

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
26 August 2004 (26.08.2004)

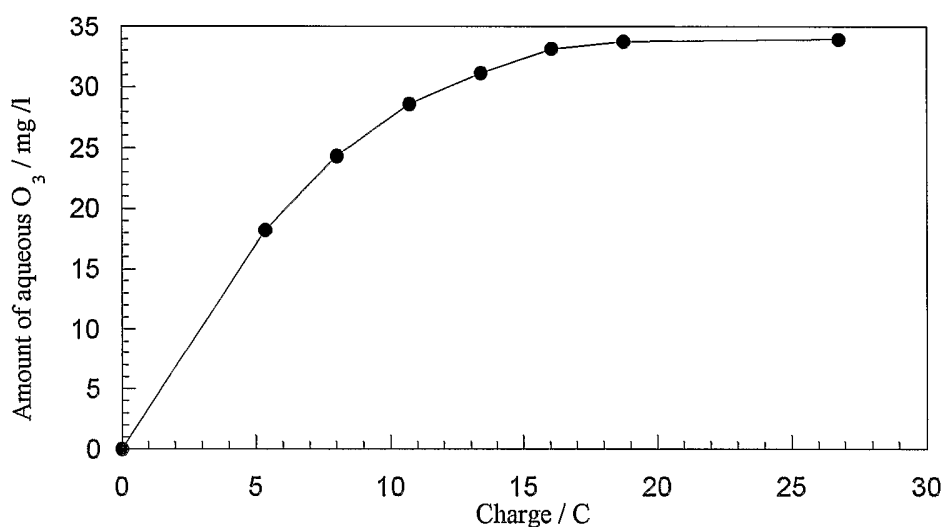
PCT

(10) International Publication Number
WO 2004/072329 A1

- (51) International Patent Classification⁷: C25B 11/04, [CN/CN]; Room 712, Nam Wai House, Nam Shan Estate, Kowloon, Hong Kong (CN).
1/13, 9/00
- (21) International Application Number: PCT/CN2004/000120
- (22) International Filing Date: 13 February 2004 (13.02.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/447,948 14 February 2003 (14.02.2003) US
- (71) Applicant (for all designated States except US): THE UNIVERSITY OF HONG KONG [CN/CN]; G18, Eliot Hall, Pokfulam Road, Hong Kong (CN).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): CHENG, Shaoan [CN/CN]; Room 321, Block 75, Qioshichun, Hangzhou 310027 (CN). CHAN, Kwongyu [CN/CN]; 15A, Block 1, 23 Sha Wan Drive, Hong Kong (CN). FUNG, Waikit
- (74) Agent: CHINA PATENT AGENT (H.K.) Ltd.; 22/F, Great Eagle Centre, 23 Harbour Road, Wanchai, Hong Kong (CN).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, 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, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: DEVICE FOR AND METHOD OF GENERATING OZONE



(57) Abstract: The present invention can provide an electrode member having a substrate member and a coating member. The substrate member can be made of a material selected from the group consisting of titanium, gold coated titanium and other inert conducting materials. The coating member can have a tin dioxide modified by antimony. The electrode member of the present invention can be used for direct generation of ozone in water or through water into a gaseous state.

WO 2004/072329 A1



Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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.

DEVICE FOR AND METHOD OF GENERATING OZONE**RELATED PATENT APPLICATION**

This patent application claims the benefit of U.S. Provisional Application No. 60/447,948 filed November 10, 2003.

5 **FIELD OF THE INVENTION**

The present invention relates generally to the generation of ozone. In particular, the present invention relates to an electrode material for generating ozone and a method of making the electrode material. The present invention also relates to a high concentration of dissolved ozone and an ozone generation system for generating the same.

10**BACKGROUND OF THE INVENTION**

Ozone has many industrial applications, such as destructing organic and inorganic contaminants in wastewater and sludge, households disinfectants, swimming pools and hospitals, bleaching paper, etching semiconductor surfaces, decolorizing water, removing odor from clothing, and terminating pests. [See, Bruno Langlais, David A. Reckhow, Deborah R. Brink; Ozone in Water Treatment application and Engineering, Lewis Publishers, INC. 1991, and references discussed therein.] Chlorination is commonly used in similar applications but will leave undesirable chlorinated organic residues. Ozone on the other hand will self disappear in time and leaves fewer potentially harmful residues.

