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(54) **DEVICE, METHOD AND SYSTEM FOR CONDUCTING AN ELECTROLYTIC PROCESS**

(57) A device for conducting an electrolytic process comprises reactor walls (6,7) defining a space (8) for accommodating an electrolyte. An electrode system (9) is arranged in the space (8) and comprises at least one first electrode (10) and an array of second electrodes (11-14). Each second electrode (11-14) surrounds the at least one first electrodes (10) and has an inward-facing major surface, an outward-facing major surface and at least one interconnect to the major surfaces. Successive second electrodes (11-14) from an inner second electrode (11) to an outer second electrode (14) surround the at least one first electrode (10) at successively larger distances. The device comprises at least one current source (18;34,35) and a current feeder arrangement providing a respective current path between each interconnect and one of the at least one current sources (18;34,35). The at least one current sources (18;34,35) are connected to the electrode system (9) such that the at least one first electrodes (10) have an opposite polarity to that of the second electrodes (11-14) and current can flow between the at least one first electrodes (10) and at least one of the major surfaces of each second electrode (11-14) through the electrolyte, in use. The current feeder arrangement and the at least one current sources (18;34,35) are configured to establish potentials at the interconnects of the inner second electrode (11) that differ from the potentials at the interconnects of at least one second electrode (12-14) other than the inner second electrode (11) by being closer to that of the at least

one first electrodes (10).

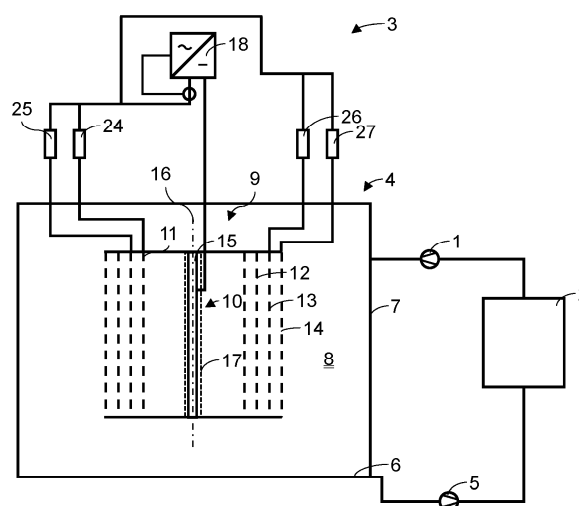


Fig. 1

Description**Technical Field**

[0001] The invention relates to a device for conducting an electrolytic process, comprising:

reactor walls defining a space for accommodating an electrolyte;
 an electrode system, arranged in the space and comprising at least one first electrode and an array of second electrodes,
 wherein each second electrode surrounds the at least one first electrodes and has an inward-facing major surface, an outward-facing major surface and at least one interconnect to the major surfaces,
 wherein successive second electrodes from an inner second electrode to an outer second electrode surround the at least one first electrode at successively larger distances;
 at least one current source; and
 a current feeder arrangement providing a respective current path between each interconnect and one of the at least one current sources,
 wherein the at least one current sources are connected to the electrode system such that the at least one first electrodes have an opposite polarity to that of the second electrodes and current can flow between the at least one first electrodes and at least one of the major surfaces of each second electrode through the electrolyte, in use.

[0002] The invention also relates to a system for regenerating a processing solution by electrochemical oxidation of an ion species in the processing solution.

[0003] The invention also relates to a method of regenerating a processing solution by electrochemical oxidation of an ion species in the processing solution using a device comprising:

an electrode system comprising at least one first electrode and an array of second electrodes,
 wherein each second electrode surrounds the at least one first electrodes and has an inward-facing major surface, an outward-facing major surface and at least one interconnect to the major surfaces,
 wherein successive second electrodes from an inner second electrode to an outer second electrode surround the at least one first electrode at successively larger distances; and
 at least one current source connected to the electrode system, the method comprising:

conveying the processing solution to a space in which the electrode system is arranged, and causing current supplied by the at least one current source to flow between the at least one first electrodes and at least one of the major

surfaces of each second electrode through the processing solution,
 wherein the at least one first electrodes are operated as cathodes and the second electrodes as anodes.

Background Art

[0004] WO 01/90442 A1 discloses a device for electrochemically regenerating permanganate etching solutions comprising at least one anode; at least one cathode; a current source for the at least one anode; as well as electric conducting lines between the current source on the one hand and the at least one anode and the at least one cathode on the other hand. The at least one cathode is formed as a rod. The at least one anode is formed as a perforated cylinder. Each cathode is arranged axisymmetrically in the centre of at least one anode.

[0005] A practical implementation of this device comprises four anodes in order to increase the yield. With more anodes, more current passes through the solution, and thus the number of desired reactions increases. However, the efficiency, the number of reactions per unit current, decreases.

Summary of Invention

[0006] It is an object of the invention to provide a device, method and system of the types defined above in the opening paragraphs that allow to increase the yield of a desired reaction occurring at the second electrodes without significantly sacrificing efficiency.

[0007] This object is achieved by the device according to the invention, which is characterised in that the current feeder arrangement and the at least one current sources are configured to establish potentials at the interconnects of the inner second electrode that differ from the potentials at the interconnects of at least one second electrode other than the inner second electrode by being closer to that of the at least one first electrodes.

[0008] It has been found that efficiency decreases with current density at the second electrodes, where the desired reaction takes place, in use. If the second electrodes are all connected to the same current source, then most of the current will flow between the first electrode and the second electrode that is closest to the first electrode. By establishing a potential at the interconnects of the inner second electrode that differs from the potential at the interconnects of at least one second electrode other than the inner second electrode by being closer to that of the at least one first electrodes, a larger potential differential between the first electrode and the second electrodes other than the inner second electrode is achieved. Thus, the larger resistance of the path through the electrolyte in the space is compensated for by the larger potential difference. As a result, a larger fraction of the total current flows between the first electrode and other second electrodes than the inner second electrode.

