.

Ozone (O_3) is a very strong oxidising agent which has many uses, including those shown in Table 1 below.

Water Treatment	Bottled water and beverages	Taste and odour improvement
------------------------	-----------------------------	-----------------------------

	Mains drinking water Water reuse and recycling Contaminant reduction	Pools and spas By-product reduction for chemical disinfection
Waste Treatment	Effluent and wastewater treatment Ground water remediation Suspended solids reduction Activated sludges	Soil remediation and treatment Ship ballast water Air conditioning recirculating water Power station cooling water
Food Treatment	Disinfection Sterilisation Deodorisation	Preservation Storage Grain treatment
Bleaching	Paper Synthetic fibres Teflon	Waxes Flour
Decontamination and disinfection	Hospitals	Infectious agent removal

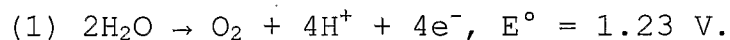
Table 1: Some applications for generated Ozone

Chlorine-based products are used for many of these purposes, but they can, in some circumstances, lead to the production of carcinogens such as trihalomethanes and chloramines. Chlorine can be unpleasant to users (e.g. in swimming pools) and can directly contaminate the environment. For example, chlorine-based products are banned from use as a bleaching agent in pulp and paper mills in a number of countries - its use in this field

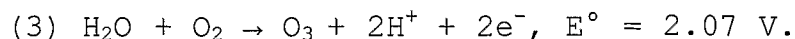
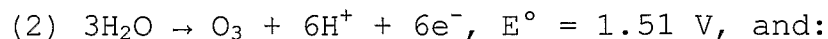
1 has fallen from 7% to 1% of total chlorine usage in the
2 US. Chlorine plays a major role in the above markets,
3 which consumed around 20% of total chlorine supply in the
4 US in 2002 (12.5M tons at \$230 per ton = \$2.9 bn).

5
6 Ozone is a safe alternative to treatment by chlorine or
7 chlorine-based products. It performs the same functions
8 without the undesirable side effects; it is not harmful
9 to the environment since it rapidly decomposes into
10 oxygen, O₂.

11
12 The electrochemical generation of ozone depends
13 critically on the proper choice of electrode material and
14 catalyst. Using conventional anodes, such as Pt, and
15 imposing a sufficiently positive potential on the
16 electrode immersed in aqueous solution will, under normal
17 circumstances, result in the generation of oxygen,
18 according to:



21
22 Ozone generation relies on suppressing this reaction
23 (e.g. by producing an anode with a "high oxygen
24 overvoltage") such that ozone can then be produced in
25 preference thus:



30
31 An advantage of this strategy is that any loss in current
32 efficiency for ozone generation will mostly lead to the

1 production of harmless oxygen which, in many cases, can
2 actually be useful.

3

4 The water oxidation reaction, equation (1), can be
5 suppressed by careful catalyst design and/or through the
6 choice of experimental conditions, both of which directly
7 influence the intermediate species which determine which
8 of steps (1) - (3) above can take place.

9

10 A number of anodes have been investigated with respect to
11 furthering research into realising a commercially useful
12 method for electrochemical ozone generation:

13

14 Pt, α -PbO₂, β -PbO₂, Pd, Au, dimensionally stable RuO₂
15 anodes (RuO₂DSA), doped diamond, and glassy carbon (GC) in
16 various electrolytes and under a range of experimental
17 conditions. Au, RuO₂DSA and GC anodes all yield current
18 efficiencies of < 1%.

19

20 The state-of-the-art with regard to development of
21 electrochemical technologies is represented by the work
22 of Putnam et al [G. L. Putnam et al, J. Electrochem.
23 Soc., 93 (1948) 211]; Foller and Tobias [P.C.Foller,
24 C.W.Tobias, J.Electrochem.Soc., 129 (1982) 506]; Cheng et
25 al, [WO 2004/072329 A1 (August 26, 2004)] and Murphy and
26 Hitchens [US-A-5,460,705 (October 24, 1995)].

27

28 An object of the present invention is to provide
29 improvements in the production of ozone and in particular
30 to develop an electrochemical process suitable for
31 commercialisation.

32

33 **Disclosure of Invention**

1
2 The invention to be more particularly described
3 hereinafter achieves effective ozone production in an
4 electrochemical cell by a modified electrode design which
5 adopts a novel catalytic component. The catalyst
6 suppresses oxygen evolution and promotes ozone production
7 by selection of particular elements which are
8 incorporated in the catalytic component to favourably
9 modify the performance of the catalyst towards the goal
10 of ozone generation. In addition, the innovations
11 dramatically increase the active lifetime of the
12 catalyst. The modified catalyst can be incorporated in an
13 electrode structure, e.g. supported upon a catalyst
14 substrate, carrier element or assembly, of a generally
15 known type but prepared in a unique way according to the
16 invention.