15
20

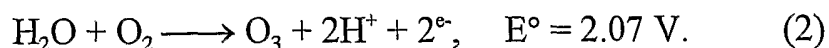
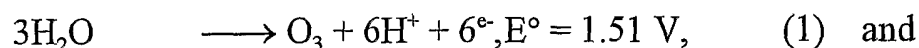
There are two main types of technologies to produce ozone. The first type of technology involves the corona discharge process, wherein ozone is formed from oxygen in air by the corona discharge in an intense and high frequency alternating electric field. This type of technology gives low

25

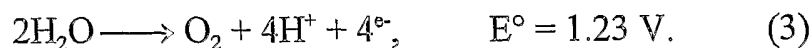
ozone concentration (about 2% to oxygen) and can produce harmful nitrogen oxides. The generation of ozone is in the gas phase and to obtain dissolved ozone, the gaseous ozone is brought into contact with water and the amount of dissolved ozone is limited by the gas phase ozone
5 concentration and the solubility.

The other type of ozone generation technology is an electrochemical and electrolytic process, wherein water is decomposed to ozone by passing an electric current through the electrodes immersed in an aqueous electrolyte. Since ozone is generated directly in water, this process can
10 provide high concentration of ozone at a high current efficiency. Over 35% current efficiency has been reported at low temperatures of -30°C to -65°C [see, P.C. Foller, C.W. Tobias, J. Electrochem. Soc., 129 (1982), 506]. A recent report discussed a 3.0 mg/l concentration of dissolved ozone [see, Tatapudi and Fenton, J. Electrochem. Soc., 140 (1993) 3527].

15 In aqueous solution, ozone is formed by electrolytic decomposition of water, represented by following equations:



The oxygen evolution reaction, a competitive process at a lower potential
20 should occur more easily according to the following equation:



Platinum, alpha and beta-PbO₂, Pd, Au, RuO₂-DSA's, and glassy carbon in different electrolytes have been considered and tested for ozone generation. Gold, RuO₂-DSA's, and glassy carbon have been found to
25 have very low current efficiency (less 1%). Platinum shows a current efficiency from 6.5% to 35% at very low temperature of about -50°C.

However the current efficiency falls to around 0.5% at room temperature. Obtaining a high current efficiency at a low temperature will require additional equipment and energy cost to make existing systems less efficient and convenient. PbO₂ electrodes can produce ozone at a current efficiency of 13% at room temperature. However, such a process releases toxic Pb ions into electrolyte solution.

Tin dioxide, a non-toxic semiconductor, has been studied for applications in sensors, batteries and oxygen evolution. Low current efficiency and instability had been reported when such tin dioxide was used for electrochemically generating ozone in concentrated sulfuric acid.

SUMMARY OF THE INVENTION

The present invention can provide an electrode member. The electrode member can comprise a substrate member and a coating member. The substrate member can be made of a material selected from the group consisting of titanium, gold coated titanium and other inert conducting materials. The coating member can comprise a tin dioxide modified by antimony. The particles of Sn and Sb can be in an atomic ratio from about 6:1 to about 10:1. Additionally or alternatively, a predetermined amount of nickel can be added in the coating member. The coating member can comprise particles from about 3 nm to about 5nm in size.

The electrode member of the present invention can be used for direct generation of ozone in water or through water into a gaseous state. The water can contain an electrolyte selected from the group consisting of HClO₄, H₂SO₄ and H₃PO₄. The electrolyte can be present in a concentration from about 0.01 M to about 0.5 M.

The present invention can also provide an ozone generation system comprising such an electrode member to generate ozone efficiently. The ozone generation system can comprise a solid polymer electrolyte, such as Nafion. Alternative, ozone can be generated in pure water, without the need of dissolved ions. The present invention can further provide a dissolved ozone with a high concentration.