[0009] Because successive second electrodes from the inner second electrode to the outer second electrode surround the at least one first electrode at successively larger distances, the inner second electrode has the smallest (geometric) surface area. As a consequence, more area is available for current to flow through the outer second electrodes. This effect somewhat counters the shielding effect due to the fact that successive second electrodes in the array are shielded from the at least one first electrode by a successively increasing number of other second electrodes in the array. Furthermore, a rise in current flowing via those other second electrodes results in a relatively small increase in current density and thus a relatively small decrease in efficiency.

[0010] Because each second electrode surrounds the at least one first electrodes, the geometric surface area of the inward-facing surface of the second electrodes is much larger than the exterior surface area of the at least one first electrodes. The ratio can be in the range of 9 to 80, inclusive. This favours the desired reaction at the surface of the second electrodes relative to the reverse reaction taking place at the first electrode. Compared to an array of planar second electrodes, this ratio can be achieved without making the electrode system significantly less compact. The disadvantage that the second electrodes do not have an inward-facing major surface with the same area, which would normally lead to most of the current flowing through the inner second electrode, is alleviated by bringing the potential of the inner second electrode closer to that of the at least one first electrode, so that less current flows via the inner second electrode. The inner second electrode may still conduct more current than the other second electrodes, but the difference is less than if all second electrodes were to be connected to the same current supply. Ordinarily, the potentials will be set such as to equalise the currents or even raise the currents through the other second electrodes to a value higher than the current flowing through the inner second electrode. In particular, the potentials will generally be set such as to equalise the current densities at the inward-facing major surfaces of the second electrodes.

[0011] In the device, reactor walls define a space for accommodating an electrolyte. The reactor walls may form a vessel or tank that is open at a top or may define a closed reactor. The device may be configured for batch or continuous operation. In the latter case, the reactor walls may define a generally tubular reactor through which electrolyte flows, in use.

[0012] An electrode system is arranged in the space. The electrode system need not be completely immersed in electrolyte in use. The electrode system comprises at least one first electrode and an array of second electrodes. The terms first and second electrode are used here to distinguish between electrodes having opposite polarities, in use. The first electrodes may be operated as cathodes and the second electrodes as anodes, for example.

[0013] Generally, there will be only one first electrode,

since the device is particularly suited for use in processes in which the desired reaction takes place at the second electrodes. A small surface area at the first electrodes has the effect of suppressing the reverse reaction without a need to use a separate catholyte and anolyte separated by a selective barrier.

[0014] Each second electrode surrounds the at least one first electrodes and has an inward-facing major surface, an outward-facing major surface and at least one interconnect to the major surfaces. Seen in an axial direction, with respect to an electrode system axis, each second electrode surrounds the at least one first electrodes in the sense that the second electrode forms a closed loop around the at least one first electrodes. The space between the inner second electrode and the at least one first electrodes may be open at one or both axial ends. The inward-facing major surface is the surface facing in the direction of the at least one first electrodes. The outward-facing major surface is the opposite surface facing away from the at least one first electrodes. The or each interconnect is the transition between an electrical current conductor along which the current flows in one direction (the direction of progression of that conductor) and the location where electrical current spreads out across the major surface or converges from across the major surface. There may be several interconnects per second electrode, e.g. at distinct axial locations with respect to the electrode system axis just mentioned.

[0015] By definition, the array of second electrodes is an ordered arrangement of the second electrodes, in which successive spaced-apart second electrodes from an inner second electrode to an outer second electrode surround the at least one first electrode at successively larger distances. It follows from this that the first second electrode in the array is the inner second electrode, which only surrounds the at least one first electrode, but at a distance thereto. The next, i.e. second, second electrode in the array surrounds both the at least one first electrode and the inner second electrode. The third second electrode surrounds the at least one first electrode, the inner second electrode and the second second electrode, etc. The second electrodes in the array are spaced apart from each other. Thus, electrolyte can enter spaces that are defined between successive second electrodes in the array. At least those second electrodes at which different potentials are established are electrically isolated from each other, but for electrolyte in the spaces between them.

[0016] The second electrodes may have an overall shape in the form of a sheet, e.g. a liquid-permeable sheet, closed on itself around at least the at least one first electrode. The overall shape has a thickness several times smaller than the extent in the remaining two dimensions. The thickness corresponds to the distance between the inward-facing major surface and the outward-facing major surface. A typical thickness may be in the range of 0.4 - 1 mm. The spacing between successive second electrodes in the array may be in the range of

1 - 3 mm, for example.

[0017] The device comprises at least one current source. The value of the current supplied or drawn by each current source is set separately from the value of the current of any other current sources. Each current may comprise its own respective current rectifier if the device is arranged to be powered by an alternating current supply or three-phase current supply at the site at which the device is operated. Alternatively, two current sources may have a current rectifier in common but at least one may comprise a DC/DC-converter specific to that current source. This would also be the case if the device is arranged to be powered by a DC power supply such as a micro-grid.

[0018] A current feeder arrangement provides a respective current path between each interconnect and one of the at least one current sources. Branches of the current paths may be shared.

[0019] The current feeder arrangement and the at least one current sources are configured to establish a potential at the interconnects of the inner second electrode that differs from the potential at the interconnects of at least one second electrode other than the inner second electrode by being closer to that of the at least one first electrodes. The interconnects of any one second electrode need not all be at the same potential, but their potential differs at least from that of corresponding interconnects of the other second electrode, i.e. those at the location corresponding most closely.

[0020] The fact that the current feeder arrangement and the at least one current sources are configured to establish a potential at the interconnects of the inner second electrode that differs from the potential at the interconnects of at least one second electrode other than the inner second electrode by being closer to that of the at least one first electrodes does not mean that adaptations have been made to both in each embodiment of the device, as will become clear.

[0021] In an embodiment, the current feeder arrangement provides current paths between a particular one of the current sources and the interconnects of a proximal set of at least one of the second electrodes having a higher resistance than current paths provided between the same current source and a distal set of at least one of the second electrodes, and the proximal set is disjoint from the distal set and comprises second electrodes surrounding the at least one first electrodes at a shorter distance than second electrodes in the distal set.

[0022] The higher resistance will generally be set by adding dedicated pre-resistors to the current paths. Because the surface area of the second electrodes increases with increasing distance to the at least one first electrode, current equalisation can be achieved with relatively small extra resistances, e.g. in the range from 0.1 to 100 m Ω , for example in the range from 0.1 to 30 m Ω . The effect of the device is therefore achieved with relatively small ohmic losses.

