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(54) **Title**: CONDUCTING POLYMER WITH ACTIVELY SWITCHABLE ABSORBENCY

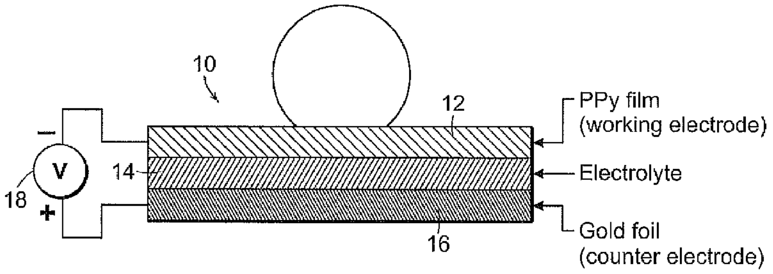

FIG. 1

(57) **Abstract**: Structure with electrically switchable wettability. The structure includes a doped conducting polymer, a counter electrode and an electrolyte disposed between the doped conducting polymer and the counter electrode. A preferred conducting polymer is polypyrroie doped with fluorinated carbon ions. A voltage between the doped conducting polymer and the counter electrode will cause the conductive polymer to switch between hydrophobic and hydrophilic states.

CONDUCTING POLYMER WITH ACTIVELY SWITCHABLE ABSORBENCY

Priority Information

This application claims priority to U.S. Utility Application No. 12/796,796, filed on June 9, 2010 which is incorporated herein by reference in its entirety.

Sponsorship Information

This invention was made with Government support under Contract No. W911NF-07-D-0004, awarded by the Army Research Office. The Government has certain rights in this invention.

Background of the Invention

The present invention relates to structure with switchable wettability and more particularly to such a structure that can be reversibly switched electrically between hydrophobic and hydrophilic states.

Materials are known whose wettability may be switched. These materials may be thermally responsive, pH responsive, and photo responsive in effecting the switch from a hydrophobic to a hydrophilic state. Another method of switching wettability is electrowetting, where an electric field applied between the material and the fluid changes the surface tension of the fluid and causes it to wet the surface. The wetting state of a surface is quantified by the contact angle that a water droplet makes with the surface – a hydrophobic surface has a contact angle greater than 90° and a hydrophilic surface has a contact angle less than 90°. Special non-wetting, or *superhydrophobic* surfaces are characterized by contact angles greater than 150°, while fully-wetting, or *superhydrophilic*, surfaces are characterized by contact angles less than 5°.

Conducting polymers offer advantages over other methods of switching wettability because of their fast electrochemical switching, low operating voltage and ease of fabrication. Polypyrrole is a conducting polymer. Previously, polypyrrole required immersion in an electrolyte in order to switch its wettability between hydrophobic to hydrophilic states by electrically inducing a change in the chemical composition of the surface. This severely limited the applications for which polypyrrole could be used.

Another conducting polymer is polyaniline. A research group has demonstrated a wettability switch with polyaniline without immersion in electrolyte but this group was able only to switch the surface between a slightly hydrophilic state (contact angle = 37°) and a more hydrophilic state (contact angle = 9°). They could not switch between superhydrophobic and superhydrophilic states. See, Isaksson, J., et al., "A Solid-State Organic Electronic Wettability Switch," Advanced Materials, 16.4(2004): 316-320.

An object of the invention, therefore, is to create a structure that allows switching of the conducting polymer such as polypyrrole from hydrophobic to hydrophilic without full immersion in an electrolyte.

Summary of the Invention

In one aspect, the structure according to the invention has electrically switchable wettability. The structure includes a doped conducting polymer, a counter electrode and an electrolyte disposed between the doped conducting polymer and the counter electrode. A preferred conducting polymer is polypyrrole. Another suitable conducting polymer is polyaniline. In a preferred embodiment, the polypyrrole is doped with fluorinated carbon ions such as perfluorooctanesulfonate and nonafluorooctancesulfonate ions. In applications where biocompatibility is important; the polypyrrole polymer may be doped with biocompatible chemicals such as sodium dodecylbenzenesulfonate (NaDBS). In this preferred embodiment a suitable counter electrode is gold foil. The structure may include a moisture sensor to trigger the switch from hydrophobic to hydrophilic or vice versa. A means is provided for establishing a voltage between the conducting polymer and the counter electrode.

The structure disclosed herein may be incorporated into consumer products such as diapers and feminine hygiene products. The structure may also be incorporated into micro-fluidics systems. Further, the structure may be coated upon a surface.

In another aspect, the structure according to the invention incorporates an electrically switchable wettability gradient portion and includes a doped conducting polymer along with a counter electrode. An electrolyte is disposed between a portion of the doped conducting polymer and the counter electrode so that a portion of the structure may be switched from a hydrophobic to hydrophilic state and back again. A wettability gradient can also be created by applying different voltages to electrically isolated portions of the polymer. This structure can be used to move a liquid droplet or to control a liquid droplet contact angle so as to make a variable refractive power lens.

Brief Description of the Drawing

Fig. 1 is a schematic diagram of one embodiment of the present invention.

Fig. 2 is a photograph of a prototype created for experimental purposes.