BRIEF DESCRIPTION OF THE DRAWINGS

The detailed description of the present invention will be better understood in conjunction with the accompanying drawings, wherein like reference characters represent like elements, as follows:

Fig. 1 is a SEM surface morphology of an antimony doped SnO_2 electrode member of the present invention;

Fig. 2 is a graph illustrating the aqueous ozone concentration as a function of electric charge; and

Fig. 3 is a graph illustrating the instantaneous aqueous ozone concentration as a function of scan potential.

DETAILED DESCRIPTION OF THE INVENTION

Exemplary electrode members and ozone generation systems embodying the principles of the present invention will now be described in detail. In the following description of various embodiments of electrode members and ozone generation system, similar elements or components thereof are designated with reference numbers having the same last two digits; redundant description is omitted.

The present invention can provide an electrode member. The electrode member can comprise a substrate member and a coating member.

In one exemplary embodiment, the substrate member can be made of a material selected from the group consisting of titanium, gold coated titanium and other inert conducting materials. For example, the substrate member is made of titanium. In an exemplary embodiment, the substrate member can be made of titanium and be spot-welded with a titanium wire. It will be appreciated that other materials of the substrate member are also within the scope of the present invention.

The coating member can be made of various materials and in various forms. In one exemplary embodiment, the coating member can comprise a tin dioxide. In an exemplary embodiment, the coating member can comprise an antimony modified tin dioxide film. For example, the coating member can comprise $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and SbCl_3 . In another exemplary embodiment, the coating member can comprise a predetermined amount of nickel. In one exemplary embodiment, the coating member can be in the form of a solution, before being affixed onto the substrate member. It will be appreciated that other materials and forms of the coating member are also within the scope of the present invention.

In another exemplary embodiment, the coating member can comprise particles of various sizes. For example, the coating member can comprise connected particles of less than 5 nm in size. In one exemplary embodiment, the connected particles can be from about 3 nm to about 5 nm in size. It will be appreciated that other sizes of the particles are also within the scope of the present invention.

In a further exemplary embodiment, the coating member can comprise particles of various ratios. In an exemplary embodiment, the particles of oxides of Sn and Sb can have an atomic ratio of more than 6:1. In another exemplary embodiment, the particles of oxides of Sn and Sb particles can have an atomic ratio of less than 10:1. In a further exemplary

embodiment, the particles of Sb and Ni can be in an atomic ratio of more than 4:1. In a still further exemplary embodiment, the particles of Sb and Ni can be in an atomic ratio of less than 10:1. It will be appreciated that other ratios of the particles are also within the scope of the present invention.

In a preferred embodiment, the electrode member can be made of titanium and coated with antimony doped tin dioxide with surface morphology composed of 3 to 5 nm particles connected and covering substantially the entire surface. In another preferred embodiment, the particles comprise Sn and Sb in a ratio from about 6:1 to about 10:1. In a further preferred embodiment, the atomic ratio of Sn:Sb:Ni can be about 500:8:1. The electrode member can yield high concentration of dissolved ozone at room temperature with high current efficiency.

The electrode member can be prepared in various manners. In one exemplary embodiment, a substrate member and a coating member of various forms can be provided, which can be similar to those described above. If desired, the substrate member can be treated or otherwise prepared by various conventional methods. For example, the substrate member can be etch cleaned in an acid solution and then rinsed and dried. It will be appreciated that other methods of treating or preparing the substrate member are also within the scope of the present invention.

The substrate member can be affixed with the coating member in various manners. For example, the substrate member can be sprayed with, dipped into, or otherwise coated with the coating member. In an exemplary embodiment, the coating member can be sprayed with solution of 2.5 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.025g SbCl_3 in 25 ml of ethanol-HCl mixture. In an exemplary embodiment, the coating member can be dipped into 25 ml ethanol-HCl mixture solution of 2.75 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.025g SbCl_3 .

It will be appreciated that other methods of affixing the coating member to the substrate member are also within the scope of the present invention.

