OIL CLEANUP AND RECOVERY SYSTEM AND METHOD

FIELD OF THE INVENTION

[0001] This invention relates to an oil cleanup and recovery system including electrochemically controllable belts capable of performing surface oil cleanup and recovery of both light and heavy oils.

BACKGROUND

[0002] Current technologies for oil cleanup can be divided into four categories: 1) chemical methods (dispersants, solidifiers), 2) in-situ burning, 3) bioremediation, and 4) mechanical recovery (booms, skimmers, and sorbents). Although some of these technologies perform well in certain applications depending on the oil's characteristics and the type of environment involved, they usually have very high material costs and sometimes have adverse effects on the environment. For example, while sorbents can trap spilled oil efficiently, they suffer from the problem of saturation.

[0003] Certain materials can be used to mop-up or scavenge oil pollution from bodies of water based on the material's surface energy, that in some materials, can be electrically modified. For example, dodecylbenzenesulfonate-doped polypyrrole (PPy(DBS)) exhibits a significant difference in surface energy under reduction or oxidation via the application of low voltages (< 1 V). When oxidized (applied with +0.6V), PPy(DBS) shows a strong affinity to organic droplets. When reduced (applied with -0.9V), PPy(DBS) switches its wettability due to the re-orientation and desorption of surfactant dopant, dramatically decreasing its affinity to oils, allowing oils to be released, (see Y.-T. Tsai, C.-H. Choi, N. Gao, and E. H. Yang, "Tunable wetting mechanism of polypyrrole surfaces and low-voltage droplet manipulation via redox," Langmuir, 27 (7), 4249–4256, (2011), and W. Xu, J. Xu, C.-H. Choi, and E. H. Yang, "In situ control of underwater-pinning of organic droplets on a surfactant-doped conjugated polymer surface," ACS Applied Materials & Interfaces, 7 (46), 25608–25617, (2015)). CNT-embedded PPy(DBS) mesh as well as PPy(DBS) film coated on conductive foam has been previously fabricated and characterized. The foam collected 7.3 ml dichloromethane ("DCM") after 60 cycles of the transportation. In this case, the absorption vs. weight ratio was 255.55 after 50 cycles (the PPy(DBS) mesh showed the

weight ratio of 1.19). See for example J. Xu, S. Fu, W. Xu and E. H. Yang, "A Carbon Nanotube-embedded Conjugated Polymer Mesh with Controlled Oil Absorption and Surface Regeneration via in situ Wettability Switch," Journal of Colloid and Interface Science, 532, 790 (2018).

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] For a better understanding of the present invention, reference is made to the following detailed description of various exemplary embodiments considered in conjunction with the accompanying drawings, in which like structures are referred to by the like reference numerals throughout the several views, and in which:

[0005] FIG. 1 is a side view, shown in cross-section, of a mobile system for collection of spilled oil from a body of water according to one embodiment of the invention; and

[0006] FIG. 2 is a perspective view of the mobile system of FIG. 1, FIG. 2 being shown in cross-section as well.

DETAILED DESCRIPTION

[0007] Before any embodiments of the invention are explained in detail, it is to be understood that the invention is not limited in its application to the details of construction and the arrangement of components set forth in the following description or illustrated in the accompanying drawings. The invention is capable of other embodiments and of being practiced or of being carried out in various ways. Also, it is to be understood that the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use of "including," "comprising," or "having" and variations thereof herein is meant to encompass the items listed thereafter and equivalents thereof as well as additional items. Unless specified or limited otherwise, the terms "mounted," "connected," "supported," and "coupled" and variations thereof are used broadly and encompass both direct and indirect mountings, connections, supports, and couplings. Further, "connected" and "coupled" are not restricted to physical or mechanical connections or couplings.

[0008] The following discussion is presented to enable a person skilled in the art to make and use embodiments of the invention. Various modifications to the illustrated embodiments will be

readily apparent to those skilled in the art, and the generic principles herein can be applied to other embodiments and applications without departing from the spirit and scope of the invention. Thus, embodiments of the invention are not intended to be limited to the embodiments shown, but are to be accorded the widest scope consistent with the principles and features disclosed herein. The following detailed description is to be read with reference to the figures, in which like elements in different figures have like reference numerals. The figures, which are not necessarily to scale, depict selected embodiments and are not intended to limit the scope of the invention's embodiments. Skilled artisans will recognize the examples provided herein have many useful alternatives and fall within the scope of embodiments of the invention.

[0009] The present invention incorporates smart membrane surfaces into a small, untethered automated surface vessel, enabling efficient and continuous collection of oil from the surface of a body of water.

[0010] In one aspect, the present invention is directed to a moveable belt adapted for use as an oil collection apparatus, and in a further aspect, the invention is directed to an apparatus including a moveable belt where an oxidation state of at least a portion of the belt can be controlled to enable collection and release of oil from a body of water. Configurations and procedures for voltage biasing for adherence and/or release of oil to the belt are explained in the following description. In an embodiment, at least a portion of the belt can possess a tunable wettability characteristic based on an oxidation or reduction state of at least a portion of the belt that can be varied in response to an applied voltage. For example, when electrochemically oxidized, (by applying a positive voltage), at least a portion of the belt's surface can include a strong adhesion to oil, thereby allowing the belt to collect oil as it is exposed to a body of water including oil. In some further embodiments, when at least a portion of the belt is reduced (by applying a negative voltage), that portion of the belt can release the trapped oil into, for example, an interior reservoir of a surface vessel. In some embodiments, the belt may be combined with a conveyor belt in a small-scale, oil-cleaning surface robot adapted to access oil spills in confined areas, such as under piers and in the small spaces between vessels and piers.

[0011] Referring to FIG. 1, showing a side cross-sectional view of a mobile system 10 for collection of spilled oil 28 from a body of water 26, and FIG. 2, showing a perspective cross-

sectional view of the mobile system 10 of FIG. 1 according to one embodiment of the invention, the system 10 comprises a segmented belt 20 that can be positioned to pass through the oil contaminated water 26, and then into a collection container 22. In some embodiments, the segmented belt 20 is an elastic segmented belt capable of providing an elastic mechanical response as a function of tension or compression of the segmented belt 20. In some embodiments of the invention, at least a portion of the segmented belt 20 can be coated with the polymer 15 which can be pre-oxidized in preparation for uptake of oil from a body of water. In this state, the segmented belt 20 can be prepared for uptake of the oil 28 onto the surface of the polymer 15 as the segmented belt 20 passes through any oil suspended in or on the water 26, causing it to attach to the segmented belt 20. Some embodiments of the invention include the following capabilities: 1) to be used for both light and heavy oils (i.e., oils that are lighter and heavier than water); 2) to provide scalability for addressing large areas covered by oil and collection of large oil volumes; and 3) to control electrical isolation to ensure the proper electrochemical state of the polymer 15 immobilized on the segmented belt 20 to allow absorption (by the polymer 15 in its oxidized state) and release (by polymer 15 in its reduced state) of oils.

