

Office de la Propriété Intellectuelle du Canada

Un organisme d'Industrie Canada Canadian Intellectual Property Office

An agency of Industry Canada

CA 2377796 A1 2001/01/11

(21) 2 377 796

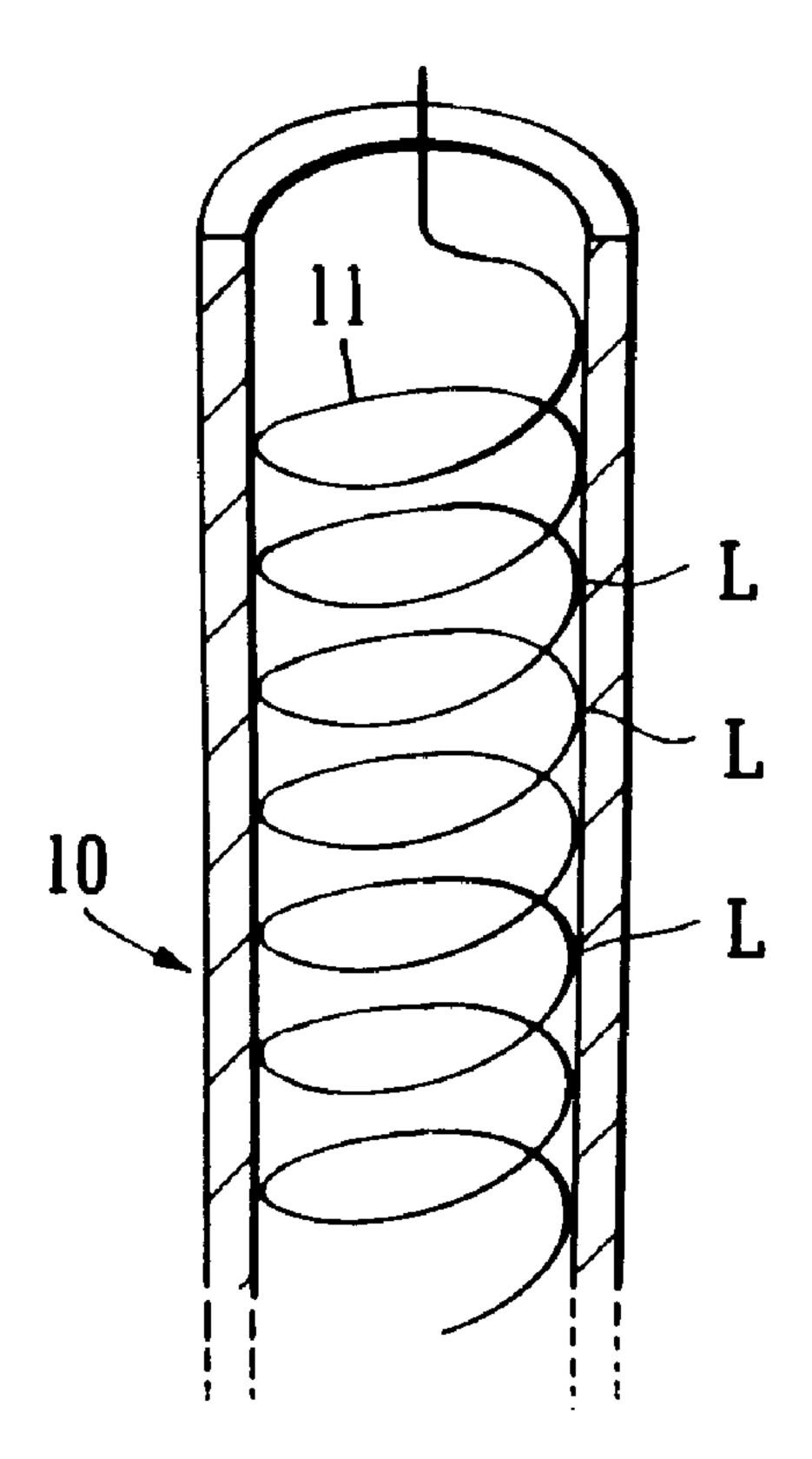
(12) DEMANDE DE BREVET CANADIEN CANADIAN PATENT APPLICATION