Figs. 3a and 3b are schematic illustrations of an embodiment of the invention in which the electrolyte region covers only a portion of the conductive polymer.

Fig. 4 is a photomicrograph of a thin film of polypyrrole.

Fig. 5 are photographs of droplets placed on polypyrrole in different doped states, showing that the surface can be switched between superhydrophobic and superhydrophilic states by reduction and oxidation.

Fig. 6 is a graph of sodium chloride concentration in water versus contact angle.

Figs. 7a-7d are photographs of a droplet moving across a wettability gradient.

Figs. 8a-8d illustrate a droplet being absorbed into the structure when the wettability is switched to hydrophilic.

Description of the Preferred Embodiment

With reference first to Fig. 1, a switchable device or structure 10 includes a polypyrrole layer 12, an electrolyte layer 14 and a gold foil counter electrode 16. The counter electrode 16 need not be gold foil. It can be any chemically inert conductive material (e.g., stainless steel). It can also be a conducting polymer such as polypyrrole. A voltage source 18 provides an electrical potential between the polypyrrole film 12 and counter electrode 16. The polypyrrole film 12 has the ability to be activated with a low voltage which may be less than 5 volts. The polypyrrole film 12 is doped with a fluorinated carbon such as perfluorooctanesulfonate or nonafluorooctanesulfonate ions which move in and out of the material with an electrical stimulus. Another fluorinated carbon ion that may be used is perfluorobutanesulfonate. The fluorinated carbon can also be a fluorosurfactant. The ionic motion changes the chemical composition and therefore the hydrophobicity of the material. An advantage of using fluorinated carbon materials as the dopant is the wide range of hydrophobic/hydrophilic conditions that are possible. The material can switch from a completely non-wetting (superhydrophobic) to a fully wetting (superhydrophilic) state.

When the material is fully doped, it is in the completely non-wetting state, and when it is undoped (concentration of dopant ions close to zero), the material is in the fully wetting state. The material can be partially doped to be in an intermediate, partially wetting state. The fully-doped material contains the maximum concentration of dopant that can be driven into the polymer.

In applications where biocompatibility is a concern (i.e., diapers, feminine hygiene products), the polymer can be doped with chemicals known to be biocompatible such as sodium dodecylbenzenesulfonate (NaDBS), and still exhibit a hydrophobic-hydrophilic switch. Those of ordinary skill in the art will recognize that a moisture sensor can be provided to cause the structure 10 to switch its state when moisture is detected. In this case, the polymer can switch into a storage mode to prevent moisture from exiting the material. In the storage mode, the polymer is completely absorbent and will absorb any moisture that contacts the polymer. The polymer can also be switched to an intermediate absorbency state, where the polymer is switched to a partially wetting state. In the intermediate absorbency state, the polymer will be able to absorb a fraction of the moisture that comes into contact with the polymer.

The electrolyte layer 14 is ionically conductive but electrically insulating. Applying a voltage between the two layers 12 and 16 will drive ions that make the material hydrophobic out of the polypyrrole, through the electrolyte 14 layer and toward the counter electrode 16 resulting in a hydrophilic surface. By reversing the voltage the ions can be driven back into the polymer resulting once again in a hydrophobic surface.

Fig. 2 is a photograph of a prototype created for experimental purposes. This prototype in Fig. 2 has demonstrated a switch from a superhydrophobic to a superhydrophilic state. The transition time can be as fast as 20 milliseconds. The transition time can be adjusted by the type of electrolyte used. Suitable electrolytes and their transition times are shown in Table 1.

Table 1: Transition times for various electrolytes

Electrolyte	Transition time
0.1 M potassium perflourooctanesulfonate + propylene carbonate + 25 wt% polymethylmethacrylate	1 – 3 sec
0.03 M potassium perfluorooctanesulfonate in cellulose-based gel	30 – 120 sec
0.015 M potassium perfluorooctanesulfonate in deionized water	20 msec

In general, the first electrolyte in Table 1 is a salt (such as potassium perfluorooctanesulfonate) dissolved in an organic solvent (such as propylene carbonate, ethylene carbonate, acetonitrile, or a combination of these solvents) with poly(methyl) methacrylate (PMMA) added as a stiffener. The second electrolyte in Table 1 is a salt dissolved into a cellulose-based gel, and the third electrolyte in Table 1 is a salt dissolved in deionized water.

With reference now to Figs. 3a and 3b, the electrolyte region 14 extends below only a portion of the polypyrrole film 12. This arrangement allows a wettability gradient to be created on the surface by controlling which regions of the film are in contact with the electrolyte. As shown in Fig. 3a, a liquid droplet 20 may be caused to move toward the right (Fig. 3b) when the region above the electrolyte becomes hydrophilic. Thus the present invention can be used to move droplets or to cause droplets to interact with one another to improve mixing. A wettability gradient can also be created by activating electrically isolated regions of the polymer, therefore switching only certain regions of the polymer.

With reference to Fig. 4, the polymer film 12 exists as a thin film with rough microstructures on its surface. The rough microstructures act to amplify the inherent hydrophobicity or hydrophilicity of the material. By varying the deposition conditions, the film thickness can be adjusted. Table 2 shows that film thickness can be adjusted by varying the current density during which the film is grown. The microstructures can be added to the material with either soft-template or hard-template methods.