The coated substrate member can then be heat treated in various manners. In one exemplary embodiment, the coated substrate member can be dried, such as at a temperature of about 100°C for about ten minutes. In another exemplary embodiment, the coated substrate member can be calcined, such as at a temperature of about 520°C in air for 5 mins. The above coating, drying, and calcining steps can be repeated. In an exemplary embodiment, these steps can be repeat for 12 times. In another exemplary embodiment, these steps can be repeat for 20 times. It will be appreciated that other heating methods including heating temperatures and/or time periods are also within the scope of the present invention.

The present invention can also provide a high concentration ozone material. In one exemplary embodiment, approximately 35 mg/l aqueous ozone can be provided with over 15% current efficiency. In an exemplary embodiment, the 15% current efficiency only accounts for the dissolved ozone. In a preferred embodiment, such an aqueous ozone can be generated in a 6 min constant potential polarization at low electrolyte concentration at room temperate. In another exemplary embodiment, a significant amount of gaseous ozone can be generated and distinctly detected by the normal smell test. The measurement of gaseous ozone can show a much high current efficiency. The solution with dissolved ozone can decolorize a dye such as indigo instantly. High overpotential of oxygen evolution was observed in cyclic voltammetry.

Various systems can be used to generate a high concentration ozone material. In one exemplary embodiment of the present invention, an ozone generation system can be in the form of an electrochemical system for generating the high concentration ozone material. In an exemplary

embodiment, the electrochemical system can comprise a cell member for containing an electrolyte material of various forms. For example, the electrolyte material can comprise $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and SbCl_3 in an ethanol-HCl mixture. In another exemplary embodiment, ozone can be generated in pure water, without the need of dissolved ions. It will be appreciated that various other types of ozone generation systems are also within the scope of the present invention.

In one exemplary embodiment, the ozone generation system can adopt the electrode member of the present invention for generating the high concentration ozone. In an exemplary embodiment, the electrode member can be used as a working electrode. For example, the electrode member can be used as an anode member in a electrochemical system. In another exemplary embodiment, the electrode member can be positioned on the bottom of the cell member. In a further exemplary embodiment, a constant potential can be applied to the electrode member, such as at room temperature. The constant potential can range from 1.5V to 3V with respect to a reference electrode. In an exemplary embodiment, the constant potential can be about 2.5V. It will be appreciated that various other forms of the ozone generation system are also within the scope of the present invention.

The present invention will now be describe in further detail in connection with the various Examples below.

Example 1

A $0.8 \times 0.8 \times 0.05 \text{ cm}^3$ titanium (Ti) sheet member spot-welded with a 1 mm dia. titanium wire was first etch cleaned in a 10% boiled oxalic acid solution for 1 hour, then rinsed with distilled water and dried. An antimony doped SnO_2 electrode member was prepared by a spray pyrolysis

technique on the pretreated Ti substrate member. The spray solution was 2.5 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.025g SbCl_3 in 25 ml of ethanol-HCl mixture. After drying the sprayed substrate member at 100°C for 10 min, the substrate member was calcined at 520°C in air for about 5 min. This treatment was repeated 12 times. The resulting electrode member showed a compact smooth surface morphology with connected particles having a diameter of about 3 to 5 nm (see Fig. 1). The atomic ratio of Sn to Sb in the film is about 7:1 by ICP analysis.

Ozone was generated in a cell with 3 ml 0.1 M HClO_4 . The prepared doped SnO_2 electrode member was used as a working electrode member positioned on the bottom of the cell. A 0.8 cm^2 platinum sheet was used as a counter electrode member positioned at the up-region of the electrolyte. An Ag/AgCl member was used as a reference electrode member and positioned closer to the working electrode member. A constant potential (vs. the Ag/AgCl member) of 2.5V was applied to the working electrode member at room temperature. About 35 g/l of ozone dissolved in the electrolyte was generated in about 6 min. (see Fig. 2). The ozone concentration was determined by UV absorption as well as a standard indigo method.