[0012] During operation of the embodiment shown in FIGS. 1 and 2, the segmented belt 20 passes from the collection container 22 according to the direction denoted by the arrows adjacent to the belt (see arrows shown in FIG. 1). Initially, the segmented belt 20 is clean of oil and is pre-oxidized by application of a negative bias (e.g., using approximately -0.9 V) followed by a positive bias (e.g., using approximately +0.6 V) to oxidize at least the surface of the segmented belt 20, thereby making it attractive to oil. In some embodiments, movement of the segmented belt 20 through the body of water 26 can be facilitated by a series of rollers 40. The non-limiting embodiment of FIGS. 1 and 2 shows a series of rollers 40, some of which are submerged in the water 26 (e.g., rollers 43), and others of which are positioned above the surface of the water 26 (e.g., rollers 41). Further, in some embodiments, the use of an alternating arrangement of submerged rollers 43 and non-submerged rollers 41 can enable the system 10 to increase the exposure of the segmented belt 20 to the surface oil 28 because the segmented belt 20 can pass through an increased area of surface oil 28, and thus can spend more time exposed to the surface oil 28.

[0013] The non-limiting embodiment illustrated in FIG. 1 shows a break-line representing the length of the segmented belt 20 and the number of rollers 40, 41, 43, it being understood that such number can be greater than that shown. Further, the submerged rollers 40, 43 are shown that can assist in conveying the segmented belt 20, which is now an oil-carrying belt, on a return path towards the collection vessel 48. In some embodiments, the segmented belt 20 can consist of a plurality of individual conductive segments positioned on an elastic backing that can be stretched to electrically separate one or more portions of the segmented belt 20 from each other. Using this arrangement, when a section of the segmented belt 20 is un-stretched, the individual segments in the section are electrically contiguous and conductive as a whole. However, under tension, the segments separate from one another and become electrically isolated. In some embodiments, this behavior allows the segmented belt 20 in the oil release area of the collection chamber 22 to be electrically isolated from the segmented belt 20 outside of the collection chamber 22, and biased negatively for oil release, which occurs in the collection chamber 22. In other embodiments, the segmented belt 20 segments can be separated by conventional mechanical linkages enabling one or more segments to be mechanically separated from one another. In some embodiments, this enables one or more segments or portions of the segmented belt 20 to be electrically isolated from one or more other segments or portions of the segmented belt 20. In one embodiment, as the oil-carrying segmented belt 20 passes into the collection vessel 48, one or more tension rollers 38 can cause one or more sections or segments of the segmented belt 20 inside the collection vessel 48 to be stretched, and to become electrically disconnected or isolated from the other sections or segments of the segmented belt 20 (i.e., those segmented belt 20 sections not within the collection vessel 48). The stretched portion of the segmented belt 20 is represented in FIG. 1 as a region 17 of the belt with a reduced diameter of the segmented belt 20.

[0014] In some embodiments, the polymer 15 applied to at least some portions of the segmented belt 20 can comprise at least one conjugated polymer. Thus, in some embodiments, an exposed surface or layer of the segmented belt 20 can include a conjugated polymer that can function to promote the collection of oil on the exposed surface of the segmented belt 20 when the conjugated polymer is oxidized. In some embodiments, when the conjugated polymer is reduced, it can function to release oil from the exposed surface of the segmented belt 20. In some embodiments, the aforementioned oxidation and reduction of the conjugated polymer can be performed electrochemically. In some embodiments, electrochemical oxidation can be performed

by applying a positive voltage to the conjugated polymer, while electrochemical reduction can be performed by applying a negative voltage to the conjugated polymer. In some embodiments, the positive electric voltage can lie in a range of from greater than 0 to about 1.5 volts, while the negative electric voltage can lie in a range of from about -0.6 to about -1.5 volts. For example, in some embodiments, the oil-coated belt section in the collection chamber 22 can be negatively biased via spring-loaded electrical contacts, releasing the oil from the belt and into the collection chamber 22, wherein it is collected as "collected oil" (see FIG. 1).

[0015] Any of the rollers shown (for example, the tension rollers 38 shown in FIG. 1) can be constructed such that the outer circumference of the roller is comprised of a conductive metallic material, or alternatively an insulating polymeric material. In embodiments where the tension rollers 38 include a conductive metallic material, the conductive surface may be used to establish electrical connection with the segmented belt 20 with which they make continuous contact. In embodiments where the rollers include an insulating surface, the insulating surface makes no electrical connection to the segmented belt 20, and thus does not change the potential of the segmented belt 20 at the point of contact.

[0016] Note that the representative rollers 38, 40, 41, 43 shown in FIGS. 1 and 2 do not encompass the entirety of rollers that would be built into the system to accommodate system design constraints such as overall system dimensions. Numerous rollers could be built into the system expressly for making redundant electrical contact; here, the rollers shown for regulating belt tension or for setting the belt path can also serve as electrical connections to the segmented belt 20. Furthermore, rollers with the characteristics described can be arbitrarily placed in any number of locations within the specific areas in which oil collection or oil release are accomplished for the purpose of setting the electrical potential in the respective location.

[0017] In some embodiments, the captured and released oil can flow to a resting position in the collection chamber 22 based on its density relative to that of the water present. For example, in one non-limiting embodiment, after passing into the collection chamber 22, at least a portion of the polymer 15 on the segmented belt 20 can be subjected to an applied negative voltage bias. For example, in some embodiments, the applied voltage bias can be approximately -0.9 V, resulting in

a reduction of at least a portion of the polymer 15 on the segmented belt 20, and the consequent "oil release" as shown in FIGS. 1 and 2.

[0018] In some embodiments, as the segmented belt 20 continues out of the collection chamber 22, and through a partition 24, a positive electric voltage can be applied to oxidize the polymer 15 of the segmented belt 20 to provide a strong adhesion toward oils as it proceeds out of the containment vessel 48 and passes into a body of water through the surface oil 28 as shown in FIGS. 1 and 2. In some embodiments, the positive electric voltage can be applied directly to the polymer 15 through an underlying electrode coated on the surface of the segmented belt 20, and the water 26 can be grounded.

[0019] In an embodiment, the conjugated polymer can be dodecylbenzenesulfonate-doped polypyrrole ("PPy(DBS)"). In some embodiments, the conjugated polymer can comprise an electrically conductive dodecylbenzenesulfonate-doped polypyrrole foam, abbreviated as "PPy(DBS) foam" having a porous 3D structure. In one embodiment, the conjugated polymer is a surfactant-doped conjugated polymer film. In an embodiment, the segmented belt 20 can comprise carbon nanotubes and/or a stainless-steel mesh. For example, in some embodiments, the segmented belt 20 can also include a substrate cooperating with and/or at least partially coupled to the conjugated polymer to form a composite structure (e.g., such as a continuous conveyor belt with an applied layer of conjugated polymer).

[0020] In some embodiments, the underwater wettability of the conjugated polymer (e.g., PPy(DBS)) can be switched in-situ upon application of voltages as low as ±1 V. For example, in some embodiments, when a positive electric voltage (e.g., 0.1 V) is applied, the PPy(DBS) surface is oxidized with a strong adhesion toward oils. As a result, the segmented belt 20 can adsorb oils by adhering the oils on their PPy(DBS) surface. In further embodiments, when a negative electric voltage (e.g., -0.9 V) is applied, the PPy(DBS) surface is reduced, whereby previously attached oil droplets can roll off the segmented belt 20 or permeate through the belt's mesh.

[0021] In some embodiments, the process described above can be actuated using very low voltages (e.g., such as voltages less than 1 V), and can be repeatable for many (e.g., hundreds) of cycles, thereby resulting in high efficiency and long durability. Furthermore, as the segmented belt 20 of the present invention can be incorporated into a conveyor belt, track, rope, or chain that runs

along the exterior hull of a small unmanned surface vessel, the present invention is also directed to a method which allows the aforementioned oil collection process to be automated. Altogether, the various aspects and embodiments of the present invention enable a versatile, highly efficient, fully-automatic oil cleanup and recovery technology that can be provided as a boom 50 extended from a vessel (e.g., such as a boat, ship, or submersible), or alternatively from an on-shore structure such as a pier, dock, or other structure situated adjacent a body of water. Further, the boom 50 and/or any related assembly including the segmented belt 20 described herein can be incorporated into an unmanned, robotic surface vessel adapted for oil cleaning and recovery from a body of oil-contaminated water.

