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12/720,102 9 March 2010 (09.03.2010) US(71) Applicants (for all designated States except US): **OHIO UNIVERSITY** [US/US]; 20 East Circle Drive, Suite 190, Athens, OH 45701 (US). **UCHICAGO ARGONNE LLC** [US/US]; 5801 South Ellis Avenue, Chicago, IL 60637 (US).

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

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(54) Title: MICROSPHERES AND THEIR METHODS OF PREPARATION

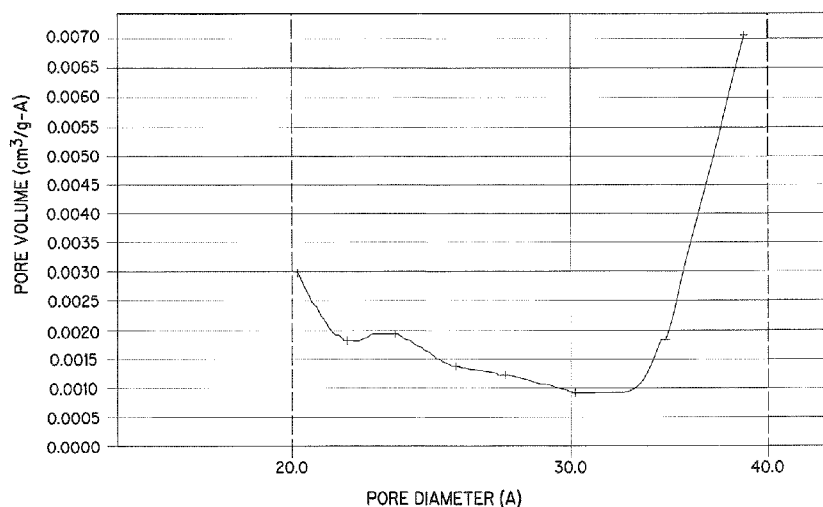


FIG. 1

(57) Abstract: Carbon microspheres are doped with boron to enhance the electrical and physical properties of the microspheres. The boron-doped carbon microspheres are formed by a CVD process in which a catalyst, carbon source and boron source are evaporated, heated and deposited onto an inert substrate.

MICROSPHERES AND THEIR METHODS OF PREPARATION

GOVERNMENT RIGHTS

[0001] This invention was made with Government support under Contract No. DE-AC02-06CH11357, awarded by the US Department of Energy, and Contract IL-26-7006-01 05P 08-282 awarded by the Department of Transportation. The Government has certain rights in this invention.

RELATED APPLICATION

[0002] This application is related to and claims the benefit of U.S. Provisional Patent Application Serial No. 61/161,580, filed March 19, 2009, the disclosure of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0003] Carbon microspheres, which generally have a particle size less than about 700 nanometers, have a wide variety of potential applications. These microspheres can be used as catalyst supports, as a medium for storing hydrogen, and as adsorbants, such as in the case of hemoperfusion and ultrafiltration membranes. These microspheres are nanoporous particles which are prepared by chemical vapor deposition. However, their use is somewhat limited by a lack of activity, in particular, electrical conductivity.

SUMMARY OF THE INVENTION

[0004] The present invention is premised on the realization that boron-doped carbon microspheres can be prepared, and can be used in a wide variety of applications including nano wiring and integrated circuits, and have superior physical properties relative to carbon microspheres.

[0005] The objects and advantages of the present invention will be further appreciated in light of the following detailed description and drawing in which:

BRIEF DESCRIPTION OF DRAWING

[0006] FIG. 1 is a graph of the BJH desorption differential pore volume distribution of boron-doped carbon microspheres (BCMS).

[0007] FIG. 2 is a diagrammatic depiction of a catalyst support.

[0008] FIG. 3 is a diagrammatic depiction of a hemoperfusion filter.

DETAILED DESCRIPTION

[0009] The boron-doped carbon microspheres of the present invention are microspheres having a diameter of less than about 700 nm and generally less than 500 nm, or less than 100 nm down to about 50 nm. The microspheres are further considered to be nanoporous wherein the spheres include pores having a diameter generally in the range of 0.6 nm to about 2 nm

[0010] These microspheres are formed from a combination of carbon and boron. The major component of the microspheres is carbon. The boron-doped carbon microspheres of the present invention are formed by chemical vapor deposition. In the chemical vapor deposition process, the reactants are injected into a flowing gas stream and are vaporized. The flowing gas stream, including the reactants, is heated further and impacted against a substrate and the carbon microspheres deposit on the substrate.

