

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 June 2006 (29.06.2006)

PCT

(10) International Publication Number
WO 2006/068444 A1

(51) International Patent Classification:

C25D 1/08 (2006.01)

(21) International Application Number:

PCT/KR2005/004487

(22) International Filing Date:

23 December 2005 (23.12.2005)

(25) Filing Language:

Korean

(26) Publication Language:

English

(30) Priority Data:

10-2004-0110900

23 December 2004 (23.12.2004) KR

(71) Applicant (for all designated States except US): **SEOUL NATIONAL UNIVERSITY INDUSTRY FOUNDATION** [KR/KR]; San 4-2, Bongcheon-dong, Gwanak-gu, Seoul 151-818 (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KIM, Hee-chan** [KR/KR]; 1-1302, Sindonga Apt., 44, Myeongil, 2-dong, Gangdong-gu, Seoul 134-786 (KR). **CHUNG, Taek**

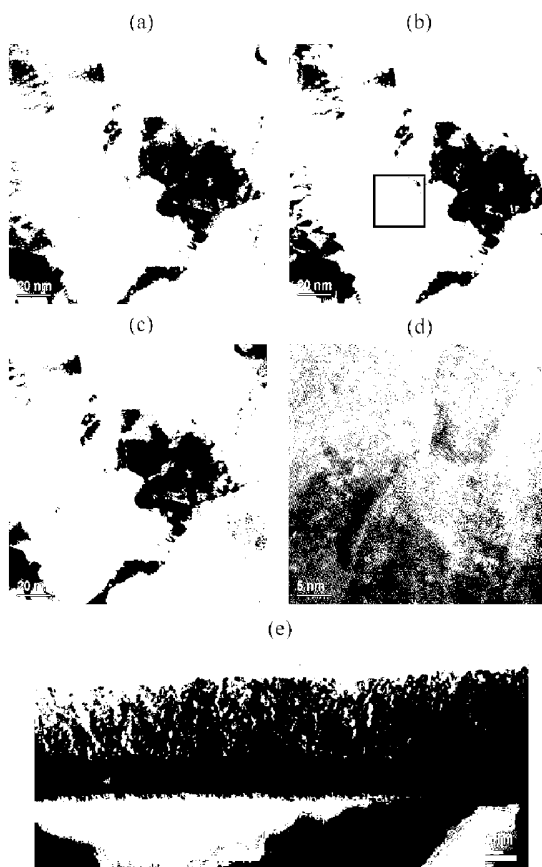
Dong [KR/KR]; 604-809, Hanyang 6-cha Apt., 59-5, Ssangmun 4-dong, Dobong-gu, Seoul 132-746 (KR). **PARK, Sejin** [KR/KR]; #114-1504, Samsung Raemian Apt., 23, Dowon-dong, Yongsan-gu, Seoul 140-748 (KR). **BOO, Hankil** [KR/KR]; #3-303, Namsan Town Apt., 884, Sindang-3-dong, Jung-gu, Seoul 100-754 (KR). **LEE, Sunyoung** [KR/KR]; 249-1, Dongseon-dong-3-ga, Seongbuk-gu, Seoul 136-053 (KR).

(74) Agents: **HAN, In-youl** et al.; #1106, Kumsan Bldg., 17-1, Youido-dong, Youngdeungpo-ku, Seoul 150-727 (KR).

(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, KM, KN, KP, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

[Continued on next page]

(54) Title: FABRICATION OF MESOPOROUS METAL ELECTRODES IN NON-LIQUID-CRYSTALLINE PHASE AND ITS APPLICATION



(57) Abstract: A method for the fabrication of a mesoporous metal electrode in a non-liquid crystalline phase was tested. Specifically, there was tested the efficacy of the method for the fabrication of a mesoporous metal electrode which comprises forming the mesoporous metal electrode on a substrate by chemical or electrochemical reduction of a mixture comprising a solvent, a structure-directing agent, and a source of a metal, characterized in that the mixture is maintained in a non-liquid crystal phase. Furthermore, the usefulness of the mesoporous metal electrode thus prepared from the non-liquid crystalline phase was also tested. The mesoporous metal electrode prepared from the non-liquid crystalline phase had a large surface area, and a roughness factor thereof was controlled by charges passed during electroplating. The method made it possible to fabricate the mesoporous metal electrode in the non-liquid crystalline phase, even more flexible than a liquid crystalline phase. The mesoporous metal electrode prepared by the method had randomly distributed mesopores on the surface thereof and retained a large roughness factor. The method was found to be a good alternative to the conventional fabrication of porous platinum films in the liquid crystalline phase. Furthermore, the method was found to be suitably applicable to automatic processes, because the mesoporous metal electrode was prepared in the highly flexible non-liquid crystalline phase. Recovery and recycling of raw materials were also improved. The mesoporous metal electrode prepared by the method can be suitably used for the detection of glucose and proton, and as a cathode or an anode of fuel cells.



(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, 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).

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.

Published:

— with international search report

Description

FABRICATION OF MESOPOROUS METAL ELECTRODES IN NON-LIQUID-CRYSTALLINE PHASE AND ITS APPLICATION

Technical Field

- [1] The present invention relates to a method for the fabrication of a mesoporous metal electrode. More specifically, the present invention relates to a method for the fabrication of a mesoporous metal electrode in a non-liquid crystalline mixture solution of a source of a metal and a structure-directing agent. The present invention also relates to a mesoporous metal electrode prepared by the method and its application.

Background Art

- [2] Metallic thin films with roughness of nano-scale are of great use and importance in the fields of energy storage materials, catalysts, and sensors. In spite of their importance, however, only a few methods have been suggested to fabricate such nanoporous metal films. The examples include chemical/electrochemical deposition in a liquid crystalline template or dealloying of alloys. U.S. patent No. 6,203,925 discloses a method for the fabrication of a porous metal electrode having a substantially regular structure and uniform pore size. The method disclosed in the U.S. patent No. 6,203,925 comprises reducing a mixture including a source of a metal; a solvent; and a structure-directing agent present in an amount sufficient to form a liquid crystalline phase in the mixture, to form a metal-organic composite, and removing the organic from the composite. Another exemplarily method for the fabrication of the mesoporous metal electrode is disclosed in U.S. patent No. 6,503,382. The method disclosed in the U.S. patent No. 6,503,382 comprises electrodepositing a metal-organic composite from a mixture onto a substrate to form a porous film, wherein the mixture comprises a source of a metal, a solvent, a structure-directing agent in an amount sufficient to form a homogeneous lyotropic liquid crystalline phase in the mixture, and removing the organic from the metal-organic composite. The method has an advantage to produce mesoporous metal electrode with a regular structure and uniform pore size. However, the methods suffered from the disadvantage that they could be applicable only to the liquid crystalline phase such as lamellar (L), hexagonal (H_1), and cubic (V_1) phase, preferably to H_1 or V_1 phase. Mixtures having the liquid crystalline phase have very high viscosity. As thus, highly viscous residues remain on the substrate even after the substrate onto which the metal-organic composite was already formed is lift off from the liquid crystalline mixture. As a result, physical removing of the residues should be performed before subjecting the substrate to the step of removing the organic from the metal-organic composite. The removal of the residues is

