(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 149 928 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
03.02.2010 Bulletin 2010/05

(21) Application number: **07808495.1**

(22) Date of filing: **23.08.2007**

(51) Int Cl.:
H01M 4/92 *(2006.01)* ***B01J 23/42*** *(2006.01)*
B01J 23/62 *(2006.01)* ***H01M 4/04*** *(2006.01)*
B01J 37/02 *(2006.01)* ***B01J 37/08*** *(2006.01)*

(86) International application number:
PCT/MX2007/000099

(87) International publication number:
WO 2008/130212 (30.10.2008 Gazette 2008/44)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK RS

(30) Priority: **23.04.2007 MX MX07004840**

(71) Applicants:
- **Universidad Autónoma Metropolitana D.F. (MX)**
- **Servicios Industriales Peñoles, S.a. De C.v. México D.F. (MX)**

(72) Inventors:
- **GONZÁLEZ MARTÍNEZ, Ignacio C.P. 09340 México D.F. (MX)**
- **NAVA MONTES DE OCA, José Luis C.P.09340 México D.F. (MX)**
- **BENAVIDEZ PÉREZ, Ricardo C.P. 64960 Monterrey Nuevo León (MX)**
- **LARA VALENZUELA, Carlos C.P. 64920 Monterrey Nuevo León (MX)**
- **RECÉNDIZ MEDINA, Alejandro C.P. 09800 Delegación Iztapalapa México D.F. (MX)**
- **RIVERA ITURBE, Fernando Felipe C.P. 09800 Delegación Iztapalapa México D.F. (MX)**

(74) Representative: **Gislon, Gabriele**
Torner, Juncosa i Associats, S.L.
C/Gran Via de les Corts Catalanes, 669bis 1r 2a
08013 Barcelona (ES)

(54) BIMETALLIC ELECTROCATALYST FOR USE IN MOLECULAR ELECTROSYNTHESIS AND PREPARATION METHOD THEREFOR

(57) The present invention relates to the mining industry and to an electrocatalyst for producing an oxidizing agent by means of the partial oxidation of sulfurous compounds, such as formamidine disulfide (FDS) from thiourea (Tu). The inventive material and process are advantageous over the materials and processes of the prior art in that they enable efficient partial oxidation of sulfurous compounds without producing parasitic reactions such as subsequent oxidations, as well as oxygen evolution. Structurally the invention consists of a bimetallic electrocatalyst having a molar ratio of between (0.8-1) Pt : (0.012-0.016) Pb on the surface of the support and the preparation method therefor consists of the use of the sol-gel technique using a polymer precursor.

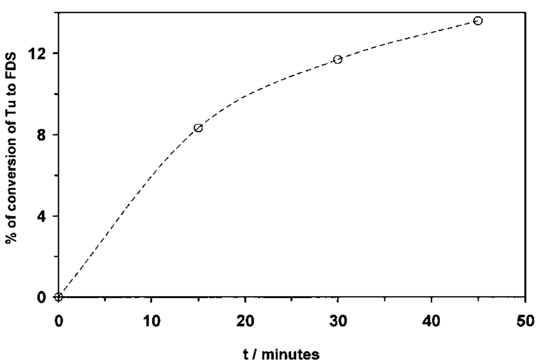

Fig. 3

Printed by Jouve, 75001 PARIS (FR)

Description

Field of the Invention

[0001] The present invention relates to the mining industry and the industry of electrosynthesis of chemical products by means of an electrocatalyst for partially oxidizing sulfurous organic molecules, for example the oxidation of thiourea (Tu) to form formamidine disulfide (FDS).

Background of the Invention

[0002] One of the applications of the invention object of this description is the mining industry, which involves different steps and processes among which the recovery of base and precious metals stands out. The recovery of these metals has traditionally been carried out by means of leaching processes with cyanide, where the metals are extracted by the presence of oxygen in the solution, whereas the cyanide complexes the dissolved metals. However, the recovery of the values by the cyanidation pathway entails an intense environmental impact.