[0011] The reactants include a carbon source gas, a boron source, as well as a catalyst. Generally, any typical catalyst suitable for use in forming carbon microspheres can be employed. Iron, nickel and cobalt catalysts can be used. One typical catalyst is ferrocene.

[0012] The carbon source can be any hydrocarbon, either saturated or unsaturated and may be aromatic. In particular, compounds such as benzene and xylene are particularly suitable for use in the present invention as a carbon source.

[0013] The boron source must be a compound that can be formed into a vapor at reaction temperatures without decomposing. Generally, a vapor is formed by dissolving a boron containing compound into an appropriate solvent, preferably a hydrocarbon solvent, and then injecting this into the chemical vapor deposition

reactor. As is described below, it is convenient to dissolve the boron source into the carbon source.

[0014] Suitable boron containing compounds include the halides, such as boron trifluoride and boron trichloride, as well as other compounds that can be dissolved in an appropriate solvent such as nitrates, and the like. Generally, the stoichiometric ratio of boron to carbon will be 1 to 20 to 1.5 to 10 generally 1 to 9 to 1 to 10.

[0015] The reaction is conducted in a chemical vapor deposition reactor with a suitable deposition substrate. The deposition substrate must be inert under reaction conditions. Suitable substrates include magnesium oxide, aluminum oxide, indium tin oxide, as well as quartz.

[0016] Chemical vapor deposition reactors include a heating zone and a reaction zone. To form the microspheres, the heating zone is maintained at a temperature sufficient to vaporize the reactants, typically about 200 °C. The reaction zone is maintained at a much higher temperature, generally above 650 °C for this reaction, typically about 850-1000 °C. The reaction is conducted by forming a solution of the reactants, including the catalyst, carbon source and boron source, in the desired stoichiometric relation. This is injected into the heating zone into a flowing gas stream.

[0017] The flowing gas stream can be a variety of inert gases, but typically are nitrogen or argon, or mixtures thereof. Hydrogen may also be included to avoid soot formation, if needed. Further, a nitrogen source gas such as ammonia may be added to facilitate boron inclusion into the microspheres.

[0018] If ammonia is added, it will generally comprise about 10% of the partial pressure of the gas stream. Hydrogen will comprise 0-20% of the partial pressure of the gas stream. Generally, the ratio of ammonia to hydrogen to inert gas (Ar) will vary from 1:1:1 to 1:4:4 by volume. The flowing gas stream draws the reactants from the heating zone where they are vaporized into the reaction zone where they form the boron-doped carbon microspheres on the selected substrate, typically quartz.

[0019] When the nitrogen source gas, ammonia, is added, it is believed that the nitrogen bonds to carbon and bonds to the boron. If ammonia is not present, the boron bonds directly to the carbon. This latter reaction is not as thermodynamically favored as the nitrogen carbide formation. Thus, the addition of ammonia increases the incorporation of boron into the microspheres.

[0020] Typically, the reactor is purged with an inert gas to remove all oxygen from the system prior to the reaction. After purging, the flow of gas is started. The reactants are then introduced in the desired ratio into the flowing gas stream. After an appropriate period of time, generally 5 minutes to 1 hour, the injection of the reactants is discontinued and the furnace cooled down to room temperature under argon and hydrogen.

[0021] The formed microspheres can be subjected to a mild oxidation in order to open the porous structure. In order to do so, the preheating zone is heated to a temperature of about 500 °C, and the reaction zone to about 850 °C. Deionized water is simply injected into the preheating zone and evaporated and transported into the reaction zone in flowing argon. This is continued again for about 30 minutes. The furnace is then cooled down to room temperature under flowing argon.

[0022] The invention will be further appreciated in light of the following detailed examples.

EXAMPLE 1: Synthesis of BCMS

[0023] Boron-doped carbon microspheres (BCMS) were prepared by a chemical vapor deposition process inside a quartz tube inserted through a low-temperature heating section (Zone I, 200 °C) and a high-temperature heating section (Zone II, 950 °C).