a manually-performed, cumbersome work and prohibits automation of the manufacturing processes. Moreover, the method requires highly concentrated metal source. According to U.S. patent Nos. 6,203,925 and 6,503,382 mentioned in the above, the concentration of the metal source reaches up to 29 wt%, based on the mixture of the solvent and the structure-directing agent (*Langmuir*, **1998**, *14*, 7340-7342, Attard et al.). However, excessive use of the metal source makes the method to be ineffective and expensive, and deteriorates the disadvantages caused by the residing of highly viscous residues on the substrate. Moreover, the temperature must be kept as low as possible in order to maintain the mixture in a liquid crystalline phase. According to the phase study by Attard et al. (*Langmuir*, **1998**, *14*, 7340-7342), octaethyleneglycol monododecylether ($C_{12}EO_8$, in which EO represents ethyleneoxide), which is a representative structure-directing agent, does give a liquid crystalline mixture at above 85°C. In addition, octylphenoxy-polyethoxy ethanol (Triton X-100TM) gives a liquid crystalline mixture only at a temperature of no more than 20-30°C (*Langmuir* **2000**, *16*, 4922-4928, Galatanu et al.). The addition of the metal source further interferes with the formation of the liquid crystalline phase. As a result, the methods disclosed in the above two U.S. patents have a limit in terms of the temperature. Low temperature retards the electroplating rate, and so it takes long time to fabricate the mesoporous metal electrode. In addition, some structure-directing agents due to the limitation of the temperature are not applicable to the methods.

- [3] Stucky et al. (*Advanced Materials*, **2003**, *15*, 2018) showed that the potential-controlled-surfactant-assembly method worked in the solution of low surfactant concentration around critical micelle concentration (*cmc*). According to their report, cylindrical/hemicylindrical micelle assembly was formed below *cmc* on electrode/solution interface by electric field and functioned as a template for nanoporous platinum thin film with pore size of ~4 nm and wall thickness of ~4 nm. In these cases, 100 nm-thick platinum films could be formed within 30 s and the problems encountered in the liquid-crystalline-template method seem to be relieved. However, the electrical field at the surface substantially affects the morphology of the plated platinum in this method. Nanoporous platinum was deposited only near 0.2 V versus Ag/AgCl (4 M KCl), where cylindrical/hemicylindrical assembly was produced. In the other potential range, bilayer assembly appeared and inhibited the nanopore formation.

Disclosure of Invention

Technical Problem

- [4] Therefore, in order to solve the above disadvantages, an object of the present invention is to provide a method for the fabrication of a mesoporous metal electrode from a non-liquid crystalline solution. Specifically, there is provided a method for the

fabrication of a mesoporous metal electrode, comprising chemically or electro-chemically reducing a mixture comprising a solvent, a structure-directing agent and a source of a metal to deposit a metal-organic composite onto a substrate to obtain the mesoporous metal electrode, characterized in that the mixture is maintained in a non-liquid crystalline phase, and the deposition of the metal-organic composite onto the substrate is performed in the non-liquid crystalline mixture.

Technical Solution

- [5] According to a preferred embodiment of the present invention, there is provided a method for the fabrication of a mesoporous metal electrode, comprising the steps of maintaining a mixture comprising a solvent, a surfactant and a source of a metal in a non-liquid crystalline phase, dipping a substrate into the mixture, reducing the mixture to deposit a metal-organic composite onto the substrate, removing residues on the substrate onto which the metal-organic composite is formed, and extracting the organic from the metal-organic composite.
- [6] According to more preferred embodiment of the present invention, there is provided a method for the fabrication of a mesoporous metal electrode, wherein the step of removing residues is preformed by air-blowing.
- [7] According to even more preferred embodiment of the present invention, the mixture is maintained in an isotropic, non-liquid crystalline phase. Specifically, the mixture is present either as a micelle phase in which the structure-directing agent is surrounded by the solvent or as a reverse micelle phase in which the solvent droplets are surrounded by the structure-directing agent. Most preferably, the mixture is present as a reverse micelle phase.
- [8] According to another preferred embodiment of the present invention, there is provided a method for the fabrication of a mesoporous metal electrode, wherein the metal is selected from the group consisting of platinum, ruthenium, gold, nickel, palladium, silver, cobalt, iron, lead, tin and iridium.
- [9] According to further another preferred embodiment of the present invention, there is provided a method for the fabrication of a mesoporous metal electrode wherein the deposition of the metal-organic composite onto the substrate is carried out by electroplating.
- [10] According to further another preferred embodiment of the present invention, there is provided a method for the fabrication of a mesoporous metal electrode wherein the non-liquid crystalline mixture comprises water, a surfactant, and a source of a metal. As a surfactant, a non-ionic surfactant is particularly preferable.
- [11] Another object of the present invention is to provide a mesoporous metal electrode prepared by the above method. The mesoporous metal electrode can be used as a

glucose sensor, a pH sensor, and a reference electrode. Also, it can be used as a cathode or an anode of fuel cells.

Advantageous Effects

- [12] The mesoporous metal electrode fabricated from the non-liquid crystalline solution of a structure-directing agent and a source of a metal has randomly distributed pores and high roughness factor. The method of the present invention is a good alternative to the conventional fabrication of porous platinum films in the liquid crystalline phase. Furthermore, the method is suitably applicable to automatic processes because the mesoporous metal electrode is prepared in the highly flexible non-liquid crystalline phase. Recovery and recycling of raw materials are also improved. Plating speed can be increased by increasing the temperature. To the contrary, the conventional method adopting the liquid crystalline phase suffers from the temperature limitation, because the liquid crystalline phase can be obtained only at low temperature. The mesoporous metal electrode of the present invention can be used as a non-enzymatic glucose sensor, a pH sensor, and a reference electrode. The electrode system with mesoporous structure provides valuable advantages in the field of electrochemical systems such as chemical sensors, biochemical sensors and micro-total-analysis-systems (μ -TAS). This system is easy to construct, less time-consuming for the manufacturing reproducible product, and is suitable for mass-production.

