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(71) Applicant: **IMPERIAL INNOVATIONS LIMITED** [GB/GB]; 52 Princes Gate, South Kensington, London Greater London SW7 2PG (GB).

(72) Inventors: **HII, King Kuok**; Imperial College London, Greater London SW7 2AZ (GB). **HELLGARDT, Klaus**; Imperial College London, Greater London SW7 2AZ (GB). **KELSALL, Geoffrey Howard**; Imperial College London, Greater London SW7 2AZ (GB). **BRAZIER, John Benedict**; Imperial College London, Greater London SW7 2AZ (GB). **ADRIO, Luis Angel**; Imperial College London, Greater London SW7 2AZ (GB).

(74) Agent: **KILBURN & STRODE LLP**; 20 Red Lion Street, London Greater London WC1R 4PJ (GB).

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(54) **Title**: APPARATUS AND METHOD FOR PRODUCTION OF OXIDANTS

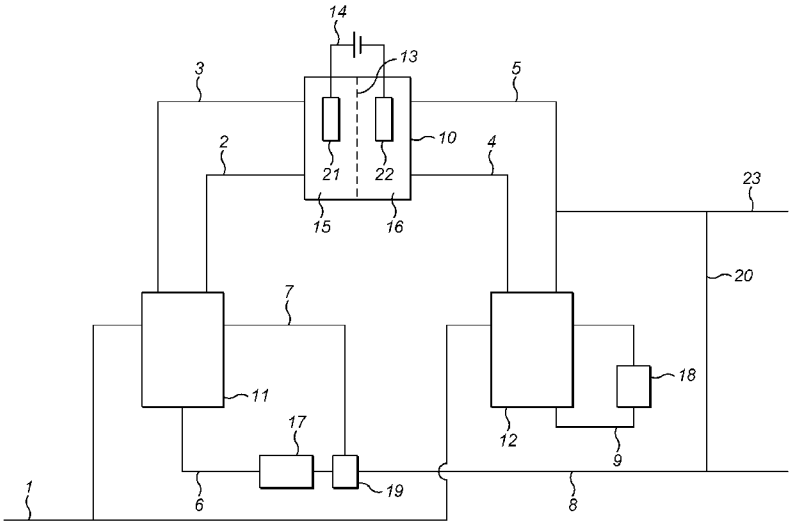


FIG. 1

(57) **Abstract**: The present invention relates to an apparatus for manufacturing oxidant, the apparatus comprising an electrochemical reactor, a feed inlet for receiving feed materials and a product outlet for the oxidant; the electrochemical reactor being in fluid communication with the feed inlet and the product outlet and comprising one or more anodes and one or more cathodes. The apparatus further comprises means for detecting oxidant within the apparatus, and flow controlling means configured to control the flow of fluid through the product outlet and to communicate with the means for detecting oxidant. The present invention also relates to a process of manufacturing oxidant using said apparatus.

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Apparatus and method for production of oxidants

The present invention relates to an apparatus and process for manufacturing oxidants.

In recent years, greater awareness of environmental and safety issues has led to increasingly stringent regulatory controls on manufacturing processes in the chemical industry, fuelling demand for green chemical technologies that can deliver greater process, and economic efficiency. To address these issues, there is substantial interest in the design and development of fully integrated continuous processes that can offer efficient chemical synthesis and that can be easily implemented at any scale.

Traditionally, liquid and solid oxidants are difficult to handle in large quantities as they are often thermally unstable and potentially explosive. As a result of these characteristics, it is important that stored oxidant is kept away from sources of heat, sources of ignition or any combustible materials. In particular, oxidants must be kept away from incompatibles such as reducing agents, organic materials, metals, acids and moisture. Because of their highly corrosive nature, great care must be taken when handling oxidants.

Storing large quantities of oxidant is therefore considered a safety hazard in many industrial and laboratory scale operations.

In addition to the safety aspects of storing large quantities of liquid or solid oxidant, another recognised problem with storing large quantities of oxidant relates to quality control. Oxidants have a limited shelf-life and expiration period, after which their use is compromised. This can pose a problem for laboratories, which typically have a large inventory of different chemicals in stock, all of which may be used in different quantities. Expiration of chemicals can therefore represent a large inefficiency in a laboratory's operations.

Few solutions are available to address these problems of storing large quantities of oxidants, and there is a recognised need for a solution which address the problems of storing oxidants and also addresses the problems that storing oxidants has on oxidant quality.

It is therefore desirable to provide a solution to alleviate the safety and quality related problems of storing oxidants.

In light of the above, the inventors of the present invention have developed an apparatus and method which enables a user to manufacture a wide variety of different species of oxidants on-demand and in-situ. For example, the apparatus and method of the present invention can be used in a laboratory or in a chemical plant, to deliver a desired oxidant type to a chemical process, at the time the oxidant is required and with user defined characteristics, for example, at a desired temperature, concentration and flow rate. The apparatus and method of the present invention thus avoids the need for oxidant storage in quantities which would be of safety and quality concern and gives the option of delivering freshly prepared oxidant which can be used immediately and in-situ.

Summary of the Invention

Accordingly, the present invention provides an apparatus for manufacturing oxidant, the apparatus comprising an electrochemical reactor, a feed inlet for receiving feed materials and a product outlet for dispensing the oxidant; the electrochemical reactor being in fluid communication with the feed inlet and the product outlet and comprising one or more anodes and one or more cathodes; and wherein the apparatus further comprises: means for detecting oxidant (an oxidant detector) within the apparatus; and flow controlling means configured to control the flow of fluid through the product outlet and to communicate with the means for detecting oxidant.

The feed material can be any suitable material which can be electrolysed to produce oxidant, for example an electrolyte solution. The feed material may alternatively be any suitable material for cleaning the apparatus, for example a cleaning fluid.

Electrolysis at a fixed electrical potential may produce a mixture of oxidants, generally with one type of oxidant dominating (being produced in a higher concentration) at a certain potential. Therefore, the term 'oxidant' as used herein may relate to a single oxidant, or a mixture of oxidants.

Preferably, the apparatus further comprises a separator configured to divide the electrochemical reactor into two or more chambers and allow the passage of ions between the chambers, wherein an anode is located within a first of the two or more chambers to form an anolyte chamber and a cathode is located within a second of the one or more chambers to form a catholyte chamber. The electrolyte solution within the anolyte chamber may be called the anolyte solution and the electrolyte solution within the catholyte chamber may be called the catholyte solution.

Dividing the electrochemical reactor using the separator in this way prevents any reaction products produced at the one or more anodes and one or more cathodes from mixing with each other to produce unwanted chemical compounds. Separating the one or more anodes from the one or more cathodes in this way helps to separate the

oxidant which is typically manufactured at the anode from the reaction product formed at the cathode, which is typically hydrogen.

Preferably, the apparatus further comprises a first reservoir (an anolyte reservoir) configured to be in fluid communication with the anolyte chamber. Preferably, the anolyte reservoir is in fluid communication with the feed inlet.

The anolyte reservoir may advantageously act as a buffer vessel for the electrolyte solution within the apparatus. If, for example, the feed inlet becomes blocked or the raw materials for producing the oxidant run out, then the buffer vessel can accommodate for the reduction or lack of electrolyte solution, and temporarily maintain an adequate amount of electrolyte solution in the electrochemical reactor, and temporarily maintain the flow rate of oxidant provided to the user.

Preferably, the means for detecting oxidant is in fluid communication with the anolyte reservoir and/or the anolyte chamber.

As mentioned above, the oxidant is typically formed at the anode. Thus, configuring the oxidant detector to be in fluid communication with the anolyte reservoir and/or the anolyte chamber enables a user of the apparatus to monitor the concentration of the oxidant in only these sections of the apparatus.

Preferably, the apparatus further comprises a second reservoir (a catholyte reservoir) configured to be in fluid communication with the catholyte chamber. Preferably, the catholyte reservoir is in fluid communication with the feed inlet. In addition to or alternatively, the catholyte reservoir is in fluid communication with a second feed inlet.

Having the catholyte reservoir in fluid communication with a second feed inlet enables a user to feed a different electrolyte solution into the catholyte reservoir. Using different electrolyte solutions in the catholyte reservoir (the catholyte solution) and the anolyte reservoir (the anolyte solution) gives the apparatus flexibility to produce a wide variety of oxidants. Using different electrolyte solutions in this way may also give economic benefits; if, for example, the reaction at the cathode involves a reduction to produce

hydrogen, then aqueous salt solution (e.g. an aqueous NaCl or KCl solution) can be used as the catholyte solution in the catholyte reservoir, while a more expensive electrolyte solution can be used as the anolyte solution to generate the oxidant. Thus, the anolyte solution and the catholyte solution may be the same, or they may be different.

The anolyte and/or catholyte reservoirs may be configured so that during operation they are able to remove electrolyte solution from general areas of the electrochemical reactor, for example from a location near the one or more anodes or a location near the one or more cathodes. This is particularly the case if the separator is not provided, as it is generally desirable to keep the reaction products at the anode and cathode separated. As mentioned above, in certain electrolysis reactions, hydrogen may be formed at the cathode, which should be kept substantially separate from oxidant being produced at the anode. Configuring the anolyte and/or catholyte reservoirs to remove/recycle electrolyte solution from a general area of the electrochemical reactor, e.g. near one of the electrodes in the electrochemical reactor, enables a certain active/desirable concentration of oxidant to be achieved.

Preferably, the apparatus further comprises a second means for detecting oxidant, configured to be in fluid communication with the catholyte reservoir and/or the catholyte chamber.

Preferably, the apparatus further comprises one or more gas detection means configured to detect the presence of any gas in the electrolyte solution. Preferably, the one or more gas detection means are configured to detect hydrogen and/or oxygen in the electrolyte solution.

During electrolysis reactions, it is common for ions within the electrolyte solution to react at the anode or the cathode to form a gas. For example, hydrogen ions present in the electrolyte solution during an electrolysis reaction may react at the cathode to form hydrogen gas, which will be evolved from the cathode. It has been found that gas detection means to detect the presence of a gas in the system can advantageously be used to provide an indication that an electrochemical reaction is occurring and thus provide an indication that oxidant is being produced.

Preferably, when a separator is provided to divide the electrochemical reactor into two or more chambers, the one or more gas detection means are configured to detect the presence of any gas in the anolyte solution and/or the catholyte solution. Preferably, the one or more gas detection means are configured to detect the presence of any gas in the anolyte chamber and/or the catholyte chamber.

Using the one or more gas detection means to detect whether gas is present in the anolyte chamber can be used advantageously to determine whether gas is being produced at the anode, or alternatively to determine whether gas is being transferred from the catholyte chamber to the anolyte chamber. Such gas transfer from the catholyte chamber to the anolyte chamber would not be desirable, and if a separator was being used within the electrochemical reaction, the presence of gas in the anolyte chamber may provide an indication to a user that the separator has become damaged and needs repairing or replacing.

As mentioned above, when the apparatus is being operated to manufacture oxidant, hydrogen gas is typically formed at the cathode. Using the one or more gas detection means to detect whether gas (e.g. hydrogen) is present in the catholyte chamber advantageously enables a user to determine whether oxidant is being produced at the anode. The readings from the one or more gas detection means (indicating that oxidant is being produced) may be compared to readings from the oxidant detector described above to verify that oxidant is being produced.

Preferably, when an anolyte reservoir is provided, the one or more gas detection means are used to detect the presence of any gas in the anolyte reservoir.

Preferably, when a catholyte reservoir is provided, the one or more gas detection means are used to detect the presence of any gas in the catholyte reservoir.

Preferably, the one or more gas detection means are configured to detect the presence of any gas in a headspace within one or more of: the electrochemical reactor, the anolyte reservoir, the catholyte reservoir. Gas detection means configured to detect any gas in the headspace may be used instead of, or in addition to gas detection means for

detecting the presence of any gas in the electrolyte solution. Preferably the gas detection means configured to detect any gas in the headspace is provided in addition to the gas detection means configured to detect the presence of gas in the electrolyte solution.

Preferably, the apparatus further comprises one or more gas removal means, configured to remove any gas present within the electrolyte solution in the apparatus. Preferably, the gas removal means is comprised in any of the one or more gas detecting means. For example, a fuel cell may be configured to detect and remove gas from the electrolyte solution in the apparatus.

Preferably, the gas removal means is an anolyte gas removal means configured to remove gas present within the anolyte chamber and/or the anolyte reservoir.

Preferably, the anolyte gas removal means is configured to remove gas from a headspace within the anolyte chamber and/or the anolyte reservoir.