[0003] In recent years, the leaching of precious metals in non-contaminating systems such as the FDS/Tu system in a sulfuric acid medium has been studied. In this process, the oxidizing agent is FDS, whereas Tu complexes the dissolved metals.

[0004] FDS production methods can be carried out through two pathways: the first one by the oxidation of Tu using oxidizing agents which are unrelated to the solution, such as ferric ion and hydrogen peroxide, and the second one by the partial oxidation of the thiourea itself by means of electrolysis in the surface of an electrocatalyst. In the first method, the FDS/Tu ratio is not very stable and tends to break down to form elemental sulfur and cyanamide, among other unwanted byproducts [Patent WO0068446]. In the second method, Tu is oxidized in the surface of an electrode to FDS by means of the following reaction:

$$\underset{\text{Tu}}{2(NH_2)_2CS} \rightarrow \underset{\text{FDS}}{[(NH_2)_2(NH_2)_2C_2S_2]^{2+}} + 2e^- \qquad (1)$$

[0005] In addition, depending on the potential and/or current density, Tu can be oxidized to cyanamide and elemental sulfur, making it useless for leaching precious metals:

$$\underset{\text{Tu}}{(NH_2)_2CS} \rightarrow \underset{\text{cyanamide}}{NH_2CN} + S^0 + 2H^+ + 2e^- \qquad (2)$$

[0006] It is important to mention that reaction (2) is irreversible, for which reason it is considered a parasitic reaction.

[0007] The state of the art of the field of this invention indicates that both reactions are carried out on the surface of a platinum electrode. However, platinum induces the oxidation of water and promotes the second reaction, for which reasons the production of FDS is not very efficient. In addition, massive platinum is very expensive. To reduce costs, the platinum must be supported on a material.

[0008] The works reported on platinum electrodes supported on certain substrates such as titanium and niobium indicate that dispersed platinum is energetically more active than massive platinum, therefore for certain applications it is necessary to modify its electrocatalytic activity by associating it with other metals such as tin, lead, palladium, for example.

[0009] The concept of preparing supported platinum bimetallic electrocatalysts is not new. However, there are works on a supported platinum bimetallic electrocatalyst which allow the partial electro-oxidation of sulfurous compounds in a selective and efficient manner.

Objectives of the Invention

[0010] One of the objectives of the present invention is preparing an electrocatalyst allowing the electro-oxidation of sulfurous compounds in a selective manner.

[0011] Another objective is providing the electrocatalyst with the quality of being efficient, preventing parasitic reactions such as subsequent oxidations and oxygen evolution, in order to achieve this efficiency and selectivity.

[0012] Other objectives and advantages of the present invention may be evident from the study of the following description and the drawings for illustrative and non-limiting purposes.

Brief Description of the Invention

[0013] Briefly, in one of its aspects the present invention is embodied as a titanium-supported platinum-lead bimetallic electrocatalyst.

[0014] In addition, the invention also relates to a preparation method for preparing the electrode by the sol-gel pathway using a polymer precursor.

[0015] In one of its applications, the platinum electrode object of this description must be doped with an element to favor only the electro-oxidation of Tu to FDS in an efficient and selective manner.

[0016] The choice of a bimetallic catalyst was made based on the available information about the electrocatalytic activity of platinum which entails the subsequent oxidation of sulfurous molecules such as the formation of elemental sulfur, in addition to the fact that platinum promotes the oxidation of water to O_2.

[0017] An attempt was then made to reduce the oxidative activity of platinum to partially oxidize sulfurous molecules in a selective manner.

[0018] With the available knowledge about bimetallic electrodes, several options of metals which achieve reducing the mentioned activity were tested.

[0019] After testing different dopants, it was found that lead reduced the activity of platinum, allowing partially oxidizing sulfurous organic molecules in a selective and efficient manner. These studies were conducted in the application of oxidation of Tu to FDS.

[0020] The Pt/Pb ratio was determined from the aforementioned tests.