Brief Description of the Drawings

- [13] Fig. 1 is a graph showing roughness factors of platinum electrodes versus the charge passed during electroplating at various potentials, temperatures, and concentrations of platinic acid.
- [14] Fig. 2 is a graph showing the dependence of roughness factors on the charge passed during electroplating. The electroplating was conducted in 5% hexachloroplatinic acid at 40°C and -0.2 V versus Ag/AgCl.
- [15] Fig. 3 are transmission electron microscopic images showing the mesoporous metal electrode of the present invention, wherein (a) is under focus view, (b) is in focus view, (c) is over focus view, (d) is closer view of the selected area of (b), and (e) is cross sectional view, respectively.
- [16] Fig. 4 are graphs of (a) current versus concentration and (b) the shape of current in the glucose solution of various concentration at 0.1 V versus mesoporous platinum oxide reference electrode.
- [17] Fig. 5 is a calibration curve for the glucose response of the mesoporous metal electrode of the present invention in 0.1 M phosphate buffer containing 0.15 M NaCl (pH 7.4). The calibration curve was constructed based on current changes dependent upon increased glucose concentrations, which are shown in an inset of the graph.

- [18] Fig. 6 is E_{oc} versus pH curve of the mesoporous metal electrode of the present invention in a stirred and air-saturated phosphate solution. In the graph, pH was decreased by adding 0.1 M H_3PO_4 to 0.1 M Na_3PO_4 ($\diamond$) and then increased by adding 0.1 M Na_3PO_4 again ($\square$).

Mode for the Invention

- [19] According to the method of the present invention, a mesoporous metal electrode is fabricated from a non-liquid crystalline phase, rather than the conventional liquid crystalline phase. Specifically, there is provided a method for the fabrication of a mesoporous metal electrode, comprising chemically or electrochemically reducing a mixture comprising a solvent, a structure-directing agent and a source of a metal to deposit a metal-organic composite onto a substrate to obtain the mesoporous metal electrode, characterized in that the mixture is maintained in a non-liquid crystalline phase, and the deposition of the metal-organic composite onto the substrate is performed in the non-liquid crystalline mixture.
- [20] In order to maintain the structure-directing agent in a liquid crystalline phase, the temperature of the mixture must be kept low. Also, the liquid crystalline phase has high viscosity. Even though the mesoporous metal electrode prepared from the liquid crystalline mixture has a regular structure and uniform pore size, high viscosity and low temperature requires manual removal of residues and deterioration of productivity due to slow plating rate. In the liquid crystalline mixture, these disadvantages are inevitable.
- [21] Surprisingly enough, it is confirmed that the mesoporous metal electrode can be prepared in a non-liquid crystalline mixture and the resulting mesoporous metal electrode shows substantially the same behaviors as the one prepared in the liquid crystalline mixture. Also, the fabrication of the mesoporous metal electrode in the non-liquid crystalline mixture solves the problems resulted from the liquid crystalline mixture. The method of the present invention has sufficient plating speed even at low concentration of the metal source, and allows elevating the temperature of the mixture sufficiently. According to the specific embodiment of the present invention, the fabrication of the mesoporous platinum electrode was successfully performed only at the low levels (1-5 wt%) of platinic acid. The use of the non-liquid crystalline mixture with low viscosity makes it possible to remove the residues by a simple work such as air-blowing, rather than manual removal. High temperature increases the plating speed and productivity of the mesoporous metal electrode.
- [22] The method for the fabrication of a mesoporous metal electrode, in accordance with the present invention, comprises the steps of maintaining a mixture comprising a solvent, a structure-directing agent and a source of a metal in a non-liquid crystalline

phase, dipping a substrate into the mixture, reducing the mixture to deposit a metal-organic composite onto the substrate, removing residues on the substrate onto which the metal-organic composite is formed, and extracting the organic from the metal-organic composite. Herein, the removal of the residues on the substrate is carried out by simple process such as air-blowing. This enables to avoid manual removal of the residues. So, the mesoporous metal electrode can be mass-produced by automation of the manufacturing processes.

- [23] The maintenance of the mixture as the non-liquid crystalline phase depends on the amount of the structure-directing agent, the temperature, and the solvent to be used. The kind of the structure-directing agent is not particularly limited. Various structure-directing agents that had been used in the art can be suitably adapted to the fabrication of the mesoporous metal electrode of the present invention. Preferable structure-directing agents are surfactants. Non-ionic surfactants are more preferable. Non-ionic surfactants are less sensitive to the electric field applied than ionic surfactants. So, there is little limitation by the voltage and the reproducibility is increased. Desirable examples of the surfactants are octylphenoxy-polyethoxy ethanol (Triton X-100TM), octaethyleneglycol monododecyl ether (C₁₂EO₈), octaethyleneglycol monoheptadecyl ether (C₁₆EO₈). Particularly desirable is octylphenoxy-polyethoxy ethanol. Besides, materials such as monoglycerides, phospholipids, glycolipids, and block-copolymers can be used as a structure-directing agent. With regard to the kind of the structure-directing agent, please refer to U.S. patent Nos. 6,203,925 and 6,503,382 mentioned in the above. The description of the two patents and documents cited are hereby incorporated by reference.
- [24] The desirable solvent in the non-liquid mixture of the present invention is water. The solvent dissolves a source of a metal (or a metal precursor). In order to increase ionic conductivity, electrolytes can be additionally dissolved. If necessary, a mixed solvent system of more than two solvents can be adopted. Sometimes, the reduction process can be carried out in a non-aqueous solvent.
- [25] Various metal thin films having mesopores, such as platinum, ruthenium, gold, nickel, palladium, silver, cobalt, iron, lead, tin and iridium can be formed on the substrate. With regard to the source of a metal to be used, please also refer to U.S. patent Nos. 6,203,925 and 6,503,382 mentioned in the above. According to the specific embodiment of the present invention, platinic acid, added in an amount of 1 - 5 wt% based on total weight of the mixture, gave satisfactory results.
- [26] The mixture according to the present invention is present as a non-liquid crystalline phase. It exists as an isotropic non-liquid crystalline phase, not as a liquid crystalline phase, that is, anisotropic metaphase. Specifically, the mixture exists either in an isotropic micelle or in an isotropic reverse micelle. In the micelle phase, the structure-

directing agent is surrounded by the solvent. In the reverse micelle phase, the solvent droplets are surrounded by the structure-directing agent. Most preferably, plating of the mesoporous thin film onto the substrate is carried out in a reverse micelle phase in which the solvent droplets are surrounded by surfactants.