[0023] In an embodiment of the device, the current

feeder arrangement provides first current paths between a first one of the current sources and a first set of at least one of the second electrodes and second current paths between a second one of the current sources and a second set of at least one of the second electrodes, wherein the first current paths are separate from the second current paths, and wherein the first set is disjoint from the second set and comprises second electrodes surrounding the at least one first electrodes at a shorter distance than second electrodes in the second set.

[0024] This embodiment also allows the effect of the device to be achieved with relatively small ohmic losses. It is possible to set the value of the total current flowing between the first set of second electrodes and the at least one first electrode separately from and independently of the total value of the current flowing between the second set of second electrodes and the at least one first electrode.

[0025] In an embodiment of the device, the second electrodes are three or more, e.g. four, in number.

[0026] It is thus possible to increase the yield of the device. Each second electrode in the array surrounds the at least one first electrodes and the preceding second electrodes in the array, counting from the inner second electrode to the outer second electrode. Thus, the device remains relatively compact. The extra shielding effect encountered by the outer second electrodes is compensated for by the measures taken to equalise the current and by the increased surface area. In particular, the current feeder arrangement and the at least one current sources are configured to establish potentials at the interconnects of the second electrodes that are equal to the potentials at the interconnects of the immediately preceding second electrode in the array or that differ from the potentials at the interconnects of the immediately preceding second electrode in the array by being less close to that of the at least one first electrodes. For example, the second electrodes may be arranged in pairs, with the potentials at the interconnects differing only between pairs. More generally, in particular in embodiments with more than four second electrodes, the second electrodes may be arranged in consecutive disjoint sub-sets of second electrodes, at least one of which sub-set has at least two second electrodes, with the potentials at the interconnects differing only between sub-sets. In that case, the number of electrodes per sub-set need not be the same for each sub-set. Alternatively, the potentials may become progressively less close to that of the at least one first electrode with each next second electrode in the array, starting at the inner second electrode.

[0027] In an embodiment, the second electrodes are liquid-pervious in a direction from the inward-facing major surface to the outward-facing major surface.

[0028] This shortens the current paths between the first and second electrodes.

[0029] In an embodiment, at least one, e.g. each, of the second electrodes comprises an electrically conducting

mesh, e.g. an expanded metal mesh.

[0030] This is a relatively uncomplicated way of providing liquid-pervious second electrodes having an overall shape of a sheet closed on itself around at least the first electrode. Expanded metal is a type of sheet metal which has been cut and stretched to form a regular pattern (often diamond-shaped) of mesh-like material. Expanded metal is relatively strong and stable compared with, e.g. a woven lattice or the like.

[0031] In an example of the embodiment in which at least one, e.g. each, of the second electrodes comprises an electrically conducting mesh, e.g. an expanded metal mesh, the mesh has a surface factor, defined as a total effective surface area per geometric area, in the range of 2.0 to 2.5.

[0032] This further increases the efficiency at a given electrical current.

[0033] In an embodiment, the second electrodes have an overall shape that is rotationally symmetrical, e.g. circle-cylindrical, over at least a majority of their dimension in axial direction with respect to an electrode system axis.

[0034] Variations in current density across the major surfaces of the second electrodes are therefore kept relatively low. The section corresponding to the majority of the dimension in axial direction corresponds to the section enveloped by the electrolyte, in use. The overall shape at the axial end may differ, however, e.g. to enable mounting of the second electrodes.

[0035] In this embodiment, the second electrodes may be arranged concentrically.

[0036] In an example of any embodiment in which the second electrodes have an overall shape that is rotationally symmetrical, e.g. circle-cylindrical, over at least a majority of their dimension in axial direction with respect to an electrode system axis, the at least one first electrodes are arranged rotationally symmetrically with respect to an axis essentially coinciding with the electrode system axis.

[0037] This minimises current density variations, including at the first electrode.

[0038] In an embodiment of the device, the at least one first electrodes are rod-shaped over at least a majority of their longitudinal dimension.

[0039] The rod may be hollow or solid. The rod-shape allows for a relatively compact electrode system and keeps the surface area of the first electrode relatively low. It will be recalled that the desired electrochemical reaction is the one taking place at the second electrodes and that it is preferred not to place a membrane separating a catholyte from an anolyte between the first electrode and the second electrodes. Thus, the surface area of the second electrodes should be larger than that of the first electrode.

[0040] In an embodiment, successive second electrodes in the array are separated from each other by at least one electrically insulating spacer, e.g. at least one annular spacer.

[0041] This allows for the use of relatively thin second electrodes placed relatively close together. The spacers help ensure that the second electrodes can be held at different potentials.

[0042] In an embodiment, the current feeder arrangement comprises at least one electrical contact device in electrical contact with at least one of the second electrodes and passing through at least one other of the second electrodes, the electrical contacting device comprising an electrically insulating mantle preventing electrical contact between the at least one other second electrodes.

[0043] Thus, the interconnects of the second electrode need not be at the axial ends (with respect to an axis about which the second electrodes are arranged in a closed overall shape). There are thus relatively small potential gradients across the major surfaces in axial direction.

[0044] In an example of this embodiment, at least one of the at least one electrical contact devices comprises an electrically conducting bushing on which the mantle is arranged and a fastener, e.g. a bolt, extending through the bushing. The fastener functions to fix both the electrical contact device and the second electrodes through which the contact device extends in position. To this end, the fastener may be arranged to exert a clamping force. Besides bolts, suitable fasteners include rivets, screws, pegs, etc. Threaded fasteners allow for the application of a relatively well-defined clamping force.

[0045] In an embodiment of the device, at least one, e.g. all, of the first electrodes comprises an electrically conducting core having an exterior surface partially exposed to the space and partially insulated therefrom by electrically insulating material.

[0046] This reduces the effective surface area of the first electrodes at which the opposite reaction to the one taking place at the major surface of the second electrodes can take place. As a consequence, the effect of the arrangement of the second electrodes around the at least one first electrode, namely that the ratio of the surface area of the second electrode to the surface area of the first electrode is relatively large, is enhanced. The electrically insulating material may be comprised in a barrier arranged around the core, e.g. a barrier made of PTFE textile material.