If the oxidant and a gas are being produced at the anode, then removing the gas may be desirable if a user of the apparatus wishes to have a product stream free from said gas, and to relieve pressure build-up. Removing the gas may also prevent unwanted side reactions from occurring with the oxidant that is being manufactured.

Preferably, in addition to, or as an alternative to the anolyte gas removal means, the apparatus further comprises a catholyte gas removal means configured to remove gas present within the catholyte chamber and/or the catholyte reservoir. Preferably, the catholyte gas removal means is comprised in any of the one or more gas detecting means present in the catholyte chamber and/or the catholyte reservoir. For example, a fuel cell may be configured to detect and remove gas from the catholyte chamber and/or the catholyte reservoir.

Preferably, the catholyte gas removal means is configured to remove any gas from a headspace within the catholyte chamber and/or the catholyte reservoir.

As mentioned above, in some cases hydrogen gas will be produced at the cathode and may therefore be present in the catholyte chamber and/or the catholyte reservoir. Hydrogen gas can be explosive in even small concentrations and therefore it is not desirable to have hydrogen gas held within the apparatus. Providing catholyte gas removal means in this way may advantageously allow the removal of any gas (e.g. hydrogen) from the catholyte chamber and/or the catholyte reservoir to reduce the likelihood of an explosion and also reduced any unwanted side reactions from occurring.

The anolyte gas removal means and/or the catholyte gas removal means and the one or more gas detection means may be in communication with each other to detect the presence of any gas and then remove the gas from the apparatus. In this way, a user may, for example, use the one or more gas detection means to detect the presence of any gas and to determine that oxidant is being produced, and then remove the gas from the apparatus using the gas removal means and/or the second gas removal means. As mentioned above, the one or more gas detection means may comprise the anolyte gas removal means and/or the catholyte gas removal means.

Preferably, the apparatus further comprises means to store gas, and wherein gas removed is stored using said means to store gas. Preferably, the means to store gas is comprised in any of the one or more gas detection means. Preferably, the means to store gas is a fuel cell.

Using means to store gas in this way is advantageous, as it prevents gas being released into the surrounding environment, and may be useful if, for example, a gas being formed within the apparatus is harmful to the environment (for example if the gas is toxic to humans, wildlife etc...), or if the gas may be useful in other applications (for example, storing hydrogen for use as a fuel).

Preferably, the means to store gas is in communication with any one of: the gas removal means, and in communication with the one or more gas detection means. Thus, the means to store gas may be used in combination with the gas removal means and the one or more gas detection means to detect the presence of any gas, to remove the gas from the apparatus, and then to store it. In this way, a user may, for example,

use the one or more gas detection means to detect the presence of gas and to determine that oxidant is being produced, then remove the gas from the apparatus using the gas removal means and then store the gas using the means to store gas.

Alternatively, the means to store gas may be used in combination with the gas removal means and/or the second gas removal means to determine whether gas is being produced, and thus to determine whether oxidant is being produced (based on whether gas is being stored in the means to store gas).

If, for example, hydrogen is produced at the cathode during operation of the electrochemical reactor, any hydrogen removed and stored by the means to store gas may be converted into water through an oxidation reaction, by either passing it through a catalyst, or preferably through a fuel cell. If a fuel cell is being used, the current produced by the fuel cell (through oxidising the hydrogen to water) can be used to provide an indication to a user that hydrogen is being produced, which in turn may be used as an indication that oxidant is being produced. Thus, a fuel cell may serve as the gas detection means, gas storage means, and gas removal means.

Preferably, the one or more anodes have an overpotential for oxygen of at least +0.5 V at a temperature of 25 °C, e.g. the overpotential for oxygen could be +0.6 V, +0.7 V, +0.8 V, +0.9 V, +1.0 V, +1.1 V etc... All overpotential values provided herein are based on overpotential under standard conditions, at a temperature of 25 °C. More preferably, the one or more anodes have an overpotential for oxygen of at least +0.6 V, and even more preferably at least +0.7 V.

Preferably, the one or more anodes comprises one or more of boron doped diamond, vitrified carbon, diamond-like carbon, lead oxide, platinum, palladium, gold, iron, silver, nickel, carbon, lead or mixtures thereof. More preferably, the anode comprises essentially boron doped diamond.

It is possible that when an aqueous electrolyte (electrolyte solution) is used, the water in the electrolyte will be oxidised. As a result of this oxidation, oxygen gas will be formed at the one or more anodes. This reduces the efficiency of the process, as the oxygen

will contaminate the electrolyte solution and ultimately the oxidant produced by the apparatus. To overcome this problem it has been found that the material used to manufacture the one or more anodes must be capable of preventing water from being oxidised during process operation. It has been found that this is possible by selecting an anode material that has a high overpotential for oxygen evolution. Overpotential is the potential difference (or voltage) between a half-reaction's determined reduction potential via the laws of thermodynamics, and the actual potential that the redox event occurs in experimentation.

It has been found that although some electrode materials may be suitable to minimise oxygen production, but may also have a high overpotential for hydrogen gas. If such a material was used for the cathode, hydrogen production at the cathode would be reduced, i.e the system will be 'cathodically limited'. The inventors of the present invention have found that this problem can be overcome by either using a different material for the cathode, or by selecting a material which has a high overpotential for oxygen evolution and also a low overpotential for hydrogen evolution.

Preferably, the one or more cathodes have an overpotential for hydrogen of – 1 V or less negative, for example -0.9 V, -0.8 V, -0.7 V, -0.6 V, -0.5 V, -0.4 V, -0.3 V, -0.2 V, -0.1 V, -0.05 V or -0.005 V. More preferably, the one or more cathodes have an overpotential for hydrogen of between -0.05 V and -0.9 V.

Preferably, the one or more cathodes comprises any material that can withstand the corrosive nature of the electrolyte solution. Preferably the one or more cathodes comprises one or more of platinum, palladium, gold, iron, silver, nickel, steel, stainless steel, or mixtures thereof. More preferably, the cathode comprises one or more of stainless steel and/or nickel.

Preferably, the separator comprises an ion exchange material which is permeable to ions but selectively impermeable to any of: gases such as hydrogen, oxygen etc..; liquids such as oxidant produced. Preferably, the separator comprises any one or more of an ionomer, a cation-exchange material, an anion-exchange material, a bipolar material or mixtures thereof. Thus, the separator may comprise, for example, a fully or partially perfluorinated ion-exchange material, a fully or partially fluorinated polymeric

material containing functional groups (e.g. sulfonic acid groups), a fully or partially sulfonated tetrafluoroethylene based fluoropolymer-copolymer material or mixtures thereof.

Preferably, the separator is a membrane, a porous membrane or a porous frit.

Although, the separator may alternatively be manufactured from any other suitable material which is capable of separating the electrochemical reactor into two or more chambers and allow selective transport of ions between the chambers. Preferably, the membrane is manufactured from a material that is chemically resistant and provided sufficient structural durability to withstand the conditions in the electrochemical reactor.

Preferably, the apparatus further comprises a waste line, configured to allow any fluid inside the apparatus to be drained. Preferably, the waste line is in fluid communication with one or more of: the anolyte chamber, the anolyte reservoir, the catholyte chamber, the anolyte reservoir.

Preferably, the apparatus further comprises one or more of temperature, flow, pH and/or concentration sensors and/or controlling means.

Preferably, the apparatus further comprises one or more pumps configured to pump electrolyte solution through the apparatus.

Preferably, the apparatus further comprises one or more depth sensors. More preferably the depth sensors are inside one or more of: the electrochemical reactor, the anolyte reservoir, the catholyte reservoir.

Preferably, the one or more depth sensors comprise a body, and a plurality of corrosion resistant sensors disposed along the longitudinal length of the body. Preferably, the plurality of corrosion resistant sensors are held into a fixed position relative to the body using a filling material.

The filling material may be any material that is capable of holding the sensors in a fixed position within and/or on the body and that can also withstand the operating conditions the depth sensor will be exposed to in the apparatus for manufacturing the oxidant. Preferably, chemically resistant filling glue is used as filling material. The corrosion resistant sensors are configured to be in fluid communication with an electrolyte solution present within the apparatus. Preferably, the corrosion resistant sensors are configured to be in fluid communication with an electrolyte solution present within the apparatus via orifices provided on body.

Preferably, the corrosion resistant sensors are plates or tubes disposed along the longitudinal length of the depth sensor.

Preferably, the plurality of corrosion resistant sensors comprises gold and/or copper. Most preferably the plurality of corrosion resistant sensors comprises gold-plated copper.

The one or more depth sensors may be used advantageously to provide an indication of liquid depth within the apparatus, and can be used to warn a user if the liquid depth is getting too low or too high.

If a separator is being used inside the electrochemical reactor, then a low depth of electrolyte solution can result in the separator becoming dry. This can result in the separator degrading or perishing. Therefore, the one or more depth sensors can be used advantageously to alert a user of the apparatus to low electrolyte solution level within the electrochemical reactor to prevent the separator becoming damaged.

Preferably, the depth sensor further comprises transmitting means to transmit data from the corrosion resistant sensors to an external device.

The one or more depth sensors may optionally be capable of communicating with other aspects of the apparatus, to correct low or high liquid levels. For example, in the case of a low electrolyte solution level within the electrochemical reactor, the one or more depth sensors may communicate with the feed inlet to ensure more electrolyte solution is

provided to the system to increase the electrolyte solution level in the reactor. In this case, the depth sensor may also prevent any electrolyte solution from leaving the apparatus until the electrolyte level has been restored to a suitable level.

Preferably, the apparatus further comprises software controlling means, configured to communicate with and/or control any aspect of the apparatus in order to manufacture oxidant according to a user's predefined requirements. For example, software controlling means may be provided to communicate with and/or control one or more of: the flow rate of electrolyte solution through the feed inlet, second feed inlet, product outlet, the two or more chambers, anolyte reservoir, catholyte reservoir; oxidant detecting means; second oxidant detecting means; flow controlling means; gas detecting means; gas removal means; gas storage means; second gas removal means, temperature sensors, pH sensors, depth sensors, concentration sensors, in order to manufacture oxidant within the apparatus according to a user's predefined requirements of oxidant type.

The controlling means may be used to operate the apparatus and produce oxidant in a batch, semi-continuous or continuous fashion. For example, the controlling means may be configured to control the amount of electrolyte solution entering the electrochemical reaction to replenish the electrolyte solution as needed to allow oxidant to be produced continuously.

Advantageously, the apparatus according to the present invention may be configured to manufacture oxidant in a batch, semi-continuously or continuously interchangeably, depending on the user's requirements.

According to another aspect of the present disclosure there is provided a process of manufacturing oxidant using an apparatus comprising an electrochemical reactor, a feed inlet for receiving feed materials and a product outlet for the oxidant; the electrochemical reactor being in fluid communication with the feed inlet and the product outlet and comprising one or more anodes and one or more cathodes; and wherein the apparatus further comprises: means for detecting oxidant within the apparatus; and flow controlling means configured to control the flow of fluid through the product outlet and to communicate with the means for detecting oxidant, the process comprising the steps of:

(a) introducing an electrolyte solution to the electrochemical reactor via the feed inlet, so as to produce oxidant by electrolysis of the electrolyte solution;

(b) using the means for detecting oxidant to monitor the oxidant concentration in the electrolyte solution; and

(c) dispensing the electrolyte solution from the apparatus via the product outlet once the oxidant concentration has reached a predetermined value in the electrolyte solution.

Again, the feed materials can be any suitable material which can be electrolysed to produce oxidant, and typically include for example, the electrolyte solution. The feed material may alternatively be any suitable material for cleaning the apparatus, for example a cleaning fluid.

The electrolyte solution may vary depending upon the oxidant species to be manufactured. This advantageously allows a wide variety of oxidants to be manufactured. The removal of the electrolyte solution once it reaches a predetermined oxidant concentration advantageously enables a user to efficiently and accurately obtain oxidant of a desired concentration consistently, which prevents, for example, the need for a person to manually prepare a diluted oxidant solution. Manually preparing oxidants in this way can be time consuming, and human error makes it difficult to produce solutions of a consistent concentration.

The oxidant detector provides an indication as to whether oxidant is being produced, and what the concentration of any oxidant is within the apparatus. This advantageously enables a user to determine what the concentration of oxidant is within the apparatus.

The flow controlling means enables a user to remove oxidant from the system once the desired oxidant composition has been achieved. According to this disclosure, the oxidant detector and the flow controlling means are capable of communicating with each other. This is advantageous as it enables the flow controlling means to control the flow to the product outlet depending on information provided by the oxidant detector.