[0021] The bimetallic electrocatalyst comprising the teachings of the present invention will achieve efficiently carrying out the partial oxidations of sulfurous compounds, such as the electrolytic synthesis of FDS from Tu. The dimensions and configuration of the electrode will depend on the electrochemical reactor to be used for said partial oxidation.

[0022] The process for preparing the electrode also represented a problem to be solved due to the fact that not all the methodologies resulted in an electrocatalyst which will achieve the partial oxidation of sulfurous organic molecules in an efficient and selective manner.

[0023] The methodology consisting of a traditional sol-gel process proved to be not very efficient due to the fact that the Pt-Pb was detached from the support. This process uses isopropanol and acetic acid in proportions such that they allow the formation of the metallic alkoxides, which after a heat treatment, when the solvents and precursors are eliminated, leave the metals dispersed on the support.

[0024] An electrodeposition methodology also showed little adherence in the fixed metals.

[0025] The sol-gel methodology using a polymer precursor allowed a fixing of platinum and lead which had not been achieved by the previously described methods.

[0026] The preparation of these electrodes consisted of using a mixture of ethylene glycol and citric acid followed by the addition of a salt of hexachloroplatinic acid and lead acetate to form the sol-gel. This material was subsequently applied to a previously conditioned titanium mesh, followed by a heat treatment in an air atmosphere.

[0027] In order to better understand the features of the invention, the drawings of an illustrative but non-limiting character described below are attached to this description as an integral part thereof.

Brief Description of the Drawings

[0028]

Figure 1 shows a diagram of the process for preparing the platinum-lead bimetallic electrocatalyst of the present invention.

Figure 2 shows the electrochemical reactor, hydraulic and electric circuit, used for the preparation of FDS from Tu.

Figure 3 shows a graph of the kinetics of formation of FDS from thiourea carried out in the installation of Figure 2.

Figure 4 shows a graph of the result of the accelerated useful life test to estimate the time the electrode will work.

[0029] In order to better understand the invention, the detailed description of some of the modalities thereof will be made, said modalities being shown in the drawings attached to this description for illustrative but non-limiting purposes.

Detailed Description of the Invention

[0030] The present invention consists, on one hand, of a novel electrode for the partial oxidation of sulfurous organic molecules.

[0031] On the other hand, the invention consists of the preparation method for preparing a titanium-supported platinum-lead bimetallic electrocatalyst by the sol-gel pathway, using a polymer precursor.

[0032] The titanium-supported platinum-lead bimetallic electrocatalyst allows achieving an efficient and selective partial oxidation of sulfurous compounds, as well as the production of FDS from Tu, preventing the formation of parasitic reactions, such as subsequent oxidations and oxygen evolution. The partial electro-oxidation of the sulfurous compound to its dimer, as in the case of Tu to FDS, can only be selective if the electrocatalyst has a molar ratio of (0.8-1) Pt: (0.012-0.016) Pb.

[0033] To that end, a sol-gel must be prepared with the following molar ratio ethylene glycol (EG)-citric acid (CA)-hexachloroplatinic acid (Pt)-lead acetate (Pb): (14-18):(0.046-0.060):(0.011-0.015):(0.0001-0.0002). And this gel is subsequently applied on the support and finally, it is given a heat treatment to volatilize the precursors.

[0034] With reference to Figure 1, the pre-treatment of the surface of the support (No. 1) is carried out according to the following process: (i) The number of titanium supports of given dimensions are placed in concentrated HCl (approximately 37%), such that the ratio approximately 0.128 cm^{-1} is met in the vessel. (ii) The HCl is heated in the range of 60-70°C, and the meshes are maintained for approximately 1 hour. (iii) The meshes are extracted from the HCl, to immerse them in concentrated HNO_3 for 5 minutes. (iv) The meshes are rinsed with abundant water and left to dry.