17
18 According to a first aspect of the invention there is
19 provided an electrode for use in an electrochemical cell
20 comprising a catalytic component applied to a substrate,
21 the catalytic component comprising a number of elements
22 selected from the group consisting of metals and
23 metalloids, and the catalytic component is applied to the
24 substrate in multiple coatings or layers, and the
25 catalytic component forming a catalytic surface being at
26 least partially disrupted by the presence of an element
27 which is relatively inactive with respect to oxygen
28 evolution in normal use of the electrode.

29
30 The electrode preferably comprises multiple coating
31 layers of catalytic component within which there is
32 preferably at least one inter-layer of a composition
33 differing from the other coating layers, e.g. one which

1 comprises Sn:Sb in the ratio 100:10. Such an inter-layer
2 may be electro-deposited.

3

4 In particular, the invention offers improvements for
5 ozone production in an electrochemical cell by adopting a
6 dimensionally stable anode which is relatively inactive
7 towards the oxidation of water to O₂, and includes at
8 least one additional element which promotes production of
9 ozone.

10

11 The anode may comprise Sb-doped SnO₂ (or Sb₂O₅/SnO₂)
12 together with an additional element selected from the
13 group consisting of metals and / or metalloids that are
14 relatively inactive with respect to oxygen evolution,
15 preferably at least one of Au, Fe, Co, Pb, and optionally
16 including a transition metal. An example of a metal
17 which is not suitable as the primary or sole additional
18 element for the purposes of this invention is Pt due to
19 its activity in oxygen evolution, but it is observed that
20 presence of Pt may offer structural advantages to promote
21 anode useful working life. A suitable ozone-promoting
22 additional element may be selected by comparing its
23 activity in oxygen evolution with Pt, those elements
24 which have significantly less activity with respect to
25 oxygen evolution than Pt being preferred. Therefore, it
26 must be understood that the presence of Pt is not
27 excluded, provided that at least one of the preferred
28 ozone-promoting additional elements is sufficiently
29 included.

30

31 The catalyst elements can be selected from the group
32 consisting of Sn, Sb, Fe, Co, Ni, Au, and Pb each in an
33 appropriate state of oxidation.

1

2 The catalyst can contain Sn, and other elements are
3 selected from a first group consisting of Sb, and Pt, and
4 also from a second group consisting of Fe, Co, Ni, Au,
5 and Pb.

6

7 Preferably the catalyst contains Sn, and at least one
8 other element is Sb, and at least one other element is
9 selected from the group consisting of Fe, Co, Ni, Au, and
10 Pb.

11

12 The catalyst can comprise a major proportion of Sn and
13 lesser amounts of Sb, a transition element and Au.

14

15 Optionally, the catalyst can comprise a major proportion
16 of Sn and lesser amounts of Sb, a transition element and
17 Pb.

18

19 Alternatively, the catalyst can comprise a major
20 proportion of Sn and lesser amounts of Sb, and at least
21 one of the transition elements Fe, Co and Ni.

22

23 The catalyst component and other elements can comprise
24 Sn:Sb:Ni:Au, in the approximate atomic/molar ratio
25 1000:16:2:0.5 to 1000:16:2:20 in an alcohol solution.

26

27 The catalyst component and other elements can comprise
28 Sn:Sb:Ni:Au, in the approximate atomic/molar ratio of
29 1000:16:2:6 to 1000:16:2:4 in an alcohol solution.

30

31 The catalyst component and other elements can comprise
32 Sn:Sb:Ni:Au, in the approximate atomic/molar ratio of
33 1000:16:2:6 in an alcohol solution.

1

2 The catalytic component can be applied in layers to the
3 substrate, and at least one inter-layer within the
4 catalytic component can comprise Sn:Sb, in the
5 approximate atomic/molar ratio 100:1 to 100:20.

6

7 The catalytic component can be applied in layers to the
8 substrate, and at least one inter-layer within the
9 catalytic component can comprise Sn:Sb, in the
10 approximate atomic/molar ratio 100:10. Furthermore, the
11 interlayer can be electro-deposited.

12

13 According to a second aspect of the present invention
14 there is provided an electrochemical cell comprising a
15 first electrode including a catalyst, the catalyst
16 composed of an antimony-doped tin composition including
17 at least one of the following elements Au, Pb, Fe, Co,
18 and Ni, a counter electrode, first and second chambers
19 for receiving electrolyte and/or water, said chambers
20 being divided by a separator or membrane, and a casing
21 for the cell, at least part of which casing is adapted to
22 collect gases.

23

24 Optionally the first electrode forms the anode located in
25 a first chamber in the cell, and the first chamber
26 contains an electrolyte in contact with the anode which
27 comprises an acid and/or water, and the counter electrode
28 forms the cathode in a second chamber in the cell, and
29 the electrolyte in contact with the cathode comprises an
30 acid and/or water.