Preferably, the apparatus used in the process is provided with a separator configured to divide the electrochemical reactor into two or more chambers and further configured to allow the passage of ions, wherein an anode is located within a first of the two or more chambers to form an anolyte chamber and a cathode is located within the second of the two or more chambers to form a catholyte chamber. Electrolyte solution within the anolyte chamber may be referred to as the anolyte solution. Electrolyte solution within the catholyte chamber may be referred to as the catholyte solution.

Preferably, the apparatus used in the process further comprises a first reservoir (an anolyte reservoir) configured to be in fluid communication with the anolyte chamber, and wherein the process further comprises recycling electrolyte solution (the anolyte solution) between said anolyte chamber and said anolyte reservoir, preferably at least until a desirable concentration of oxidant has been reached.

Recycling the electrolyte solution (anolyte solution) between the anolyte chamber and the anolyte reservoir in this way also ensures that there is good mixing of the anolyte solution within the anolyte chamber to ensure that the reaction at the electrodes occurs efficiently. The means for detecting oxidant may be employed to detect the oxidant concentration within the apparatus (including the anolyte chamber and anolyte reservoir). In this case, the mixing effect provided by the recycling of the electrolyte solution advantageously improves the accuracy of the means for detecting oxidant, as the mixed solution provides an accurate representation of the bulk oxidant concentration present within the anolyte chamber and anolyte reservoir.

Preferably, the electrolyte solution in step (c) is dispensed from the anolyte reservoir once the oxidant in the electrolyte solution has reached the predetermined concentration.

Preferably, the anolyte reservoir is in further fluid communication with the feed inlet, and the process further comprises feeding the electrolyte solution into the anolyte reservoir via the feed inlet and introducing the electrolyte solution to the anode in the anolyte chamber from said anolyte reservoir.

Preferably, the means for detecting oxidant is configured to be in fluid communication with the anolyte reservoir and/or the anolyte chamber, and said means for detecting oxidant is used to monitor whether any oxidant is present in the anolyte reservoir and/or the catholyte chamber.

Preferably, the apparatus used in the process further comprises a second reservoir (a catholyte reservoir) configured to be in fluid communication with the catholyte chamber, and wherein the process further comprises recycling the electrolyte solution = between said catholyte chamber and said catholyte reservoir.

Preferably, the catholyte reservoir is in further fluid communication with the feed inlet, and wherein the process further comprises feeding the electrolyte solution into the catholyte reservoir via the feed inlet and introducing the electrolyte solution to the cathode in the catholyte chamber from said catholyte reservoir.

Preferably, the catholyte reservoir is in further fluid communication with a second feed inlet for receiving second feed materials, and a second electrolyte solution is fed into the catholyte reservoir via the second feed inlet and the second electrolyte solution is introduced to the cathode in the catholyte chamber from said catholyte reservoir.

The second feed materials can be any suitable materials which can be electrolysed, for example an electrolyte solution. The second feed materials may alternatively be any suitable materials for cleaning the apparatus, for example a cleaning fluid.

Preferably, the apparatus used in the process further comprises one or more gas detection means, and wherein said one or more gas detection means are used to detect the presence of gas within the apparatus. Preferably, the one or more gas detection means are used to detect the presence of hydrogen and/or oxygen in the apparatus.

Preferably, the process further comprises using the one or more gas detection means to detect the presence of gas in the anolyte chamber and/or the catholyte chamber.

Preferably, the process further comprises using the one or more gas detection means to detect the presence of gas in the anolyte reservoir.

Preferably, the process further comprises using the one or more gas detection means to detect the presence of gas in the catholyte reservoir.

Preferably, the process further comprises using the one or more gas detection means to detect the presence of gas in a headspace of one or more of: the electrochemical reactor, the catholyte reservoir and the anolyte reservoir. Gas detection means configured to detect any gas in the headspace may be used instead of, or in addition to gas detection means for detecting the presence of any gas in the electrolyte solution. Preferably the gas detection means configured to detect any gas in the headspace is provided in addition to the gas detection means configured to detect the presence of gas in the electrolyte solution.

Preferably, the process further comprises using the one or more gas detection means to determine whether oxidant is being manufactured based on the presence of any gas.

Preferably, the apparatus is further provided with one or more gas removal means, and wherein the process further comprises using said gas removal means to remove gas present within the electrolyte solution in the apparatus. Preferably, the gas removal means is comprised in any of the one or more gas detecting means. For example, a fuel cell may be used which is configured to detect and remove gas.

Preferably, the gas removal means is an anolyte gas removal means and the process further comprises using the anolyte gas removal means to remove gas present within the anolyte chamber and/or the anolyte reservoir.

Preferably, the anolyte gas removal means are used to remove gas from a headspace within the anolyte chamber and/or the anolyte reservoir.

Preferably, in addition to, or as an alternative to the anolyte gas removal means, the apparatus further comprises a catholyte gas removal means configured to remove gas present within the catholyte chamber and/or the catholyte reservoir. Preferably, the catholyte gas removal means is comprised in any one of the one or more gas detecting means present within the catholyte chamber and/or the catholyte reservoir. For example, a fuel cell may be used which is configured to detect and remove gas.

Preferably, the catholyte gas removal means are used to remove any gas present within the electrolyte solution in the apparatus from a headspace within the catholyte chamber and/or the catholyte reservoir.

Preferably, the apparatus is provided with means to store gas, and wherein the process further comprises using said means to store any gas which is removed by the gas removal means. Preferably, the means to store gas is comprised in the gas detecting means. For example, a fuel cell may be used to detect, store and remove gas.

If, for example, hydrogen is produced during the operation of the electrochemical reactor, any hydrogen removed and then stored by the means to store gas may be converted into water either by passing it through a catalyst or passing it through a fuel cell prior to venting into the atmosphere. This advantageously prevents explosive risks. Preferably, a current generated in the fuel cell is used to give an indication of the system's operation, and rate of production of hydrogen.

Preferably, the apparatus is provided with one or more anodes with an overpotential for oxygen of at least +0.5 V, e.g. +0.6 V, +0.7 V, +0.8 V, +0.9 V, +1.0 V, +1.1 V etc... More preferably, the one or more anodes have an overpotential for oxygen of at least +0.6 V, and even more preferably at least +0.7 V.

Preferably, the one or more anodes comprises one or more of boron doped diamond, vitrified carbon, diamond-like carbon, lead oxide, platinum, palladium, gold, iron, silver, nickel, carbon, lead or mixtures thereof. More preferably, the anode comprises boron doped diamond.

Preferably, the one or more cathodes have an overpotential for hydrogen of – 1 V or less negative, for example -0.9 V, -0.8 V, -0.7 V, -0.6 V, -0.5 V, -0.4 V, -0.3 V, -0.2 V, -0.1 V, -0.05 V or -0.005 V. More preferably, the one or more cathodes have an overpotential for hydrogen of between -0.05 V and -0.9 V.

Preferably, the one or more cathodes comprise any material that can withstand the corrosive nature of the electrolyte solution. Preferably the one or more cathodes comprise one or more of platinum, palladium, gold, iron, silver, nickel, steel, stainless steel or mixtures thereof. More preferably, the cathode comprises one or more of stainless steel and/or nickel.

Preferably, the separator comprises an ion exchange material which is permeable to ions but selectively impermeable to any of: gases such as hydrogen, oxygen etc..; liquids such as oxidant produced. Preferably, the separator comprises any one or more of an ionomer, a cation-exchange material, an anion-exchange material, a bipolar material or mixtures thereof. Thus, the separator may comprise, for example, a fully or partially perfluorinated ion-exchange material, a fully or partially fluorinated polymeric material containing functional groups (e.g. sulfonic acid groups), a fully or partially sulfonated tetrafluoroethylene based fluoropolymer-copolymer material or mixtures thereof.

Preferably, the separator is a membrane, a porous membrane or a porous frit.

Preferably, the apparatus is further provided with one or more of temperature, flow, pH and/or concentration sensors.

Preferably, the temperature of the electrolyte solution within the apparatus is in the range 0 – 50 °C, e.g. the temperature range may be 0 °C up to a maximum of 30 °C, 25 °C, 20 °C, 15 °C, 10 °C, 8 °C, 6 °C, 4 °C or 2 °C. More preferably, the temperature of the electrolyte solution within the apparatus is in the range 5 – 15 °C, and even more preferably 8 – 12 °C. Providing a temperature in this range has been found to inhibit decomposition of oxidant produced within the electrochemical reactor.

Preferably, the average pressure within the system is in the range 0 – 5 bar, more preferably the system pressure is about 1 bar.

Preferably, the process is a batch, semi-continuous and/or continuous process.

During batch operation, the apparatus is used to manufacture oxidant in a batch, wherein a predefined volume of the electrolyte solution is introduced to the electrochemical reactor in step (a). During continuous operation, the apparatus is used to manufacture oxidant continuously, wherein the flow rate of electrolyte solution entering the electrochemical reactor in step (a) is controlled to replenish the electrolyte solution as needed, in order to allow a continuous production of oxidant.

Preferably, the process further comprises a self-cleaning step for the apparatus, comprising the steps:

(a) draining the apparatus of any solution inside;
(b) filing the apparatus with cleaning fluid via the feed line;
(c) circulating the cleaning fluid around the apparatus for time t; and
(d) draining the cleaning fluid from the apparatus.

Preferably, the apparatus is further provided with a waste line, and the process further comprises draining the cleaning fluid from the apparatus via said waste line in step (d) of the self-cleaning step.

The present invention may be carried out in various ways and a preferred embodiment of a process and apparatus for manufacturing oxidant in accordance with the invention will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 – shows a schematic diagram of an apparatus for manufacturing oxidant in accordance with the present invention;

Figures 2a, 2b, 3a, 3b – illustrate an aspect of Linear Sweep Voltammetry (LSV) calibration;

Figure 4 – is a perspective view of an embodiment oxidant detector;

Figure 5 – is a different perspective view of the oxidant detector shown in Figure 4;

Figure 6 – is a perspective view of an electrode for use in the oxidant detector shown in Figures 4 and 5;

Figure 7 – is a perspective view of an embodiment of a depth sensor for us in an apparatus for manufacturing oxidant

Figure 8 – shows the results of example 1

Detailed description

An example of an apparatus according to the present invention is shown generally in Figure 1. It is envisaged that the apparatus may be employed to produce oxidants in-situ on a small lab scale, or may be scaled up to produce oxidants in-situ on a larger industrial scale. The apparatus described herein may be used to produce oxidant in a batch-type fashion or continuously and thus may be used, for example, for chemical manufacturing processes, water treatment purposes, sanitation, soil and ground water remediation or other application where oxidant is required or would be useful in either a constant stream or large amounts. However, the invention is not only limited to these uses.

The apparatus of the present invention is not limited to production of a single type of oxidant, but allows a user to produce a multitude of different oxidants, suitable for the user's specific requirements. The apparatus can give the user control of parameters such as oxidant type, and concentration, flow rate, temperature, and pH of the oxidant produced.

As can be seen from Figure 1, the apparatus comprises an electrochemical reactor 10, an anolyte reservoir 11, a catholyte reservoir 12, oxidant detector 17 and flow control means 19.

The electrochemical reactor 10 comprises a pair of electrodes 21 and 22 and is connectable to an electrical supply 14. The electrochemical reactor 10 may comprise a membrane 13, which divides the electrochemical reactor 10 into two chambers, an anolyte chamber 15 comprising the anode and a catholyte chamber 16 comprising the cathode.

Suitable materials for the electrodes include, boron doped diamond, vitrified carbon, diamond-like carbon (DLC), lead oxide or compounds comprising platinum, palladium, gold, iron, silver, nickel, carbon, lead and mixtures thereof.

The membrane 13 (or separator) is a material that is configured to separate the anolyte and catholyte zones (the anolyte zone relating to a zone in the substantially immediate vicinity of the anode, and the catholyte zone relating to a zone in the substantially immediate vicinity of the cathode) into an anolyte chamber 15 and catholyte chamber 16, but at the same time allowing ions to be exchanged between the anolyte and catholyte zones, preferably the membrane 13 selectively allows the passage of cations, hence enabling an electrochemical reaction to occur. Separating the electrochemical reactor into an anolyte chamber and catholyte chamber as described above acts to prevent mixing of any reaction products from an electrochemical reaction , for example it prevents the mixing of gases or oxidant produced at the electrodes, which could lead to unwanted side reactions. The membrane may also, for example, prevent any oxidant produced at the anode from being subsequently reduced at the cathode.