[0035] The preparation of the sol-gel (ink), containing the platinum and lead, (No. 2) is carried out according to the following methodology: (i) the proportions of EG and CA described above are added; the mixture is subsequently heated to 60-70°C, with stirring, until complete dilution. (ii) A salt of hexachloroplatinic acid and lead acetate, with the ratio described above, is added to the mixture, the temperature is subsequently raised to 70-90°C, maintaining it for approximately 30 minutes, the temperature is then reduced stirring. (iii) The solution is maintained under stirring and it is ready to be applied. The ratio of the four components, before the volatilization of the precursors, has already been mentioned.

[0036] The application of the ink and heat treatment on the support (No. 3) consisted of: (i) The ink is applied with a brush on one of the pre-conditioned titanium meshes, until the layer is uniform. (ii) The meshes are placed in the muffle at 100°C for approximately 5 minutes, for the purpose of polymerizing the coating. (iii) Steps (i) and (ii) are repeated six times. (iv) Process (i) is repeated once. (v) After the previous step, the mesh is introduced in the muffle and maintained from 350 to 450°C for approximately 30 minutes.

[0037] The dimensions of the electrocatalyst and configuration thereof will depend on the electrochemical reactor to be used for the electro-oxidation, but any electrode dimension, configuration will achieve efficiently carrying out the partial oxidation of sulfurous compounds. This invention in particular does not intend to be limited to a certain electrode size and shape.

Examples

Example 1. Electro-oxidation of Tu to FDS using the platinum-lead bimetallic electrocatalyst.

[0038] The composition of the solution of Tu from which FDS is produced by electrolysis was 0.2 M Tu at pH = 2. The electrolysis was carried out in a filter-press type electrochemical reactor in a batch operation with recirculation, see diagram in Figure 2. The electrochemical reactor (No. 1) is made up of the platinum-lead electrocatalyst (No. 2), a cathode (3), both separated by an anionic membrane (No. 4). The anodic tank (No. 6) contains the Tu to be electrolyzed, whereas the cathodic tank (No. 7) contains 0.01 M H_2SO_4, both with a capacity of 1000 cm^3. The hydraulic system consists of two centrifugal pumps (No. 8), flow valves (No. 9) and two flowmeters (No. 10). The power is supplied by a potentiostat-galvanostat (No. 5).

[0039] The dimensions of each channel, separated by the membrane, forming the electrochemical reactor, have a cross-sectional area of AT = (3.1 cm x 1.2 cm) =3.72 cm^2, with a length L = 7.9 cm, which gives a volume of each channel of 29.39 cm^3. The anode used consists of five platinum-lead bimetallic electrocatalysts which are inserted in the anodic compartment of the electrochemical reactor, whereas the cathode is a platinized titanium plate.

[0040] The electrochemical reactor is divided with an anionic membrane to prevent the FDS, produced in the anodic compartment, from passing to the cathodic compartment and being reduced.

[0041] The electrolysis was carried out in the electrochemical reactor applying a current of 0.9 Amperes for 45 minutes, at a Reynolds number Re = 190 ($Re=ud_p/((1-\varepsilon)\nu)$), where u is the average velocity of the solution in the channel, d_p is the size of the particle formed by the mesh, ε is the porosity and ν is the kinematic viscosity of the solution. In addition, a Re = 513 was used in the anodic compartment.

[0042] Figure 3 shows the percentage of conversion of Tu to FDS as a function of the electrolysis time. It is observed that for the first 15 minutes the production of FDS has linear kinetics, the kinetics subsequently decrease, it being observed that in 45 minutes 13.8% of conversion to FDS is reached without the irreversible destruction of Tu. It is important to emphasize that the efficiency of the electrolysis current was approximately 100%, indicating that the oxidation of Tu to FDS was selective, and that parasitic reactions were not generated.

Example 2. Determination of the average lifetime of the platinum-lead bimetallic electrocatalyst.

[0043] Accelerated life tests were carried out for the purpose of evaluating the chemical stability of these electrodes, and evaluating the time that the electrodes last working in electrolysis. These tests were carried out in extreme electrolysis conditions, applying an electrolysis current density of 1 A cm^{-2} in 0.5 M H_2SO_4, which is equivalent to 286 times the current density of a normal electrolysis.