[0024] 0.34 g Ferrocene was dissolved in 23.63 g boron trichloride solution 1.0 M in p-xylene (both from Sigma-Aldrich) and used as precursor for BCMS synthesis. The solution was injected and vaporized in Zone I. A hydrogen and argon mixture (60 ml/min and 90 ml/min, respectively) was used to transport the vapor from Zone I to Zone II. The BCMS were formed over a polished quartz plate inside Zone II. After 30 minutes, the solution injection was stopped and the furnaces were cooled down to room temperature with the argon and hydrogen flowing.

EXAMPLE 2: Activation of BCMS

[0025] The boron-doped carbon microspheres (BCMS) formed in Example 1 were activated in steam to open the pore structure. For this purpose, Zone I and Zone II were heated and kept at 500 °C and 850 °C, respectively. Deionized water was injected into and evaporated inside the quartz tube in the middle of Zone I at the rate of 0.225 ml/min. Flowing argon (140 ml/min) was used to carry the steam to

Zone II and react with BCMS, which were synthesized as disclosed in Example 1. The injection of water lasted for 30 minutes. After stopping the injection of water and turning off the temperature controller, the furnace was cooled down to room temperature with flowing argon.

[0026] The boron-doped carbon microspheres formed from the above examples were spherical particles with uniform particle size. TEM images reveal that the microspheres have an onion structure, and x-ray photon electron spectrum indicated they are comprised of carbon, boron and oxygen an impurity. Generally, the boron to carbon ratio is approximately from 1:4 - 1:12.

[0027] The microspheres are high purity uniform spheres of about 700 nanometers or less in diameter, and reasonably high surface area of about 220 m²/g measured via nitrogen absorption.

[0028] Further, thermogravimetric analysis demonstrates that the oxidation stability is comparable to pure multiwall nanotubes. The activated microspheres contain a large number of mesopores and the BET surface area is about 213 m²/g, which is the same range as standard carbon black, but higher than multiwall carbon nanotubes. The sheet resistance of the microspheres is lower than that formed from multiwalled carbon nanotubes. The micropore surface area was 107 m²/g and the total pore volume was 0.163 cm³/g. The micropore volume was 0.054 cm³/g and the median micropore diameter was 0.62 nm. Fig. 1 shows the pore size distribution of the activated microspheres. The activated microspheres clearly contain a large number of mesospheres.

EXAMPLE 3: Incorporation of Nitrogen

[0029] 0.5 g Ferrocene was dissolved in 28.0 g boron trichloride solution in 1.0 M p-xylene (both from Sigma-Aldrich) and used as precursor for BCMS synthesis. The solution was injected into the same reactor as in Example 1 and fully vaporized in the low-temperature zone I (200 °C). A carrier gas mixture containing ammonia, hydrogen and argon with pre-set volume ratio (volume ratio NH₃/H₂/Ar = 1/1.33/4 and total flow rate of 190 ml/min) was added through upstream of zone I. BCMS formed on the surface of a quartz substrate positioned in the high-temperature zone at 900 °C. The growth process lasted for 30 minutes until the liquid precursor injection stopped. The carrier gas continued to flow for another 20 minutes before the reactor was cooled down.

[0030] The boron-doped carbon microspheres of the present invention can be used in a variety of different applications. In particular, these can be used in fuel cells, which are devices that convert chemical energy of fuels, such as hydrogen, directly into electrical energy. The proton exchange membrane fuel cell is one type of fuel cell that can utilize the boron-doped carbon microspheres of the present invention. The boron-doped carbon microspheres can be used in any fuel cell operating at less than 500 °C. These can be combined with an electron conducting resin or used on other supports.

[0031] Also, the boron-doped carbon microspheres of the present invention can provide a durable catalyst support. The uniform pore size of the microspheres allow the microspheres to carry gases through their porous structure. In particular, the unique spherical structure and high thermal stability and oxidation resistance of the boron-doped carbon microspheres compared to carbon black, carbon fibers or carbon nanotubes, enable this product to be used as a catalyst support in which its uniform rate of gas transport does not degrade. Thus, the microspheres can be used as supports for electrolytic cell cathodes or anodes. These would be used in the electrolysis of water, ammonia or dissolved organic material.

[0032] The catalyst support can take the configuration shown in FIG. 2 in which a porous conductive support layer 11 is coated with a layer 12 of the boron-doped carbon nanospheres. This layer is in turn coated with a catalyst 13 such as a noble metal. The catalyst can be deposited by well known methods such as vapor deposition, electrochemical deposition and chemical deposition. Exemplary catalysts include platinum, iridium, ruthenium, rhenium, palladium, gold, silver, nickel, iron, lanthanides and alloys of these. Basically, any catalyst can be supported by these microspheres, including nonmetallic catalysts as well as metallic catalysts.