(13) **A1**

- (86) Date de dépôt PCT/PCT Filing Date: 2000/07/03
- (87) Date publication PCT/PCT Publication Date: 2001/01/11
- (85) Entrée phase nationale/National Entry: 2001/12/31
- (86) N° demande PCT/PCT Application No.: GB 2000/002553
- (87) N° publication PCT/PCT Publication No.: 2001/002626
- (30) Priorités/Priorities: 1999/07/01 (9915420.5) GB;
 - 1999/07/20 (9917015.1) GB

- (51) Cl.Int.⁷/Int.Cl.⁷ C25B 9/04, C02F 1/461
- (71) Demandeur/Applicant: ATRAVERDA LIMITED, GB
- (72) Inventeur/Inventor: HILL, ANDREW, GB
- (74) Agent: ROBIC

(54) Titre: ELECTRODE (54) Title: ELECTRODE



(57) Abrégé/Abstract:

An electrode comprises an elongate hollow tube (5) made of porous titanium suboxide the inside wall of which is contacted at spaced apart locations by an electrical conductor (11, 12) so that the current is substantially uniformly distributed along the length of the electrode.





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

(19) World Intellectual Property Organization International Bureau





(43) International Publication Date 11 January 2001 (11.01.2001)

PCT

(10) International Publication Number WO 01/02626 A1

(51) International Patent Classification⁷: C02F 1/461

C25B 9/04,

(21) International Application Number: PCT/GB00/02553

(22) International Filing Date: 3 July 2000 (03.07.2000)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

9915420.5 9917015.1 1 July 1999 (01.07.1999) GB 20 July 1999 (20.07.1999) GB

(71) Applicant (for all designated States except US):
ATRAVERDA LIMITED [GB/GB]; 11B Stephenson
Road, Speedwell Industrial Estate, Staveley, Derbyshire
S43 3JN (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): HILL, Andrew [GB/GB]; Atraverda Limited, 11B Stephenson Road, Speedwell Industrial Estate, Staveley, Derbyshire S43 3JN (GB).

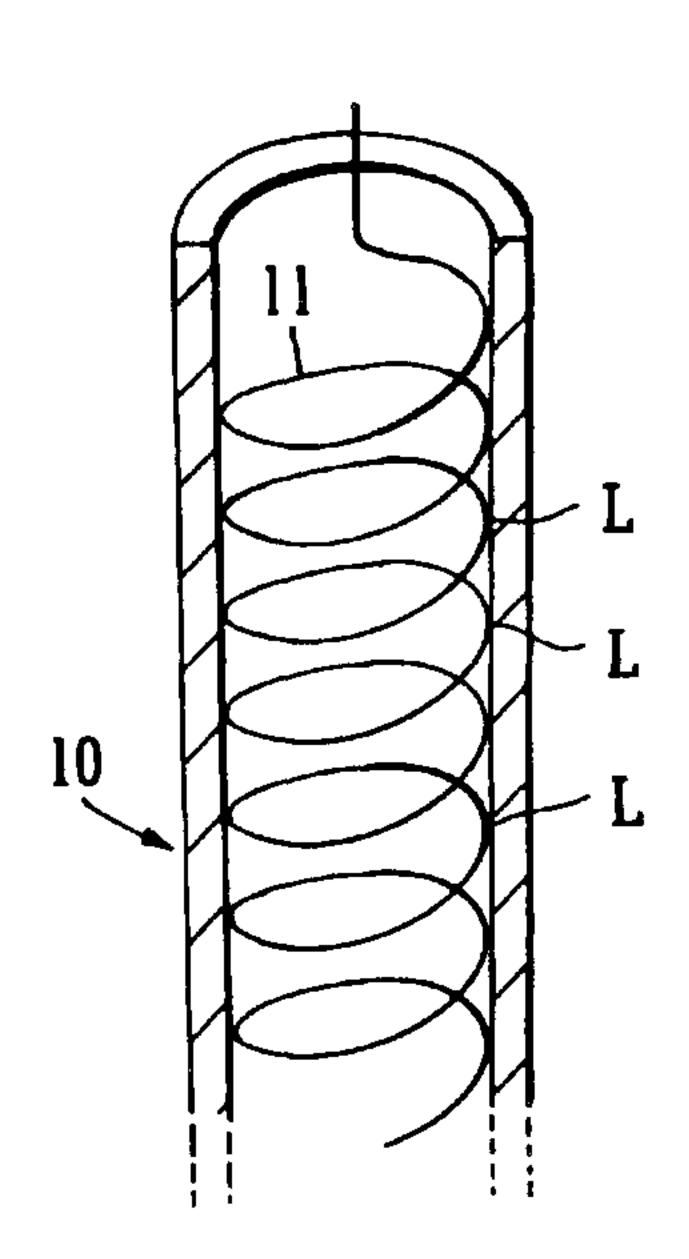
- (74) Agent: SHAW, Laurence; Laurence Shaw & Associates, 5th floor, Metropolitan House, 1 Hagley Road, Edgbaston, Birmingham B16 8TG (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