31

32 The anode and cathode can both be in close contact with
33 the two sides of a proton exchange membrane (forming a

1 membrane electrode assembly), and, in this case, air or
2 oxygen can be in contact with the cathode, as
3 alternatives to an acid and/or water.
4

5 According to a third aspect of the present invention
6 there is provided a catalytic component for use in an
7 electrochemical cell for ozone production comprising a
8 substrate upon which a catalyst is supported, the
9 catalyst consisting of an antimony-doped tin composition
10 containing at least one additional element selected from
11 Au, Pb, Fe, Ni, and Co.
12

13 The catalyst can be applied in multiple layers, at least
14 one of which layers may have a composition differing from
15 the other layers.
16

17 A surface layer of the catalyst may present Au as an
18 element embedded in the surface.
19

20 Alternatively, a surface layer of the catalyst presents
21 Pb as an element embedded in the surface.
22

23 A surface layer of the catalyst may present Fe as an
24 element embedded in the surface.
25

26 Alternatively a surface layer of the catalyst may present
27 Co as an element embedded in the surface.
28

29 Preferably at least one layer comprising tin catalyst and
30 antimony, which is substantially free of any other active
31 element, is included as an interlayer in the catalytic
32 coating.
33

1 Optionally substantially all of the catalytic layers
2 include Ni.

3

4 The catalyst applied to the substrate may be derived from
5 a coating solution in which the atomic/mole ratio of the
6 elements tin: antimony: nickel: gold is 1000:16:2:6.

7

8 At least one layer comprising tin and antimony can be
9 derived from a coating solution in which the atomic/mole
10 ratio of the elements tin: antimony is 100:10.

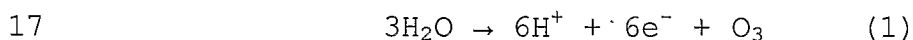
11

12 Modes for Carrying Out the Invention

13

14 The following reactions at the anode of this invention
15 are contemplated:

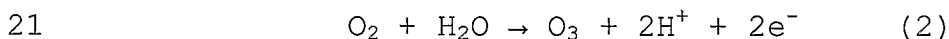
16



18

19 Or, more efficiently:

20



22

23 A conventional structure for the electrode may be adopted
24 e.g. forming a carrier substrate for the doped catalytic
25 electrode surface. A titanium mesh may be suitable for
26 this purpose, but another inert material, even a ceramic,
27 may be useful as the core for the active surface of the
28 electrode. It will be understood that the functional
29 catalytic layer of doped surface material may be applied
30 as multiple coating layers or depositions to provide a
31 suitable coverage over the carrier substrate, e.g. 20
32 such layers or depositions may offer a commercially
33 durable anode. A minimum or maximum level is not

1 specified but a sufficient amount must be applied to
2 provide a functional anode coating over the carrier
3 substrate, and this can be readily determined by simple
4 trial experimentation with the materials.

5
6 The type of catalyst which is currently considered
7 suitable for performance of the invention is one such as
8 that described in WO 2004/072329, which teaches an anode
9 electrocatalyst (based on an empirical composition
10 Ni:Sb:Sn 1:8:500, requiring connected nanoparticles with
11 a size [diameter] distribution in the range 3-5 nm) has,
12 to date resulted in (for a limited period) a current
13 efficiency for ozone generation of over 36% at room
14 temperature, corresponding to 34 mg L⁻¹ of dissolved
15 ozone. This is the highest current efficiency that the
16 inventor's are aware of for the electrocatalytic
17 generation of ozone in an aqueous medium at room
18 temperature. Initially, upon start-up, ozone generation
19 efficiency can be in excess of 80%, but after a period of
20 use this level typically falls to from 30% to 35%. Such
21 catalysts are, however, found to fail after a period of
22 operation and it is an objective of this invention to
23 overcome such failure.

24
25 Such a catalyst is surface modified to achieve the
26 benefits obtainable by the invention to be more fully
27 described herein. Valuable modification include use of
28 Au or Pb as additional surface elements to promote ozone
29 production whilst avoiding enhanced oxygen production,
30 and inclusion of an interlayer within the catalyst layers
31 to improve operational life and performance. Typically,
32 the surface of the modified catalyst is smoother than the

1 unmodified catalyst, with particle sizes in the range of
2 5 nm to 20nm.

3
4 Typically, an apparatus for producing ozone will comprise
5 a multi-compartment electrochemical cell, the
6 compartments defining at least a cathode chamber and an
7 anode chamber, said chambers being divided by at least
8 one separator, and each including an electrode, wherein
9 at least one chamber receives an electrode of the
10 aforementioned type according to the invention.