[0033] The boron-doped carbon microspheres of the present invention can also be used as an adsorbant to store gases such as hydrogen. In this application, hydrogen is typically stored under elevated pressure, and frequently at reduced temperatures, causing the hydrogen to migrate into the boron-doped carbon microspheres. The boron, in particular, enhances the hydrogen absorption via a non-classical chemical binding mechanism in which the two undissociated H atoms in the molecule and the B form a 3-body center sharing two common electrons. Further the high surface area increase H₂ absorption.

[0034] Also, due to the ability of the microspheres to absorb organic compounds, the microspheres of the present invention can be used as a drug delivery system, absorbing pharmacologically active organic compounds, and gradually releasing them subsequent to administration.

[0035] In another application, the boron-doped carbon microspheres of the present invention can be used as adsorbants in a wide variety of different applications, and, in particular, in hemoperfusion applications. The uniform size of these spheres, along with their porous structure, both facilitate in use in hemoperfusion in place of activated carbon.

[0036] As shown in FIG 2, the hemoperfusion filter 20 would include a porous support layer 22 coated with a layer of the boron-doped carbon microspheres 24. Blood or other fluid would flow through the filter 20 in the direction of arrow 26. Organic molecules will tend to bond to the microspheres thereby filtering the fluid.

[0037] The boron-doped carbon microspheres possess a much higher electrical conductivity than carbon nanotubes while being stable at higher temperatures. For that reason, the microspheres can be used in a variety of different applications.

[0038] These microspheres are particularly useful in batteries as a conductive surface and/or support. The microspheres can form conductive surfaces in metal ion batteries as well as metal hydride batteries and other batteries such as metal/air batteries. These microspheres can also replace carbon in the cathodes and anodes in batteries, fuel cells and electrolytic cells. They can also comprise nonometer size conductors or nano wiring for micro circuits.

[0039] The boron-doped carbon microspheres can be used in any application requiring electrical conductivity, and, in particular can be used to replace indium tin oxide in a variety of different applications, including solar panels, and the like. In particular, the boron-doped carbon microspheres can be added to photoactive compositions and used to form thin layer solar panels.

[0040] Thus, the boron-doped carbon microspheres of the present invention can be used in a wide variety of different applications because of their enhanced support stability through boron doping, enhanced catalyst support interaction providing improved stability, high electronic conductivity, spherical particle shape permitting uniform packing density.

[0041] This has been a description of the present invention along with the preferred method of practicing the present invention. However, the invention itself should only be defined by the appended claims, WHEREIN WE CLAIM:

WHAT IS CLAIMED IS:

1. Carbon microspheres having an average diameter of less than 700 nm wherein microspheres are doped with boron.
2. The carbon microspheres claimed in claim 1 wherein the boron to carbon ratio of said microspheres is at least 1:20.
3. The carbon microspheres claimed in claim 2 wherein the boron to carbon ratio of said carbon microspheres is less than 1.5 to 10.
4. The carbon microspheres claimed in claim 3 wherein the boron to carbon ratio of said microspheres is from about 1:4 - 1:12.
5. The carbon microspheres claimed in claim 1 further comprising nitrogen.
6. A separator for an electrolytic cell comprising a support containing the carbon microspheres claimed in claim 1.
7. A method of forming boron-doped carbon microspheres comprising heating a carbon source and a boron source and a catalyst in a gas stream to a temperature effective to vaporize said sources and said catalyst thereby forming a reactant vapor mixture; and
further heating said vapor mixture to a second temperature effective to cause said boron source and said carbon source to react and depositing boron-doped microspheres onto a substrate.
8. The method claimed in claim 7 wherein said gas stream comprises one of H₂, N₂, Ar, and mixtures thereof.
9. The method claimed in claim 7 wherein said gas stream further includes NH₃.