20 Example 2

An antimony doped SnO_2 electrode was prepared by dipping a Ti substrate with the same area as described in Example 1 into 25 ml ethanol-HCl mixture solution of 2.75 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.025g SbCl_3 . Before drying the dipped the Ti substrate at 100°C, excess solution on the substrate surface was removed to leave a thin uniform liquid layer on the substrate surface. The substrate member was calcined at about 520°C. The time periods for drying and calcining were the same as in Example 1. The above process was repeated 30 times. The surface morphology of the

resulting electrode was similar to that shown in Fig. 1. The ratio of Sn to Sb in the film is about 10:1 by ICP analysis.

Ozone was generated using the same system as in Example 1. SnO₂ electrode was performed by cyclic voltammetry in a potential ranging from 1.5 V to 3 V (vs. the Ag/AgCl member) at the scan rate of 1 mV/s at room temperature. Fig. 3 shows the ozone generated against scan potential.

Example 3

A solution of 1 molar SnCl₄·5H₂O, 0.016 molar SbCl₃, and 0.002 molar NiCl₂·6H₂O in absolute ethanol was used as the coating solution. A titanium sheet can be coated in the same manner by dip coating and pyrolysis, as described in Example 1. The coating and pyrolysis was repeated 7 times. The resulting Ni-Sb doped SnO₂ coated electrode member was tested to give better ozone generation. The current efficiency can reached more than 25% at room temperature using 0.1 molar perchloric acid electrolyte and with applied electric potential of 2.2 V (vs. the Ag/AgCl member). The ozone generation and measurement was the same as described in Example 1.

It will be appreciated that the various features described herein may be used singly or in any combination thereof. Therefore, the present invention is not limited to only the embodiments specifically described herein. While the foregoing description and drawings represent a preferred embodiment of the present invention, it will be understood that various additions, modifications, and substitutions may be made therein without departing from the spirit of the present invention. In particular, it will be clear to those skilled in the art that the present invention may be embodied in other specific forms, structures, arrangements, proportions, and with other elements, materials, and components, without departing

from the spirit or essential characteristics thereof. One skilled in the art will appreciate that the invention may be used with many modifications of structure, arrangement, proportions, materials, and components and otherwise, used in the practice of the invention, which are particularly
5 adapted to specific environments and operative requirements without departing from the principles of the present invention. The presently disclosed embodiments are therefore to be considered in all respects as illustrative and not restrictive.

WHAT IS CLAIMED IS:

1. An electrode member, comprising a substrate member and an antimony modified tin dioxide film coating member,
wherein the coating member comprises connected particles from about
5 3 nm to about 5 nm in size, and
wherein the particles comprise Sn and Sb in a ratio from about 6:1 to about 10:1.
2. The electrode member according to claim 1, wherein the substrate member is made of a material selected from the group consisting of
10 titanium, gold coated titanium and other inert conducting materials.
3. The electrode member according to claim 1, wherein the substrate member is made of titanium.
4. The electrode member according to claim 3, wherein the substrate member is spot-welded with a titanium wire.
- 15 5. An electrode member comprising a substrate member and a coating member, wherein the coating member comprises a tin dioxide modified by antimony.
6. The electrode member according to claim 5, wherein the coating member comprises connected particles of less than 5 nm in size.
- 20 7. The electrode member according to claim 6, wherein the connected particles are from about 3 nm to about 5 nm in size.
8. The electrode member according to claim 5, wherein the coating member comprises connected particles of Sn and Sb.

9. The electrode member according to claim 8, wherein the Sn and Sb are in an atomic ratio of more than 6:1.
10. The electrode member according to claim 8, wherein the Sn and Sb are in an atomic ratio of less than 10:1.
- 5 11. The electrode member according to claim 5, wherein the coating member comprises nickel.
12. The electrode member according to claim 11, wherein the Sb and Ni are in an atomic ratio of less than 10:1.
13. The electrode member according to claim 11, wherein the Sb and
10 Ni are in an atomic ratio of more than 4:1.
14. A method of making an electrode member for use in generating ozone, comprising:
- providing a substrate member comprising an inert conducting material;
- 15 providing a coating member comprising an antimony modified tin dioxide;
- affixing the substrate member with the coating member;
- drying the coated substrate member at about 100°C for about ten
minutes;
- 20 calcining the coated substrate member at about 520°C;
- repeating the above coating, drying, and calcining steps.
15. The method according to claim 14, wherein the coating member comprises $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and SbCl_3 in an ethanol-HCl mixture.