Table 2: The film thickness can be adjusted by varying the current density that the film is grown at.

Current Density (A/m^2)	Underlying Film Thickness (nm)	Micro-structures height (µm)
0.5	50	10-25
1.0	70	10-25
1.5	178	15-30
2.0	180	25-40
2.5	160	35-40

The polymer can be switched between superhydrophobic (contact angle greater than 150°) and superhydrophilic (0° contact angle) states. Fig. 5 illustrates that the surface can be switched from superhydrophobic to superhydrophilic states by reduction and oxidation.

The structure 10 disclosed herein can be used to repel and absorb a variety of fluids including water. The polymer has demonstrated superhydrophobicity with other high surface tension fluids, such as glycerol and saltwater (aqueous NaCl solution). The polymer disclosed herein has demonstrated a high hydrophobicity to salt water with salinity comparable to seawater (0.6 M NaCl in H_2O) with a contact angle of 142°. Fig. 6 is a graph showing the effect of NaCl concentration on contact angle. Table 3 shows contact angles of various fluids on the polymer.

Table 3: Contact angles of various fluids on the polymer

Name	Surface Tension, γ_{lv}, at 20°C (mN/m)	Contact Angle (deg)
Water	72.8	164
Glycerol	64.0	146
Ethylene glycol	47.7	51
Propylene glycol	38.0	0
Oil	20-25	0
6.0 M NaCl in water	82.55	76

The switchable structure disclosed herein retains its switchability for at least 100 cycles with only slight degradation occurring. Table 4 illustrates that the polymer can last at least 100 cycles.

Table 4: The polymer can last at least 100 cycles

Cycle Number	$\theta^*_{oxidized}$	$\theta^*_{reduced}$
0 (initial)	161	0
10	154	0
50	155	0
100	148	0

Experiments have been conducted to establish the efficacy of the structure disclosed herein. Figures 7a-7d illustrate the movement of a droplet of liquid toward the right as the wettability is switched. Figs. 8a-8d show a liquid droplet being absorbed when the structure is switched from hydrophobic to hydrophilic.

Those of ordinary skill in the art will recognize that the structure disclosed herein will have myriad applications. In addition to diapers and feminine hygiene products, mops and sponges could benefit from the structure of the invention. In the diaper context, an absorbency gradient can be employed so that certain areas of the product can be more absorbent than others. For example, a diaper with a superabsorbent bottom and a dry waistline may be desired to contain moisture and prevent leaks. There can thus be zones of absorbency and non-absorbency as needed and these zones can have the ability to change location due to the switchable hydrophobicity of the structure disclosed herein.

Other applications of the structure disclosed herein can be used in the field of microfluidics such as lab-on-a-chip devices. The structure disclosed herein can be used to drive fluid droplets across a surface without the need for channels. This functionality can result in less contamination and more flexibility in fluid delivery since the fluid can be driven to any point on the surface and not limited by paths set by channels. This functionality has many applications including drug, fluid, and nutrient delivery, cell and tissue culture platforms, and high-throughput assays.

The structure of the invention can also be used in a micro-mixing context. The device can be used to drive two micro-droplets together to promote mixing. The active mixing process is much faster than the passive diffusion process. The present invention can also be used for coatings for microfluidic channels to allow researchers to control the fluid flow inside a channel. Fluid flow can be stopped and started on command.

The present invention can also be used in smart cooling systems in which water droplets are delivered to hot spots that can develop on heat exchangers and electrical circuits. The structure disclosed herein provides a faster, more efficient method of cooling. The invention can also be used for water harvesting. Water droplets can collect and grow on hydrophilic regions of the structure. Once the droplets have grown to an appropriate size they can be released and collected as the surface is switched to hydrophobic.

The present invention may also be used to make liquid lenses having infinitely-variable refractive index by controlling the liquid contact angle and without the need for any moving parts. The invention can also be used to form self-cleaning surfaces. The polymer can be used as a coating on any surface. When water droplets contact the coating, they will roll off when the polymer is tilted at a low angle (10°), and collect any dirt or particles that have collected on a surface.

Another important use for the structure disclosed herein is for low friction surfaces or surfaces with variable friction characteristics. For example, the polymer can be used as a coating on pipes, submarines, boats, or any other water vehicle. In the superhydrophobic, non-wetting state, the friction coefficient between water and the polymer is extremely low. In the superhydrophilic wetting state, the friction coefficient between water and the polymer is high. The polymer can be switched to the non-absorbent state thereby allowing the vehicle to move very fast since drag has been reduced. When the polymer is switched to the absorbent state, drag is increased and the vehicle can slow down much faster than without the coating. It will also be apparent that weatherproof materials can utilize the polymer coated on clothing or other products such as camping gear, umbrellas, and boots that need to be waterproof.

The polymer disclosed herein exhibits oleophilic (oil-absorbent) properties. In the non-wetting state, the polymer can absorb oil and repel water which can be used for oil and water separation or filtering applications. The polymer can absorb both oil and water when switched to the wetting state.