[0044] Figure 4 shows a typical accelerated life test for the titanium-supported platinum-lead bimetallic electrocatalyst. The potential starts at approximately 2.0 V, the latter remains constant, until a time of approximately 65 hours, where the value of this potential starts increasing upwardly, indicating that the electrode has been deactivated, i.e., it has stopped being efficient. The lifetime of the electrocatalyst according to the accelerated life test will be 2 years 3 months. This average lifetime is very similar to the one of dimensionally stable electrodes (DSA), used in multiple applications.

[0045] Having described this invention in detail, the contents of the following claims are considered as novelty and claimed as belonging exclusively to the inventors:

Claims

1. A titanium-supported platinum-lead bimetallic electrocatalyst for use in molecular electrosynthesis, **characterized in that** the electrocatalyst has a molar ratio of between (0.8-1) Pt : (0.012-0.016) Pb on the surface of the support.

2. The electrocatalyst as claimed in the previous claim, **characterized in that** it is applied in the partial electro-oxidation (dimerization) of sulfurous compounds.

3. The electrocatalyst as claimed in the previous claim, **characterized in that** it is applied in the electro-oxidation of Tu to FDS.

4. A preparation method for preparing the electrocatalyst claimed in clam 1, **characterized in that** it consists of using a mixture of ethylene glycol (EG) and citric acid (CA) followed by the addition of a salt of hexachloroplatinic acid (Pt) and lead acetate (Pb) to form the sol-gel with a molar ratio: (14-18):(0.046-0.060):(0.011-0.015):(0.0001-0.0002); this material is subsequently applied to a previously conditioned titanium mesh, followed by a heat treatment at a temperature of between 350 to 450°C, in an air atmosphere.