[0022] As discussed earlier, in some embodiments, voltages can be applied directly to the polymer through an underlying electrode coated on the surface of the conveyer belt, and the water is grounded. In some embodiments, the segmented belt 20 can include PPy(DBS)-polymer-coated conductive segments on an insulating elastic support belt. In some embodiments, at rest, i.e., without intentionally stretching the belt, these segments can come together, forming an electrically contiguous belt. However, under sufficient tension, the segments can be drawn apart, becoming electrically isolated from one another and allowing different sections of the belt to be maintained at disparate electrical potentials.

[0023] In FIG. 1, the tension rollers 38 on the left and right sides of the chamber 22 (only the left ones are labeled as 38), can allow a portion of the belt inside the chamber 22 to be electrically isolated from the section of the segmented belt 20 outside the chamber 22. The electrical isolation occurs in the belt section just between pairs of rollers. Thus, the portion of the segmented belt 20 inside the chamber 22 is biased for oil release, while the portion of the segmented belt 20 outside is biased for collection. In some embodiments, the segmented belt 20 can have an appearance similar to that of the track of a tracked military vehicle (such as a tank), or alternatively an escalator in a department store, i.e., segmented sections that move together with the proximity of segments to one another controlled by a system of tensioning rollers. The segments can be intentionally separated to produce a selective electrical isolation at that point. The purpose of the tension rollers 38 is to provide the means for electrical isolation of the belt into distinct sections, functioning separately for oil collection and oil recovery.

[0024] Some embodiments include a suction tube 34 extending from a pump 32 to the collection chamber 22. In some embodiments, the suction tube 34 can be adjusted in height to allow it to access the oil in the collection chamber 22, and to then remove it by pumping through an outlet pipe 33 (shown as oil recovery 30). Some further embodiments include a vent-or-pressure line 36 that is used to allow the system pressure in the collection chamber 22 to equilibrate with the ambient pressure. Alternatively, the pressure can be raised in the collection chamber 22 by the introduction of compressed air, nitrogen or other inert gas to provide more favorable conditions for oil removal by pumping via the pump 32.

[0025] In an embodiment, the substrate of the segmented belt 20 can be a stainless-steel mesh that can further include carbon nanotubes. In some embodiments, the carbon nanotubes can be grown thereon via chemical vapor deposition. In embodiments in which carbon nanotubes are used, the conjugated polymer may be coated on the carbon nanotubes via electro-polymerization. In another embodiment, the substrate of the segmented belt 20 can include an electrically conductive carbon foam having a porous 3D structure. In such an embodiment, the conjugated polymer can be applied to the substrate so that the conjugated polymer inherits the porosity of the conductive carbon foam.

[0026] In an embodiment, multi-walled carbon nanotubes (CNTs) can be grown directly from 304 stainless steel (SS) mesh (e.g., size 200 x 200, McMaster-Carr, Robbinsville, NJ) using atmospheric pressure chemical vapor deposition ("APCVD"). For example, the SS mesh can be cut, rinsed, dried and then placed in the center of a 200-mm inner diameter quartz tube in a horizontal three zone chemical vapor deposition (CVD) furnace and heated to 750 °C under the flow of 60 sccm hydrogen (H_2) (e.g., sourced from Praxair, Newark, NJ) and 500 sccm Argon (Ar), (e.g., sourced from Praxair, Newark, NJ). Then, additional ethylene (C_2H_4). (e.g., sourced from Praxair, Newark, NJ) was fed through the system at flow rates of 100 sccm for 7 minutes for CNTs growth. Subsequently, the samples were rapidly cooled to room temperature by blowing air into the furnace.

[0027] After CNT growth, PPy(DBS) film was electro-polymerized atop the CNT-covered SS mesh surface. First, 1 mL pyrrole monomer (reagent grade, 98%, Sigma-Aldrich, St. Louis, MO) was thoroughly mixed with 150 mL 0.1 mol/L sodium dodecylbenzenesulfonate (NaDBS,

technical grade, Sigma-Aldrich, St. Louis, MO) solution. Then, a CNT-covered SS mesh, saturated calomel electrode (SCE, Fisher Scientific Inc., Pittsburgh, PA), and another SS mesh (5 cm x 5 cm) were submerged in the solution as the working (i.e., reference) electrode and counter electrode, respectively. The coating of PPy(DBS) surfaces was carried out using a potentiostat (263A, Princeton Applied Research, Oak Ridge, TN) by applying 0.7 V to the working electrode (vs. SCE) and stopped once surface charge density reached 1 C/cm^2. Instead of CNTs, SS meshes were deposited with 10 nm chromium (Cr) and 30 nm gold (Au) films using an e-beam evaporator (Explorer 14, Denton Vacuum, Moorestown, NJ), and then also coated with PPy(DBS) surfaces. After fabrication, the PPy(DBS) mesh surfaces were rinsed and dried in air overnight before any further characterizations.

[0028] It should be noted that CNTs are optional in the foregoing embodiment. However, the CNTs are preferred, as the in-situ switch time decreases because the CNTs allow for a higher surface area, which increases the amount of DBS molecules desorbed from PPy(DBS) surfaces under reduction, thereby facilitating more rapid decrease of oil/water interfacial tension and retention force.

[0029] In another embodiment, a conductive carbon foam can be used directly for PPy(DBS) electro-polymerization after necessary cutting and dicing. The pristine carbon foam is extremely porous, has a 3D microstructure, and is also lightweight. A 2.5 x 0.5 x 0.2 cm sized carbon foam weighs only 0.025 g, compared to a 2 x 3 cm PPy(DBS) mesh, which weighs 0.2 g. After PPy(DBS) electro-polymerization, the whole surface of carbon foam can be evenly and uniformly covered with PPy(DBS) surfaces. Results show that the PPy(DBS) surface inherits the 3D porous structure of the carbon foam without blocking the pores. By fabricating PPy(DBS) surfaces on conductive carbon foam, the absorption capacity of absorbent made of PPy(DBS) material significantly increases.

[0030] It will be appreciated by those skilled in the art that while the invention has been described above in connection with particular embodiments and examples, the invention is not necessarily so limited. Numerous other embodiments, examples, uses, modifications and departures from the embodiments, examples and uses are intended to be encompassed by the

description and figures attached hereto, as well as the entire disclosure of International Publication Number WO 2019/113126A1 shown in the attached APPENDIX included herewith.