Heretofore, a significant disadvantage of the polypyrrole conducting polymer was that it required immersion in an electrolyte in order for it to be switched. The inventors herein are aware of no group that has of yet been able to switch the wettability of polypyrrole without immersion in an electrolyte and without a mechanical change in surface features. The present invention thus makes conducting polymers a viable candidate as a material to be used in the above-mentioned applications.

Modifications and variations of the invention disclosed herein will be apparent to those of ordinary skill in the art. It is intended that all such modifications and variations be included within the scope of the appended claims.

What is claimed is:

CLAIMS

1. Structure with electrically switchable wettability comprising:

a doped conducting polymer;
a counter electrode; and
an electrolyte disposed between the doped conducting polymer and the counter electrode.

2. The structure of claim 1 wherein the conductive polymer is polypyrrole.

3. The structure of claim 1 wherein the conductive polymer is doped with fluorinated carbon ions.

4. The structure of claim 3 wherein the fluorinated carbon ions are perfluorooctanesulfonate or nonafluorobutanesulfonate.

5. The structure of claim 1 where in the conducting polymer is doped with NaDBS.

6. The structure of claim 1 where in the counter electrode is gold foil.

7. The structure of claim 1 further including a moisture sensor to switch the wettability state.

8. The structure of claim 1 further including means for establishing a voltage between the conducting polymer and the counter electrode.

9. The structure of claim 1 wherein the electrolyte is a salt dissolved in an organic solvent further including addition of a stiffener.

10. The structure of claim 1 wherein the electrolyte is a salt dissolved in a gel.

11. The structure of claim 1 wherein the electrolyte is a salt dissolved in deionized water.

12. The structure of claim 1 wherein the electrolyte is potassium perfluorooctanesulfonate, propylene carbonate, and polymethylmethacrylate.

13. The structure of the claim 1 wherein the electrolyte is potassium perfluorooctanesulfonate in cellulose-based gel.

14. The structure of claim 1 wherein the electrolyte is potassium perfluorooctanesulfonate in deionized water.

15. Structure with an electrically switchable wettability gradient comprising:

a doped conducting polymer;
a counter electrode; and
an electrolyte disposed between a portion of the doped conducting polymer and the counter electrode.