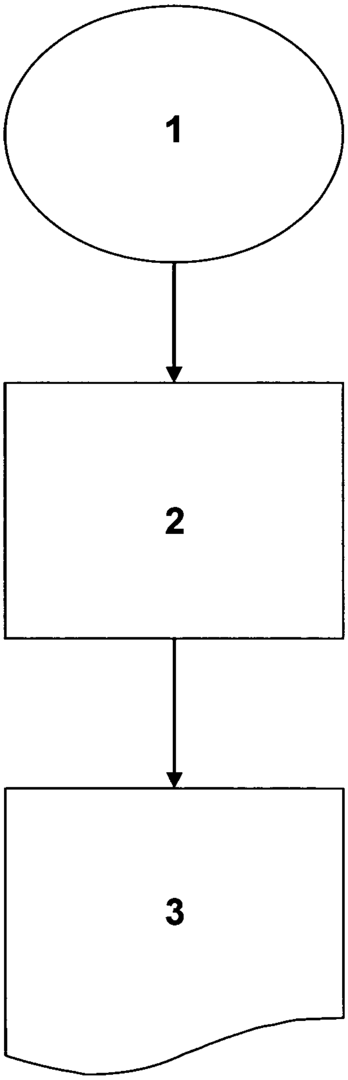

Fig. 1

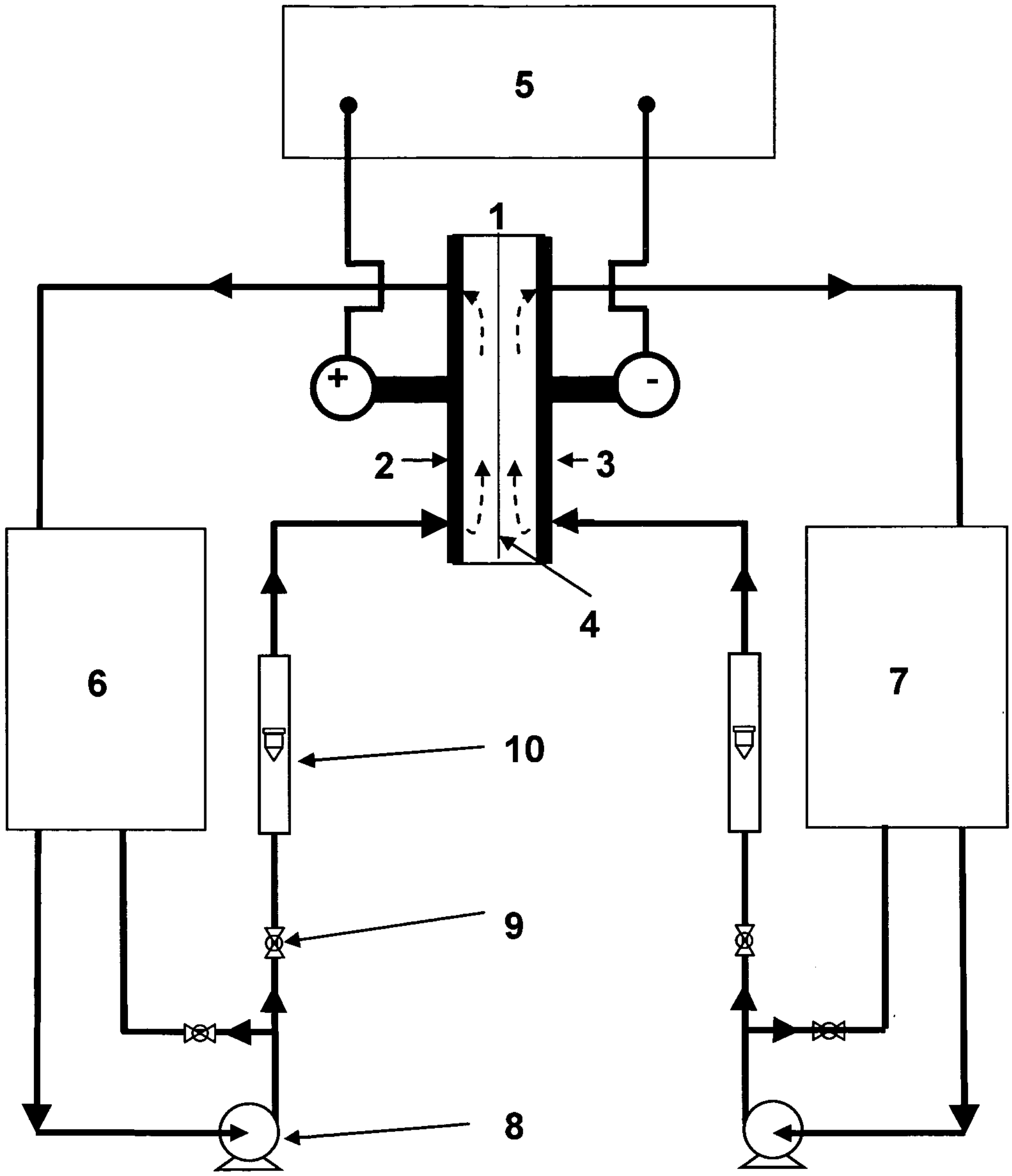

Fig. 2

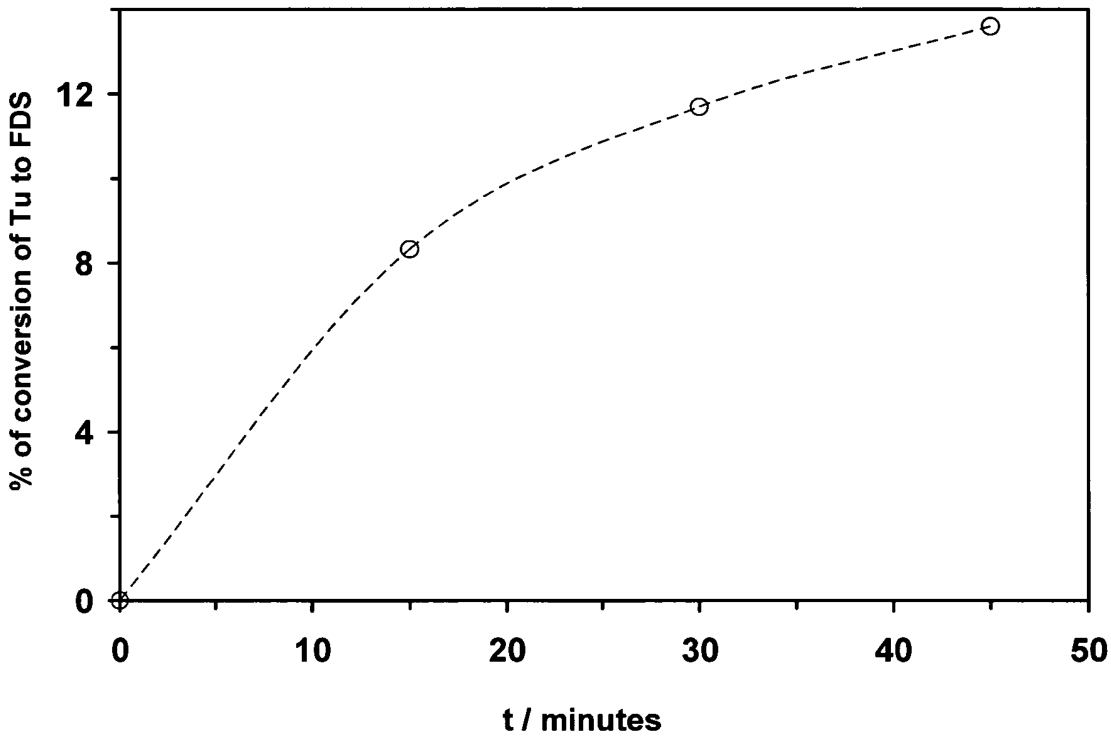

Fig. 3

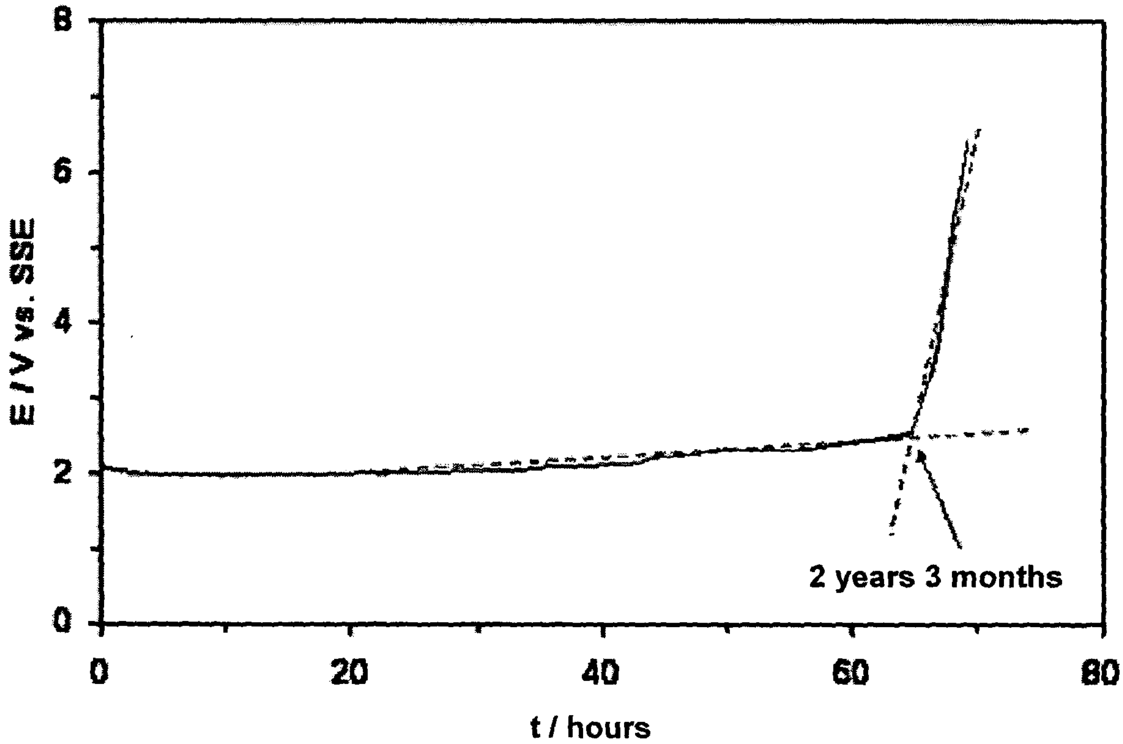

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ MX 2007/000099

A. CLASSIFICATION OF SUBJECT MATTER

see extra sheet

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M, B01J

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)

CIBEPAT,EPODOC, WPI, HCAPLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004021486 A2 (UNIV NEWCASTLE VENTURES LTD ; SCOTT KEITH ; CHENG HUA) 11.03.2004, page 5, line 14 - page 6, line 2; page 12, lines 22-25; page 15, lines 6-12, lines 20-25; page 17, lines 9-13; page 19, lines 8-14; page 33, lines 2-13;	1-4
A	US 6676919 B1 (FISCHER et al.) 13.01.2004, column 3, lines 37-46;column 3, line 64 - column 4, line 6; column 4, lines 33-41, lines 52-64; column 5, lines 66-67; column 7, line 66 - column 8, line 10; column 8, lines 37-40; column 9, lines 37-54;column 10, line 32 - column 11, line 11; column 11, lines 42-56; example IC2.	1-4

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance.