11
12 The apparatus may comprise a membrane divided cell. In
13 such a cell the anodic chamber(s) and the cathodic
14 chamber(s) are divided by a membrane which may be a
15 proton-exchange membrane (PEM), and the electrodes are
16 positioned in an operational functional position close
17 to, but usually not in contact with the
18 separator/membrane. Specifically, if the electrolyte is
19 acidic then the electrodes and membrane need not be in
20 contact. However, if the electrolyte is water then the
21 closer the electrodes are to the membrane the better, due
22 to resistance. Finally, when the electrolyte is air or
23 oxygen then the electrodes and membrane must be in
24 contact.

25
26 In an embodiment of the invention, a series of chambers
27 is arranged in a "battery" of cells wherein alternating
28 chambers include an electrode for generating ozone, or an
29 electrode for generating hydrogen. Appropriate ducting
30 is provided with separators to direct evolved gases to
31 collectors.

32

1 The anode and cathode chambers may be divided one from
2 the other by a membrane assembly comprising a proton
3 exchange membrane in close contact with catalytic
4 material (for example, on the surface of an electrode,
5 embedded in a paste electrode or suspended in a carbon
6 granular electrode), and arranged within the chambers to
7 contact fluids introduced to the cell chambers in use.

8 The proton exchange membrane is not permeable to gas. A
9 fluid and gas permeable material is preferably arranged
10 to overlie the catalytic coating. The fluid and gas
11 permeable material may be a porous metal.

12
13 The cell may comprise a casing adapted to snap-fit around
14 the separator assembly and incorporate fluid seals
15 therebetween. Alternatively, corresponding casing parts
16 may be presented about the separator assembly, suitable
17 seals to avoid fluid-leakage are introduced, and the
18 casing parts closed using fastening means, e.g. rivets,
19 adhesive, welds, or threaded fasteners. The fastening
20 means may compress the seals, which may be custom gaskets
21 or O-rings depending upon the configuration of the casing
22 parts. Obviously, the person skilled in the art will
23 understand that care should be taken to select materials
24 resistant to ozone for the chamber housing the anode
25 where ozone is to be generated. Proprietary materials
26 such as the fluorinated polymers VITON®, KYNAR and
27 TEFLON®, may be useful for surfaces liable to contact
28 ozone, and NYLON fasteners may be suitable with such
29 materials.

30
31 In the method according to the invention, a cell
32 analogous to that of the typical fuel cell design is
33 adapted to generate ozone electrochemically by passing a

1 current through a particular membrane assembly, by means
2 of electrodes arranged on either side of the membrane,
3 the electrodes respectively being in contact with an
4 electrolyte or water, and air, oxygen, water, or an
5 electrolyte. Ozone and oxygen are generated around the
6 electrode in contact with the electrolyte/water and
7 protons pass through the membrane. The protons combine
8 to form hydrogen at the second electrode if it is in
9 contact with an electrolyte or water, or to form water if
10 it is in contact with oxygen or air. Use of a particular
11 catalyst in the membrane assembly allows superior
12 performance over that anticipated for other
13 electrochemical methods of producing ozone.

14
15 **Brief Description of Drawings**

16
17 The invention will now be described by way of
18 illustrative example with reference to the accompanying
19 drawings, in which:

20
21 Figure 1 is a schematic sectional view through an
22 electrochemical cell suitable for performance of the
23 invention;

24
25 Figure 2 is a schematic sectional view of an embodiment
26 of electrode plate design;

27
28 Figure 3 is a graph illustrating performance of a test
29 embodiment of the invention in terms of current
30 efficiency and absorbance; and

31
32 Figure 4 is a graph that compares the solution phase
33 ozone generated by a commercial PbO_2 cell with that

1 generated by an Au doped anode electrode of the present
2 invention in a glass PEM cell.

3

4 **Example**

5

6 In an embodiment of the invention, a catalytic component
7 is prepared for use in an electrode, using a titanium
8 mesh substrate cleaned with oxalic acid. An intermediate
9 electro-deposited (ED) coating of Sn:Sb (100:10) in an
10 alcohol solution is applied to form an ED interlayer.
11 Catalytic coatings are then applied sequentially to
12 gradually build up a stable coating, each coating being
13 heat treated at 500°C to 600°C. Perhaps 20 or so coatings
14 are needed depending upon the technique applied. The
15 composition of the coatings is based upon Sn:Sb:Ni:Au in
16 an approximate atomic/mole ratio of between 1000:16:2:0.5
17 to 1000:16:2:20 in an alcohol solution. The composition
18 of the coatings can be based upon Sn:Sb:Ni:Au in an
19 approximate atomic/mole ratio of 1000:16:2:6 to
20 1000:16:2:4 in an alcohol solution. The composition of
21 the coatings is advantageously based upon Sn:Sb:Ni:Au in
22 an approximate atomic/mole ratio of 1000:16:2:6 in an
23 alcohol solution. The elements are each in an
24 appropriate oxidation state.