[0047] In an embodiment, an electrically conducting part of at least one of the first and second electrodes is made of stainless steel.

[0048] This enhances the suitability of the device for use with alkaline electrolytes.

[0049] Similarly, the reactor walls may comprise walls made of stainless steel.

[0050] According to another aspect of the invention, there is provided a system for regenerating a processing solution by electrochemical oxidation of an ion species in the processing solution, comprising:

a device according to the invention, wherein the at

least one current sources are arranged to operate the at least one first electrodes as cathodes and the second electrodes as anodes; and
at least one pump for at least one of supplying the solution to and removing the solution from the space.

[0051] The system is suited to electrochemical oxidation at the second electrodes without necessitating a separate catholyte, is relatively compact and provides a relatively high treatment capacity with relatively good efficiency.

[0052] According to another aspect, the method of regenerating a processing solution by electrochemical oxidation of an ion species in the processing solution is establishing potentials at the interconnects of the inner second electrode that differ from the potentials at the interconnects of at least one second electrode other than the inner second electrode by being closer to that of the at least one first electrodes.

[0053] The method provides the effects of the system. The method may use a device according to the invention, just as the device according to the invention is suitable for use in the method according to the invention.

[0054] In an embodiment of the method, the potentials are set such as to equalise the current densities at the inward-facing major surfaces of the second electrodes.

[0055] The current density determines the efficiency. In this embodiment, the maximum total current for a given efficiency is conducted through the processing solution.

[0056] In an embodiment of the method, the processing solution is an alkaline processing solution, e.g. an alkaline etchant.

Brief Description of Drawings

[0057] The invention will be explained in further detail with reference to the accompanying drawings, in which:

Fig. 1 is a schematic drawing of a first system for regenerating a processing solution comprising a device for conducting an electrolytic process;

Fig. 2 is a perspective view of an electrode system and feeders comprised in the device;

Fig. 3 is a detailed cross-sectional view showing a contacting device for supplying current to one of four anodes comprised in the electrode system;

Fig. 4 is a diagram relating efficiency to current density at different manganese concentrations as determined in tests conducted using a single anode;

Fig. 5 is a diagram relating simulated efficiency to manganese concentration for the device at a particular total current value and for three alter-

native devices at the same current value and the device of Figs. 1-3 at double the total current value; and

Fig. 6 is a schematic drawing of a variant of the system of Fig. 1.

[0058] A first system (Fig. 1) for regenerating a processing solution by electrochemical oxidation of an ion species in the processing solution comprises a first pump 1 for supplying processing solution to be regenerated from a processing station 2 to a first electrolysis device 3, in particular a tank 4 comprised in the first electrolysis device 3. The system further comprises a second pump 5 for returning the regenerated processing solution to the processing station 2.

[0059] The processing station 2 may be a processing station 2 for carrying out a desmear process using an alkaline etching solution. Such a process is, for example, carried out in a production line for the production of printed circuit boards subsequent to a step in which holes are drilled through the printed circuit board. Here, the example of an alkaline etching solution comprising permanganate will be used. The etching solution is used to remove smear from the drilled holes generated during drilling. The permanganate decomposes (is reduced) to manganate in the processing station 2. The regeneration comprises a process of electrolytically oxidising the manganate back to permanganate.

[0060] In the illustrated embodiment, the tank 4 makes the system suitable for carrying out the regeneration process as a batch process. It is also possible to implement the process as a continuous process, in which case the tank 4 may be replaced by a continuous reactor and one of the first and second pumps 1,5 may be dispensed with. The same is the case if there is a level difference between the processing station 2 and the tank 4.

[0061] The tank 4 has at least a bottom wall 6 and side wall 7 defining a space 8 for accommodating the processing solution, which functions as an electrolyte in the electrolytic process. In view of the alkaline nature of the processing solution, the walls 6,7 may be made of stainless steel.

[0062] An electrode system 9 is accommodated in the space 8. An alternative electrolysis device comprises multiple electrode systems 9 of the same configuration, e.g. from two to six electrode systems 9. The electrode system 9 may be in the form of an assembly forming a unit that can be taken out of and inserted into the first electrolysis device 3 as a module.

[0063] In the illustrated first electrolysis device 3, the electrode system 9 comprises a single first electrode 10 that is arranged to function as a cathode. The electrode system comprises an array of second electrodes 11-14 that are arranged to function as anodes. The desired oxidation reaction takes place at the second electrodes 11-14.

[0064] The first electrode 10 comprises an electrically

conducting core 15 having an elongate shape, e.g. in the form of a solid rod. A longitudinal axis of the first electrode 10 essentially coincides with an electrode system axis 16. At least the core 15 is rotationally symmetric with respect to the longitudinal axis. The core 15 may be made of stainless steel, for example. An apertured sheath 17 is provided around the core 15 along at least a section of the length of the core 15. This section encompasses at least the section of the first electrode 10 exposed to the electrolyte, in use. The material of the apertured sheath 17 has a lower electrical conductivity than that of the core 15, e.g. being electrically insulating. An example of a suitable material is Polytetrafluoroethylene (PTFE). In an example, the apertured sheath 17 comprises a mesh, e.g. a mesh made of PTFE. Instead of an apertured sheath 17, an electrically insulating coating could be applied to sections of the exterior surface of the core 15.

[0065] Due to the apertured sheath 17, less than all of the area of an exterior surface of the core 15 is exposed to the space 8, and thus the electrolyte, in use. Some of the exterior surface is insulated therefrom. This increases the current density at the exposed parts of the exterior surface. An effect is that the dominant reaction at the first electrode 10 is the decomposition of water into hydrogen (H_2) and hydroxide (OH^-). In addition, the space between the inner second electrode 11 and the first electrode 10 is free of ion-selective barriers (such as membranes). This is because there is no need for separation of an anolyte and a catholyte, there being just one electrolyte.

[0066] The array of second electrodes 11-14 comprises an inner second electrode 11 and an outer second electrode 14. The illustrated array comprises a further two second electrodes 12, 13 arranged between the inner second electrode 11 and the outer second electrode 14.