The membrane 13 in Figure 1 is shown as being substantially in the centre of the electrochemical reactor 10. However, this disclosure is not limited to such a membrane configuration. The membrane 13 may be in any suitable configuration inside electrochemical reactor 10, and in any position in relation to the electrodes (not shown on Figure 1).

The membrane 13 may comprise any material suitable for use in the highly corrosive environment inside the electrochemical reactor, for example, metals, metal alloys (e.g. stainless steel), asbestos, cloth, polymers (e.g. fiberglass, nylon, terylene, rubber, plastic sheets of polyethylene, polyvinyl chloride (PVC) and polytetrafluoroethylene (PTFE), synthetic rubber, fluoropolymer elastomer mixtures, perfluoroalkoxy alkanes

(PFA), polyvinylidene difluoride (PVDF), ethylene tetrafluoroethylene (ETFE), polypropylene (PP)). Preferably, the membrane 13 comprises any one or more of an ionomer, a cation-exchange material, an anion-exchange material, a bipolar material, a fully or partially perfluorinated ion-exchange material, a fully or partially fluorinated polymeric material containing functional groups (e.g. sulfonic acid groups), a fully or partially sulfonated tetrafluoroethylene based fluoropolymer-copolymer material or mixtures thereof.

The wettable components of the apparatus (the components which are exposed to electrolyte solution within the apparatus) (e.g. any component of the electrochemical reactor, the anolyte and/or catholyte chambers and any of the sensors, pumps, detectors, internal pipes etc...) may comprise any suitable corrosion resistant material which would be capable of withstanding the highly corrosive environment inside the apparatus, and may comprise for example, metals, metal alloys (e.g. stainless steel), polymers (e.g. fiberglass, nylon, terylene, rubber, polyethylene, polyvinyl chloride (PVC) and polytetrafluoroethylene (PTFE), synthetic rubber, fluoropolymer elastomer mixtures, perfluoroalkoxy alkanes (PFA), polyvinylidene difluoride (PVDF), ethylene tetrafluoroethylene (ETFE) or polypropylene (PP)).

The anolyte reservoir 11 receives electrolyte solution from an electrolyte storage or electrolyte feed (not shown) via line 1. Once the electrolyte solution has entered the anolyte reservoir 11 it becomes part of an 'anolyte solution'. The anolyte reservoir 11 feeds anolyte solution into the anolyte chamber of the electrochemical reactor 10 via line 3. The anolyte reservoir 11 receives return anolyte solution from the anolyte chamber 15 of electrochemical reactor 10 via line 2. As line 2 is returning from the reactor, the composition of this line may comprise some reaction products from the electrochemical reaction at the anode 21, carried out in the electrochemical reactor 10. Therefore, it should be understood that the composition of the anolyte solution may comprise reaction products as well as the electrolyte solution.

The reaction products being returned to the anolyte reservoir 11 via line 2 are not limited to only reaction products produced at the anode 21. The reaction products may, for example include reaction products from the cathode 22. However, employing the porous membrane 13 can minimise or completely eliminate the presence of reaction

products from the cathode 22/catholyte chamber 16 entering the anolyte chamber 15 and anolyte reservoir 11.

The catholyte reservoir 12 receives electrolyte solution from an electrolyte storage or electrolyte feed (not shown) via line 1. Once the electrolyte solution has entered the catholyte reservoir 12 it becomes part of a 'catholyte solution'. The catholyte reservoir 12 feeds catholyte solution into the catholyte chamber of the electrochemical reactor 10 via line 5. The catholyte reservoir 12 receives return catholyte solution from the catholyte chamber 16 of the electrochemical reactor 10 via line 4. As line 4 is returning from the reactor, the composition of this line may comprise some reaction products from the electrochemical reaction at the cathode 22, carried out in the catholyte chamber 16 of the electrochemical reactor 10. Therefore, it should be understood that the composition of the catholyte solution may comprise reaction products as well as the electrolyte solution.

Although Figure 1 shows that the anolyte reservoir 11 and the catholyte reservoir 12 are fed electrolyte solution via line 1. The anolyte reservoir 11 and catholyte reservoir 12 may be alternatively fed electrolyte solution via separate feed lines (not shown in the example of the apparatus shown in Figure 1).

During batch operation of the apparatus, the electrolyte solution received by the anolyte reservoir 11 and catholyte reservoir 12 via line 1, or via separate feed lines (not shown), may be in a volume which is defined by the user's batch requirements. In continuous operation, the anolyte reservoir 11 and catholyte reservoir 12 may receive the electrolyte solution on a continuous or semi-continuous basis via line 1, or via separate feed lines (not shown), so that the apparatus may produce and remove oxidant at a constant rate. Preferably, during continuous operation, the flow rate of the electrolyte solution entering the apparatus is equal to the flow rate of oxidant being removed from the apparatus.

The reaction products being returned to the catholyte reservoir 12 via line 4 are not limited to only reaction products produced at the cathode 22. The reaction products may, for example include reaction products from the anode 21. However, as mentioned above, employing the porous membrane 13 can minimise or completely eliminate the

presence of reaction products from the anode 21/anolyte chamber 15 entering the catholyte chamber 16 and catholyte reservoir 12.

As discussed above, an aspect of the present invention is that a user can select any type of oxidant to be produced by the apparatus. As a result, the electrolyte solution used may vary greatly. The electrolyte solution may be any suitable solution which may be electrolysed to produce oxidant through electrolysis, for example, it may be acidic, basic or neutral aqueous solutions which have been generated from inorganic salts. For example: ammonium sulfate and sulfuric acid may be electrolysed to form ammonium persulfate; brine may be electrolysed to give hypochlorite; potassium manganate may be electrolysed to form potassium permanganate; solutions of chlorate salts may be electrolysed to form perchlorate salts; carbonate may be electrolysed to form peroxycarbonate; phosphates may be electrolysed to form peroxyphosphates. The electrolyte solution used for the anolyte side and the catholyte side of the apparatus may be the same, or may alternatively be different.

The electrochemical reactor 10, anolyte reservoir 11, and catholyte reservoir 12 may be equipped with conventional internal features, for example, temperature control and sensing devices, pH sensing devices, depth sensing devices, and/or fluid agitation devices.

The oxidant detector 17 (also known as an electrochemical detector) is employed to detect the effective concentration of oxidant in an electrolyte solution. The oxidant detection means 17 may be any suitable device that can be used for the detection of oxidants, and is preferably configured to work in highly corrosive solutions, for example in the presence of strong acids or bases and oxidants. Preferably the oxidant detector 17 can monitor the concentration of oxidant present in the anolyte solution in line 6 in an online basis, wherein the concentration is displayed for the user to see.

An example of an oxidant detector 17 according to the present invention is shown generally in Figures 4 and 5 at item 40. The oxidant detector 17 comprises an electrode cover 42, an electrode holder 44 and an electrode 46.

The electrode holder 44 holds electrode 46 in place relative to the electrode holder 44. The electrode holder 44 is substantially rectangular cuboid in shape. The electrode holder 44 is also provided with four substantially straight threaded cylindrical members 48. These cylindrical members 48 may alternatively be any non-threaded members or partially threaded members. The electrode holder 44 may be provided with orifices 50 that enable the oxidant detector 17 to be secured to a surface by way of screws, nails, bolts etc.

The electrode holder 44 may be provided with a depression on it's planar surface which is substantially the same shape as electrode 46, and which enables the electrode 46 to fit inside the depression such that the electrode 46 fits flush or semi-flush with the planar surface of the electrode holder 44.

Cover 42 of the oxidant detector 17 is substantially rectangular cuboid in shape, and is provided with four orifices 52, which travel continuously from one face of the cover 42 to the opposite face of cover 42 in a substantially straight line, such that the substantially straight threaded cylindrical members 48 may extend through the orifices 52 so that cover 42 and electrode holder 44 are mated together. The cylindrical members 48 are of a sufficient length to allow a portion to extend out of cover 42 sufficiently to enable a securing means, for example a threaded nut or wing nut, to be threaded onto the four threaded cylindrical members when the cover 42 is such that the cover 42 is tightly fixed to the electrode holder 44, while allowing the flowing electrolyte to come into contact with the electrode surface.

The cover 42 is provided with cavity (not shown) that is positioned so that it is in fluid communication with the electrode 46 when the cover 42 and electrode holder 44 are fixed together in the manner described above. The cavity is in fluid communication with an inlet 54 and an outlet 56. When the cover 42 and electrode holder 44 are tightly fixed together, the cavity of cover 42 is watertight apart from the inlet 54 and outlet 56. To help form a watertight seal, a seal or O-ring may be used inbetween the cover 42 and electrode holder 44.

The cover 42 and electrode holder 44 may be manufactured from any suitable chemically resistant material, for example metals, metal alloys, polymers or ceramics.

Preferably the cover 42 and electrode holder 44 are manufactured from polytetrafluoroethylene (PTFA).

The electrode is shown generally in Figure 6 at item 46. The electrode 46 comprises an electrode plate 70, a working electrode 64, counter electrode 62, a reference electrode 66 and transmitting means 68.

The electrodes may be manufactured from any suitable material that conducts electricity. Metal compounds are particularly well suited for use as electrodes, and some preferred materials include aluminium, brass, graphite and carbon, copper, gold, silver, tin, lead, platinum, palladium, compounds including these materials, and mixtures thereof. Preferably, the working electrode 64 and counter electrode 62 are manufactured from gold and the reference electrode 66 is manufactured from silver or silver chloride.

The transmitting means 68 may be any device that allows the data provided by the electrodes to be transmitted to an external device so that the oxidant concentration of a fluid being tested may be calculated. The transmitting means may be connectable to an external device to transmit data from the electrodes via a wired or a wireless connection. Preferably, the data from the electrodes is transmitted to an external device via a USB plug and socket.

In operation, a fluid to be tested for oxidant enters the oxidant detector 17 via inlet 54. The fluid enters the downstream cavity, where it is introduced to the electrode 46 which analyses the fluid to be tested. Once the electrode has tested the fluid for oxidant, the fluid exits the oxidant detector via outlet 56.

A plurality of depth sensors may be used within the apparatus for process control, to monitor electrolyte solution depth in any part of the apparatus, for example the anolyte reservoir 11, anolyte chamber 15, catholyte reservoir 12 or the catholyte chamber 16. In particular, depth sensors may be used as a method of leak detection or may be in communication with a raw material feed control to control the volume of raw material being fed into the apparatus.

The inventors of the present invention found that due to the highly corrosive nature that the internal components of the apparatus disclosed herein is exposed to; a depth sensor capable of withstanding highly corrosive environments had to be developed. An example of a depth sensor according to the present invention is shown generally in Figure 7, item 80.

The present disclosure provides a depth sensor 80 suitable for highly corrosive environments, comprising a body 84, and a plurality of corrosion resistant sensors 82 disposed along the longitudinal length of the body 84. The plurality of corrosion resistant sensors 82 are held into a fixed position relative to the body 84 using a filling material 88. The filling material 88 may be any material that is capable of holding the sensors in a fixed position in the body 84 and that can also withstand the operating conditions the depth sensor will be exposed to in the apparatus for manufacturing the oxidant. Preferably, chemically resistant filling glue is used as filling material 88. The corrosion resistant sensors 82 are configured to be in fluid communication with a fluid (electrolyte solution) via orifices provided on body 84. The depth sensor 80 is also provided with transmitting means 86 to transmit data from the corrosion resistant sensors 82 to an external device.

The height of the chemically resistant sensors 82 along the body 84 is known, and therefore in operation, the depth sensor 80 is able to calculate the depth of a fluid by analysis of which of the plurality of corrosion resistant sensors 82 are sensing the presence of the fluid solution, based on electrical resistance readings. The depth sensor is capable of transmitting the depth of a fluid via any means, for example electronically to a computer system or to a visual display.

The sensors may take any suitable form, for example they may be in the form of plates or tubes disposed along the longitudinal length of the depth sensor.

The plurality of corrosion resistant sensors may comprise any suitable corrosion resistant material, for example gold and/or copper. Preferably, the plurality of corrosion resistant sensors comprise gold-plated copper.

The electrochemical reactor 10, the anolyte reservoir 11, and the catholyte reservoir 12 may comprise temperature controlling means, for example a heat exchanger or thermal insulation. Any suitable heat exchange techniques may be used, for example internal piping, baffles or plate heat exchangers.

The electrochemical reactor 10, the anolyte reservoir 11, and the catholyte reservoir 12 may comprise fluid agitation means, to agitate the fluid and obtain good mixing.