25

26 Finishing of the coated substrate to render it suitable
27 for use as an electrode is carried out using conventional
28 techniques using for example conductive connectors e.g.
29 titanium wire and or conductive plate. This forms the
30 basis for a dimensionally stable anode (DSA).

31

32 A production cell **1** for producing ozone using the DSA
33 comprises inert walls **2** and a base **2b** defining a

1 container for electrolyte and configured to receive a
2 separator **3** to define therein a plurality of chambers **4**,
3 **5**, alternate ones of which receive the DSA **6**. The cell
4 is covered by a manifold **2a** adapted to collect and convey
5 gases away from the cell. The manifold has provision for
6 attachment of electrical connections (not shown). Cells
7 may be connected in parallel within a common casing. The
8 materials chosen are ozone resistant e.g. fluorocarbon
9 based structural and sealing components. Fluid
10 connections (not shown) for adding electrolyte, water,
11 etc. are provided. The connections provide for flow-
12 through to facilitate a continuous or extended batch run
13 process.

14
15 The separator is an assembly of components including a
16 proton-exchange membrane (PEM) **7**, and gaskets **8** for
17 sealing and spacing purposes. Provision is made for
18 completing the assembly with conductive plate components
19 **9**. Configuration of the plates is such as to partially
20 envelope the PEM to assist with positioning and assembly.
21 The PEM and associated gaskets act as the electrical
22 insulator between the conductive plate components which
23 serve as electrodes.

24
25 The assembled cell may be oriented in any position, and
26 connected to fluids supply.

27
28 In use of the cell, a nominal voltage of 2.7 V is applied
29 for a chosen time period, and evolved gases (O₃ and H₂)
30 are collected separately. During one test (40 days)
31 current and absorbance (OD) were monitored. The current
32 was maintained above 0.09 A. Figure 3 is representative
33 of the results of the test.

1
2 Illustrated in Figure 4 is a graph that compares data for
3 ozone production by a standard lead dioxide (PbO_2)
4 electrode and by an electrode according to the present
5 invention (WEXIIIED-Au), both operating at 2.7V and in
6 the same conditions. It is clear from Figure 4 that the
7 electrode of the present invention acts to generate a
8 greater volume of ozone over a shorter timescale than
9 electrodes known to the art. In particular, Figure 4
10 illustrates that the electrode of the present invention
11 will advantageously produce ozone at a significantly
12 lower current than that necessary for electrodes of the
13 prior art (0.3 A for the present invention versus 1.1 A
14 for PbO_2). Therefore if, for example, the PbO_2 electrode
15 is operating at a typical current efficiency of 1 - 10%,
16 then the electrodes of the present invention are clearly
17 vastly superior to those known to the art.

18
19 In addition to the data provided in Figure 4, the outcome
20 of a range of tests (not reported here) suggests that the
21 catalyst, electrode, and cell made available by the
22 invention described herein represent a significant step
23 forward in electrolytic methods of ozone production.

24 25 Industrial Applicability

26
27 The invention finds utility in a wide range of fields,
28 including potable water management, food production,
29 waste treatment, hygiene and health care, raw material
30 processing, and environment management.
31 Improvements and modifications may be incorporated herein
32 without deviating from the scope of the invention.

CLAIMS

1. An electrode for use in an electrochemical cell, said electrode comprising a catalytic component applied to a substrate, the catalytic component comprising a number of elements selected from the group consisting of metals and metalloids, and the catalytic component being applied to the substrate in multiple coatings or layers, and the catalytic component forming a catalytic surface being at least partially disrupted by the presence of an element which is relatively inactive with respect to oxygen evolution in normal use of the electrode.
2. An electrode as claimed in claim 1 wherein the multiple coating layers of catalytic component comprise at least one inter-layer of a composition differing from the other coating layers.
3. An electrode as claimed in claims 1 or 2 wherein at least one inter-layer within the catalytic component comprises Sn:Sb, in the approximate atomic/molar ratio 100:1 to 100:20.
4. An electrode as claimed in claim 3 wherein at least one inter-layer within the catalytic component comprises Sn:Sb, in the approximate atomic/molar ratio 100:10.
5. An electrode as claimed in any preceding claim wherein the inter-layer is electro-deposited.