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.

(54) Title: ELECTRODE



(57) Abstract: An electrode comprises an elongate hollow tube (5) made of porous titanium suboxide the inside wall of which is contacted at spaced apart locations by an electrical conductor (11, 12) so that the current is substantially uniformly distributed along the length of the electrode.

VO 01/026 A1

WO 01/02626 PCT/GB00/02553

ELECTRODE

The invention relates to an electrode formed of low conductivity material. Typically such electrodes take the form of an elongate hollow body. Preferably the body is made of a substoichiometric oxide of titanium or the like in which case it is likely that the most effective manufacturing route will result in the body being porous.

It has been calculated, by way of illustration, based on a tubular body 500 mm long, 18 mm outside diameter with a 3 mm wall thickness, made of a material with a volume resistivity of 30 m Ω .cm, operating with an electrical connection at the one end, supplied with a current of 2.83 Amps (intended to provide a current density of 100A/m² at all points along its length) that there will be a voltage drop of about 750mV between the ends of such an electrode. In many electrochemical applications and as a result of this voltage drop there may be regions of the electrode where the potential is insufficient to perform its intended function. In the case of an electrolytic process operating at low voltages of the order of 1 to 5V between anode and cathode (the preferred situation since this leads generally to lower electrical costs) it cannot be guaranteed that all the surface area of the electrode will be equally effective, or effective at all. This is particularly true of electrolytic processes, such as water treatment, which are favoured by electrode surfaces which exhibit high gassing overpotential (such as titanium suboxides, lead dioxide, doped tin dioxide etc). In such cases, the actual current density can be shown to vary by more than 50% between the ends of such an electrode.

It is one object of this invention to provide a method of making an electrical connection to such an electrode which will solve this problem, particularly in the context of the electrode body being made of a porous material.

In one aspect the invention provides an electrode comprising an elongate generally hollow body formed of porous relatively low electrical conductivity material, and connection means comprising an elongate electrically conductive member for being connected to a power source, the connection means extending along inside the body and contacting the inner wall surface of the body at a plurality of spaced apart locations along the length of the body for causing the electrical current from the power source to be distributed substantially uniformly along the electrode.

The electrically conductive member has an electrical conductivity substantially higher (at least 2 orders of magnitude) than that of the electrode body. In one form the connection means is a coiled length of spring wire shaped so as to mechanically urge the coils into contact with the inner wall surface of the hollow body at regular intervals. In another embodiment separate conductor lengths are present at longitudinal spaced apart locations and each contacts the inner wall of the body.

The hollow body may be formed from a range of materials. Most preferably the electrode body is formed of a substoichiometric oxide of titanium of the form TiO_x where x is from about 1.99 to about 1.7. Such a body is generally porous since the more most cost-effective manufacturing routes to a cylindrical or hollow body of such materials results in a porous structure. Catalytic elements may be present. In a preferred embodiment the electrode body is formed of the substoichiometric oxide of titanium and the electrode conductor is a valve metal, whereby a durable electrical connection is made.