16. The structure of claim 1 incorporated into a diaper.

17. The structure of claim 1 incorporated into a feminine hygiene product.

18. The structure of claim 1 incorporated into a microfluidics system.

19. The structure of claim 1 coated upon a surface.

20. The structure of claim 1 used to control a liquid droplet contact angle to make a variable refractive power lens.

21. The structure of claim 1 used to separate oil from water.

22. The structure of claim 19 wherein the surface is a pipe, boat, submarine, or other water vehicle.

23. The structure of claim 19 wherein the surface is clothing.

24. The structure of claim 15 wherein the structure is used to move a droplet.

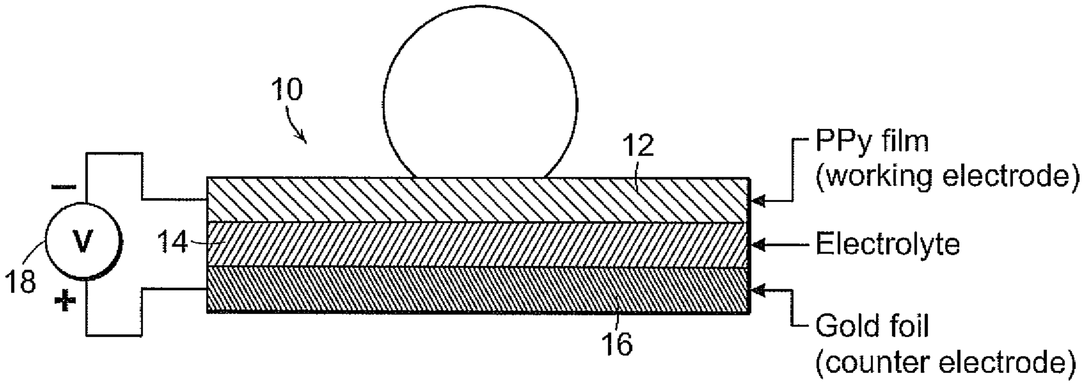

FIG. 1

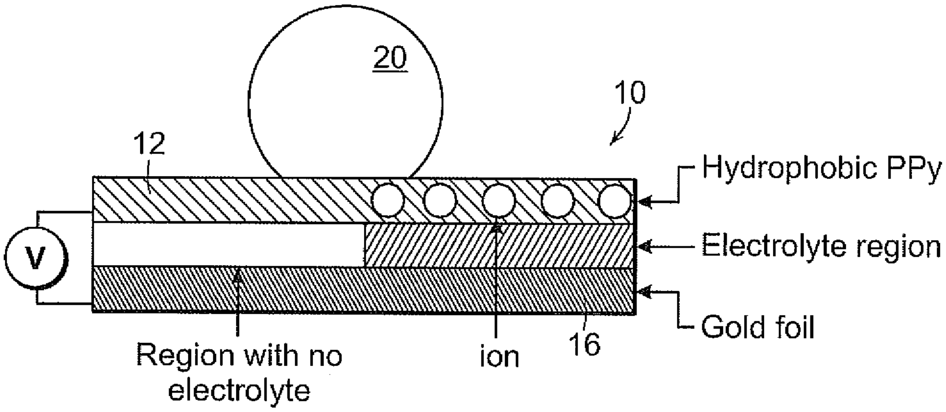

FIG. 3a

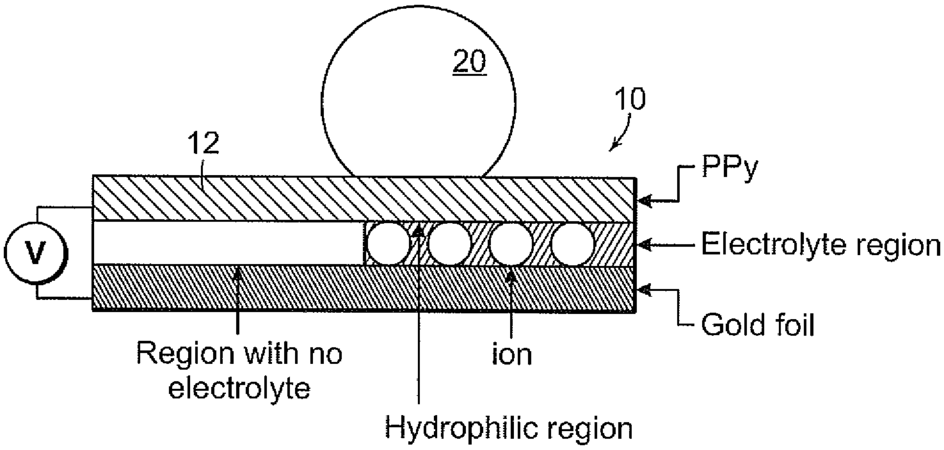

FIG. 3b

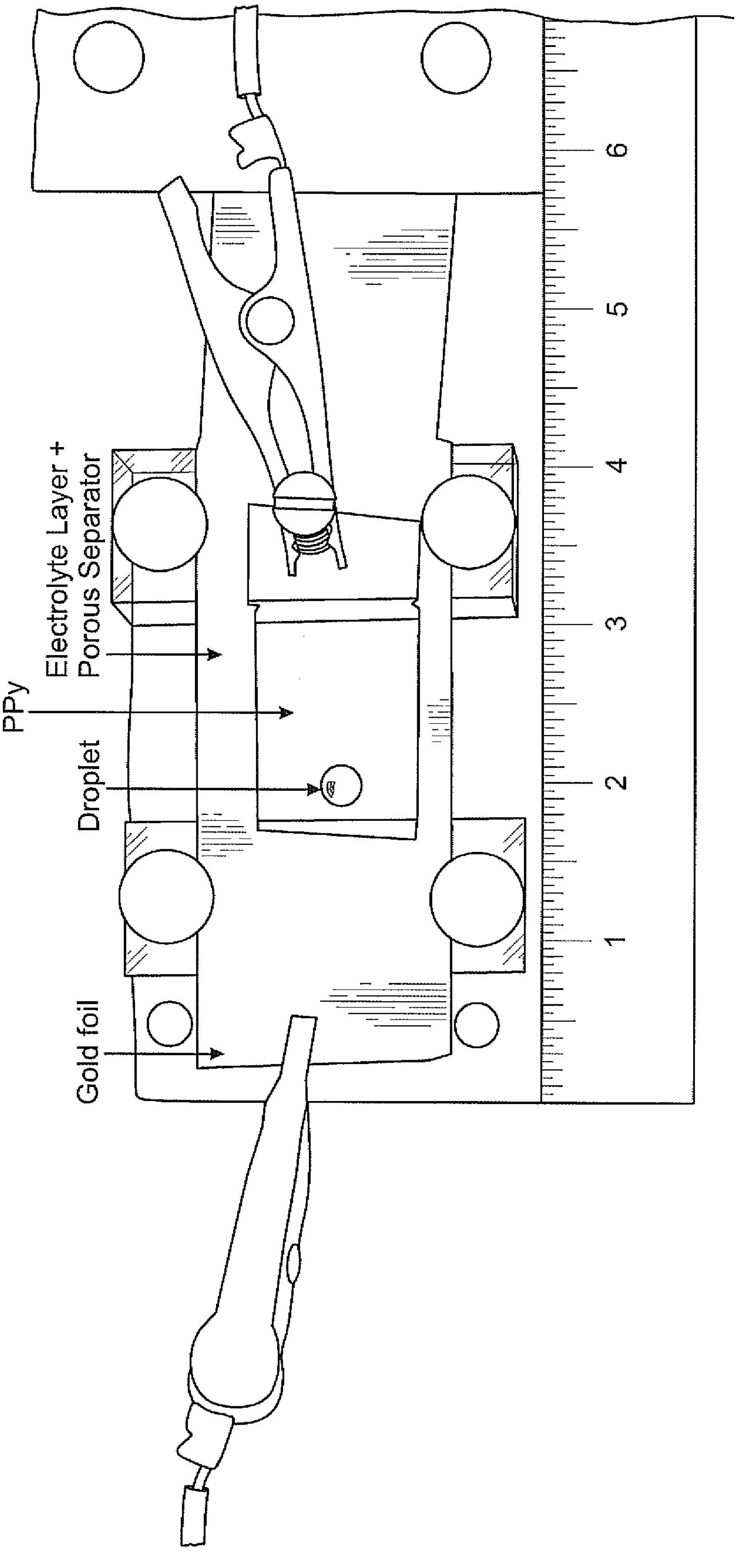
Electrolyte Layer +
Porous Separator
PPy
Droplet
Gold foil
1
2
3
4
5
6