- 1 6. An electrode as claimed in any preceding claim
2 wherein the electrode comprises Sb-doped SnO_2 .
3
- 4 7. An electrode as claimed in any preceding claim
5 wherein the electrode comprises Sb_2O_5 and SnO_2 .
6
- 7 8. An electrode as claimed in any preceding claim
8 wherein the elements which are relatively inactive
9 with respect to oxygen evolution are at least one of
10 Au, Fe, Co, and Pb.
11
- 12 9. An electrode as claimed in any preceding claim
13 wherein the electrode further comprises a transition
14 metal.
15
- 16 10. An electrode as claimed in any preceding claim
17 wherein the elements of the catalytic component are
18 selected from the group consisting of Sn, Sb, Fe,
19 Co, Ni, Au, and Pb each in an appropriate state of
20 oxidation.
21
- 22 11. An electrode as claimed in claims 1 to 9 wherein the
23 catalytic component contains Sn, and other elements
24 are selected from a first group consisting of Sb,
25 and Pt, and also from a second group consisting of
26 Fe, Co, Ni, Au, and Pb.
27
- 28 12. An electrode as claimed in claims 1 to 9 wherein the
29 catalytic component contains Sn, and at least one
30 other element is Sb, and at least one other element
31 is selected from the group consisting of Fe, Co, Ni,
32 Au, and Pb.
33

1 13. An electrode as claimed in claims 9 to 12 wherein
2 the catalytic component comprises a major proportion
3 of Sn and lesser amounts of Sb, a transition element
4 and Au.

5

6 14. An electrode as claimed in claims 9 to 13 wherein
7 the catalytic component comprises a major proportion
8 of Sn and lesser amounts of Sb, a transition element
9 and Pb.

10

11 15. An electrode as claimed in claims 9 to 14 wherein
12 the catalytic component comprises a major proportion
13 of Sn and lesser amounts of Sb, and at least one of
14 the transition elements Fe, Co and Ni.

15

16 16. An electrode as claimed in claim 13 wherein the
17 catalytic component and other elements comprises
18 Sn:Sb:Ni:Au, in the approximate atomic/molar ratio
19 1000:16:2:0.5 to 1000:16:2:20.

20

21 17. An electrode as claimed in claim 13 wherein the
22 catalytic component and other elements comprises
23 Sn:Sb:Ni:Au, in the approximate atomic/molar ratio
24 of 1000:16:2:6 to 1000:16:2:4.

25

26 18. An electrode as claimed in claim 13 wherein the
27 catalytic component and other elements comprises
28 Sn:Sb:Ni:Au, in the approximate atomic/molar ratio
29 of 1000:16:2:6.

30

31 19. An electrode as claimed in claims 16 to 18 wherein
32 the catalytic component and other elements are
33 applied in a coating solution.

1

2 20. An electrode as claimed in claim 19 where the
3 coating solution is an alcohol solution.

4

5 21. An electrochemical cell comprising a first electrode
6 including a catalyst, the catalyst composed of an
7 antimony-doped tin composition including at least
8 one of the following elements Au, Pb, Fe, Co, and
9 Ni, a counter electrode, first and second chambers
10 for receiving electrolyte and/or water, said
11 chambers being divided by a separator or membrane,
12 and a casing for the cell, at least part of which
13 casing is adapted to collect gases.

14

15 22. An electrochemical cell as claimed in claim 21
16 wherein the first electrode forms the anode located
17 in a first chamber in the cell, and the first
18 chamber contains an electrolyte in contact with the
19 anode which comprises an acid and/or water, and the
20 counter electrode forms the cathode in a second
21 chamber in the cell, and the electrolyte in contact
22 with the cathode comprises an acid and/or water.

23

24 23. An electrochemical cell as claimed in claim 22
25 wherein the anode is the electrode described in
26 claims 1 to 20.

27

28 24. A catalytic component for use in an electrochemical
29 cell for ozone production comprising a substrate
30 upon which a catalyst is supported, the catalyst
31 consisting of an antimony-doped tin composition
32 containing at least one additional element selected
33 from Au, Pb, Fe, Ni, and Co.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32

25. A catalytic component as claimed in claim 24 wherein the catalyst is applied in multiple layers, at least one of which layers has a composition differing from the other layers.
26. A catalytic component as claimed in claim 25 wherein the differing layer comprises tin and antimony, is substantially free of any other active element, and is included as an inter-layer in the catalytic coating.
27. A catalytic component as claimed in claims 24 to 26 wherein a surface layer of the catalyst may present Au as an element embedded in the surface.
28. A catalytic component as claimed in claims 24 to 27 wherein a surface layer of the catalyst presents Pb as an element embedded in the surface.
29. A catalytic component as claimed in claims 24 to 28 wherein a surface layer of the catalyst presents Fe as an element embedded in the surface.
30. A catalytic component as claimed in claims 24 to 29 wherein a surface layer of the catalyst presents Co as an element embedded in the surface.
31. A catalytic component as claimed in claims 24 to 30 wherein substantially all of the catalytic layers include Ni.