The body is preferably at least 200 mm long when the invention is valuable for use with materials for which the volume resistivity is higher than about $20m\Omega$.cm. If the material of the body is of higher resistivity then the invention is valuable for use where the body is at least 150 mm long.

The electrode of the invention is useful in many processes where cylindrical electrode geometry is advantageous, such as in the treatment of fluids to remove pollutants, and in the in-situ remediation of contaminated soils. Generally, water pollutants can be grouped in seven classes as follows:

- 1. Sewage and other oxygen-demanding wastes
- 2. Infectious agents
- 3. Plant nutrients
- 4. Exotic organic chemicals
- 5. Inorganic minerals and chemical compounds
- 6. Sediments
- 7. Radioactive substances.

Sewage and other oxygen-demanding wastes are generally carbonaceous organic materials that can be oxidised biologically (or sometimes chemically) to carbon dioxide and water. These wastes can be problematic. Infectious agents are usually found in waste water from municipalities, sanatoriums, tanning and slaughtering plants and boats. This type of pollutant is capable of producing disease in man and animals, including livestock.

Plant nutrients, (e.g. nitrogen and phosphorus) are capable of stimulating the growth of aquatic plants which interfere with water usage and which later decay to produce annoying odours and increase the amount of oxygen-demanding waste in the water.

Exotic organic chemicals include surfactants used in detergents, pesticides, various industrial products and the decomposition products of other organic compounds. Some of these compounds are known to be toxic to fish at very low concentrations. Many of these compounds are not readily biologically degradable.

Inorganic minerals and chemical compounds are generally found in water from municipal and industrial waste waters and from urban run-off. These pollutants can kill or injure fish and other aquatic life and can also interfere with the suitability of water for drinking or industrial use. A prominent example is the occurrence of mercury in water. Another example is salt pollution used to de-ice roads in winter in the northern, colder climates.

Sediments are soil and mineral particles washed from the land by storms and floodwaters, from croplands, unprotected forest soils, overgrazed pastures, strip mines, roads and bulldozed urban areas. Sediments fill stream channels and reservoirs; erode power turbines and pumping equipment, reduce the amount of sunlight available to aquatic plants; plug water filters; and blanket fish nests, spawn and food supplies, thereby reducing the fish and shell fish populations.

Radioactive substances in water environments usually result from the wastes of uranium and thorium mining and refining; from nuclear power plants and from industrial, medical, scientific utilisation of radioactive materials.

In another aspect the invention provides apparatus for use in electrolytic treating of a liquid comprising a chamber containing the fluid to be treated, an anode and a cathode at least one of which is an electrode as disclosed herein, and a supply of electrical current.

The invention is seen to particularly good effect in the treatment of water or aqueous media. In such a case electrical current is passed between an anode and a cathode across a small gap, through which the water is passed. Because of the structure of an electrode of the invention one can guarantee that a predetermined minimum voltage, e.g. 3V will be present along the length of the electrode.

Electrodes made of titanium suboxide has a high gassing overpotential, i.e. the voltage required before any appreciable current passes because of the low catalytic activity of the surface for splitting water into hydrogen and hydroxyl radicals. This level is in excess of 1V unless the surface is catalysed, so the effective driving force for current is at most about 2V (if the overall voltage is 3V as above) near the connector and 1.25 volts at the other end due to the voltage drop along the electrode in the absence of this invention, under the conditions described above.

In yet another aspect the invention provides a method of operating apparatus as disclosed herein, including supplying a current from the power source to the electrode of low conductivity at a current density of more than 10 A.m² of external anode area, whereby the voltage variation between any two points on the electrode is less than 200 mV.

In order that the invention may be well understood it will now be described by way of example with reference to the accompanying diagrammatic drawings, in which

Figure 1 is a diagram showing a representative electrochemical cell for the treatment of water;

Figure 2 is an enlarged view partly in section of one embodiment shown in the diagram of Figure 1 and Figure 3 is the same of another embodiment.