- [27] The temperature can be suitably chosen regarding the solvent to be used, the amount of the structure-directing agent, and the amount of the platinic acid. For example, when 5 w% of platinic acid was added to the mixture of water and octylphenoxy-polyethoxy ethanol (Triton X-100TM) in a ratio of 45:50(wt/wt) at 40°C, the reverse micelle phase was obtained. As the amount of octylphenoxy-polyethoxy ethanol was decreased up to above critical micelle concentration, the micelle phase was obtained.
- [28] Formation of the metal-organic composite on a substrate is carried out by reducing the mixture into which the substrate is inserted. Herein, the reduction can be accomplished in a chemical or electrochemical method. Please refer to U.S. patent No. 6,203,925 for the details of the chemical reduction. Electrochemical reduction is preferable. The electrochemical reduction is carried out by applying the electric field while the substrate is dipped into the mixture. This is simple and suitable for the improvement of the characteristics of the electrode obtained. Please refer to U.S. patent No. 6,503,382 for more details.
- [29] The substrate onto which the metal-organic composite are formed is lift off from the mixture solution, and residues on the substrate are removed. The residues can be easily removed due to its low viscosity. Simple process such as air-blowing can be adopted, instead of manual removal. Thereafter, the substrate subjects to an extraction. By the extraction process, the organic is removed from the metal-organic composite, and a mesoporous metal electrode is obtained.
- [30] According to the test results in various conditions, it was confirmed that the mesoporous metal electrode prepared from the non-liquid crystalline mixture exhibits substantially the same characteristics as the one prepared from the conventional liquid crystalline mixture.
- [31] In the following, the present invention will be more fully explained referring to Examples. However, it should be understood that the examples are suggested for the purpose of illustration. The present invention is not limited thereto.

[32]

[33] **Examples**

[34] **- Materials**

[35] Triton X-100TM (Sigma), hexachloroplatinic acid hydrate (Aldrich), D-(+)-glucose (Sigma) and sulfuric acid were used without further purification. Gold and platinum disk electrodes were used. Another platinum disk electrode was used as flat platinum

electrode after polished with alumina (0.3 μ).

[36] **- Instruments**

[37] Electrochemical experiments were performed using an electrochemical analyzer (Model CH660, CH Instruments Inc., Austin, TX 78733). As an exemplarily sample, a gold or platinum rod electrode (0.0079 cm²) was employed as a substrate electrode for the deposition of mesoporous platinum film. Ag/AgCl (3 M KCl) and a platinum wire were used as a reference electrode and a counter electrode, respectively.

[38] **- Preparation of the non-liquid crystalline mixture**

[39] Triton X-100TM, a distilled water into which conductive electrolytes are dissolved, and hexachloroplatinic acid hydrate were mixed in a ratio of 50:50- x : x by weight, in which x has a value in a range of from 1 to 10. Then, the mixture was heated up to 40°C. Polarization microscopic test revealed that the mixture had a reverse micelle phase. Into the homogeneous mixture, the substrates were dipped.

[40] **- Fabrication of the mesoporous platinum electrode by electroplating of a platinum-organic composite onto the substrate followed by extraction**

[41] Electroplating was carried out onto a polished platinum disk electrode, by applying a constant potential in a range of -0.1 and -0.25 V versus Ag/AgCl. The thickness of the platinum-organic composite was found to be proportional to the electroplating time, the temperature and the potential passed. The substrate electrode onto which the platinum-organic composite was formed was lift off from the mixture and residues residing on the substrate was removed by air-blowing. The resulting nanoporous platinum electrode was placed in distilled water for 1 h to extract the organics (Triton X-100TM), and the extraction procedure was repeated 3-4 times. The electrode as treated was then electrochemically cleaned by cycling potential between +1.2 and -0.22 V versus Ag/AgCl in 1.0 M sulfuric acid until reproducible cyclic voltammograms were obtained. The mesoporous metal electrode thus obtained was named as L₂-ePt.

[42] **- Morphology analysis of the mesoporous metal electrode prepared from the non-liquid crystalline mixture**

[43] The surface area of L₂-ePt was determined by measuring the area under the hydrogen adsorption/desorption peaks of the cyclic voltammograms (scan rate, 0.2 V sec⁻¹) in 1.0 M sulfuric acid solution. A conversion factor of 210 C cm⁻² was used to determine the electrode area. The L₂-ePt prepared from the non-liquid crystalline mixture showed largely increased surface area, compared to H₁-ePt manufactured by Attard et al. Specifically, the cyclic voltammogram measured in 1M H₂SO₄ showed very large hydrogen adsorption/desorption peaks. Fig. 1 is the graph showing the results of the test on the roughness factor of the platinum electrode versus the charge passed during the electroplating at various potentials, temperatures, and concentrations

of platinic acid. Fig. 2 is the graph showing the dependence of roughness factors on the charge passed during electroplating. The results showed that the roughness factor of the platinum film increases as the charges passed is increased, and the roughness factor can be controlled by the charge passed. Figs. 1 and 2 showed that the roughness factor of the mesoporous platinum film reaches to several hundreds under various platinum concentrations and potentials applied.

- [44] To observe the surface structure of the mesoporous film, transmission electron microscopic images were attained. Fig. 3 are transmission electron microscopic images showing mesoporous metal electrode of the present invention, wherein (a) is under focus view, (b) is in focus view, (c) is over focus view, (d) is closer view of the selected area of (b), and (e) is cross sectional view, respectively. The TEM images showed that the pore size was in a range of 1.5-3 nm, and the pore-pore distance was 1.5-3 nm. The closer view of Fig. 3(d) showed that the pores were randomly distributed without any lattice. These are critically distinguished from the mesoporous metal electrodes manufactured from the liquid crystalline phase by Attard et al. and the mesoporous metal electrode from potential controlled surfactant assembly by Stucky et al.

[45] - **Use of the mesoporous platinum electrode as a glucose sensor**

- [46] Glucose sensor with L_2 -ePt as a working electrode was manufactured. In the Korean Patent application No. 2002-0005774, PCT/KR03/00884 and the paper (*Analytical Chemistry*, **2003**, 75(13), 3046), usefulness and principles of a mesoporous metal electrode as a glucose sensor are well described. The key idea behind the present study is based on the fact that the roughness of the mesoporous electrodes is even smaller than the scale of the chronoamperometric diffusion field in most cases. Since the diffusion layers reach several micrometers away from the electrode surface in milliseconds, reactants inside the mesopores (2-50 nm in diameter) are depleted in diffusion-controlled electrochemical systems. As a result, for rapidly oxidizable and/or reducible reactants, the faradaic current is proportional to the apparent geometric area of the electrode regardless of the mesoporous roughness. On the other hand, faradaic current associated with kinetic-controlled electrochemical events is sensitive to the nanoscopic area of the electrode rather than its geometric area. Thus, the mesoporous Pt electrode can be used to selectively enhance the faradaic current from a sluggish reaction.

- [47] According to the glucose measuring method of the present invention, the biosensor was inserted into the buffer solution containing glucose, and then constant potential was applied to measure the current change. As a buffer solution, phosphate buffer solution or phosphate buffered saline solution was used. Potential was applied between -0.1 V and 0.6 V vs. Ag/AgCl. Outside the range, side reactions such as adsorption/

desorption of hydrogen, oxidation of platinum or reduction of platinum oxide, reduction of oxygen prevail rather than glucose oxidation, and so that it gets difficult to measure the glucose concentration. As a reference electrode, Ag/AgCl electrode was used.