[0067] Each of the second electrodes 11-14 surrounds the first electrode 10. Each second electrode 11-14 has one major surface facing inwards towards the first electrode 10 and one major surface facing in the opposite direction, away from the first electrode 10. In use, electrical current flows to the second electrodes 11-14 via a feeder arrangement, an arrangement of electrical conductors, to one or more interconnects to the major surfaces of the second electrodes 11-14. At the interconnect, the electrical current spreads out in multiple directions, whereas there is a single respective direction of current flow in the conductors of the feeder arrangement. The present explanation will proceed on the basis that there are two interconnects per second electrode 11-14. For example, there may be one proximate one axial end of the second electrodes 11-14 and one proximate an opposite axial end of the second electrode 11-14, with respect to the electrode system axis 16.

[0068] Each second electrode 11-14 comprises a mesh. Thus, each second electrode 11-14 is liquid-permeous in a direction from the inward-facing major surface to the outward-facing major surface (and *vice versa*). An alternative is conceivable in which this is not the case for the outer second electrode 14.

[0069] The mesh may be an expanded metal mesh. The mesh may be made of stainless steel.

[0070] The mesh may have a surface factor, defined as a total effective surface area per geometric area, in the range of 2.0 to 2.5, e.g. from 2.2 to 2.3. The effective surface area can be obtained by summing the surface area of the individual strands of a piece of mesh having a length L and a width W, the geometric area being two times the product of the length L and the width W.

[0071] The second electrodes 11-14 are arranged around the electrode system axis 16. They, or at least their respective meshes, have an overall shape that is rotationally symmetrical over at least a majority of their axial dimension with respect to an axis essentially coinciding with the electrode system axis 16. They are thus arranged concentrically. It is the overall shape that is rotationally symmetric, not necessarily the electrode or mesh itself, because the latter may have interruptions of the mesh pattern at certain locations, e.g. where part of the feeder arrangement is integrated into the mesh or there is an aperture in the mesh. Generally, the shape will be circle-cylindrical, as illustrated. A cylindrical shape with a convex, e.g. regular, polygonal cross-section perpendicular to the electrode system axis 16 is also possible, in particular where this polygonal shape is an n-gon with n higher than four.

[0072] The first electrolysis device 3 comprises a single electrical current source 18. The current supplied by the electrical current source 18 can be set individually. Where the electrical current source 18 is configured to be powered by an alternating current supply or three-phase current supply, the electrical current source 18 will generally comprise a current rectifier specific to the electrical current source 18 and/or a DC/DC converter specific to the electrical current source 18. The latter would generally be the case if the electrical current source 18 is powered by a DC current supply, e.g. from a Direct Current microgrid. In any case, the value of the current supplied can be set independently of the value of the current supplied by any other electrical current sources comprised in the first electrolysis device 3.

[0073] Membrane electrolysis experiments at different current densities have been performed with an anode in the form of a metal sheet with a covered outward-facing surface and a cathode in a membrane box, in order to investigate how the current efficiency varies with current density. The results are shown in Fig. 4, where a first graph 19 corresponds to a manganate concentration of 6 g/l, a second graph 20 to a concentration of 8 g/l, a third graph 21 to a concentration of 10 g/l, a fourth graph 22 to a concentration of 14 g/l and a fifth graph 23 to a concentration of 16 g/l. One can see that the efficiency is higher at lower current densities. Increasing the current to increase the yield thus comes at a cost of lower efficiency, unless the anode is also made larger.

[0074] Without further measures, most of the current supplied by the electric current source 18 would flow via the inner second electrode 11, leading to a relatively high

current density at the inner second electrode 11. This is because there is a shielding effect due presence of other second electrodes between the first electrode 10 and each of the outer, second and third second electrodes 12-14. This negates the effect of the increasing surface area. For this reason, the current feeder arrangement and the electric current source 18 are configured to establish a potential at corresponding interconnects of the second electrodes 11-14 that is closer to that of the first electrode 10 with each successive second electrode, starting from the outer second electrode 14. In other words, the magnitude of the differential to the potential of the first electrode 10 increases with each successive second electrode, starting from the inner second electrode 11.

[0075] Where the second electrodes 11-14 comprise multiple interconnects, the corresponding interconnects are those closest in location in axial direction.

[0076] In the first system (Fig. 1), the different potentials are established by means of pre-resistors 24-27. The resistance values decrease progressively from a pre-resistor 24 in a current path to the inner second electrode 11 to a pre-resistor 27 in a current path to the outer second electrode 14. Of course, the latter pre-resistor 27 could be omitted. The pre-resistor may be situated anywhere between the electric current source 18 and the interconnect. Where a second electrode 11-14 has multiple interconnects, there may be one pre-resistor per interconnect or the current paths between those interconnects and the current source 18 may partially overlap and pass through a common pre-resistor.

[0077] The pre-resistors 24-27 may be integral parts of the second electrodes 11-14 in the manner set out in WO 2024/223646 A1, herein incorporated by reference. Equally, the pre-resistors 24-27 need not be discrete components. It is, for example possible to provide feeder bars having at least one of a different length a different cross-sectional area and a different resistivity in the respective current paths to the second electrodes 11-14.

[0078] Furthermore, although not quite optimal, it is conceivable to use different resistance values in current paths between the common electric current source 18 and sets of multiple adjacent second electrodes 11-14 in the array, e.g. one for the innermost two and one for the outermost two. Alternatively, the pre-resistors 25-27 to the outermost three second electrodes 12-14 may be omitted.

[0079] The result in each case is that the current density at at least the inward-facing major surfaces of the second electrodes 11-14 is made more equal than if they were to be connected to the same current source 18 via current paths of approximately equal resistance.

[0080] The effect due to the features of the first electrolysis device 3 has been investigated through simulation using a resistor network model similar to the model described in WO 2024/223646 A1. The model has variable resistors representing the anodic and cathodic reactions at the surfaces of the first electrode 10 and the

second electrodes 11-14 and resistances for the sections of the current path through the electrolyte between the second electrodes 11-14 and between the inner second electrode 11 and the first electrode 10, as well as resistances for each section of the current path through one of the second electrodes 11-14, i.e. from the outward-facing major surface to the inward-facing major surface thereof. The results of the tests on which the graphs 19-23 are based were used as a basis for the model.