FIG. 2

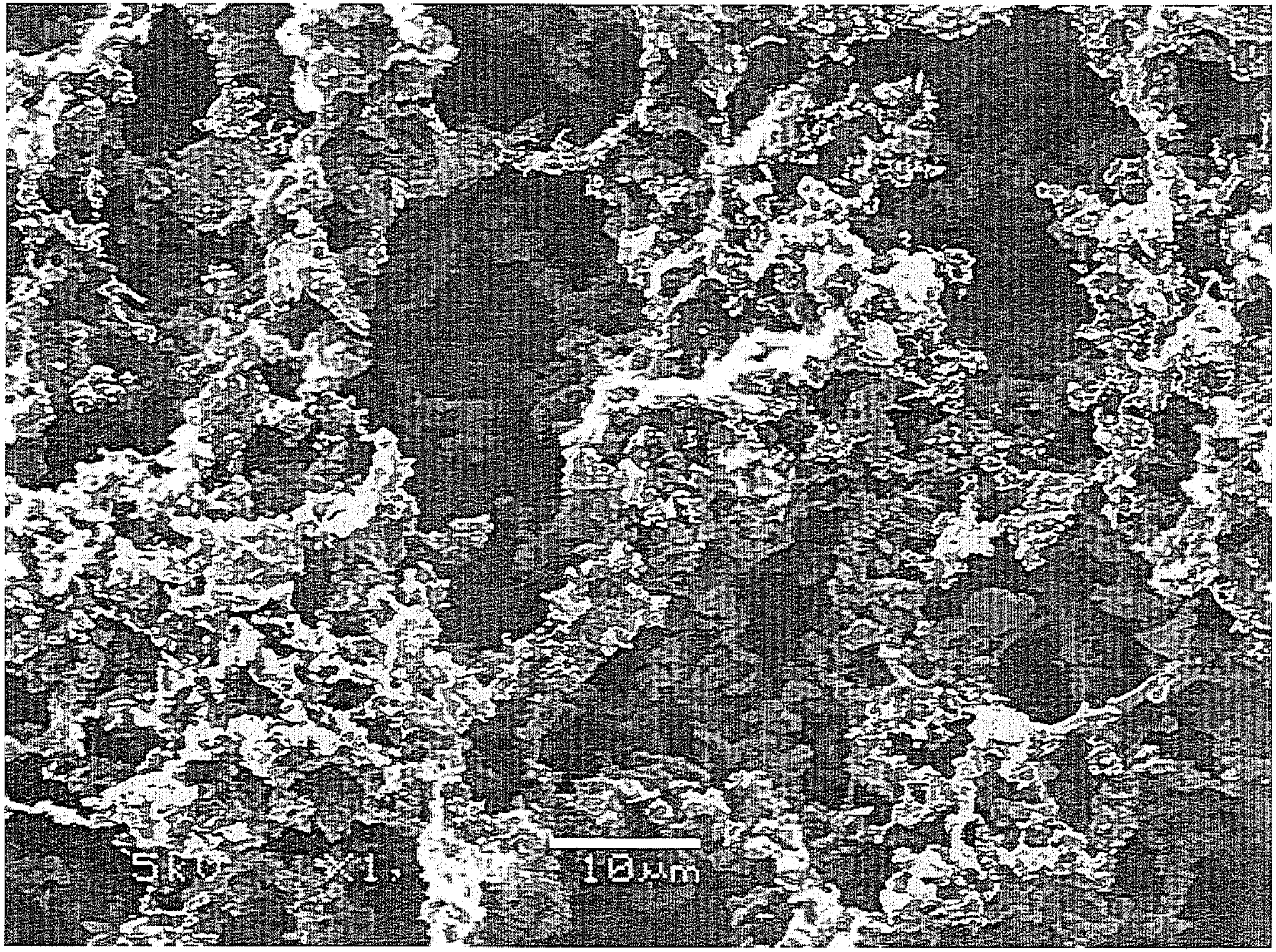

FIG. 4

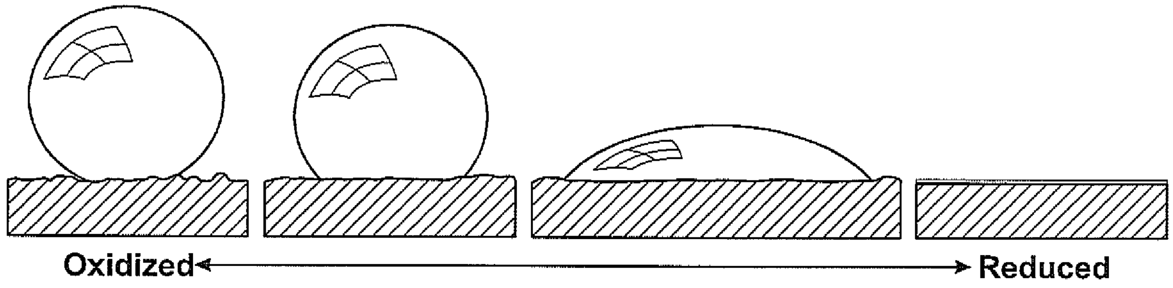
Oxidized
Reduced

FIG. 5

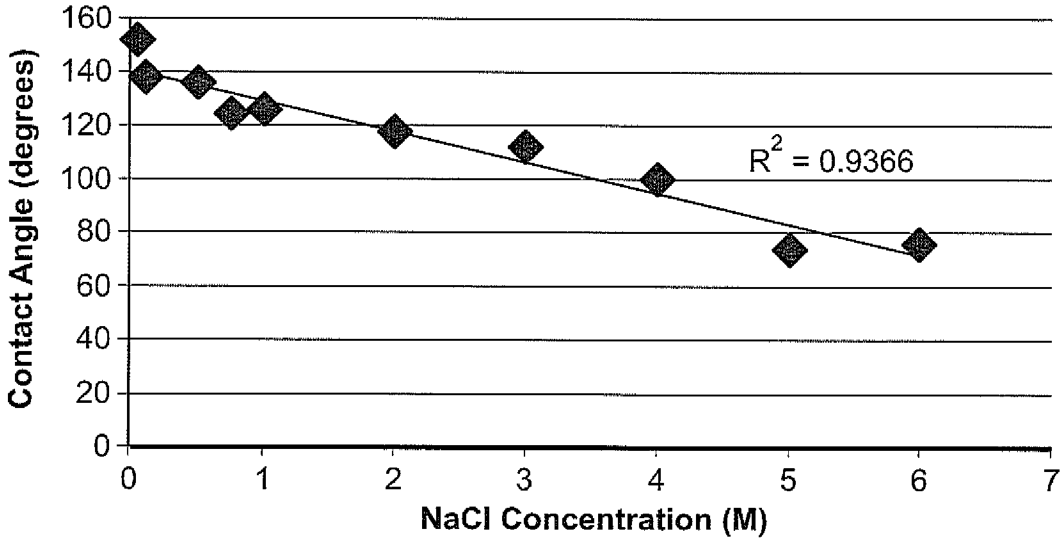
160
140
120
100
80
60
40
20
0
Contact Angle (degrees)
0
1
2
3
4
5
6
7
NaCl Concentration (M)
$R^2 = 0.9366$