[48] Fig. 4 shows graphs of (a) current versus concentration and (b) the shape of current of various glucose concentrations in 0.1 M PBS solution containing 0.15 M chloride ion (pH 7.3) at 0.1 V versus mesoporous platinum oxide reference electrode. As illustrated in Fig. 4, the mesoporous platinum electrode of the present invention showed linear responses to the glucose concentration (increasing of the current with increasing of the glucose concentration), and negligible sensitivity for interfering agents. From these results, it was demonstrated that the glucose sensor selectively responses to glucose. The mesoporous platinum electrode showed selective responses to glucose even in the presence of high concentration (0.15 M) of chloride ion. This addresses the problem that the activities of the conventional electrochemical sensors are seriously decreased by the presence of the chloride ion, and implies that the mesoporous platinum of the present invention can be suitable for biosensors operating in bio-materials containing high levels of chlorides. Further, the mesoporous platinum electrode is mechanically or chemically robust, and is easily reproduced by electrochemical cleaning.

[49] Another example is depicted in Fig. 5. Fig. 5 is the calibration curve for glucose in 0.1 M phosphate buffer saline solution containing 0.15 M NaCl (pH 7.4). As shown in Fig. 5, the mesoporous metal electrode of the present invention showed linear response to the glucose concentration.

[50] - **Use of the mesoporous platinum electrode as a pH sensor**

[51] pH sensor was manufactured by using the large surface area of mesoporous L_2 -ePt. This example shows that the mesoporous metal electrode from the non-liquid crystalline phase can be effectively applied for the quantification of hydrogen ion concentration. Please refer to Korean patent application No. 2004-110819 and the paper (*Analytical Chemistry*, **2005**, 77(23), 7695) for detailed explanation of the operation principle of the mesoporous platinum as pH sensor. In the documents, detailed description for the utility of the mesoporous metal electrode made in the liquid crystalline phase as pH sensor was suggested.

[52] According to the pH measuring method of the present invention, oxidized L_2 -ePt was inserted and zero current potential (E_{oc}) was measured in a standard buffer for glass electrode calibration (pH 4, 7, 10), PBS (pH 7.4), and NaOH solution (pH 13.8), respectively. The oxidation of L_2 -ePt was conducted by applying 0.8 V vs. Hg/Hg_2SO_4 reference electrode for a constant time (typically 300 s) in 1.0 M H_2SO_4 solution. Fig. 6 is the E_{oc} versus pH curve of the mesoporous metal electrode of the present invention

in a stirred and air-saturated phosphate solution. In the graph, pH was decreased by adding 0.1 M H_3PO_4 to 0.1 M Na_3PO_4 ($\diamond$) and then increased by adding 0.1 M Na_3PO_4 again ($\square$). As shown in Fig. 6, the mesoporous metal electrode of the present invention exhibited increased exchange current, and improved sensitivity, stability, and response rate to hydrogen ion.

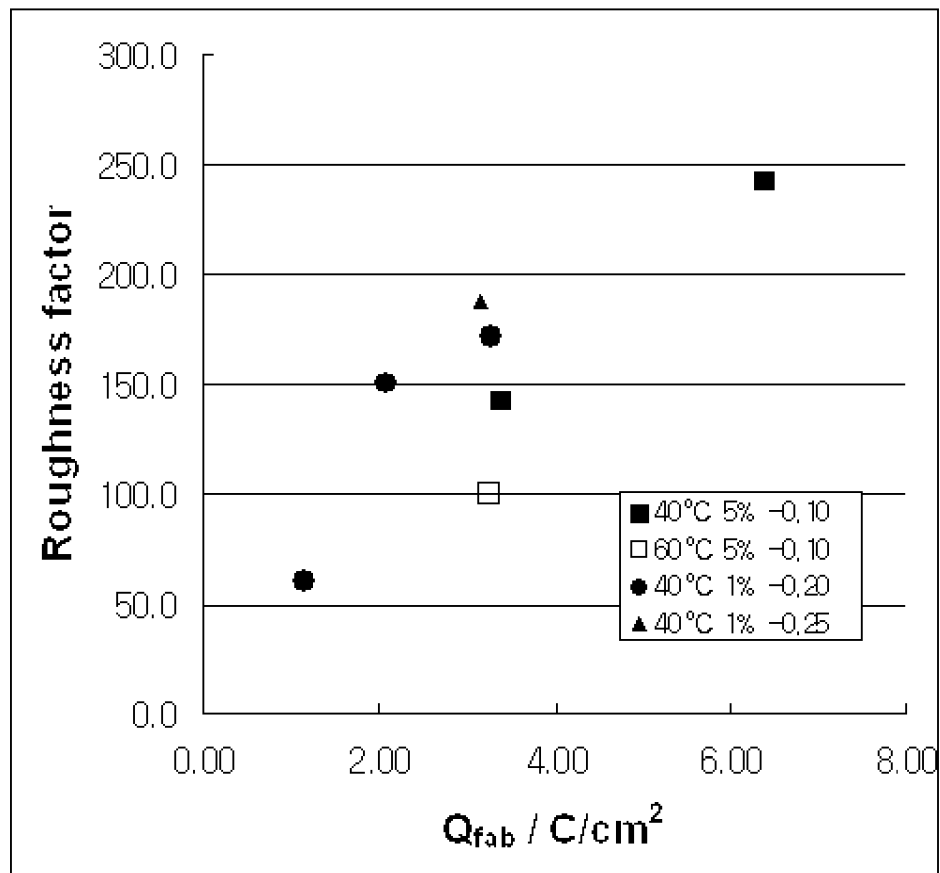
[53] - **Use of the mesoporous platinum electrode as a reference electrode**

[54] The usefulness of the mesoporous metal electrode prepared from the non-liquid crystalline phase as a reference electrode was tested. The L_2 -ePt whose surface was oxidized can be used as a reference electrode in electrochemical detection system, as Ag/AgCl or Hg/Hg₂SO₄ does. Pay attention to the fact that the oxidized L_2 -ePt was used instead of a commercial reference electrode in Fig. 4. Fig. 4 showed that electrochemical system operates successfully even though the oxidized L_2 -ePt was used.