[0081] Fig. 5 shows the efficiency at different manganate concentrations for different combinations of electrolysis device configuration and total current supplied by the electric current source 18. A first graph 28 relates to a configuration in which the pre-resistors 24-27 are omitted, only the innermost two second electrodes 11,12 are present, the surface factor of the mesh is 1.7 and the total current is 120 A. This is an implementation of an electrolysis device as disclosed in WO 01/90442 A1 and serves as a baseline. A second graph 29 relates to the same configuration, but with the surface factor of the meshes increased from 1.7 to 2.25. A third graph 30 relates to a configuration in which the pre-resistors 24-27 are omitted, all four second electrodes 11-14 are present, the surface factor of the mesh is 2.25 and the total current is 120 A. A fourth graph 31 relates to the configuration of the first electrolysis device 3, including the pre-resistors 24-27, the surface factor being 2.25 and the total current 120 A. The pre-resistor values were obtained using the model with the constraint that the current density at the inward-facing major surface is equal for each of the second electrodes 11-14. Therefore, a current profile with a low current at the inner second electrode 11 and a high current at the outer second electrode 14 is obtained. A fifth graph 32 shows the effect of increasing the total current to 240 A. It will be apparent that the efficiency is approximately equal to that of the baseline configuration at half the total current. In other words, the permanganate formation rate is approximately double at the same efficiency.

[0082] Such an effect is also achievable with the second system (Fig. 6), in which like parts are referred to by the same reference signs. The second system comprises a second electrolysis device 33, which differs from the first electrolysis device 3 by comprising multiple, in this example two, independent electric current sources 34,35. The value of the current supplied by one of the electric current sources 34,35 is independent of the value of the current supplied by the other. The description of the electric current source 18 of the first electrolysis device 3 applies also to the electric current sources 34,35 of the second electrolysis device 33.

[0083] The current feeder arrangement provides first current paths between a first electric current source 34 and a first set of at least one of the second electrodes and second current paths between a second electric current source 35 and a second set of at least one of the second electrodes 11-14. The first current paths are separate from the second current paths, i.e. they do not share a

branch. The first set is disjoint from the second set and comprises second electrodes 11-14 surrounding the first electrode 10 at a shorter distance than second electrodes 11-14 in the second set. In the illustrated second electrolysis device 33, the first set comprises only the inner second electrode 11. The second set comprises the remaining second electrodes 12-14. Alternatively, the first set may comprise the innermost two second electrode 11,12 and the second set comprise the remaining two second electrodes, 13,14.

[0084] The second electrolysis device 33 retains the pre-resistors 25-27 in the current paths to the second electrodes 12-14 in the second set, because they are connected to a common electric current source 35. In a less optimal variant, these pre-resistors 25-27 may be omitted or have equal values.

[0085] A practical implementation (Figs. 2, 3) of the array of second electrodes 11-14, for use in either of the first and second electrolysis devices 3,33 makes use of a separate respective current feeder bar 36-39 for each second electrode 11-14. Each current feeder bar 36-39 is connected to the associated second electrode 11-14 by two electrical contact devices 40 (Fig. 3).

[0086] The illustrated electrical contact device 40 connects the second second electrode 12 to the associated current feeder bar 37 and passes through the outermost two second electrodes 13,14. The electrical contact device 40 comprises an electrically insulating mantle 41 preventing electrical contact between the electrical contact device 40 and the outermost two second electrodes 13,14.

[0087] The mantle 41 is arranged on an electrically conducting bushing 42 through which a bolt 43 extends. The bolt 43 passes through a bore in the current feeder bar 37 and is secured by a nut 44. The bolt 43 clamps the bushing 42 between the second second electrode 12 and the current feeder bar 37. An aperture 45 provides a tool (not shown) with access to a bolt head 46 of the bolt 43.

[0088] Electrically insulating spacers 47a-c made of material having a lower electrical conductivity than the material of the second electrodes 11-14 and the feeder arrangement separate successive second electrodes 11-14 in the array from each other. The electrically insulating spacers 47a-c may be annular in shape or multiple spacers may be arranged at angular intervals in the space between successive second electrodes 11-14.

[0089] Thus, the interconnects, which are at the junctions between the electrical contact devices 40 and the associated second electrode 11-14 can have different potentials such that the differential to the potential of the first electrode 10 increases from one second electrode to the next in the array of second electrode 11-14, starting at the inner second electrode 11. The currents are thereby equalised or at least made more equal, allowing for a relatively large total current without sacrificing efficiency too much.

[0090] The invention is not limited to the embodiments described above, which may be varied within the scope of

the accompanying claims. For example, although the illustrated electrode systems 9 are open at their opposite axial ends, one or both axial ends may be closed by barriers preventing liquid flow. Conversely, there may be a further pump inside the tank 4 for promoting flow through the electrode system 9. It is conceivable for the second electrodes 11-14 to comprise an electrically conducting mesh in the form of a lattice instead of an expanded metal mesh. The expanded metal mesh is relatively strong and durable, however.

[0091] Although the description of the electrolysis devices 3,33 has focused on their suitability for conducting a process of electrolytic oxidation of ions such as manganese species, the devices are also suitable for electrochemical water splitting to obtain hydrogen, for electroplating, for electroplating and for plating out ions from solutions, to name a few examples.