Due to the corrosive nature of oxidant species, the components and sensing devices of the present apparatus must be manufactured from suitable corrosion resistant materials. Any suitable corrosion resistant materials may be used. Suitable materials for the components and sensing devices include but are not limited to metals such as stainless steel, thermoplastics such as polyvinyl chloride (PVC), chlorinated polyvinylchloride (CPVC), polyvinylidine difluoride (PVDF), polyethylene, polytetrafluoroethylene (PTFE), ethylene tetrafluoroethylene (ETFE), acrylonitrile butadiene styrene (ABS) polymer blends, organofluorine compounds, for example perfluoroalkoxy alkanes (PFA), synthetic rubber and fluoropolymer elastomer mixtures, perfluoroalkoxy alkanes (PFA), polypropylene (PP).

The apparatus may be operated in the following way. During operation of the apparatus i.e. when the apparatus is in the process of manufacturing oxidant, a stream of anolyte solution is continuously fed into the anolyte chamber 15 of the electrochemical reactor 10 from the anolyte reservoir 11 via line 3, and a stream of catholyte solution is continuously fed into the catholyte chamber 16 of the electrochemical reactor 10 from the catholyte reservoir 12 via line 5. By doing this, the anolyte solution and the catholyte solution are introduced to the anode and cathode respectively.

The anolyte and catholyte solutions may be fed into the electrochemical reactor 10 via lines 3 and 5 respectively at any suitable flow rate. The anolyte and catholyte solutions may be fed into the electrochemical reactor via lines 3 and 5 respectively at the same or different flow rates. The flow rates through lines 3 and 5 may be determined by a predefined flow rate of oxidant required by the user of the apparatus, or may be determined by the residence time required for the anolyte and catholyte solutions in the electrochemical reactor.

The anolyte solution is continuously fed from the anolyte chamber 15 to the anolyte reservoir 11 via line 2, at a flow rate suitable to maintain an appropriate depth in the anolyte chamber 15. The catholyte solution is continuously fed from the catholyte chamber 16 to the catholyte reservoir 12 via line 4, at a flow rate suitable to maintain an appropriate depth in the catholyte chamber 16. Thus, during operation the anolyte and catholyte solutions are circulated between the anolyte and catholyte chambers 15 and 16 and the anolyte and catholyte reservoirs 11 and 12 respectively. The rate at which the anolyte and catholyte solutions are fed via lines 2 and 4 respectively can be varied, and is preferably the same rate as the anolyte and catholyte solution flowing into the electrochemical reactor 10 via lines 3 and 5 respectively. An appropriate depth of anolyte and catholyte solution in the electrochemical reactor 10 is such that the depth is sufficient to allow an electrochemical reaction to occur; preferably the anolyte and catholyte solutions encompass most, if not all, of the available surface area of the anode and cathode inside the electrochemical reactor 10.

The anolyte reservoir 11 is in fluid communication with an oxidant detection means 17 via line 6. The oxidant detection means 17 can detect the concentration of oxidant in the anolyte solution from the anolyte reservoir 11. During operation the anolyte solution from anolyte reservoir 11 flows through line 6, through the oxidant detection means 17, and can either be recycled back to the anolyte reservoir via line 7, or can be removed from the system via the product line 8. The scope of the present invention is not limited to this specific embodiment; line 7 may alternatively recycle anolyte solution from the oxidant detection means 17 to any other part of the apparatus, for example the anolyte chamber 15.

If the concentration of oxidant in line 6 is not as the user predefined then the anolyte solution may be returned to the reactor via recycle line 7. If the concentration of the oxidant in the anolyte solution meets the user's specifications, then the anolyte solution may be fed through product line 8, to be delivered for use.

A flow controlling means 19 is provided to control the flow of the anolyte solution by directing the flow via recycle line 7, or through product line 8. The flow controlling means may take any suitable form which allows the redirection of fluid, for example a valve.

The flow controlling means 19 may also be capable of controlling whether anolyte solution flowing through line 8 is partially or fully diverted through line 20. Diverting the flow of anolyte solution through line 20 in this way may be required if removal of the anolyte solution from the system is required via waste line 23.

The flow controlling means 19 may be provided with communication means such that it can transmit information in connection with the direction of flow and/or flow rate. The flow controlling means 19 may also be provided with receiving means to receive signals from other components of the apparatus, for example the oxidant detector 17, the gas detecting means 18, any oxygen sensing devices, depth sensing devices, temperature sensing devices or pressure sensing devices. The flow controlling means may then direct the flow of the anolyte solution appropriately, depending on the signal it has received.

For example, if a user requires a certain oxidant concentration within the anolyte solution, the flow controlling means 19 can direct the flow of the anolyte solution through recycle line 7, and back into the anolyte reservoir 11. Once the oxidant concentration has reached the desired value then the flow controlling means 19 can direct the anolyte solution through product line 8.

The flow controlling means 19 may alternatively direct the anolyte solution flowing though line 6 such that simultaneously, a portion of the anolyte solution is directed through product line 8 and a portion of the anolyte solution is directed through recycle line 7.

The volume of anolyte and catholyte solution within the apparatus is mainly contained in the anolyte reservoir 11 and catholyte reservoir 12 respectively, but a certain volume is also contained in the anolyte chamber 15 and catholyte chamber 16. These volumes may act as a buffer volume to avoid an interruption in production of oxidant in the case of a leak or in the case where the apparatus is starved of a raw material feed through line 1.

The apparatus and process disclosed herein is suitable for continuous or batch production of oxidant. In the case of continuous operation, having a buffer volume enables a user to demand an increase in oxidant flow rate for a certain time period through product line 8. In this case, the anolyte reservoir 11 acts as a buffer vessel to accommodate for the increased oxidant flow rate demand.

In continuous operation, a buffer capacity may be used in connection with one or more depth sensors, for example in the anolyte or catholyte reservoirs 11, 12 or anolyte or catholyte chambers 15, 16, to pre-warn and alert a user to low levels of anolyte or catholyte solution in the system. This may be needed if the electrolyte solution feed stops during operation, if for example the source of the electrolyte solution becomes exhausted. The benefit of this is that the user has the opportunity to restore the electrolyte solution feed to the system before the process is stopped due to lack of fresh electrolyte solution.

Figure 1 provides that the oxidant detector 17 is upstream from the flow controlling means 19. However, the oxidant detector 17 does not have to be at this location relative to the flow controlling means, and it may, for example be located downstream of the flow controlling means along recycle line 7, or configured to be in direct fluid communication with the electrochemical reactor, in fluid communication with the catholyte reservoir 12 or the catholyte chamber 16. Optionally, a plurality of oxidant detection means 17 may be provided to the apparatus.

Electrochemical reactions at the cathode commonly produce a gas as a reaction product, which will bubble from the cathode and become entrained in the catholyte solution. For example, in aqueous systems, a reduction reaction occurs at the negatively charged cathode, with electrons from the cathode being given to hydrogen cations to form hydrogen gas. The gas in the catholyte solution will flow from the catholyte chamber 16 into catholyte reservoir 12. The production of such gas at the cathode can be used as an indicator that an electrochemical reaction is occurring. Therefore, a gas detection device 18 is used to detect the presence of gas in the catholyte solution. The catholyte reservoir 12 is in fluid communication with the gas detection device 18 via line 9, the gas detection device 18 being configured to detect the presence of any gas in the catholyte solution flowing through line 9. The gas

detection device 18 may alternatively be located in the head space of the catholyte reservoir 12. The gas detection means 18 does not have to be in fluid communication with the catholyte reservoir 12, and may for example be in fluid communication with the catholyte chamber 16 of the electrochemical reactor 10.

Optionally, any number of gas detection means may be employed in the apparatus to detect the presence of gas. For example, a gas detection means may be configured to detect whether a gas is being produced in the anolyte chamber 15, which may be used to indicate to a user that gas from the catholyte chamber 16 is being entrained into the anolyte chamber 15, or alternatively that gas is being produced at the anode 21.

Without any means of removal, the gas produced at the cathode 22 may accumulate in the system. Accumulation of gas in the system is not desirable as it may lead to increased system pressure which could lead to an explosion, or, if the gas being produced is flammable, then there could be a risk of fire.

In most cases of oxidant production using the apparatus and process described herein, the gas produced at the cathode 22 will be hydrogen gas. Hydrogen gas is highly flammable and is known to burn even in very low concentrations. If any hydrogen is formed at the cathode, it is therefore desirable to remove the hydrogen gas from the system, preferably via an oxidation catalyst or fuel cell that can convert it to water vapour.

To prevent an accumulation of gas, a gas removal device may be employed to continuously remove any gas produced within the system.

Alternatively, a gas storing device may be employed to continuously remove any gas from the system and store it so that it is not released to the surrounding atmosphere. Such a gas storage device may be in fluid communication with the catholyte reservoir 12, and be used to detect the presence of gas in the catholyte solution. Such a gas storage device would therefore have a similar function to the gas detection device 18 of detecting when an electrochemical reaction is occurring. The gas storage device may take any suitable form that allows gasses to be removed from the catholyte solution.

Removal and storage of gas in this way can be advantageous, as the gas can be used in other applications or, it can be subjected to further treatment. If the gas being stored is hydrogen gas then preferably, it is converted to water or it is used in other application, for example as a fuel. Optionally, to maintain the level of gas present in the apparatus to a suitably low level, it may be necessary to have a constant bleed of the catholyte and/or anolyte solutions (comprising the gas) from the system, via waste stream 23. The catholyte and/or anolyte solutions may then be subjected to downstream treatment to recycle or process the catholyte and/or anolyte solutions so that they can be returned to the process or safely disposed of.

Product line 8 (via line 20) and line 5 (from the catholyte reservoir 12 to the catholyte chamber 16) are in fluid communication with waste stream 23, which enables the anolyte reservoir 11 and/or the catholyte reservoir 12 to be bled. If necessary the waste stream 23 allows the entire apparatus to be bled.

The apparatus according to the present invention is configured such that it is able to self-clean after operation. The self-cleaning operation comprises: (i) draining the apparatus of any previous process fluid (electrolyte solution) remaining in the apparatus using waste stream 23; (ii) filling the apparatus with a cleaning fluid via feed line 1, or alternatively via a cleaning line (not shown on Figure 1); (iii) circulating the cleaning fluid around the apparatus for a period of time; and (iv) draining the cleaning fluid from the apparatus using waste stream 23.

The self-cleaning process may be used in a batch-type way or a continuous-type way. When being operated in a batch-type way, the entire apparatus is filled with the cleaning fluid, which is circulated around the apparatus, and then drained from the apparatus once the self-cleaning process has completed. If the self-cleaning process is being operated in a continuous way, then it is similar to being operated in a batch-type way, but with a continuous bleed and feed of the cleaning fluid via waste line 23 and feed line 1 (or via the cleaning line now shown on Figure 1) respectively.

Various modifications may be made to the described embodiment without departing from the scope of the invention.

Examples

Determination of Oxidants: Linear Sweep Voltammetry (LSV)

The oxidant detection means of the present disclosure employs Linear Sweep Voltammetry (LSV) to determine the concentration of oxidant within the apparatus. LSV is a voltammetric method employing three electrodes (a working electrode, a counter electrode and a reference electrode). A potential scan is applied to a working electrode and the current generated is registered. Oxidation or reduction of species is registered as a peak or a trough in the current signal at the potential at which the species begins to be oxidised or reduced (as can be seen in Figures 2a and 2b). This current is therefore proportional to the concentration of anolyte in a solution.

To calibrate the oxidant detection means, LSV can be performed on known concentrations of oxidant to produce a calibration curve, which can then be used to test for unknown concentrations of that oxidant species.

Example 1

The apparatus according to this disclosure was used to produce and manufacture ammonium persulfate ($(NH_4)_2S_2O_8$)). In this example, an aqueous solution of ammonium sulfate ($(NH_4)_2SO_4$) and sulfuric acid (H_2SO_4) was fed into the apparatus for use as the anolyte solution and catholyte solution. Boron doped diamond electrodes were employed within the electrochemical reactor. The electrochemical reactor comprised a cation exchanging membrane (a NAFION^{TM} N-424 membrane separator), which was used to divide the electrochemical reactor into two chambers, each chamber comprising an electrode. The anode used comprised boron doped diamond. The cathode comprised stainless steel. A heat exchanger was used to maintain the temperature of the electrochemical reactor and anolyte reservoir at 0 – 20 °C. An oxidant detector according to the present disclosure was used to monitor the concentration of $(NH_4)_2S_2O_8$ within the system, based on the concentration of persulfate ($[S_2O_8]^{2-}$). To calibrate the system, LSV was performed on various $(NH_4)_2S_2O_8$/ H_2SO_4

solutions of known concentrations. Figures 3a and 3b show the LSV calibration results obtained, and the calibration curve produced using these results.