FIG. 6

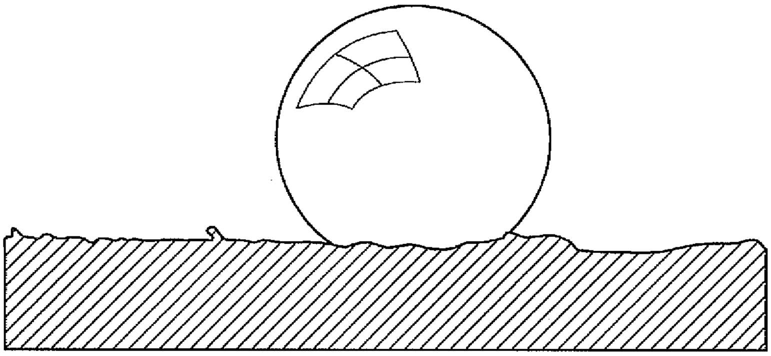

FIG. 7a

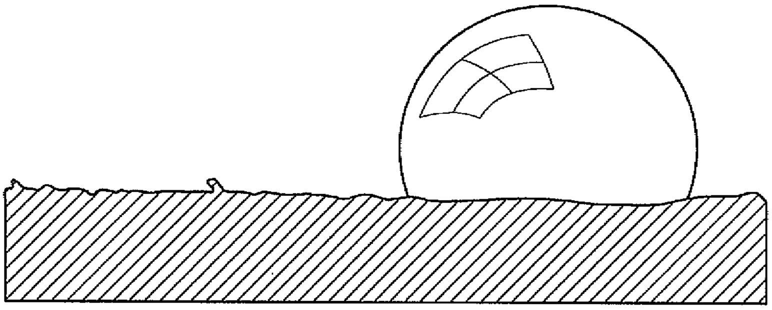

FIG. 7b

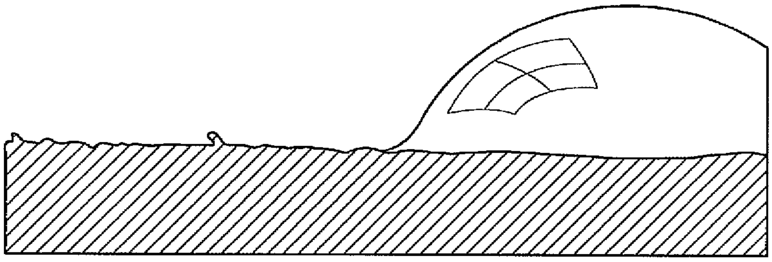

FIG. 7c

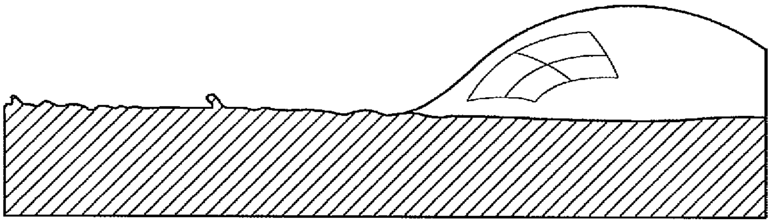

FIG. 7d

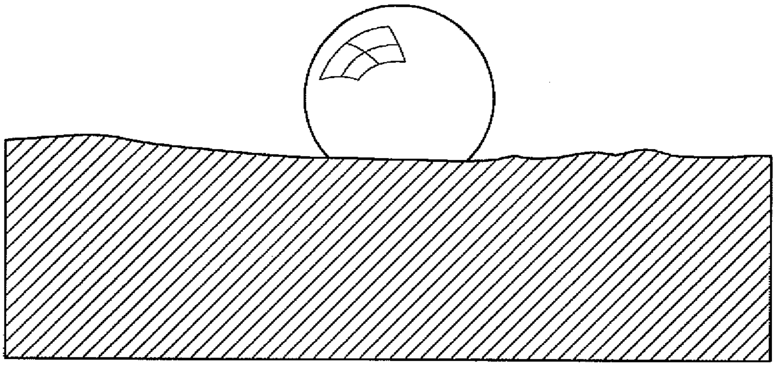

FIG. 8a

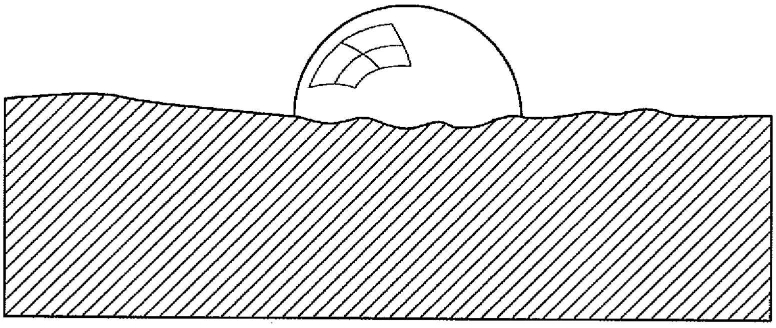

FIG. 8b

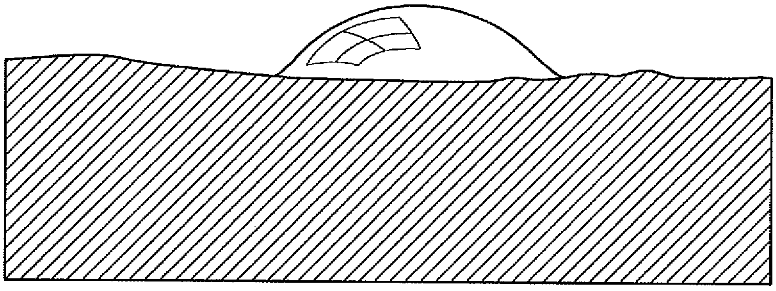

FIG. 8c

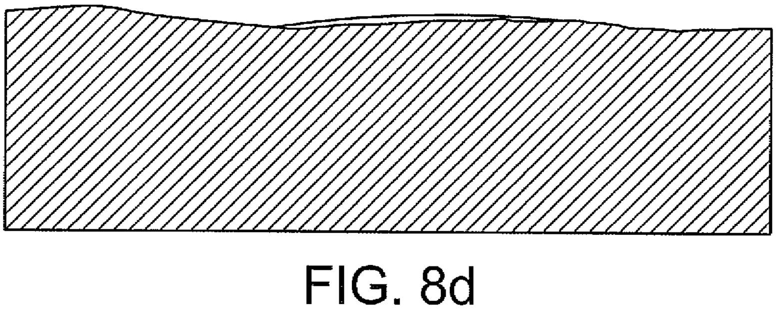

FIG. 8d

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/036757

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01B1/12 F03G7/00
ADD.

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)
H01B F03G

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/053836 A1 (ACREO AB [SE]; ISAKSSON JOAKIM [SE]; ROBINSON NATHANIEL [US]; BERGGREN) 16 June 2005 (2005-06-16) page 4, lines 9-30 page 5, lines 17-28 page 8, lines 3-15 page 12, lines 30-32 page 16, line 31 - page 17, line 13 page 20, lines 27-33 page 21, lines 20-23 page 22, lines 16-21 page 24, lines 2-28 page 25, lines 9-12 page 31, lines 15-29 page 37, lines 21-27; figures 2B,12 ----- -/--	1,2,5, 7-11, 15-18, 20,21, 23,24

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search 21 July 2011	Date of mailing of the international search report 01/08/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Delaporte, P

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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