- 1 32. A catalytic component as claimed in claims 24 to 31
2 wherein the substrate is derived from a coating
3 solution in which the atomic/mole ratio of the
4 elements tin: antimony: nickel: gold is 1000:16:2:6.
5
- 6 33. A catalytic component as claimed in claims 24 to 32
7 wherein at least one layer comprising tin and
8 antimony is derived from a coating solution in which
9 the atomic/mole ratio of the elements tin: antimony
10 is 100:10.

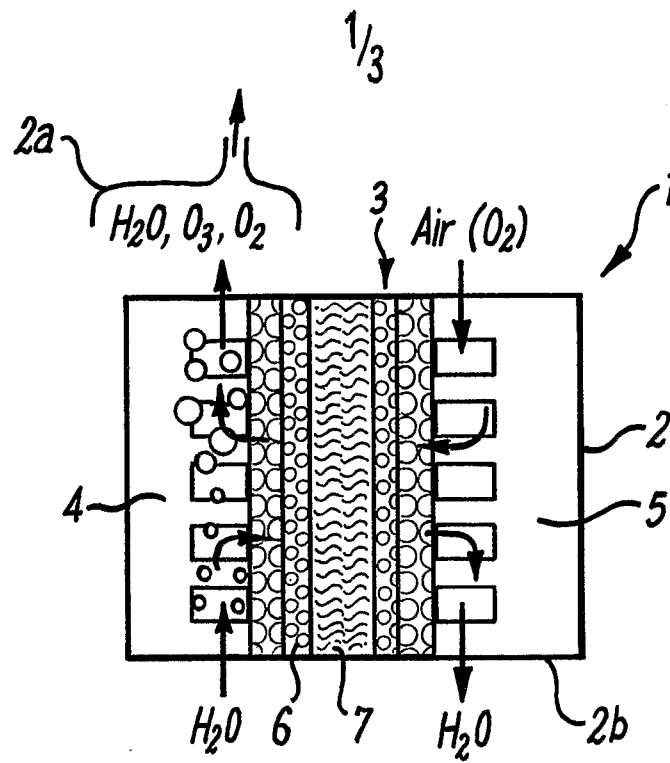
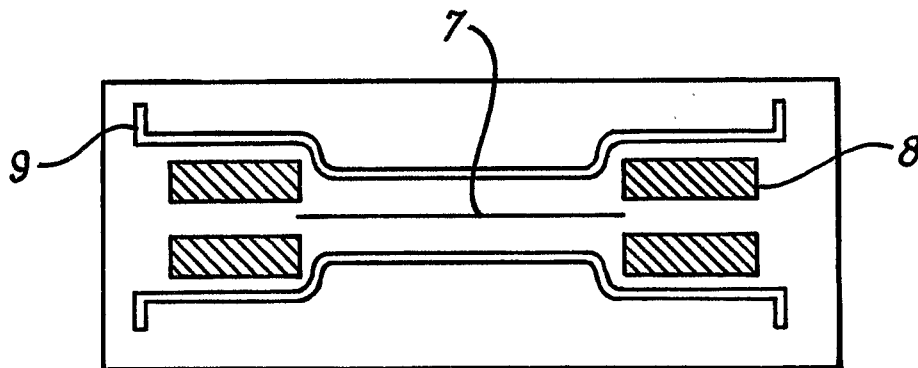
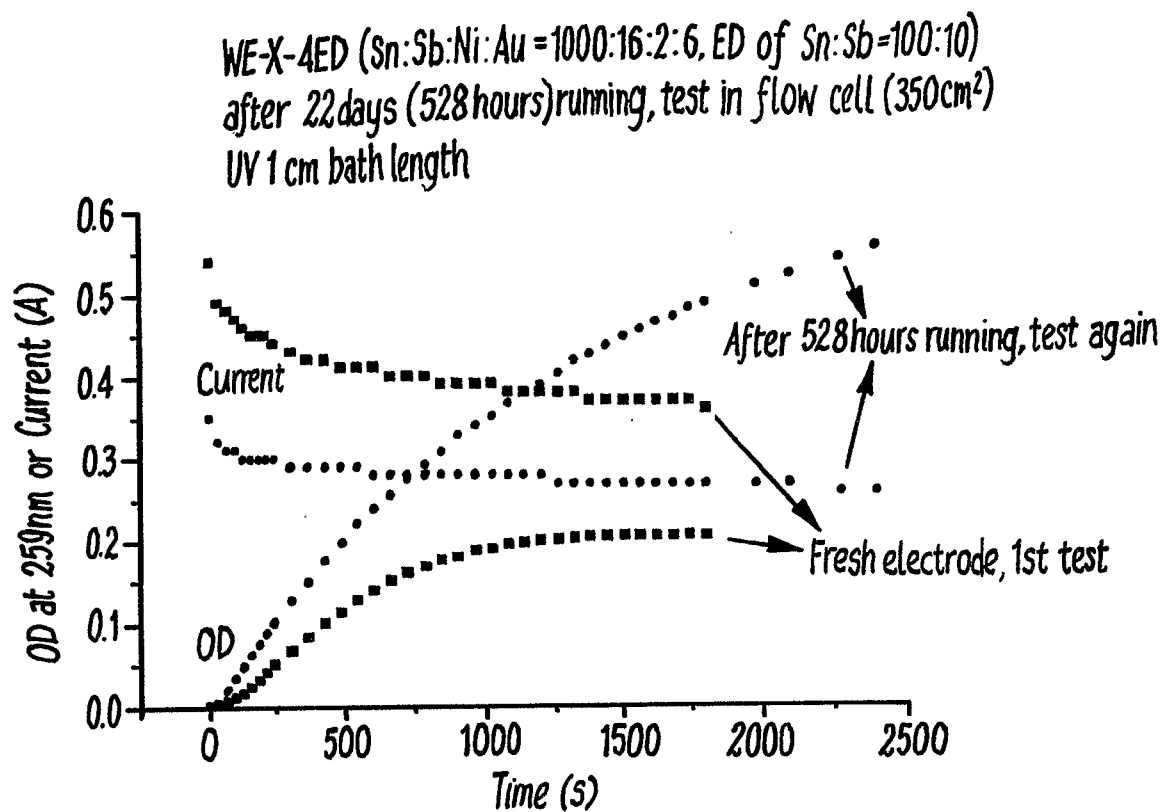