List of reference numerals

[0092]

- | | |
|----|--|
| 1 | - First pump |
| 2 | - Processing station |
| 3 | - 1 st electrolysis device |
| 4 | - Tank |
| 5 | - 2 nd pump |
| 6 | - Bottom wall |
| 7 | - Side wall |
| 8 | - Space |
| 9 | - Electrode system |
| 10 | - First electrode |
| 11 | - Inner second electrode |
| 12 | - 2 nd second electrode |
| 13 | - 3 rd second electrode |
| 14 | - Outer second electrode |
| 15 | - Core |
| 16 | - Electrode system axis |
| 17 | - Apertured sheath |
| 18 | - Current source |
| 19 | - 1 st graph (manganese concentration 6 g/l) |
| 20 | - 2 nd graph (manganese concentration 8 g/l) |
| 21 | - 3 rd graph (manganese concentration 10 g/l) |
| 22 | - 4 th graph (manganese concentration 14 g/l) |
| 23 | - 5 th graph (manganese concentration 16 g/l) |
| 24 | - Inner electrode pre-resistor |
| 25 | - 2 nd electrode pre-resistor |
| 26 | - 3 rd electrode pre-resistor |
| 27 | - Outer electrode pre-resistor |
| 28 | - 1 st graph (two second electrodes, no pre-resistors, surface factor 1.7, total current 120 A) |
| 29 | - 2 nd graph (two second electrodes, no pre-resistors, surface factor 2.25, total current 120 A) |
| 30 | - 3 rd graph (four second electrodes, no pre-resistors, surface factor 2.25, total current 120 A) |
| 31 | - 4 th graph (four second electrodes, pre-resistors, surface factor 2.25, total current 120 A) |
| 32 | - 5 th graph (four second electrodes, pre-resis- |

- tors, surface factor 2.25, total current 240 A)
- 33 - Second electrolysis device
 - 34 - First current source
 - 35 - Second current source
 - 36 - Inner electrode current feeder bar
 - 37 - 2nd electrode current feeder bar
 - 38 - 3rd electrode current feeder bar
 - 39 - Outer electrode current feeder bar
 - 40 - Electrical contact device
 - 41 - Mantle
 - 42 - Bushing
 - 43 - Bolt
 - 44 - Nut
 - 45 - Aperture
 - 46 - Bolt head
 - 47a-c - Spacers

Claims

1. Device for conducting an electrolytic process, comprising:

reactor walls (6,7) defining a space (8) for accommodating an electrolyte;
 an electrode system (9), arranged in the space (8) and comprising at least one first electrode (10) and an array of second electrodes (11-14), wherein each second electrode (11-14) surrounds the at least one first electrodes (10) and has an inward-facing major surface, an outward-facing major surface and at least one interconnect to the major surfaces,
 wherein successive second electrodes (11-14) from an inner second electrode (11) to an outer second electrode (14) surround the at least one first electrode (10) at successively larger distances;
 at least one current source (18;34,35); and
 a current feeder arrangement providing a respective current path between each interconnect and one of the at least one current sources (18;34,35),
 wherein the at least one current sources (18;34,35) are connected to the electrode system (9) such that the at least one first electrodes (10) have an opposite polarity to that of the second electrodes (11-14) and current can flow between the at least one first electrodes (10) and at least one of the major surfaces of each second electrode (11-14) through the electrolyte, in use,
characterised in that
 the current feeder arrangement and the at least one current sources (18;34,35) are configured to establish potentials at the interconnects of the inner second electrode (11) that differ from the potentials at the interconnects of at least one second electrode (12-14) other than the inner second electrode (11) by being closer to that of

the at least one first electrodes (10).

2. Device according to claim 1,

wherein the current feeder arrangement provides current paths between a particular one of the current sources (18;35) and the interconnects of a proximal set of at least one of the second electrodes (11-14) having a higher resistance than current paths provided between the same current source (18;35) and a distal set of at least one of the second electrodes (11-14), and
 wherein the proximal set is disjoint from the distal set and comprises second electrodes (11-14) surrounding the at least one first electrodes (10) at a shorter distance than second electrodes (11-14) in the distal set.

3. Device according to claim 1 or 2,

wherein the current feeder arrangement provides first current paths between a first one of the current sources (34,35) and a first set of at least one of the second electrodes (11-14) and second current paths between a second one of the current sources (34,35) and a second set of at least one of the second electrodes (11-14), wherein the first current paths are separate from the second current paths, and
 wherein the first set is disjoint from the second set and comprises second electrodes (11-14) surrounding the at least one first electrodes (10) at a shorter distance than second electrodes (11-14) in the second set.

4. Device according to any one of the preceding claims, wherein the second electrodes (11-14) are three or more, e.g. four, in number.

5. Device according to any one of the preceding claims, wherein the second electrodes (11-14) are liquid-pervious in a direction from the inward-facing major surface to the outward-facing major surface.

6. Device according to any one of the preceding claims, wherein at least one, e.g. each, of the second electrodes (11-14) comprises an electrically conducting mesh, e.g. an expanded metal mesh.

7. Device according to any one of the preceding claims, wherein the second electrodes (11-14) have an overall shape that is rotationally symmetrical, e.g. circle-cylindrical, over at least a majority of their dimension in axial direction with respect to an electrode system axis (16).

8. Device according to claim 7,

wherein the second electrodes (11-14) are arranged concentrically.

9. Device according to claim 7 or 8,
wherein the at least one first electrodes (10) are arranged rotationally symmetrically with respect to an axis essentially coinciding with the electrode system axis (16). 5
10. Device according to any one of the preceding claims, wherein successive second electrodes (11-14) in the array are separated from each other by at least one electrically insulating spacer (47a-c), e.g. at least one annular spacer. 10
11. Device according to any one of the preceding claims,
wherein the current feeder arrangement comprises at least one electrical contact device (40) in electrical contact with at least one of the second electrodes (11-14) and passing through at least one other of the second electrodes (11-14),
the electrical contacting device (40) comprising an electrically insulating mantle (41) preventing electrical contact between the at least one other second electrodes (11-14). 15 20 25
12. Device according to claim 11,
wherein at least one of the at least one electrical contact devices (40) comprises an electrically conducting bushing (42) on which the mantle (41) is arranged and a fastener, e.g. a bolt (43), extending through the bushing (42). 30
13. System for regenerating a processing solution by electrochemical oxidation of an ion species in the processing solution, comprising:
a device (3;33) according to any one of the preceding claims, wherein the at least one current sources (18;34,35) are arranged to operate the at least one first electrodes (10) as cathodes and the second electrodes (11-14) as anodes; and
at least one pump (1,5) for at least one of supplying the solution to and removing the solution from the space (8). 35 40 45
14. Method of regenerating a processing solution by electrochemical oxidation of an ion species in the processing solution using a device, e.g. a device according to any one of claims 1-12, comprising:
an electrode system (9) comprising at least one first electrode (10) and an array of second electrodes (11-14),
wherein each second electrode (11-14) sur- 50 55

rounds the at least one first electrodes (10) and has an inward-facing major surface, an outward-facing major surface and at least one interconnect to the major surfaces,
wherein successive second electrodes (11-14) from an inner second electrode (11) to an outer second electrode (14) surround the at least one first electrode (10) at successively larger distances; and
at least one current source (18;34,35) connected to the electrode system (9), the method comprising:

conveying the processing solution to a space (8) in which the electrode system (9) is arranged, and
causing current supplied by the at least one current source (18;34,35) to flow between the at least one first electrodes (10) and at least one of the major surfaces of each second electrode (11-14) through the processing solution,
wherein the at least one first electrodes (10) are operated as cathodes and the second electrodes (11-14) as anodes, **characterised by**
establishing potentials at the interconnects of the inner second electrode (11) that differ from the potentials at the interconnects of at least one second electrode (12-14) other than the inner second electrode (11) by being closer to that of the at least one first electrodes (10).