Appendix

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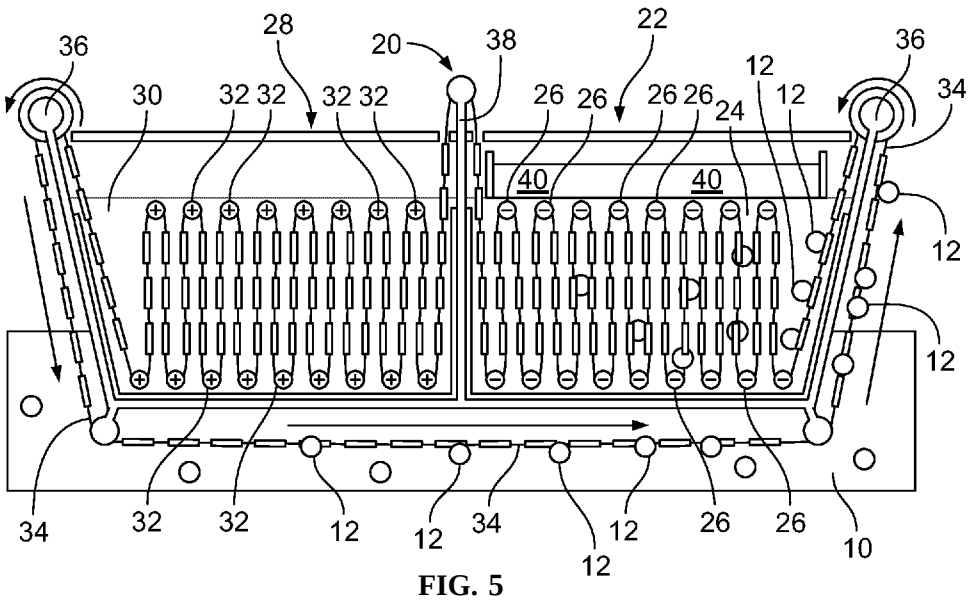

FIG. 5

(57) Abstract: Smart membranes (14) are integrated into a small, unmanned surface vessel (20) to enable the efficient, automated cleanup of oil spills. Such a vessel (20) has the potential to provide a low-cost, modular solution for day-to-day oil-spill cleanup operations, especially in confined aquatic areas, such as under piers and in the small spaces between marine vessels and piers. The smart membranes (14) are provided on the surface of a conveyor belt (34) that circulates the membranes (14) through the surrounding body of water (10) for oil collection, as well as through an internal reduction chamber (22) of the vessel (20) for oil release. The smart membranes (14) are adapted to attract and repel oil (12) in response to low-voltage commands applied across the conveyor belt (34), using a process that is repeatable for a number of cycles, offering high efficiency and long durability.

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[Continued on next page]

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SMART POLYMER INTEGRATED MEMBRANE FOR SURFACE OIL CLEANUP AND RECOVERY

Statement Regarding Federally Sponsored Research

This invention was made with government support under Grants ECCS-1202269 and EEC-l 138244 awarded by the National Science Foundation and Grant FA9550-1 1-1-0272 awarded by the Defense ETniversity Research Instrumentation Program. The government has certain rights in the invention.

Cross-Reference to Related Application

This application claims priority to U.S. Provisional Patent Application Serial No. 62/594,485 filed December 4, 2017, the entire disclosure of which is incorporated herein by reference.

Field of the Invention

This invention relates to smart membranes, and, more particularly, to such membranes adapted for integration into a surface vessel for performing surface oil cleanup and recovery operations.

Background of the Invention

There is persistent, day-to-day oil spillage into U.S. waterways that results from many sources outside of the petroleum industry, including nearly 6,000 barrels annually from marine vessels, more than 4,000 from coastal marine facilities, and more than 350,000 from urban runoff, comprised of leakage from road vehicles and other land-based sources. When oil is

spilled into the ocean, waves, water currents, and wind force the oil slick to drift over larger areas, impacting the open ocean, coastal areas, and marine/terrestrial habitats in the path of the drift.

Current technologies for oil cleanup can be divided into four categories: 1) chemical methods (dispersants, solidifiers), 2) in situ burning, 3) bioremediation, and 4) mechanical recovery (booms, skimmers, and sorbents). Although some of these technologies perform well in certain applications depending on the oil's characteristics and the type of environment involved, they usually have very high material costs and sometimes have adverse effects on the environment. For example, while sorbents can trap spilled oil efficiently, they suffer from the problem of saturation.

In many ports and harbors, preventative measures are employed to minimize the impact of a potential spill. One of the most commonly used measures is pre-booming, the practice of deploying an oil boom in advance, to contain any potential spillage for easy skimming and disposal. When pre-booming is not possible due to space constraints, response vessels equipped with booms are often on standby. However, even when booms can be deployed effectively, not all areas within the boom are easily reached by a skimmer, which pumps oily water via a hose to the shore or to a larger vessel.

Summary of the Invention

In one aspect, the present invention is directed to a membrane adapted for use as an oil collection apparatus. An exposed surface of the membrane includes a conjugated polymer that functions to promote the collection of oil on the exposed surface of the membrane when the

conjugated polymer is oxidized. When the conjugated polymer is reduced, it functions to release oil from the exposed surface of the membrane.

The aforementioned oxidation and reduction of the conjugated polymer can be performed electrochemically, for example. Electrochemical oxidation can be performed by applying a positive voltage to the conjugated polymer, while electrochemical reduction can be performed by applying a negative voltage to the conjugated polymer. The positive electric voltage can lie in a range of from greater than 0 to about 1.5 volts, while the negative electric voltage can lie in a range of from about -0.6 to about -1.5 volts.

In an embodiment, the membrane possesses a wettability characteristic that can be varied in response to the voltage applied to the conjugated polymer during oxidation and reduction. In an embodiment, the conjugated polymer can be dodecylbenzenesulfonate-doped polypyrrole. In an embodiment, the conjugated polymer is a surfactant-doped conjugated polymer film. Alternatively, the conjugated polymer can be a freestanding, porous film fabricated via 3D printing of the conjugated polymer.

The membrane can also include a substrate cooperating with the conjugated polymer to form a composite structure. In an embodiment, the substrate can be a stainless steel mesh. The stainless steel mesh can further include carbon nanotubes grown thereon via chemical vapor deposition. In embodiments in which carbon nanotubes are used, the conjugated polymer may be coated on the carbon nanotubes via electropolymerization.

In another embodiment, the substrate can include an electrically conductive carbon foam having a porous 3D structure. In such an embodiment, the conjugated polymer would be applied to the substrate so that the conjugated polymer inherits the porosity of the conductive carbon foam.

In accordance with another aspect of the present invention, the membrane can be incorporated in a surface vessel for in situ oil clean-up of, and recovery from, a body of oil-contaminated water. The vessel can include a reduction chamber with a first reservoir of electrolyte and a first set of electrodes designed to generate a negative electric voltage. The vessel may also include an oxidation chamber with a second reservoir of electrolyte and a second set of electrodes designed to generate a positive electric voltage. A conveyor belt, which includes the aforementioned membrane and a plurality of similar membranes, can be employed in connection with an inventive method which involves the steps of: (1) passing the membranes, while in an oxidized state, through a body of oil-contaminated water to collect oil; (2) passing the membranes, with collected oil thereon, through the first reservoir of electrolyte in the reduction chamber to reduce the membranes and thereby release collected oil therefrom; and (3) then passing the membranes through the second reservoir of electrolyte in the oxidation chamber to oxidize the membranes and thereby regenerate the membranes for reuse as oil-collection agents.

The membranes carried by the conveyor belt can be electrochemically reduced by applying a negative electric voltage to the first set of electrodes as the conveyor belt carries the membranes through the first reservoir of electrolyte in the reduction chamber, thereby releasing collected oil into the first reservoir of electrolyte. When the conveyor belt carries the membranes from the reduction chamber to the oxidation chamber, the membranes are then electrochemically oxidized as a result of a positive electric voltage applied by the first set of electrodes, whereby surface regeneration of the membranes is effected in preparation for their reuse as oil-collection agents.

In an embodiment, the first reservoir of electrolyte in the reduction chamber and the second reservoir of electrolyte in the oxidation chamber are separated by a partition positioned between the oxidation chamber and the reduction chamber. The partition inhibits oil collected in the reduction chamber from migrating into the oxidation chamber.