16. A method of generating ozone using the electrode member made according to claim 1, comprising:

using the electrode member as a working electrode;

5 applying a constant potential to the electrode member at room temperature;

wherein the ozone generated is dissolved in an electrolyte.

17. The method of claim 16, wherein the constant potential to the electrode member applied to the electrode member ranges from about 1.5V to about 3.0V.

10 18. A use of the electrode according to claim 1 for direct generation of ozone in water or through water into a gaseous state.

19. The use of the electrode according to claim 18 for electrochemical generation of ozone at a concentration of electrolyte from about 0.01 M to about 0.5 M.

15 20. The use of the electrode according to claim 19, wherein the electrolyte is selected from the group consisting of HClO_4 , H_2SO_4 and H_3PO_4 .

21. An ozone generation system comprising an electrode according to claim 1 for electrochemical generation of ozone.

20 22. The ozone generation system according to claim 21, further comprising a solid polymer electrolyte.

23. The ozone generation system according to claim 22, wherein the solid polymer electrolyte is Nafion.

24. An ozone material comprising approximately 35 mg/l aqueous ozone with over 15% current efficiency.
25. The ozone material according to claim 24, wherein the 15% current efficiency only accounts for the dissolved ozone.
- 5 26. The ozone material according to claim 24, wherein the aqueous ozone is generated in a 6 min constant potential polarization at low electrolyte concentration at room temperate.