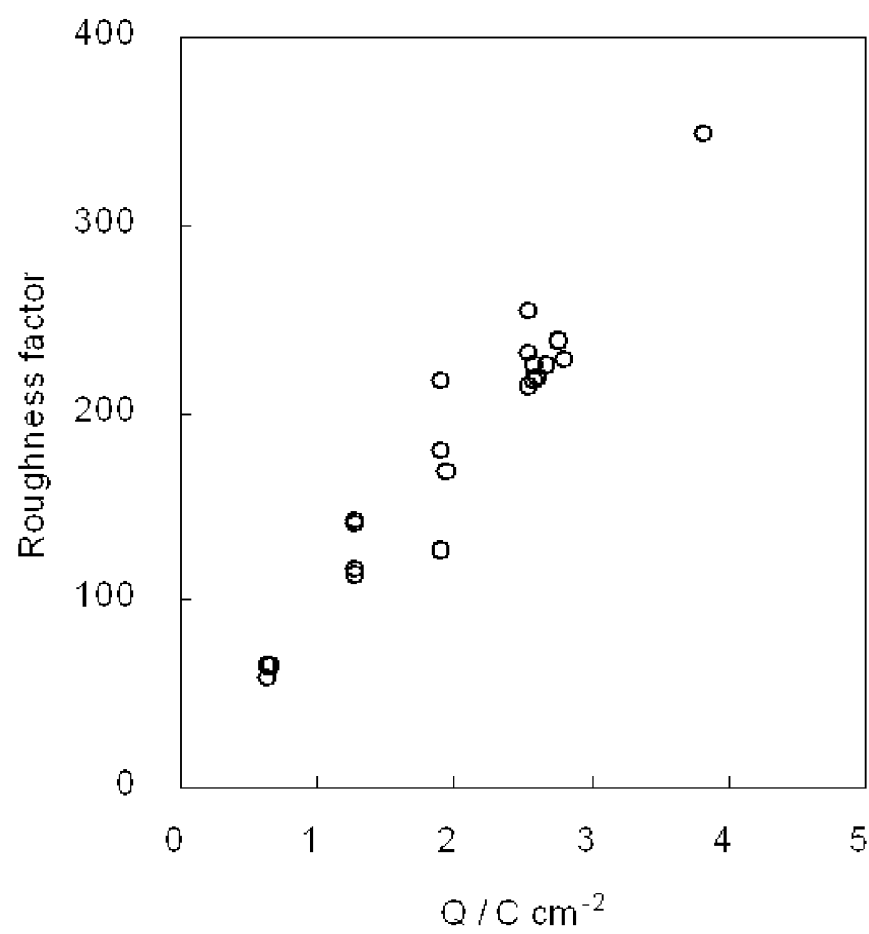
Claims

- [1] A method for the fabrication of a mesoporous metal electrode which comprises chemically or electrochemically reducing a mixture comprising a solvent, a structure-directing agent and a source of a metal to deposit a metal-organic composite onto a substrate to obtain the mesoporous metal electrode, characterized in that the mixture is maintained in a non-liquid crystalline phase, and the deposition of the metal-organic composite onto the substrate is performed in the non-liquid crystalline mixture.
- [2] The method as set forth in claim 1, comprising the steps of:
(a) maintaining a mixture comprising a solvent, a surfactant and a source of a metal in a non-liquid crystalline phase;
(b) dipping a substrate into the mixture and reducing the mixture to deposit a metal-organic composite onto the substrate;
(c) removing residues on the substrate onto which the metal-organic composite is formed; and
(d) extracting the organic from the metal-organic composite.
- [3] The method as set forth in claim 1, wherein the mixture is present as an isotropic, non-liquid crystalline phase.
- [4] The method as set forth in claim 3, wherein the mixture is present either as an isotropic micelle phase or as an isotropic reverse micelle phase.
- [5] The method as set forth in claim 4, wherein the mixture is present as an isotropic reverse micelle phase.
- [6] The method as set forth in claim 1, wherein the metal is selected from the group consisting of platinum, ruthenium, gold, nickel, palladium, silver, cobalt, iron, lead, tin and iridium.
- [7] The method as set forth in claim 1, wherein the deposition of the metal-organic composite onto the substrate is carried out by electroplating.
- [8] The method as set forth in claim 1, wherein the solvent is water and the structure-directing agent is a surfactant.
- [9] The method as set forth in claim 1, wherein the structure-directing agent is a non-ionic surfactant.
- [10] A mesoporous metal electrode fabricated by the method of claim 1, comprising a substrate onto which a thin film having randomly distributed mesopores is formed.
- [11] The mesoporous metal electrode as set forth in claim 10, being used for the detection of glucose or hydrogen ion, or for a cathode or anode of a fuel cell.

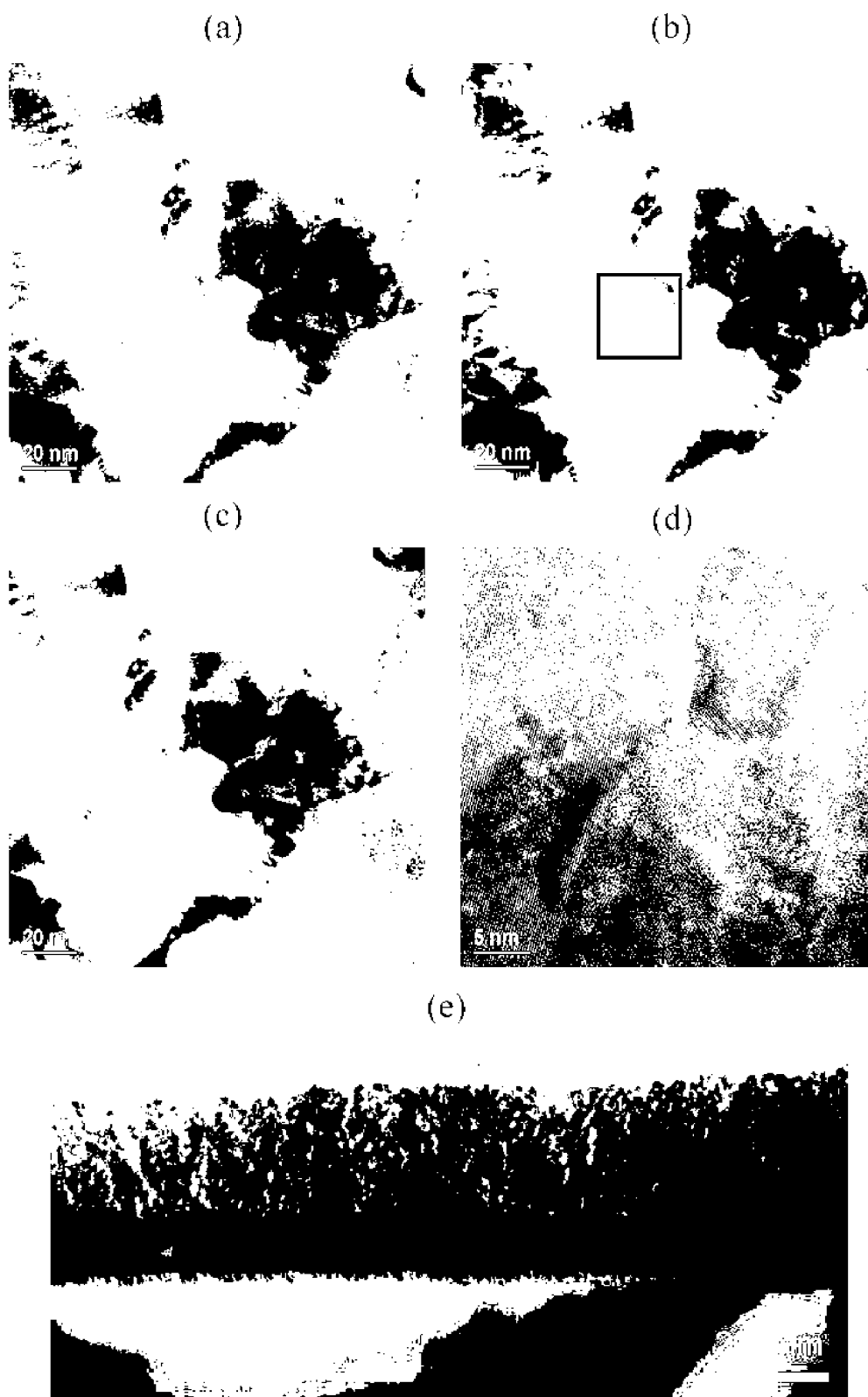
[Fig. 1]