Unlike the existing technologies listed in the background section hereinabove, the present invention involves the utilization of smart membranes that may be combined with a conveyor belt in a small-scale, oil-cleaning surface robot adapted to access oil spills in confined areas, such as under piers and in the small spaces between vessels and piers. In an embodiment, the smart membranes comprise: (1) conjugated polymer (e.g., dodecylbenzenesulfonate-doped polypyrrole, abbreviated as PPy(DBS)); (2) carbon nanotubes (CNTs); and (3) stainless steel (SS) mesh.

The present invention provides a potential low-cost, modular solution for day-to-day oil-spill cleanup operations in confined aquatic areas, such as those described above. Unlike current cleanup solutions, such as skimmers, which pump large volumes of oily water by hose into storage barges, the present invention incorporates smart membrane surfaces into a small, untethered automated surface vessel, enabling efficient and continuous collection of oil from the surface of a body of water. In addition to providing a solution for accessing oil spills in confined areas, a small-scale, oil-cleaning surface robot may also serve as a counter-measure for rapid water clean-up, especially in situations where a boom cannot be deployed, as such a robot can patrol the area in the vicinity of a fuel transfer.

In an embodiment, the smart membranes of the present invention exhibit tunable wettability, in the form of in situ switching of underwater wettability (i.e., affinity for organic liquid in an aqueous environment), as an oil collection agent. When electrochemically oxidized

(by applying a positive voltage to the conjugated polymer), the membranes' surface has strong adhesion to oil, thereby allowing the membranes to collect oil. When reduced (by applying a negative voltage to the conjugated polymer), the membranes' surface releases the trapped oil into, for example, an interior reservoir of a surface vessel. The conjugated polymer (e.g., PPy(DBS)) switches its underwater wettability in situ upon application of voltages as low as ± 1 V. When a positive electric voltage (e.g., 0.1 V) is applied, the PPy(DBS) surface is oxidized with a strong adhesion toward oils. As a result, the membranes can adsorb oils by adhering the oils on their PPy(DBS) surface. When a negative electric voltage (e.g., -0.9 V) is applied, the PPy(DBS) surface is reduced, whereby previously attached oil droplets can roll off the membranes or permeate through the membranes' mesh.

The process described above can be actuated using very low voltages (< 1 V) and is repeatable for a number (e.g., hundreds) of cycles, thereby resulting in high efficiency and long durability. Furthermore, as the smart membranes of the present invention can be incorporated into a conveyor belt that runs along the exterior hull of a small unmanned surface vessel, the present invention is also directed to a method which allows the aforementioned oil collection process to be automated. Altogether, the various aspects and embodiments of the present invention enable a versatile, highly efficient, fully-automatic oil cleanup and recovery technology.

Brief Description of the Drawings

For a better understanding of the present invention, reference is made to the following detailed description of various exemplary embodiments considered in conjunction with the

accompanying drawings, in which like structures are referred to by the like reference numerals throughout the several views, and in which:

FIG.l is a schematic illustration of a body of oil-contaminated water;

FIG. 2 is a schematic illustration of a plurality of oxidized polymer mesh membranes constructed in accordance with an embodiment of the present invention and operating to collect oil as a conveyor transports the membranes through the body of oil-contaminated water shown in FIG. 1;

FIG. 2A is a detailed schematic illustration showing an oil droplet adhered to the oxidized polymer surface of one of the mesh membranes illustrated in FIG. 2;

FIG. 3 is a schematic illustration showing the polymer mesh membranes of FIG. 2 in a reduced stated in which collected oil is being released therefrom and therethrough;

FIG. 3A is a detailed schematic illustration showing an oil droplet being released from (e.g., by sliding or permeating) the reduced polymer surface of one of the mesh membranes illustrated in FIG. 3;

FIG. 4 is a schematic illustration showing the polymer mesh membranes of FIG. 3 in an oxidized state and ready for reuse after they have been regenerated;

Figure 5 is a schematic illustration of an oil-cleaning surface vessel constructed in accordance with an embodiment of the present invention and showing the vessel's oxidation and reduction chambers and their interactions with a conveyor belt which comprises membranes that are similar in construction and function to those illustrated in FIGS. 2-4; and

Figure 6 is a rear schematic illustration of the surface vessel depicted in FIG. 5 showing the vessel's catamaran hull form and steering mechanism.

Detailed Description of Exemplary Embodiments

The following disclosure is presented to provide an illustration of the general principles of the present invention and is not meant to limit, in any way, the inventive concepts and embodiments contained herein. All terms defined herein should be afforded their broadest possible interpretation, including any implied meanings as dictated by a reading of the specification as well as any words that a person having skill in the art and/or a dictionary, treatise, or similar authority would assign thereto.

Further, it should be noted that, as recited herein, the singular forms “a”, “an”, and “the” include the plural referents unless otherwise stated. Additionally, the terms “comprises”, “comprising”, “includes”, “including”, “has” and the like, when used herein specify that certain features are present in that embodiment; however, such terms should not be interpreted to preclude the presence or addition of additional steps, operations, features, components, and/or groups thereof.

With specific reference now to the accompanying drawings, FIGS. 1-4 represent schematic illustrations of a method involving the trap-and-release of oils and the regeneration of smart membrane surfaces in accordance with one embodiment of the present invention. In Figure 1, a body of water (e.g., seawater) 10 is contaminated with oil 12, which is shown schematically in the form of bubbles or droplets. FIG. 2 shows the oil 12 trapped within oxidized mesh membranes 14. Figure 2A shows an oil droplet 12 adhered to the oxidized polymer surface of one of the mesh membranes 14 illustrated in FIG. 2, wherein a DBS group 16 of the polymer has its hydrophobic tail exposed. As shown in FIG. 3, reduced polymer surfaces of the membranes 14 cause collected oil droplets 12 to be released from the membranes 14 (through sliding or permeating). Fig. 3A shows an oil droplet 12 being released from (e.g., by sliding or permeating)

the reduced polymer surface of one of the mesh membranes 14 illustrated in FIG. 3, wherein the DBS group 16 of the polymer has its hydrophilic head exposed. FIG. 4 shows the membranes 14 after they have been oxidized to thereby regenerate their membrane surfaces in preparation for reuse of the membranes 14 as oil collection agents.

In an embodiment, a substrate cooperates with a conjugated polymer to form a composite mesh structure. The result is a smart membrane that includes: (1) conjugated polymer; (2) CNTs; and (3) SS mesh. On the SS mesh, CNTs are directly grown using chemical vapor deposition to form the substrate for the conjugated polymer. Finally, the surfactant-doped conjugated polymer film is coated atop the CNTs using electropolymerization to complete the composite mesh structure.

In an embodiment, multiwalled carbon nanotubes (CNTs) can be directly grown from 304 stainless steel (SS) meshes (Size 200 x 200, McMaster-Carr, Robbinsville, NJ) using atmospheric pressure chemical vapor deposition (APCVD). SS meshes were cut, rinsed, dried and then placed in the center of a 200 quartz tube in a horizontal three zone chemical vapor deposition (CVD) furnace and heated to 750 °C under the flow of 60 seem hydrogen (H2, Praxair, Newark, NJ) and 500 seem Argon (Ar, Praxair, Newark, NJ). Then, additional ethylene (C2H4, Praxair, Newark,NJ) was fed through the system at flow rates of 100 seem for 7 mins for CNTs growth. Subsequently, the samples were rapidly cooled to room temperature by blowing air into the furnace.