"E" earlier document but published on or after the international filing date
"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)
"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

"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
"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
"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 documents , such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 November 2007 (20.11.2007)	(22/01/2008)
Name and mailing address of the ISA/ O.E.P.M. Paseo de la Castellana, 75 28071 Madrid, España. Facsimile No. 34 91 3495304	Authorized officer J. A. Peces Aguado Telephone No. +34 913496870

Form PCT/ISA/210 (second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MX 2007/000099

C (continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3630961 A (WILHELM et al.) 28.12.1971, column 1, lines 13-20, lines 41-54; column 3, lines 29-52; column 4, lines 30-42;column 7, line 67 - column 8, line 10;column 8, line 46 - column 9, line 3;column 9, line 45 - column 10, line 30.	1-4

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/ MX 2007/000099

Patent document cited in the search report	Publication date	Patent family member(s)	Publication date
WO 2004021486 A	11.03.2004	CA 2497105 A	11.03.2004
		AU 2003259369 A	19.03.2004
		EP 1537617 A	08.06.2005
		EP 20030791028	27.08.2003
		KR 20050083660 A	26.08.2005
		JP 2005537618 T	08.12.2005
		US 2006099482 A	11.05.2006
US 6676919 B	13.01.2004	WO 0059635 A	12.10.2000
		CA 2368149 A	12.10.2000
		DE 19915681 A	12.10.2000
		AU 4544500 A	23.10.2000
		KR 20010105411 A	28.11.2001
		ID 30550 A	20.12.2001
		EP 1169129 A	09.01.2002
		MXPA01009978	28.02.2002
		CN 1354690 A	19.06.2002
		CN 1144620 C	07.04.2004
		ZA 200109145 A	06.11.2002
		JP 2002540921 T	03.12.2002
US 3630961 A	28.12.1971	US 3723554 A	27.03.1973

Form PCT/ISA/210 (patent family annex) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/ MX 2007/000099

CLASSIFICATION OF SUBJECT MATTER

H01M 4/92 (2006.01)
B01J 23/42 (2006.01)
B01J 23/62 (2006.01)
H01M 4/04 (2006.01)
B01J 37/02 (2006.01)
B01J 37/08 (2006.01)

Form PCT/ISA/210 (extra sheeet) (April 2007)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 0068446 A **[0004]**