Electrode reactions in the system of Example 1:

Reaction at the Anode (oxidation): $(NH_4)_2SO_4 + H_2SO_4 \longrightarrow (NH_4)_2S_2O_8 + 2H^+ + 2e^-$

Reaction at the Cathode (reduction): $2H^+ + 2e^- \longrightarrow H_2$

The calibrated oxidant detector was used to calculate the concentration of $(NH_4)_2S_2O_8$) over time. Figure 8 shows the results obtained for the generation of persulfate oxidant over time, using different compositions of anolyte solution and applying different current densities. The data points are experimental values and the trend lines are predicted values using a model.

Claims:

1. An apparatus for manufacturing oxidant, the apparatus comprising an electrochemical reactor, a feed inlet for receiving feed materials and a product outlet for the oxidant;
the electrochemical reactor being in fluid communication with the feed inlet and the product outlet and comprising one or more anodes and one or more cathodes;
and wherein the apparatus further comprises:
means for detecting oxidant within the apparatus; and
flow controlling means configured to control the flow of fluid through the product outlet and to communicate with the means for detecting oxidant.

2. The apparatus according to claim 1, further comprising a separator configured to divide the electrochemical reactor into two or more chambers and allow the passage of ions, wherein an anode is located within a first of the two or more chambers to form an anolyte chamber and a cathode is located within a second of the two or more chambers to form a catholyte chamber.

3. The apparatus according to claim 2, further comprising an anolyte reservoir configured to be in fluid communication with the anolyte chamber.

4. The apparatus according to claim 3, wherein the anolyte reservoir is in fluid communication with the feed inlet.

5. The apparatus according to claim 3 or claim 4, wherein the means for detecting oxidant is in fluid communication with the anolyte reservoir and/or the anolyte chamber.

6. The apparatus according to any one of claims 2 to 5, further comprising a catholyte reservoir configured to be in fluid communication with the catholyte chamber.

7. The apparatus according to claim 6, wherein the catholyte reservoir is in fluid communication with the feed inlet.

8. The apparatus according to claim 6 or claim 7, wherein the catholyte reservoir is in fluid communication with a second feed inlet.

9. The apparatus according to any preceding claim, further comprising one or more gas detection means.

10. The apparatus according to any one of claims 6 to 8, further comprising one or more gas detection means and wherein the one or more gas detection means are configured to detect the presence of gas in the catholyte chamber and/or the catholyte reservoir.

11. The apparatus according to any preceding claim, further comprising gas removal means, configured to remove gas present within an electrolyte solution in the apparatus.

12. The apparatus according to any one of claims 6 to 10, further comprising one or more gas removal means, configured to remove gas present within one or more of: the anolyte chamber, the catholyte chamber, the anolyte reservoir, the catholyte reservoir.

13. The apparatus according to any one of claims 11 to 12, further comprising means to store gas, which is configured to store gas present within an electrolyte solution within the apparatus.

14. The apparatus according to any preceding claim, wherein the one or more anodes have an overpotential for oxygen of at least +0.5 V.

15. The apparatus according to any preceding claim, wherein the one or more anodes comprise one or more of: boron doped diamond, vitrified carbon, diamond-like carbon, lead oxide, platinum, palladium, gold, iron, silver, nickel, carbon, lead or mixtures thereof.

16. The apparatus according to any preceding claim, further comprising one or more depth sensor.

17. The apparatus according to any preceding claim, further comprising a fuel cell configured to detect, remove and store gas present within the apparatus.

18. A process of manufacturing oxidant using an apparatus comprising an electrochemical reactor, a feed inlet for receiving feed materials and a product outlet for the oxidant; the electrochemical reactor being in fluid communication with the feed inlet and the product outlet and comprising one or more anodes and one or more cathodes; and wherein the apparatus further comprises: means for detecting oxidant within the apparatus; and flow controlling means configured to control the flow of fluid through the product outlet and to communicate with the means for detecting oxidant, the process comprising the steps of:
    a. introducing an electrolyte solution to the electrochemical reactor via the feed inlet, so as to produce oxidant by electrolysis of the electrolyte solution;
    b. using the means for detecting oxidant to monitor the oxidant concentration in the electrolyte solution; and
    c. dispensing the electrolyte solution from the apparatus via the product outlet once the oxidant concentration has reached a predetermined value in the electrolyte solution.

19. The process according to claim 18, wherein the apparatus is provided with a separator configured to divide the electrochemical reactor into two or more chambers and further configured to allow the passage of ions, wherein an anode is located within a first of the two or more chambers to form an anolyte chamber and a cathode is located within a second of the two or more chambers to form a catholyte chamber.

20. The process according to claim 19, wherein the apparatus further comprises an anolyte reservoir configured to be in fluid communication with the anolyte chamber, and wherein the process further comprises recycling the electrolyte solution between said anolyte chamber and said anolyte reservoir.

21. The process according to claim 20, wherein the electrolyte solution in step (c) is dispensed from the anolyte reservoir once the oxidant in the electrolyte solution has reached the predetermined concentration.

22. The process according to claims 20 or 21, wherein the anolyte reservoir is in further fluid communication with the feed inlet, and wherein the process further comprises feeding the electrolyte solution into the anolyte reservoir via the feed inlet to introduce the electrolyte solution to the anode in the anolyte chamber.

23. The process according to claims 20 to 22, wherein the means for detecting an oxidant is configured to be in fluid communication with the anolyte reservoir and/or the anolyte chamber, and wherein the process further comprises using said means for detecting an oxidant to monitor whether any oxidant is present in the anolyte reservoir and/or the anolyte chamber.

24. The process according to any one of claims 19 to 23, wherein the apparatus further comprises a catholyte reservoir configured to be in fluid communication with the catholyte chamber, and wherein the process further comprises recycling the electrolyte solution between said catholyte chamber and said catholyte reservoir.

25. The process according to claim 24, wherein the catholyte reservoir is in further fluid communication with the feed inlet, and wherein the process further comprises feeding the electrolyte solution into the catholyte reservoir via the feed inlet to introduce the electrolyte solution to the cathode in the catholyte chamber.

26. The process according to any one of claims 18 to 25, wherein the apparatus further comprises one or more gas detection means, and wherein the process further comprises using said one or more gas detection means are used to detect the presence of any gas within the apparatus.

27. The process according to any one of claims 24 or 25, wherein the apparatus further comprises one or more gas detection means, and wherein the process further comprises using the one or more gas detection means to detect the presence of any gas in the catholyte chamber and/or catholyte reservoir.

28. The process according to any one of claims 24 to claim 27, wherein the apparatus further comprises gas removal means, and wherein the process further comprises using said gas removal means to remove gas present within one or more of: the

anolyte chamber, the catholyte chamber, the anolyte reservoir, the catholyte reservoir.

29. The process according to claim 28, wherein the apparatus further comprises means to store gas, and wherein the process further comprises using said means to store gas to store removed gas.

30. The process according to any one of claims 18 to 29, wherein the temperature of the electrolyte solution within the apparatus is in the range 0 – 50 °C.

31. The process according to any one of claims 18 to 30, wherein the process is a batch, semi-continuous, or continuous process.

32. The process according to any one of claims 18 to 31, further comprising a self-cleaning step for the apparatus, comprising the steps:
    a. draining the apparatus of any solution inside;
    b. filing the apparatus with cleaning fluid via the feed line;
    c. circulating the cleaning fluid around the apparatus for time t; and
    d. draining the cleaning fluid from the apparatus.

33. The process according to claim 32, wherein the apparatus further comprises a waste line, and the process further comprises draining the cleaning fluid from the apparatus via said waste line.