After CNT growth, PPy(DBS) film was electropolymerized atop the CNT-covered SS mesh surface. First, 1 mL pyrrole monomer (reagent grade, 98%, Sigma-Aldrich, St. Louis, MO) was thoroughly mixed with 150 mL 0.1 mol/L sodium dodecylbenzenesulfonate (NaDBS, technical grade, Sigma-Aldrich, St. Louis, MO) solution. Then, a CNT-covered SS mesh, a

saturated calomel electrode (SCE, Fisher Scientific Inc., Pittsburgh, PA), and another SS mesh (5 cm x 5 cm) were submerged in the solution as the working, reference, and counter electrode, respectively. The coating of PPy(DBS) surfaces was carried out using a potentiostat (263A, Princeton Applied Research, Oak Ridge, TN) by applying 0.7 V to the working electrode (vs. SCE) and stopped once surface charge density reached 1 C/cm^2. Instead of CNTs, SS meshes were deposited with 10 nm chromium (Cr) and 30 nm gold (Au) films using an e-beam evaporator (Explorer 14, Denton Vacuum, Moorestown, NJ), and then also coated with PPy(DBS) surfaces. After fabrication, the PPy(DBS) mesh surfaces were rinsed and dried in air overnight before any further characterizations.

It should be noted that CNTs are optional in the foregoing embodiment. However, the CNTs are preferred, as the in situ switch time decreases because the CNTs allow for a higher surface area, which increases the amount of DBS molecules desorbed from PPy(DBS) surfaces under reduction, thereby facilitating more rapid decrease of oil/water interfacial tension and retention force.

In another embodiment, a conductive carbon foam can be used directly for PPy(DBS) electropolymerization after necessary cutting and dicing. The pristine carbon foam is extremely porous and has a 3D microstructure. It is also lightweight. The 2.5 × 0.5 × 0.2 cm carbon foam weighs only 0.025g, compared to a 2 x 3 cm PPy(DBS) mesh, which weighs 0.2g. After PPy(DBS) electropolymerization, the whole surface of carbon foam can be evenly and uniformly covered with PPy(DBS) surfaces. Results show that the PPy(DBS) surface inherits the 3D porous structure of the carbon foam without blocking the pores. In testing conductive carbon foam as a substrate for PPy(DBS) electropolymerization, results further show that the resulting PPy(DBS) foam exhibits much higher absorbing capacity compared with the PPy(DBS) mesh. To

summarize, the PPy(DBS) foam had 3 times more absorption capacity with only 1/10 of the weight, versus the PPy(DBS) mesh. Such higher absorption capacity is attributed to the abundant surface area in the 3D porous structure of the foam. By fabricating PPy(DBS) surfaces on conductive carbon foam, the absorption capacity of absorbent made of PPy(DBS) material significantly increases.

The PPy(DBS) foam's longevity was tested, and it still absorbed and released DCM oil after 100 redox cycles. Additionally, the foam proved in tests its ability to absorb and release hexane and diesel. Such 3D printed PPy(DBS) has the potential for further improving the absorbing capacity and tailoring absorbent structure for different oil cleanup scenarios, as well as the development of other applications using PPy(DBS) surfaces and its wettability characteristic that can be varied in response to changing parameters (i.e., tunable wettability).

In another embodiment, 3D printing is used to directly print PPy(DBS) materials with a 3D porous structure to form PPy(DBS) absorbents. In this way, the structure and physical/mechanical properties of PPy(DBS) absorbents can be tailored and the mass production of PPy(DBS) absorbents will be possible. In order to test the feasibility of 3D printing of PPy(DBS), the PPy(DBS) solution was prepared and later cast on flat substrates (i.e., glass slides, Au-coated Si) to form freestanding PPy(DBS) films. Then, the resulting freestanding PPy(DBS) films were tested for their tunable wettability and switchable adhesion toward oils.

To prepare the PPy(DBS) solution, PPy(DBS) surfaces must be dissolved in organic solvents. However, it is suggested that electropolymerized PPy(DBS) is insoluble in either organic or inorganic solvents due to its high degree of cross-linking. Thus, electrochemical oxidization is used instead to prepare PPy(DBS) material, in which the polymerization is started

by adding oxidants (e.g., iron(III) chloride, FeCb) into the solution with pyrrole monomer and NaDBS.

With careful controlling of the molecular ratio/concentration of pyrrole/NaDBS/$FeCl_3$ and the polymerization duration, PPy(DBS) particles were synthesized and precipitated, which were then filtered out and thoroughly rinsed and dried. For example, 0.5 mL (0.0075 mL) of pyrrole monomer was mixed with 75 mL of 0.1 mol/L NaDBS solution for one hour. Then, 5 mL of 0.25 mol/L FeCb solution was added dropwise to start the polymerization process. After 10 minutes, the precipitates were filtered out using centrifugation, washed extensively with water three times, and dried in air at 60°C for 72 hours. Subsequently, the PPy(DBS) particles were dissolved in dimethylformamide (DMF) to form a stable suspension. To test the tunable wettability of PPy(DBS) made from electrochemical oxidization, one drop of such suspension was applied on a glass slide and dried overnight to form a freestanding film. The resulting PPy(DBS) freestanding film was then tested for tunable wettability.

This initial result suggests that the PPy(DBS) films made by a casting PPy(DBS) particle solution also exhibit tunable wettability, demonstrating the feasibility of making an oil absorbent via the 3D printing of PPy(DBS). Thus, with a careful design of the structure based on the oil cleanup requirement, the PPy(DBS) oil absorbent can be fabricated using 3D printing. Such oil absorbent can have both high absorbing capacity, as well as in situ surface regeneration ability, making it suitable for highly efficient next generation oil cleanup technology.

By way of example, DCM droplets on freestanding PPy(DBS) surfaces are characterized by a spherical shape and contact angle of ~60° when no voltage was applied to the surface. However, when -0.9V was applied, the DCM droplet exhibited flattening behavior, similar to the shape change observed in those droplets on the reduced electropolymerized PPy(DBS) surface.

A DCM droplet once adhered to the oxidized PPy(DBS) surface rolled away after 60 seconds of reduction, demonstrating tunable adhesion.

Any of the smart membranes described hereinabove can be incorporated into an unmanned, robotic surface vessel adapted for oil cleaning and recovery from a body of oil-contaminated water. For purposes of discussion only, the membranes 14 will be described in connection with one practical, potentially commercial embodiment of such a vessel 20, which is shown schematically in FIGS. 5 and 6.

With particular reference now to FIGS. 5 and 6, the vessel 20 includes a reduction chamber 22 with a reservoir 24 of electrolyte and a plurality of electrodes 26 in the form of passive rollers having a negative electric voltage. The vessel 20 also includes an oxidation chamber 28 with a reservoir 30 of electrolyte and a plurality of electrodes 32 in the form of passive rollers having a positive electric voltage.

A conveyor belt 34 includes a plurality of the smart membranes 14, which are spaced apart and electrically insulated from one another along the entire length of the conveyor belt 34. Active (i.e., driven) rollers 36 function as motive means for assisting in the performance of a method which includes the following steps: (i) passing the oxidized membranes 14 through the body of oil-contaminated water 10, where the lowest submerged portion of the membranes' surface (stable in the oxidized state) collects oil droplets 12 from the body of water 10; (ii) passing the membranes 14 through the reservoir 24 of electrolyte in the reduction chamber 22, where the membranes 14 are electrochemically reduced to thereby release collected oil droplets 12 with an assist from the simultaneous application of a dynamic pressure; and (iii) passing the membranes 14 through the reservoir 30 of electrolyte in the oxidation chamber 28, where the

membranes 14 are oxidized to thereby regenerate them for reuse as oil-collection agents when they are subsequently passed back into the body of oil-contaminated water 10.