10. The method claimed in claim 7 further comprising contacting said microspheres with steam to activate said microspheres.
11. The microspheres claimed in claim 1 further comprising a gas stored in said microspheres.
12. The microspheres claimed in claim 11 wherein said gas is H₂.
13. A fuel cell including a membrane;
said membrane comprising an electron conducting resin in combination with boron-doped carbon microspheres.
14. A catalyst structure comprising a layer of boron-doped carbon microspheres coated with a catalyst.
15. The catalyst structure claimed in claim 13 wherein said catalyst is a metal.
16. The catalyst structure claimed in claim 14 wherein said structure is an electrode in an electrolytic cell.
17. A method of storing H₂ with boron-doped carbon microspheres at superatmospheric pressure and at subambient temperatures, thereby causing said H₂ to be absorbed into said microspheres.
18. A hemoperfusion device having a filter;
said filter comprising a layer of boron-doped carbon microspheres supported on a porous substrate.
19. A delayed release composition comprising an active pharmaceutical composition adsorbed onto a boron-doped carbon microsphere.
20. A photovoltaic device comprising a layer comprising a photoactive composition adsorbed onto boron-doped carbon microspheres.

21. An electrical conductor formed from carbon microspheres claimed in claim 1.
22. The electrical conductor claimed in claim 21 wherein said conductor is in a battery.
23. The electrical conductor claimed in claim 22 wherein said conductor is an electrode.
24. The electrical conductor claimed in claim 21 wherein said conductor comprises nano wiring.