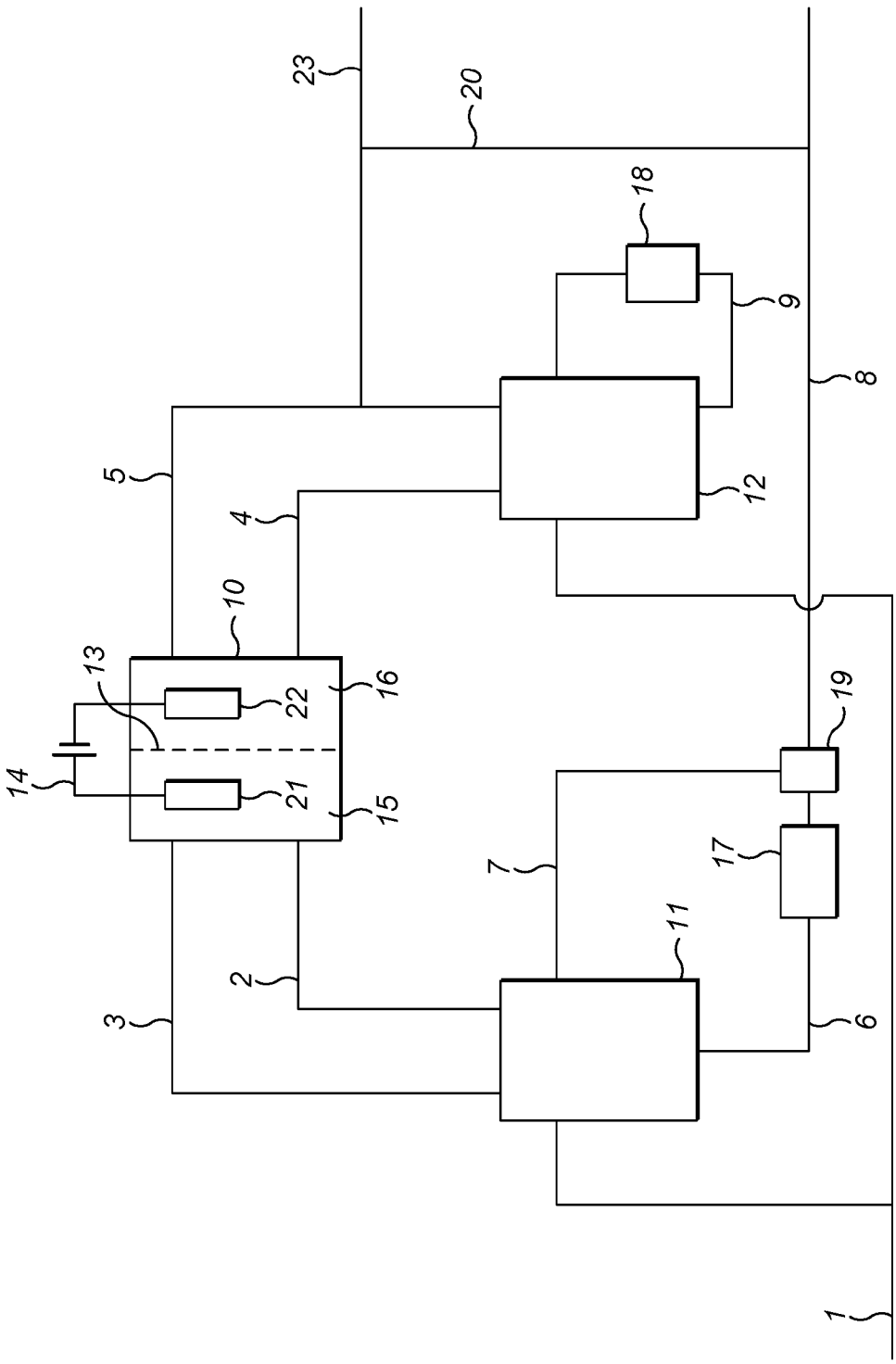


FIG. 1

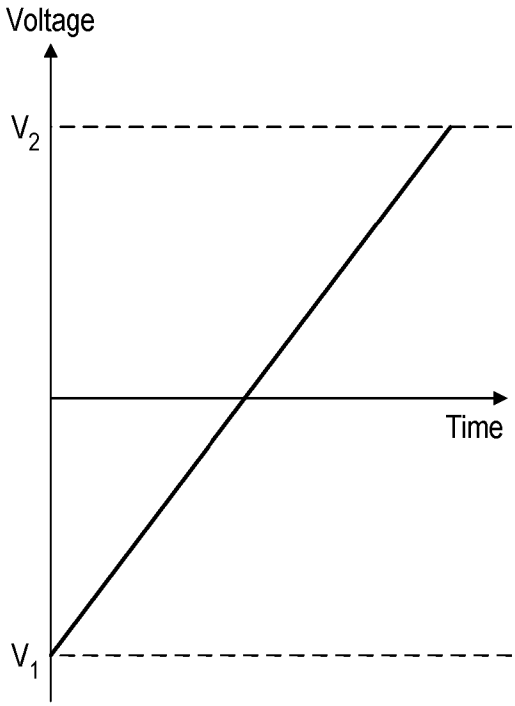


FIG. 2a

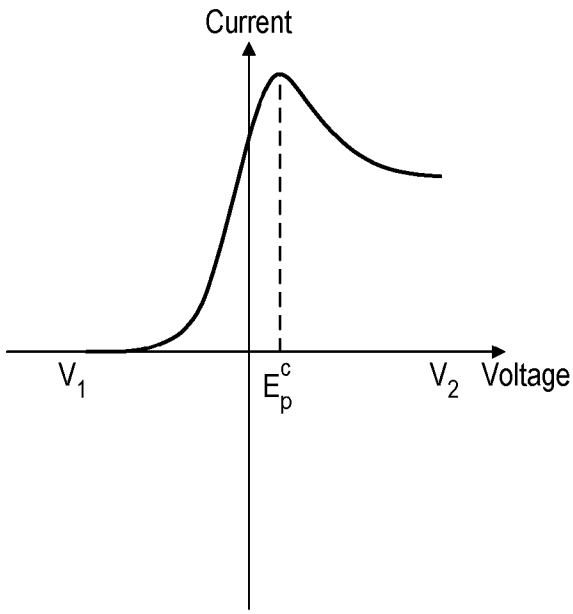


FIG. 2b

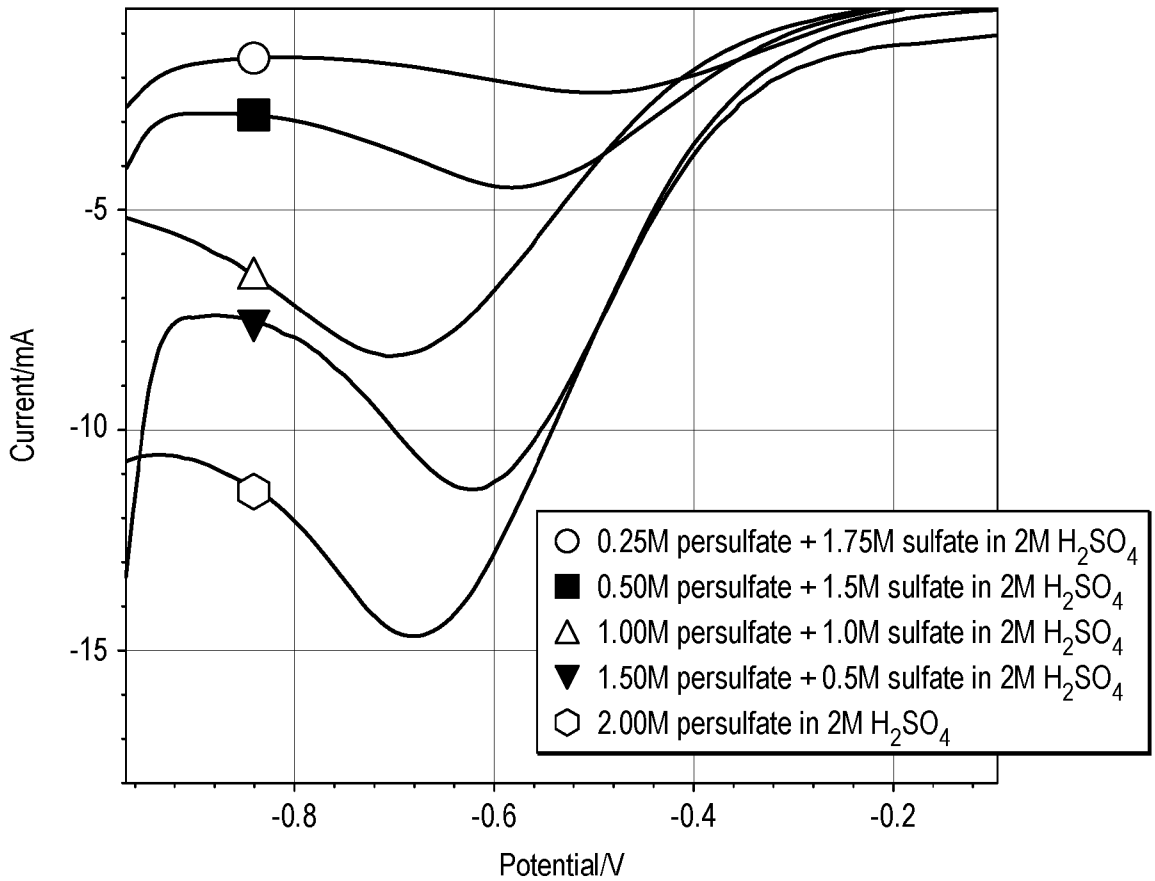

Current/mA
-5
-10
-15
-0.8
-0.6
-0.4
-0.2
Potential/V
0.25M persulfate + 1.75M sulfate in 2M H_2SO_4
0.50M persulfate + 1.5M sulfate in 2M H_2SO_4
1.00M persulfate + 1.0M sulfate in 2M H_2SO_4
1.50M persulfate + 0.5M sulfate in 2M H_2SO_4
2.00M persulfate in 2M H_2SO_4

FIG. 3a

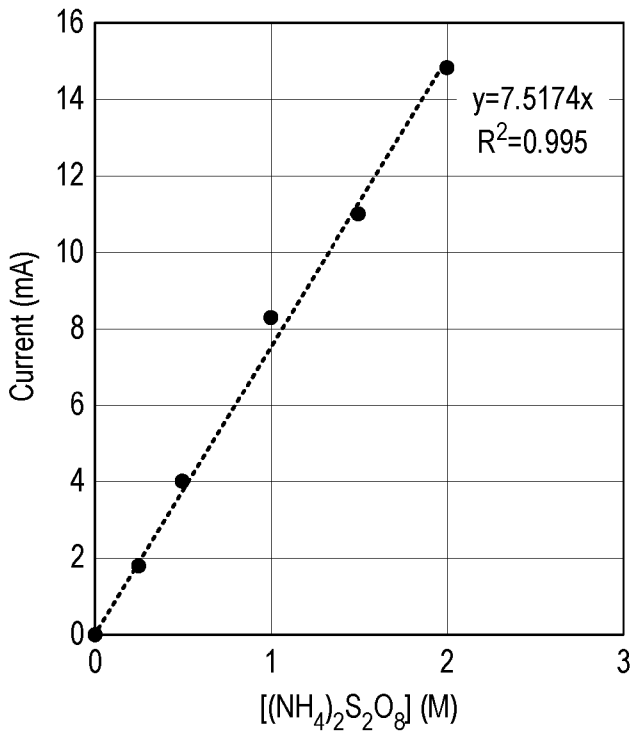

Current (mA)
0
2
4
6
8
10
12
14
16
0
1
2
3
$[(NH_4)_2S_2O_8]$ (M)
y=7.5174x
R^2=0.995