In connection with the performance of the aforementioned method, the membranes 14 can be reduced in the reduction chamber 22 by applying a negative voltage (e.g., -0.9 volts) to the rollers/electrodes 26 versus a 13 mm x 35 mm platinum (Pt) mesh (i.e., counter-electrode). The subsequent oxidation of the membranes 14 can be achieved by applying a positive voltage (e.g., 0.1 volt) to the rollers/electrodes 32 versus a 13 mm x 35 mm platinum (Pt) mesh (i.e., counter-electrode).

A partition 38 between the reduction chamber 22 and the oxidation chamber 28 electrically insulates the two chambers from each other so that the requisite and appropriate negative and positive voltages may be applied to the membranes 14 as they pass between the reduction chamber 22 and the oxidation chamber 28, respectively. The partition 38 also creates a physical barrier that inhibits collected oil 40 in the reduction chamber 22 from migrating to the oxidation chamber 28. The collected oil 40 may be cleaned in the reduction chamber 22 to thereby avoid re-contaminating the body of water 10 outside the vessel 20.

The rollers/electrodes 26, 32 are arranged inside the reduction and oxidation chambers, 22, 28 respectively, so as to maximize the amount of collected oil 40 housed within the vessel 20. The rollers/electrodes 26, 32 also serve to support the conveyor belt 34 as it passes through the reduction and oxidation chambers 22, 28, respectively.

In addition to the active rollers 36, which function as motive means (i.e., a drive system) for the conveyor belt 34, the vessel 20 includes a simple electric propulsion system (not shown), an onboard microcontroller (not shown) supporting remote control of the drive and propulsion systems, and a lithium polymer battery (not shown). The vessel 20 is designed to be sufficiently

positively buoyant to take on additional weight during the performance of an oil-collection operation.

It will be understood that the embodiments described herein are merely exemplary and that a person skilled in the art may make many variations and modifications without departing from the spirit and scope of the invention. All such variations and modifications are intended to be included within the scope of the invention as defined in the appended claims.

Claims

1. A membrane adapted for use as an oil-collection agent, said membrane comprising an exposed surface which includes a conjugated polymer that is capable of functioning to collect oil on said exposed surface when said conjugated polymer is oxidized and that is capable of functioning to release oil from said exposed surface when said conjugated polymer is reduced.

2. The membrane of Claim 1, wherein said conjugated polymer is capable of being oxidized and reduced electrochemically.

3. The membrane of Claim 2, wherein said conjugated polymer is capable of being electrochemically oxidized by applying a positive electric voltage to said conjugated polymer and wherein said conjugated polymer is capable of being electrochemically reduced by applying a negative electric voltage to said conjugated polymer.

4. The membrane of Claim 3, wherein said positive electric voltage lies in a range of from greater than 0 volts to about 1.5 volts and wherein said negative electric voltage lies in a range of from about -0.6 volts to about -1.5 volts.

5. The membrane of Claim 4, wherein said conjugated polymer exhibits a wettability characteristic variable in response to the voltages selected from said positive and negative electric voltage ranges.

6. The membrane of Claim 1, wherein said conjugated polymer is a surfactant-doped conjugated polymer film.

7. The membrane of Claim 1, wherein said conjugated polymer is dodecylbenzenesulfonate-doped polypyrrole.

8. The membrane of Claim 1, wherein said conjugated polymer is a freestanding, porous film.

9. The membrane of Claim 8, wherein said freestanding, porous film is fabricated via 3D printing of said conjugated polymer.

10. The membrane of Claim 1, further comprising a substrate which cooperates with said conjugated polymer to form a composite structure.

11. The membrane of Claim 10, wherein said substrate includes a stainless steel mesh.

12. The membrane of Claim 11, wherein said substrate further includes carbon nanotubes.

13. The membrane of Claim 12, wherein said carbon nanotubes are grown on said stainless steel mesh via chemical vapor deposition.

14. The membrane of Claim 13, wherein said conjugated polymer is coated on said carbon nanotubes via electropolymerization.

15. The membrane of Claim 10, wherein said substrate includes electrically conductive carbon foam having a porous 3D structure.

16. The membrane of Claim 1, wherein said membrane is integrated into a surface vessel adapted to perform an oil cleanup and recovery operation on a body of oil-contaminated water.

17. The membrane of Claim 16, wherein said surface vessel includes a reduction chamber, which includes a first reservoir of electrolyte and a first set of electrodes; an oxidation chamber, which includes a second reservoir of electrolyte and a second set of electrodes; a conveyor belt, which includes said membrane; and motive means for moving said conveyor belt such that said membrane (i) passes beneath said surface vessel and through a body of oil-contaminated water to collect oil thereon, (ii) passes through said first reservoir of electrolyte in said reduction chamber after passing through the body of oil-contaminated water, and (iii) passes through said second reservoir of electrolyte in said oxidation chamber after passing through said first reservoir of electrolyte in said reduction chamber.

18. The membrane of Claim 17, wherein said membrane is electrochemically reduced by applying a negative electric voltage to said first set of electrodes as said conveyor belt carries said membrane through said first reservoir of electrolyte in said reduction chamber and wherein said membrane is electrochemically oxidized by applying a positive electric voltage to said second set of electrodes as said conveyor belt carries said membrane through said second reservoir of electrolyte in said oxidation chamber.

19. The membrane of Claim 18, wherein said first reservoir of electrolyte in said reduction chamber is separated from said second reservoir of electrolyte in said oxidation chamber by a partition positioned between said oxidation chamber and said reduction chamber.

20. The membrane of Claim 19, wherein said partition inhibits oil collected in said reduction chamber from migrating into said oxidation chamber.