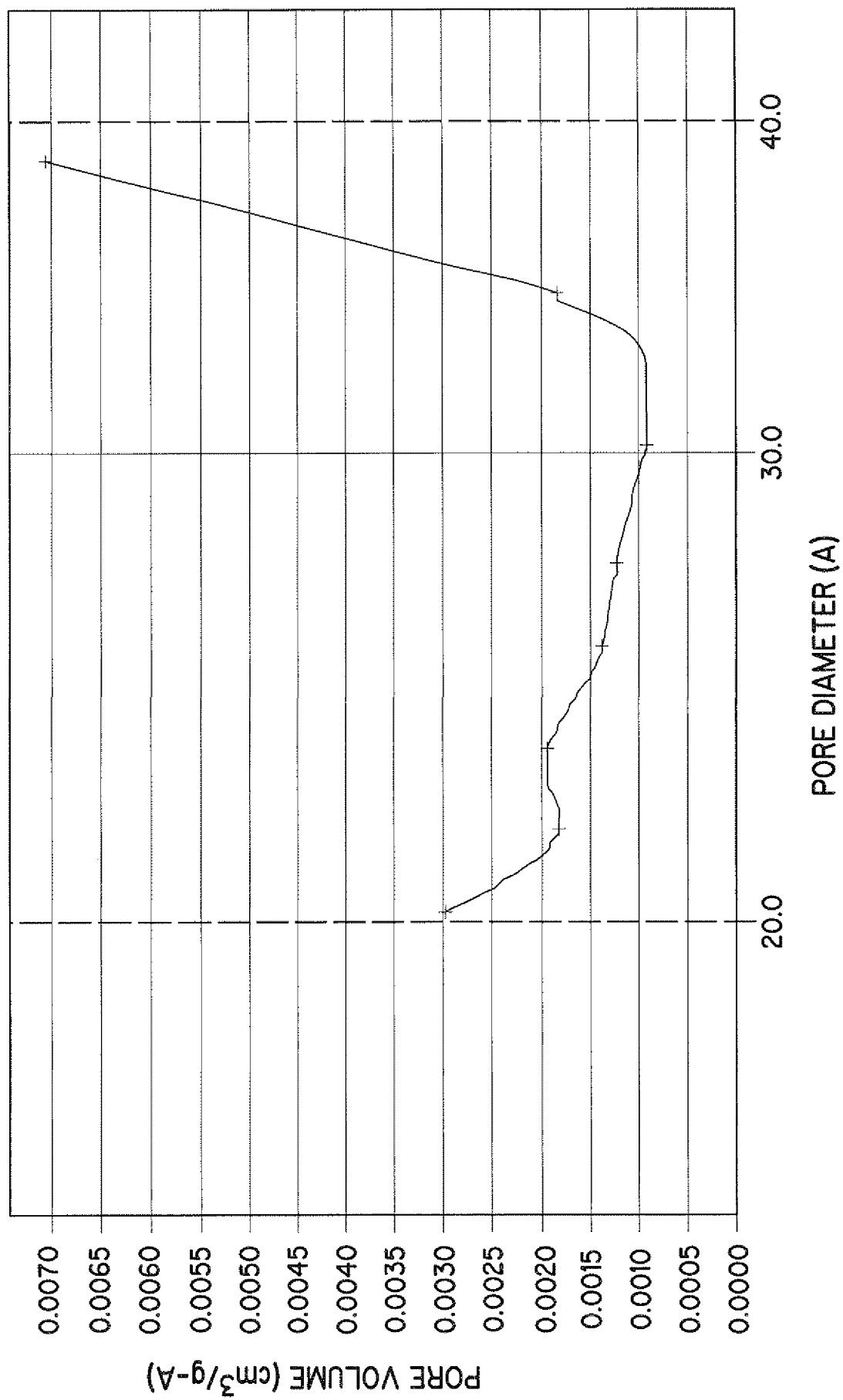


FIG. 1

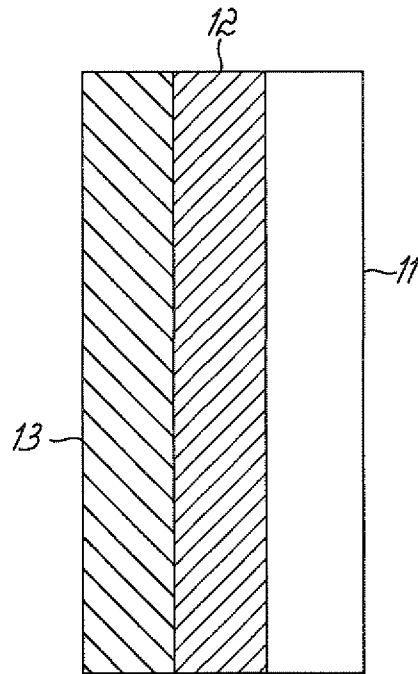


FIG. 2

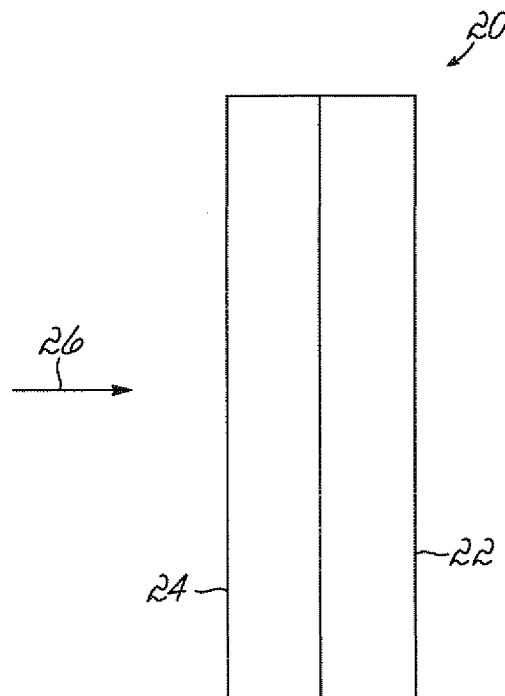


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 10/27293

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - H01B 1/04 (2010.01) USPC - 428/402; 252/502 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) IPC- H01B 1/04 (2010.01); USPC- 428/402; 252/502 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Patents and NPL Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWest (US Pat, PgPub, EPO, JPO: classification, keyword), GoogleScholar; search terms: carbon, microsphere, micro, nano, sphere, particle, boron, dope, electrode, battery, nanowire, gas storage																							
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US 5,908,896 A (MAYER et al.) 01 June 1999 (01.06.1999), col 2, ln 62-65; col 3, ln 19; col 5, ln 1-8; col 2, ln 58-61; col 5, ln 9-28, col 7, ln 5-25</td> <td>1, 21-23</td> </tr> <tr> <td>Y</td> <td></td> <td>2-6, 11, 12, 24</td> </tr> <tr> <td>Y</td> <td>US 2005/0025970 A1 (STIPANOVIC) 03 February 2005 (03.02.2005), para [0006], [0010], [0017], [0018], [0022]-[0029], [0060], [0062], [0074]</td> <td>2-6, 11, 12</td> </tr> <tr> <td>Y</td> <td>US 2004/0132220 A1 (FISH) 08 July 2004 (08.07.2004), para [0021], [0113], [0121], [0128]</td> <td>24</td> </tr> <tr> <td>A</td> <td>WO 2005/122285 A2 (NUZZO et al.) 22 December 2005 (22.12.2005), entire document</td> <td>1-6, 11, 12, 21-24</td> </tr> <tr> <td>A</td> <td>US 6,716,525 B1 (YADAV et al.) 06 April 2004 (06.04.2004), entire document</td> <td>1-6, 11, 12, 21-24</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 5,908,896 A (MAYER et al.) 01 June 1999 (01.06.1999), col 2, ln 62-65; col 3, ln 19; col 5, ln 1-8; col 2, ln 58-61; col 5, ln 9-28, col 7, ln 5-25	1, 21-23	Y		2-6, 11, 12, 24	Y	US 2005/0025970 A1 (STIPANOVIC) 03 February 2005 (03.02.2005), para [0006], [0010], [0017], [0018], [0022]-[0029], [0060], [0062], [0074]	2-6, 11, 12	Y	US 2004/0132220 A1 (FISH) 08 July 2004 (08.07.2004), para [0021], [0113], [0121], [0128]	24	A	WO 2005/122285 A2 (NUZZO et al.) 22 December 2005 (22.12.2005), entire document	1-6, 11, 12, 21-24	A	US 6,716,525 B1 (YADAV et al.) 06 April 2004 (06.04.2004), entire document	1-6, 11, 12, 21-24
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☐ Further documents are listed in the continuation of Box C. ☐																							
<table border="0"> <tr> <td> * 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 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 </td> <td> "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 </td> </tr> </table>			* 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 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 such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family																			
* 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 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 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 07 June 2010 (07.06.2010)		Date of mailing of the international search report 06 JUL 2010																					
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774																					

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/27293