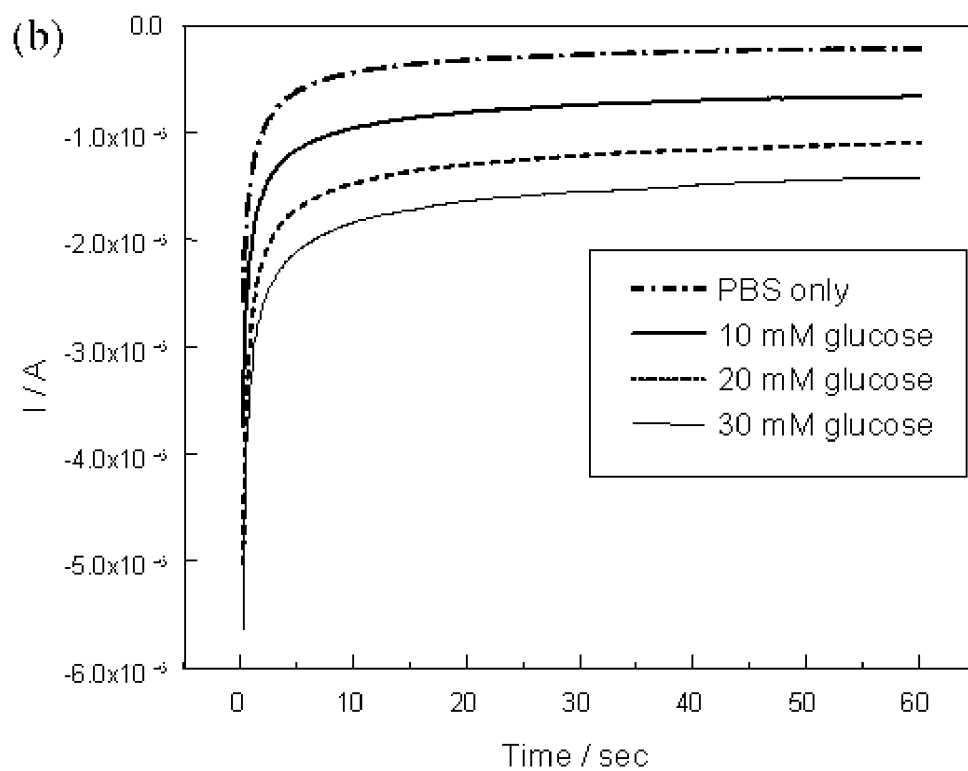
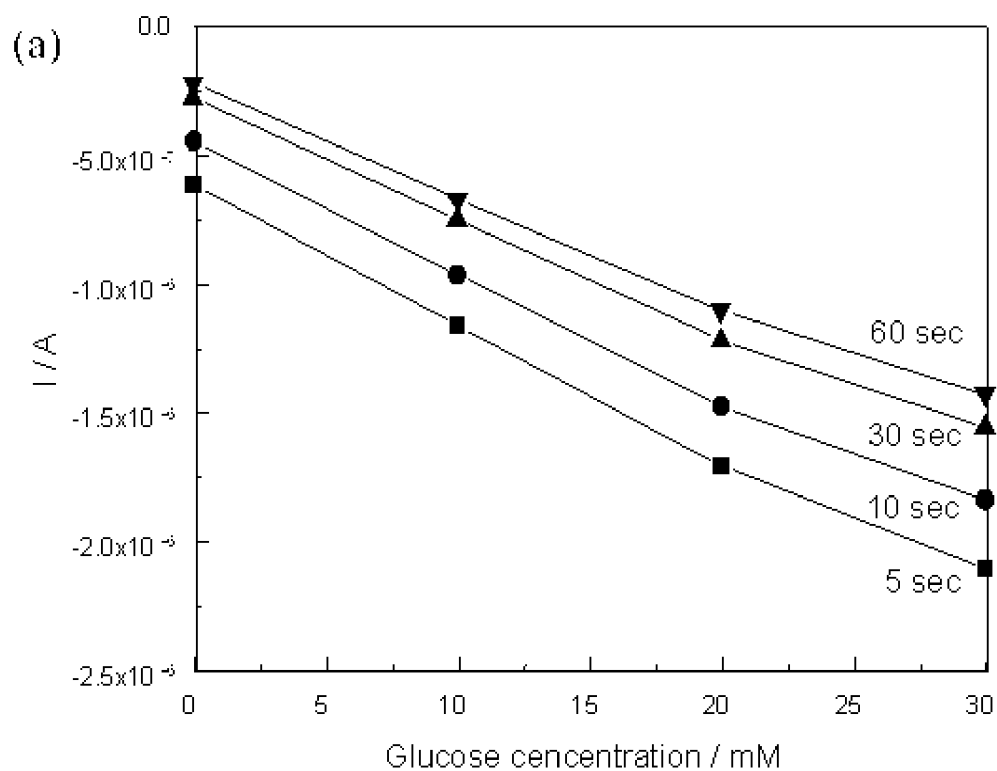
[Fig. 2]