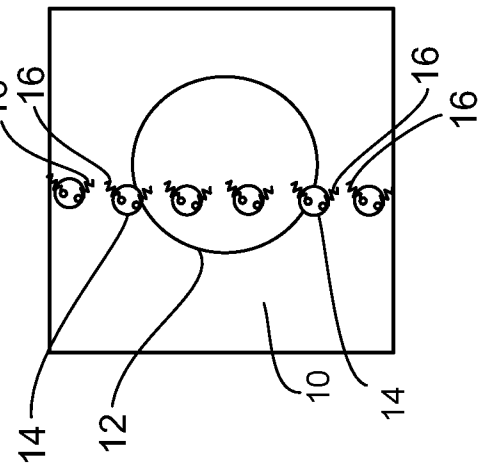


FIG. 2A

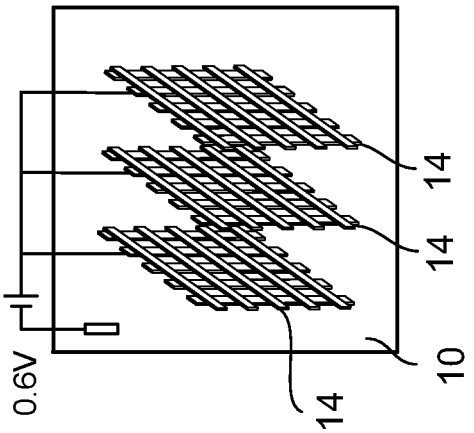


FIG. 4

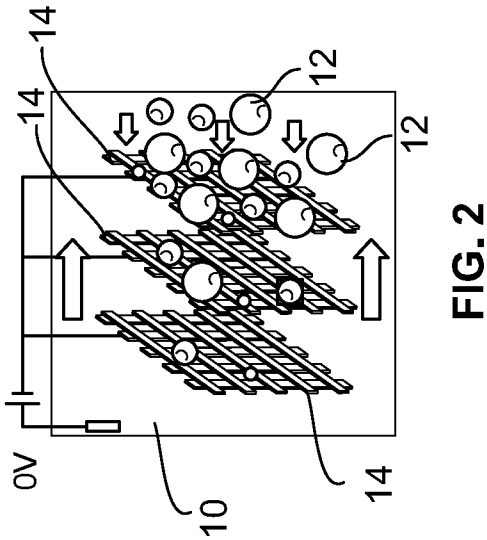


FIG. 2

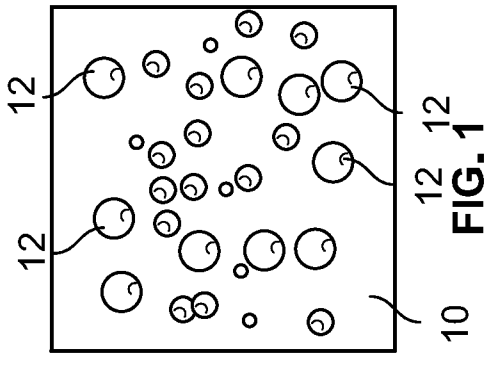
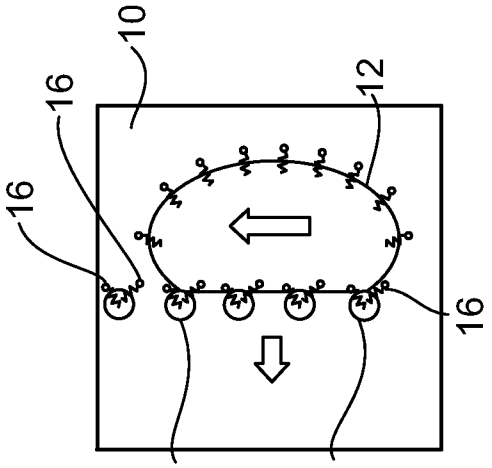


FIG. 1



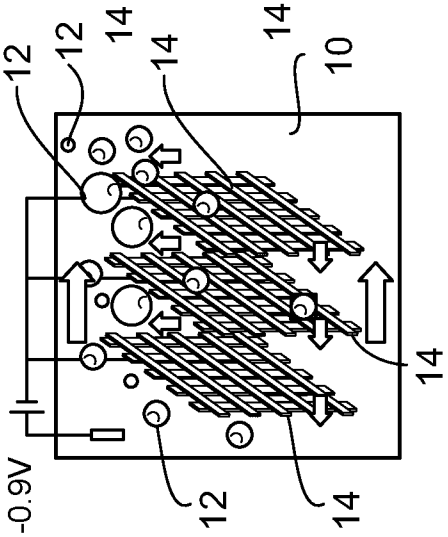


FIG. 3A

FIG. 3

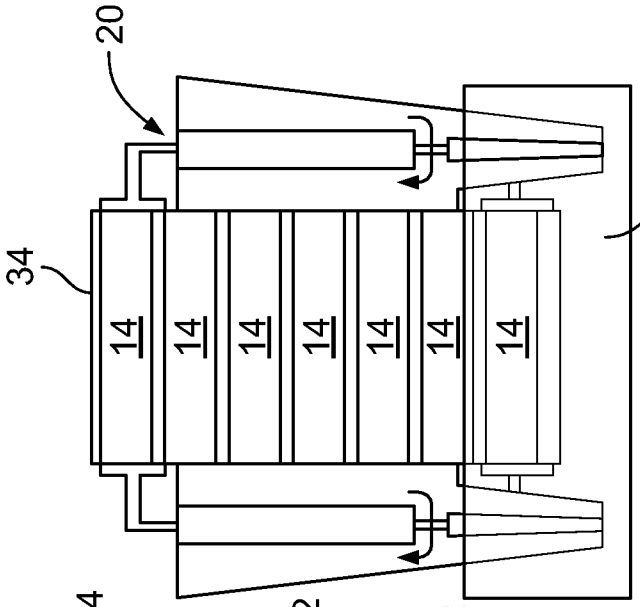

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FIG. 6

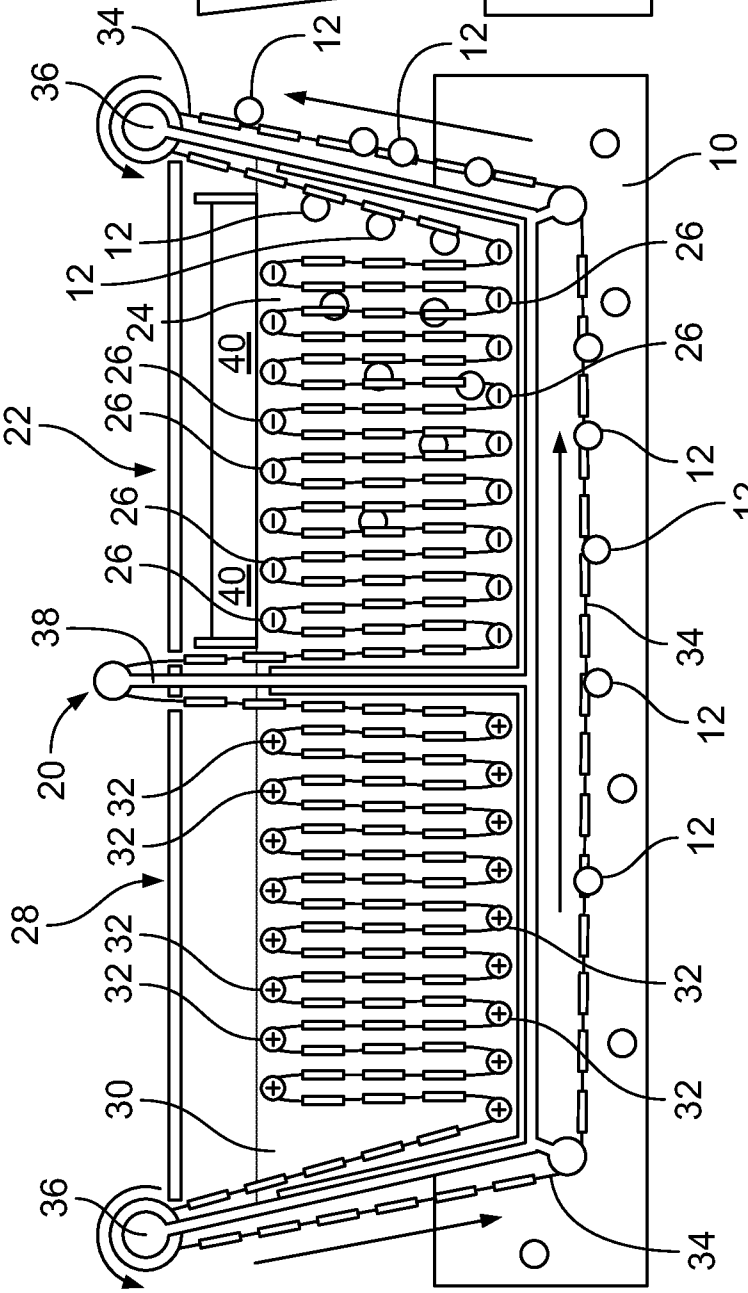
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FIG. 5