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see Extra Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-6, 11-12, 21-24

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Box No. III, Observations where unity of invention is lacking:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-6, 11-12, 21-24 directed to carbon microspheres having an average diameter of less than 700 nm wherein microspheres are doped with boron.

Group II: claims 7-10 directed to a method of forming boron-doped carbon microspheres comprising heating a carbon source and a boron source and a catalyst in a gas stream to a temperature effective to vaporize said sources and said catalyst thereby forming a reactant vapor mixture; and further heating said vapor mixture to a second temperature effective to cause said boron source and said carbon source to react and depositing boron-doped microspheres onto a substrate.

Group III: claims 13, 15 directed to a fuel cell including a membrane; said membrane comprising an electron conducting resin in combination with boron-doped carbon microspheres.

Group IV: claims 14, 16 directed to a catalyst structure comprising a layer of boron-doped carbon microspheres coated with a catalyst.

Group V: claims 17 directed to a method of storing H₂ with boron-doped carbon microspheres at superatmospheric pressure and at subambient temperatures, thereby causing said H₂ to be absorbed into said microspheres.

Group VI: claims 18 directed to a hemoperfusion device having a filter; said filter comprising a layer of boron-doped carbon microspheres supported on a porous substrate.

Group VII: claims 19 directed to a delayed release composition comprising an active pharmaceutical composition adsorbed onto a boron-doped carbon microsphere.

Group VIII: claims 20 directed to a photovoltaic device comprising a layer comprising a photoactive composition adsorbed onto boron-doped carbon microspheres.

The inventions listed as Groups I-VIII do not relate to a single general inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding technical features for the following reasons:

Groups II-VIII do not include the average diameter of less than 700 nm of group I.

Groups I, III-VIII do not include the heating source material with a catalyst at different temperatures of group II.

Groups I, II, IV-VIII do not include the fuel cell including a membrane of group III.

Groups I-III, V-VIII do not include the catalyst structure comprising a layer of boron-doped carbon microspheres coated with a catalyst of group IV.

Groups I-IV, VI-VIII do not include the storing H₂ at superatmospheric pressure and at subambient temperatures of group V.

Groups I-V, VII-VIII do not include the hemoperfusion device having a filter of group VI.

Groups I-VI, VIII do not include the a delayed release composition comprising an active pharmaceutical composition of group VII.

Groups I-VII do not include the photovoltaic device of group VIII.

The common feature of boron-doped carbon microspheres of Groups I-VIII is taught by US 5,908,896 A to Mayer et al. issued 01 June 1999 (col 2, ln 42- to col 3, ln 32); therefore the common feature is not an improvement over the prior art.

None of these technical features are common to the other groups, nor do they correspond to a special technical feature in the other groups. Therefore, unity of invention is lacking.