Fig. 1



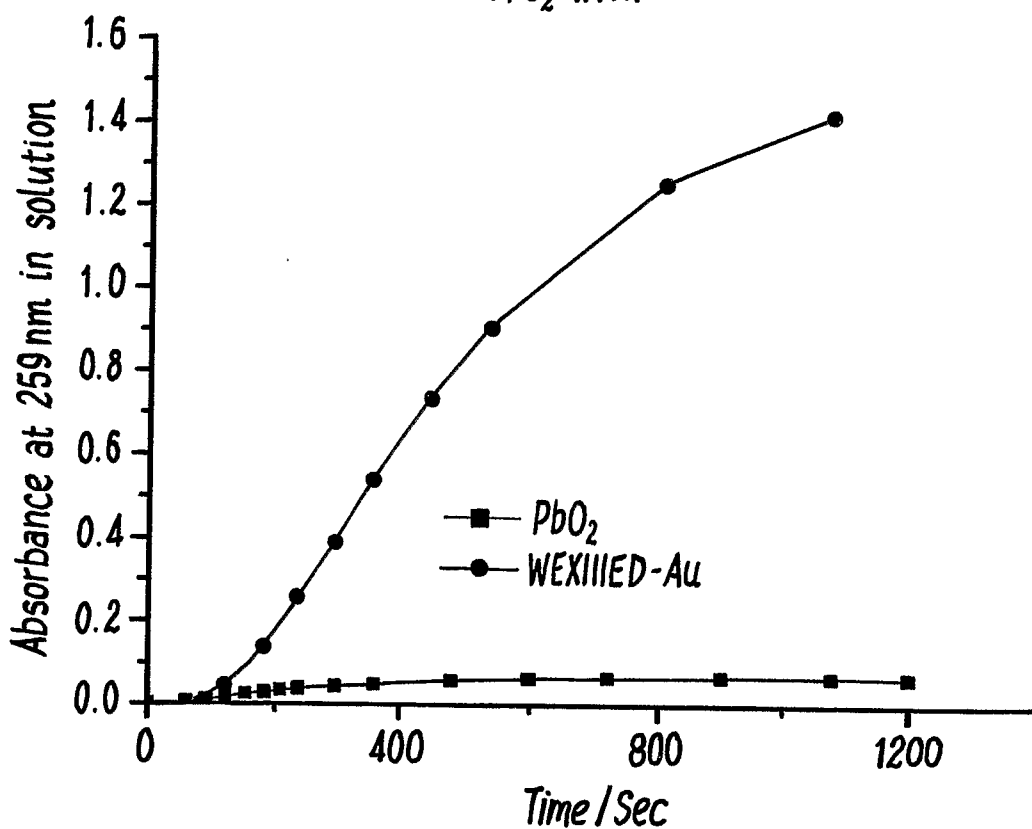
File 2

2/3

**FIG. 3**

3/3

Comparison of PbO_2 data (9May06) with run 3 WEXIIED-Au (14June 06)
2.7 V vs CE, PbO_2 anolyte ca. 50cm^3 0.1M H_2SO_4 , WEXIIED-Au 100cm^3
0.5M H_2SO_4 ; WEXIIED-Au, glass PEM cell. Average current WEXIIED 0.3A,
 PbO_2 1.1A.

**Fig. 4**