The water treatment system includes a cell whereby the water being treated is introduced to the annular space 2 between two elongate tubular bodied electrodes, with a small annular clearance in between. Each electrode is typically 500 mm long and is connected to the respective poles of a D.C. supply 4 so that one electrode is a cathode 5 and the other (in illustration, the inner electrode) an anode 6. The inner electrode is typically 18 mm outside diameter and the annular space is typically 2 mm. When current is passed through the electrodes an electrolytic reaction takes place, such as treating the water to remove pollutants. The water passes in the annular clearance between the electrodes. Typically the electrical connection is made to one end of the inner electrode and a current of about 2.83 amps is supplied. If the inner electrode is made of a titanium suboxide tube with a wall thickness of 3 mm and which has a volume resistivity of $\sim 30 \text{m}\Omega$.cm, a voltage drop of about 750mV will occur down the length of the inner electrode in the absence of this invention, so that the cell potential at one end will be about 3V and at the other 2.25V.

According to the invention the anode 6 of Figure 1 comprises an elongate tube 10 formed of titanium suboxide by moulding, extrusion or the like. The tube is about 500 mm long, having an inner diameter of 12 mm and an outer diameter of 18 mm, i.e. a wall thickness of about 3 mm.

WO 01/02626 PCT/GB00/02553

7

According to one embodiment of the invention and as shown in Figure 2, the current feeder comprises a length of titanium spring wire 11 which extends along the inner bore of the tube. One end of the wire 11 is connected to the power source 4, the other end may be sealed by an end cap. The coils of the spring are mechanically urged into contact with the inner wall of the tube at longitudinally spaced apart locations L whereby the supply is distributed substantially uniformly along the length of the tube. As a result the cell voltage is substantially the same along the entire length of the cell and hence the entire length is effective in its electrochemical function, such a killing micro-organisms, oxidising and/or reducing contaminants.

The cathode may be the same shape as the anode or it may be of standard design.

In the embodiment shown in Figure 3, the coil spring is replaced by a series of individual connectors 12 spaced apart along the length of the tube.

The invention is not limited to the embodiment shown. The water treatment apparatus may comprise banks of cells, and include other treatments. The electrode need not be circular in section. Although the invention has been described in relation to water treatment, the electrode has value in any situation where an elongate electrode is useful. Such applications include in-situ soil remediation, and electrochemical synthesis reactions, e.g. a redox system.

CLAIMS

- 1. An electrode comprising an elongate generally hollow body (5) formed of porous relatively low electrical conductivity material, and connection means (11, 12) comprising an elongate electrically conductive member for being connected to a power source (4), the connection means extending along inside the body (5) and contacting the inner wall surface of the body at a plurality of spaced apart locations along the length of the body for causing the electrical current from the power source to be distributed substantially uniformly along the electrode.
- 2. An electrode according to Claim 1, wherein the connection means (11) is an elongate spring made from spring wire shaped so as to mechanically urge the coils into contact with the inner wall surface of the body (5) at longitudinally spaced apart locations.
- 3. An electrode according to Claim 1, wherein the conductor means (12) comprise separate conductors in contact with the inner wall surface of the body (5) at respective longitudinal spaced apart locations.
- 4. An electrode according to any preceding Claim, wherein the electrically conductive member has a conductivity at least two orders of magnitude higher than that of the body.
- 5. An electrode according to any preceding Claim, wherein the electrode body is formed of a substoichiometric suboxide of titanium of the form TiO_x where x is from 1.99 to about 1.7.

- 6. An electrode according to any preceding Claim, wherein the body is at least 200 mm long.
- 7. An electrode according to any preceding Claim, wherein the electrical conductor means is made of a valve metal.
- 8. Apparatus for use in electrolytic treatment of a liquid, the apparatus comprising a chamber containing the liquid to be treated, an anode and a cathode at least one of which is an electrode according to any one of Claims 1 to 7.
- 10. A method of operating apparatus according to Claim 8 or 9 including supplying a current from the power source to the electrode at a density of above 10 A.m² of external anode area, whereby the voltage variation between any two points on the electrode is less than 200 mV.
- 11. An in-situ soil remediation system incorporating an electrode according to any of Claims 1 to 7.
- 12. Apparatus for performing a redox type reaction, incorporating an electrode according to any of Claims 1 to 7.

WO 01/02626 PCT/GB00/02553