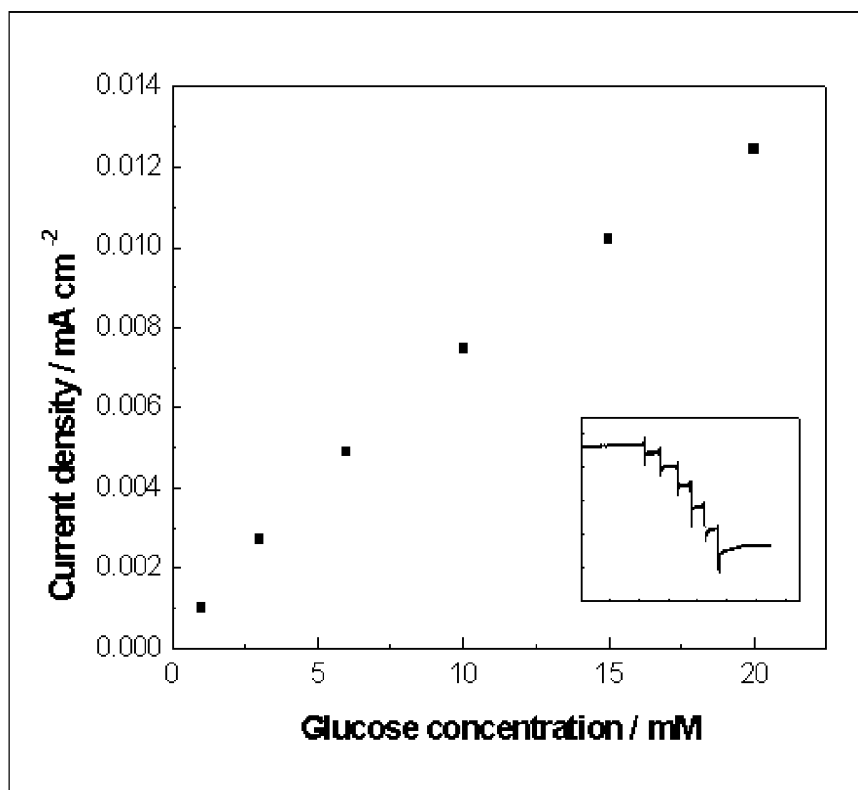
[Fig. 3]



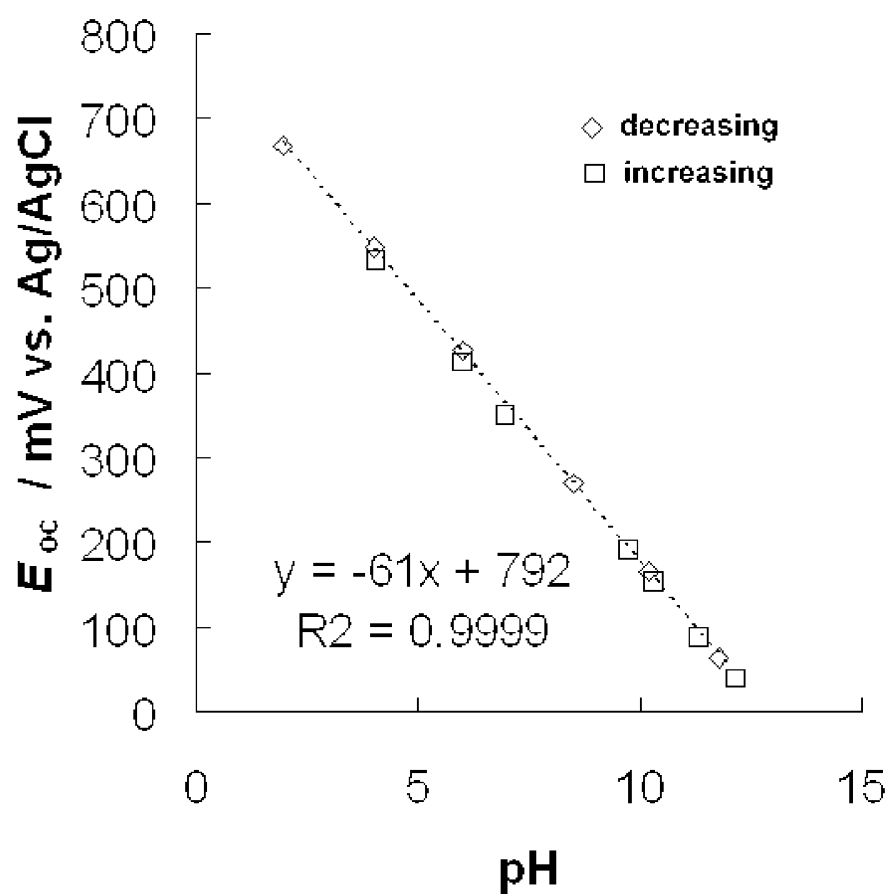
[Fig. 4]



[Fig. 5]



[Fig. 6]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2005/004487**A. CLASSIFICATION OF SUBJECT MATTER***C25D 1/08(2006.01)i*

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)

IPC8 C25D 1/08, C23C 22/78, B32B 5/18, H01M 4/90, B05D 5/06, C08J 7/18

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

Korean Patents and applications for inventions since 1975.

Korean Utility models and applications for Utility models since 1975.

Japanese Utility models and applications for Utility models since 1975.

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

Patent and Utility Search System at KIPO.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US6203925B1 (UNIVERSITY OF SOUTHAMPTON) 20 March 2001 See the abstract and claims 1 to 10	1 - 11
Y	US6420063B1 (MOBIL OIL CORP.) 16 July 2002 See the abstract, claims 1 to 8 and column 5, lines 46 to 56	1 - 11
Y	US5858457A (SANDIA CORP.) 12 January 1999 See the abstract and claims 1 to 15	1 - 11
Y	US6395350B1 (UNIV. TEXAS) 28 May 2002 See the abstract and claims 1 to 22	1 - 11
Y	WO02075826A2 (XOLIOX SA et al.) 26 September 2002 See the abstract and claims 1 to 21	1 - 11



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 application or patent 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 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 such 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

03 APRIL 2006 (03.04.2006)

Date of mailing of the international search report

03 APRIL 2006 (03.04.2006)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
920 Dunsan-dong, Seo-gu, Daejeon 302-701,
Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

CHUNG, SANG IK

Telephone No. 82-42-481-8145



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2005/004487

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US6203925B1	20.03.2001	AT303219E	15.09.2005
		AU743153B2	17.01.2002
		CA2282528A1	03.09.1998
		DE69831401C0	06.10.2005
		EP963266B1	31.08.2005
		ES2247680T3	01.03.2006
		GB9703920A0	16.04.1997
		JP2001513147T2	28.08.2001
		W09837997A2	03.09.1998
US6420063B1	16.07.2002	AU200075761A1	17.04.2001
		CA2384751A1	22.03.2001
		EP1237829A1	11.09.2002
		JP15509323	11.03.2003
		W00119752A1	22.03.2001
US5858457A	12.01.1999	AU9670398A	12.04.1999
		EP1028817A1	23.08.2000
		IL135228A	24.06.2003
		JP2001517595T	09.10.2001
		TW434186B	16.05.2001
US6395350B1	28.05.2002	W09915280A1	01.04.1999
		AU1206999A1	17.05.1999
		US6120891A	19.09.2000
		W09921923A1	06.05.1999
W002075826A2	26.09.2002	CA2441125AA	26.09.2002
		EP1374325A2	02.01.2004
		JP16533702	04.11.2004
		KR1020030093252	06.12.2003
		US20040131934A1	08.07.2004