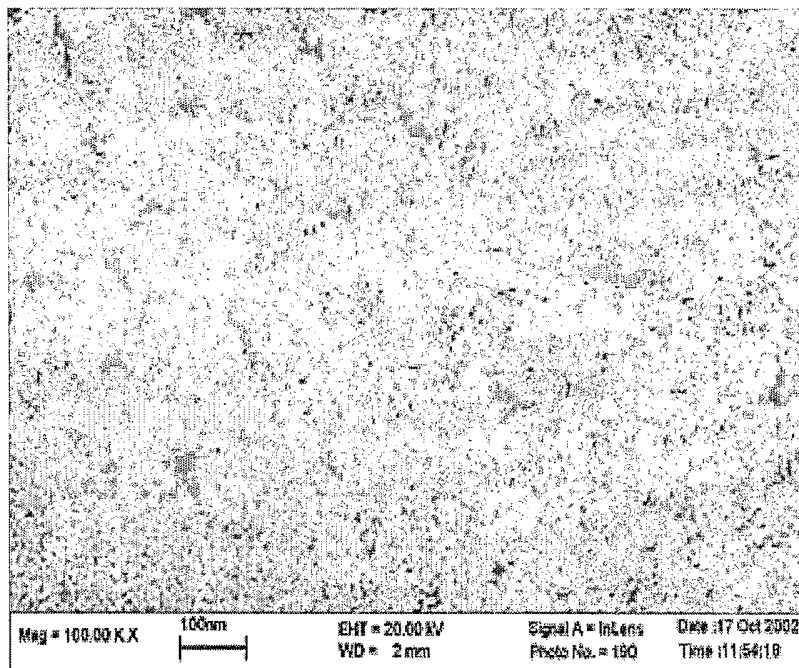


FIG. 1

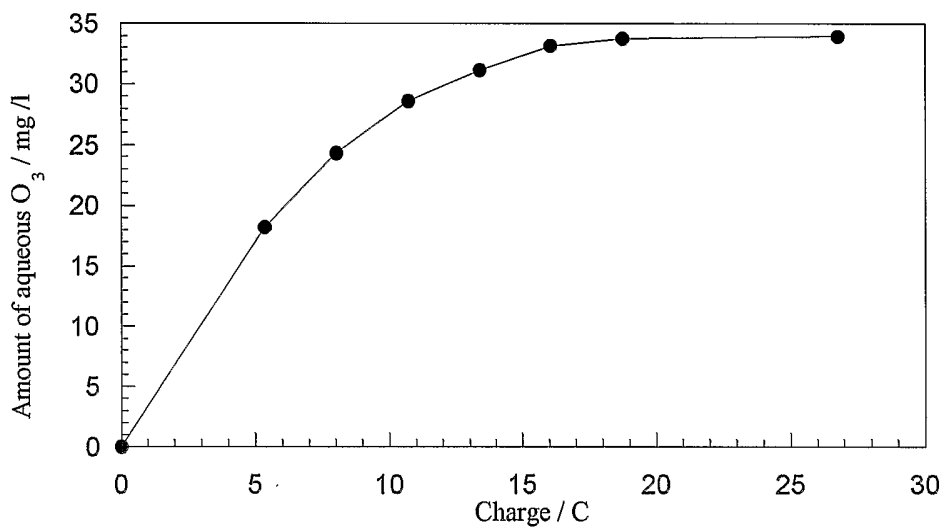


FIG. 2

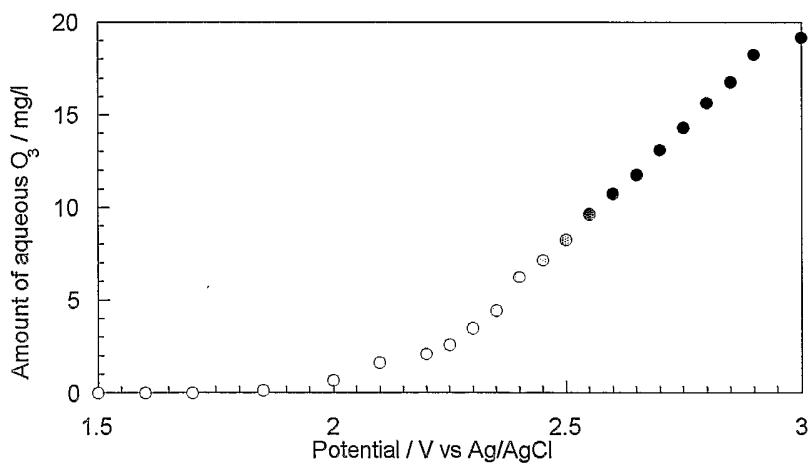


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2004/000120

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C25B 11/04, 1/13, 9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

IPC 7 C25B11, C25B1, C25B9, C02F1, C01B13, G01N27

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI EPODOC PAJ CNPAT CNKI tin oxide, tin dioxide, SnO₂, Sb, antimony, ozone, O₃, electrode, titanium, Ti

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US4839007A(published on 13 June 1989, by BBC BROWN BOVERI & CIE AG) see column 2 line 47-54, examples, and claims 1-9.	5-9, 14, 15
A	JP11221570A(published on 17 Aug. 1999, by MATSUSHITA ELECTRIC IND CO LTD) see column 5 line25- column 6 line 3, column 6 line 40- column 8 line 38, column 9 line 36- column 12 line 30, figs. 1-4, and claims 1-9.	1-15
A	JP2001300561A(published on 30 Oct. 2001, by SHIODA HIROICHI) see column 4 line 30- column 16 line 17, figs. 1-3, and claims 1-7.	1-23

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“A” document defining the general state of the art which is not considered to be of particular relevance	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“E” earlier application or patent but published on or after the international filing date	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	“&” document member of the same patent family
“O” document referring to an oral disclosure, use, exhibition or other means	
“P” document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
17 May 2004(17. 05. 2004)

Date of mailing of the international search report
10 · JUN 2004 (10 · 06 · 2004)

Name and mailing address of the ISA/CN
6 Xitucheng Rd., Jimen Bridge, Haidian District,
100088 Beijing, China
Facsimile No. 86-10-62019451

Authorized officer
ZHOU, Quan
Telephone No. 86-10-62084687



INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2004/000120

Patent document cited in search report	Publication date	patent family members	Publication date
US4839007A	1989-06-13	EP0280926A JP63221888A CH671408A	1988-09-07 1988-09-14 1989-08-31
JP11221570A	1999-08-17	NONE	
JP2001300561A	2001-10-30	NONE	