FIG. 3b

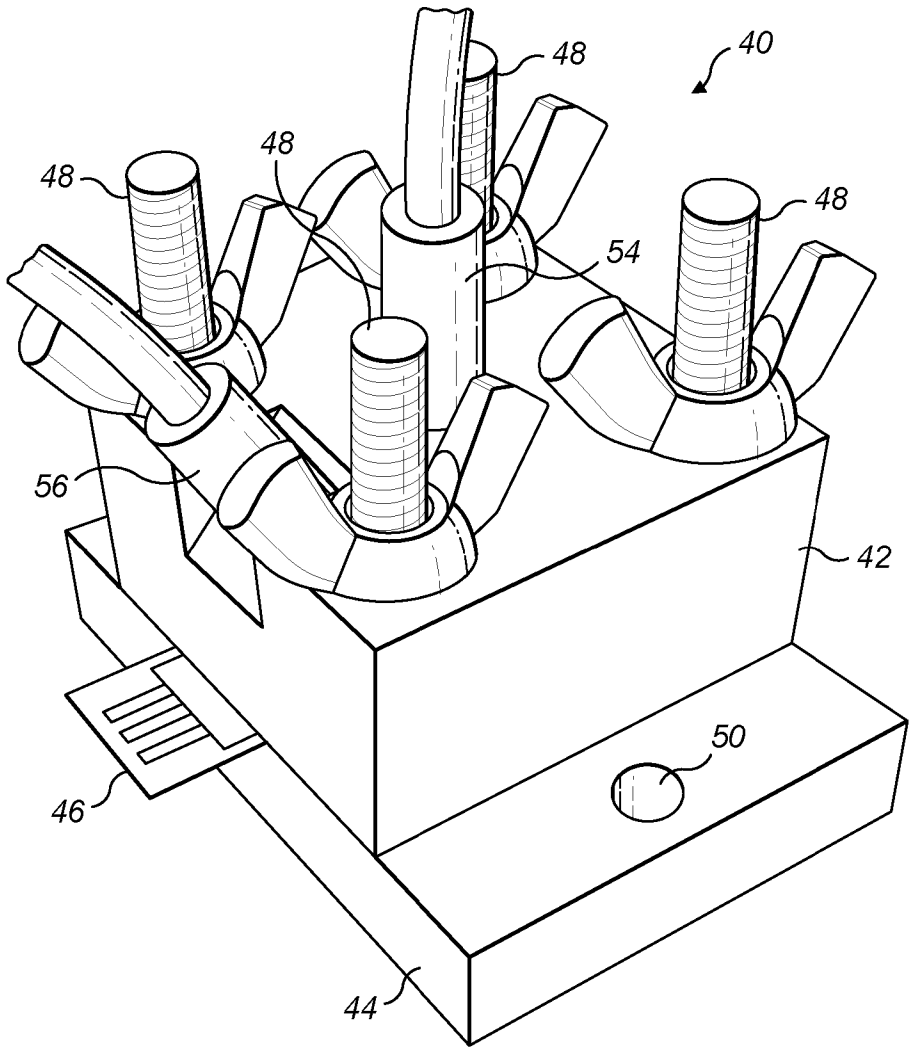


FIG. 4

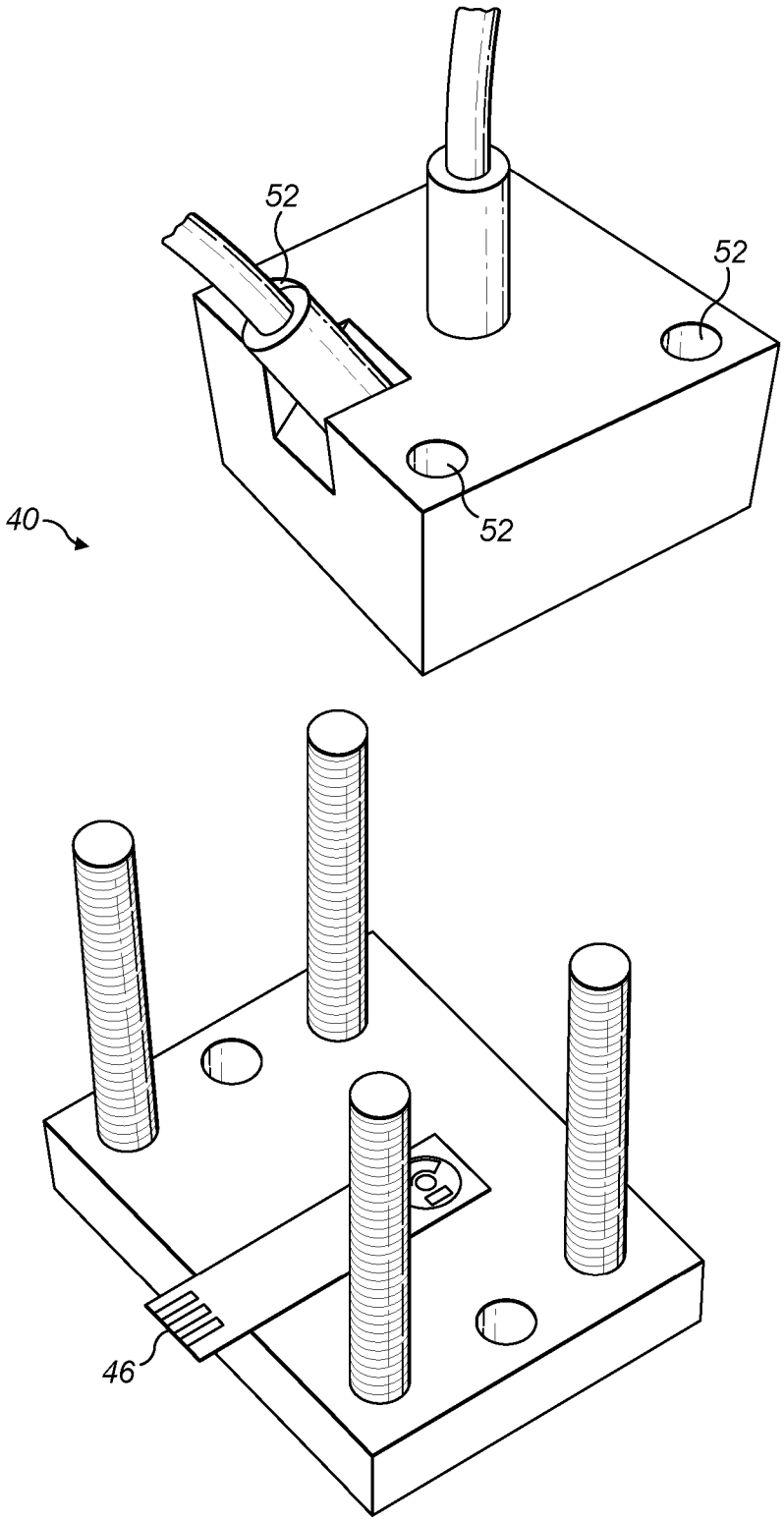


FIG. 5

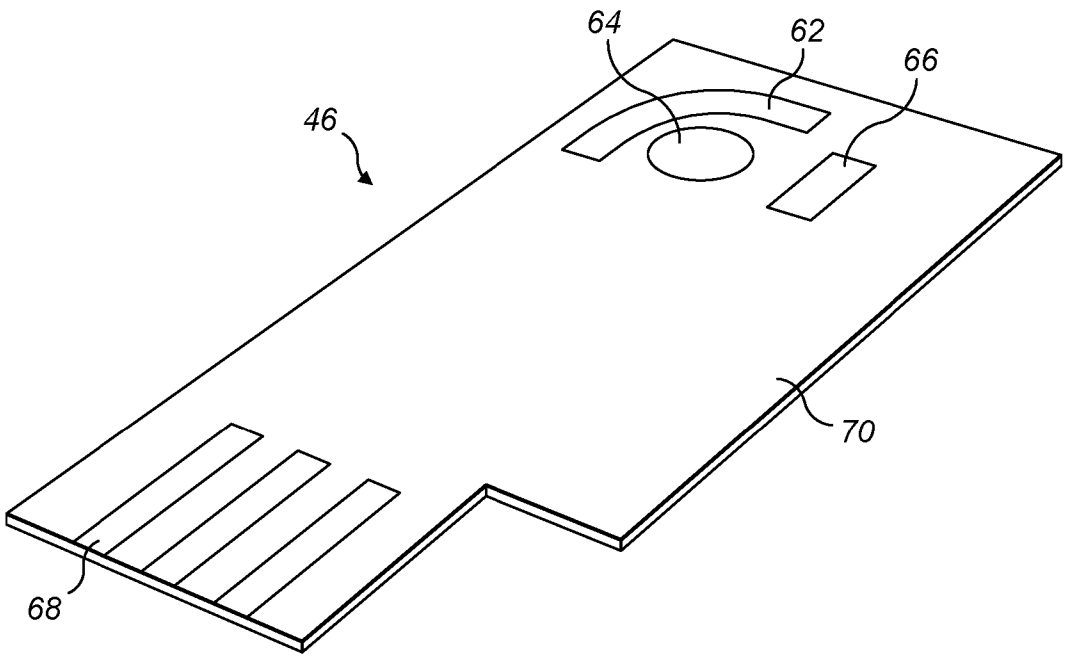


FIG. 6

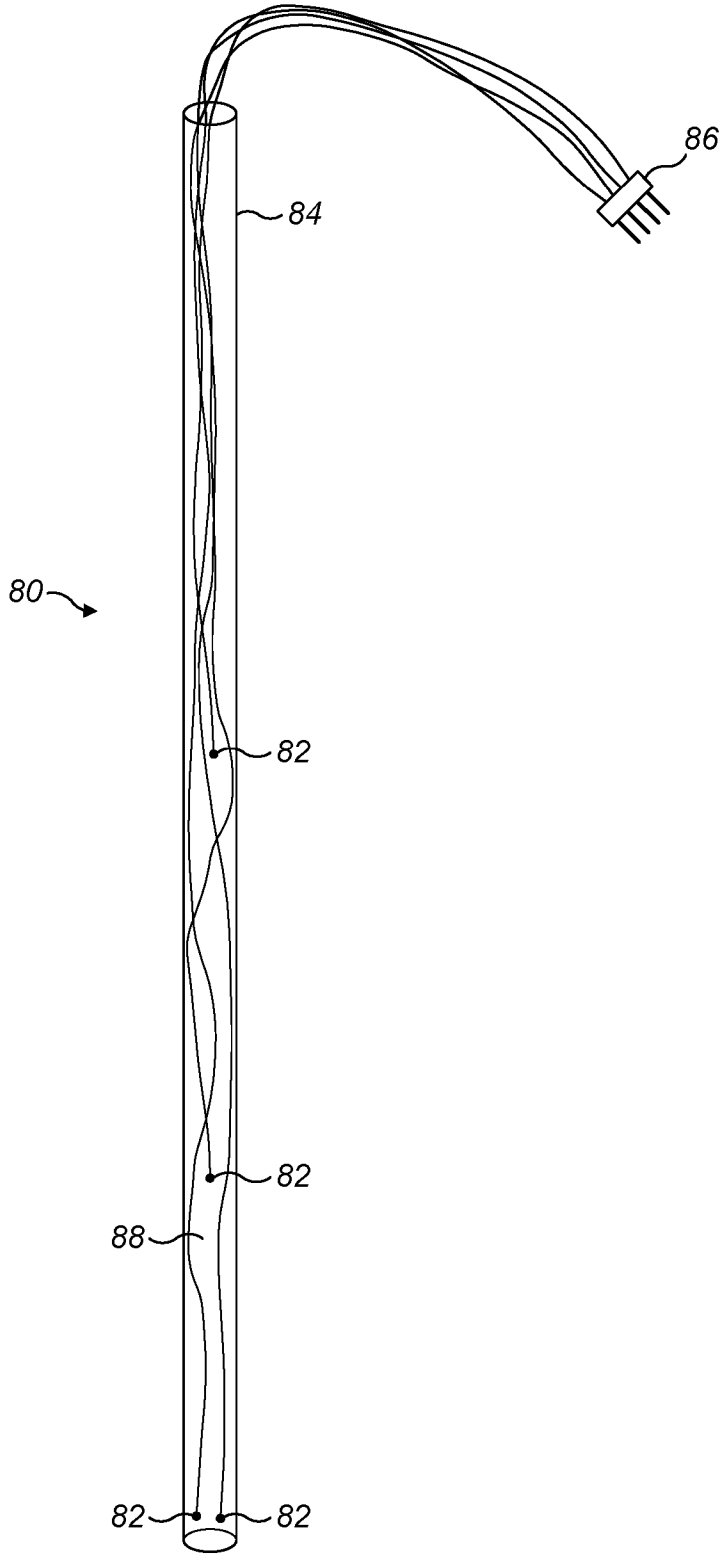


FIG. 7

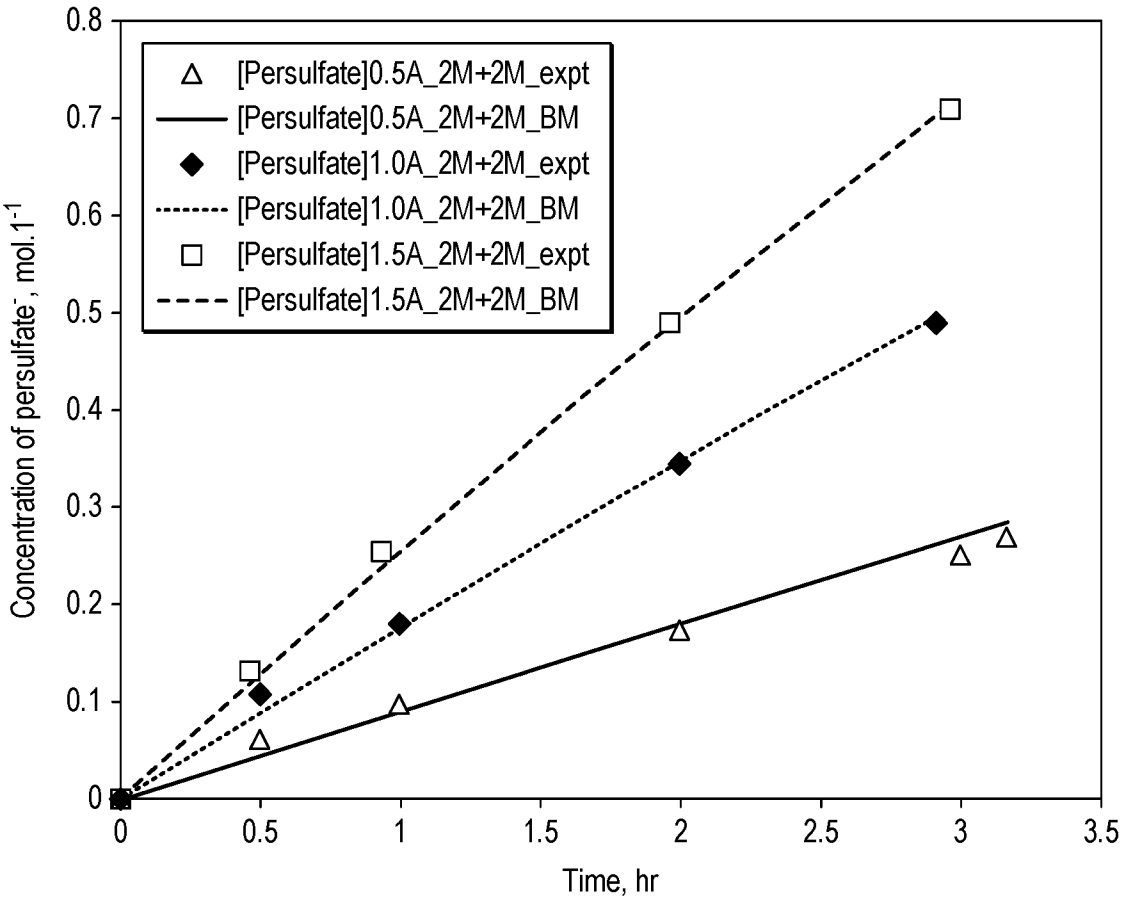

[Persulfate]0.5A_2M+2M_expt
[Persulfate]0.5A_2M+2M_BM
[Persulfate]1.0A_2M+2M_expt
[Persulfate]1.0A_2M+2M_BM
[Persulfate]1.5A_2M+2M_expt
[Persulfate]1.5A_2M+2M_BM
Concentration of persulfate-, mol.l-1
Time, hr
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.5
1
1.5
2
2.5
3
3.5

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/051631

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25B15/02 C25B1/26 C25B1/28
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)
C25B C02F

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
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	US 2014/026971 A1 (ROACH KENNETH J [US] ET AL) 30 January 2014 (2014-01-30)	1-3,5,6, 8,16,18, 19,21, 23,30-33
Y	paragraphs [0023], [0034] - [0037]; claims 1,5,6; figure 1	4,7, 9-15,17, 20,22, 24-29
X	WO 2011/073714 A1 (CM VENTURES LTD [IE]; CARRAGHER GEOFF [IE]; KOPHAMEL JEFF [IE]; CARRAG) 23 June 2011 (2011-06-23) page 7, line 4 - page 8, line 8; figure 5	1-3,5,6

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
4 August 2016	16/08/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Hammerstein, G

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 688 385 A (RHEES RAYMOND C [US] ET AL) 18 November 1997 (1997-11-18) column 9, line 18 - column 10, line 35; figure 3 column 8, lines 22-27	4,7, 9-15,20, 22,24-29
Y	US 2009/266706 A1 (FUKUI KENJL [JP] ET AL) 29 October 2009 (2009-10-29) paragraphs [0022], [0023], [0029] - [0031]; figures 5,6	17
A	EP 0 133 920 A1 (OLIN CORP [US]) 13 March 1985 (1985-03-13) page 4, line 24 - page 5, line 20; claims 8,10; figures 1,3	1-33

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2016/051631

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