15. Method according to claim 14,
wherein the processing solution is an alkaline processing solution, e.g. an alkaline etchant. 35

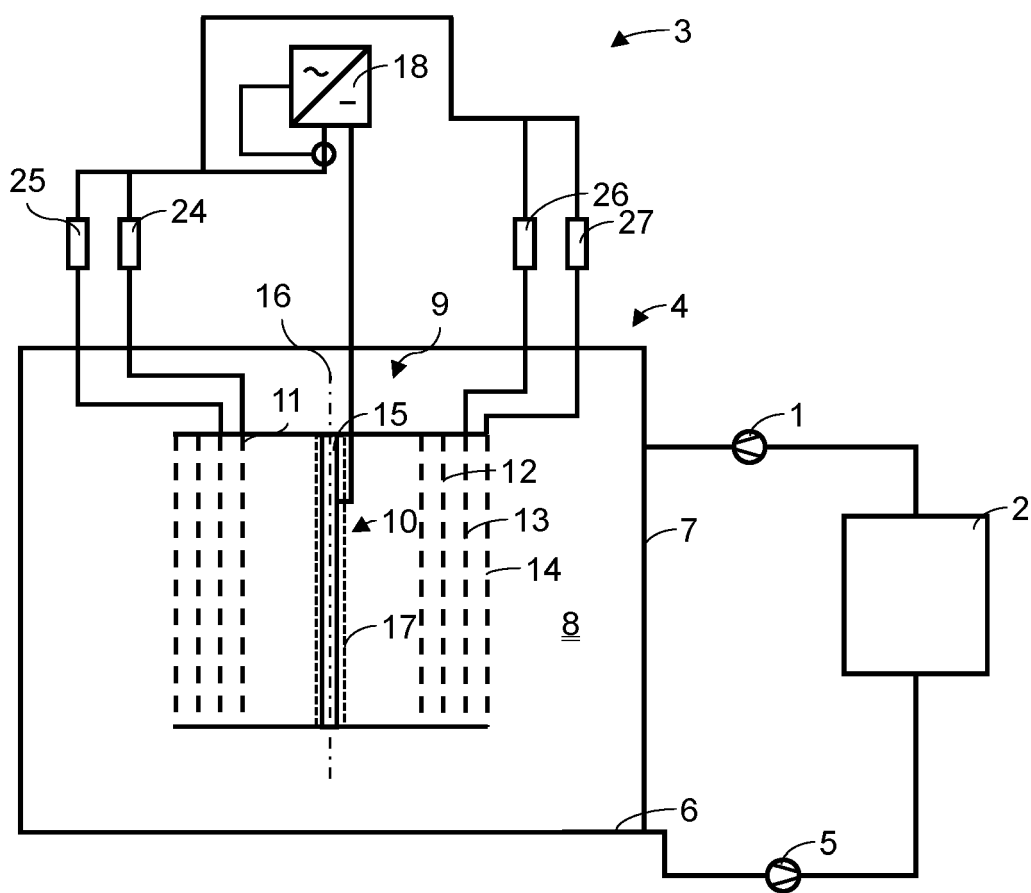


Fig. 1

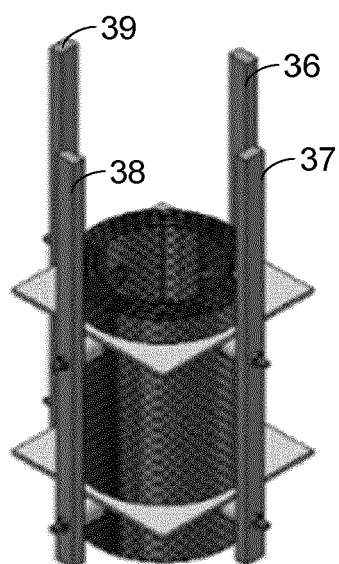


Fig. 2

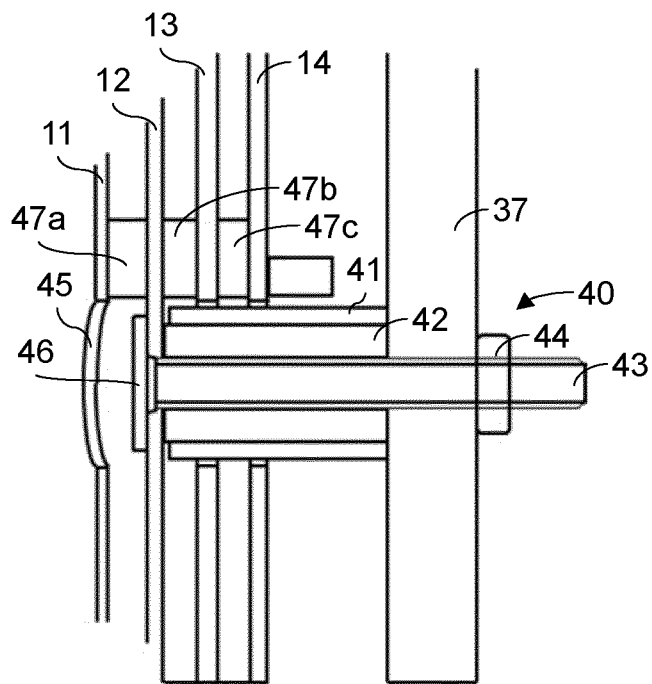


Fig. 3

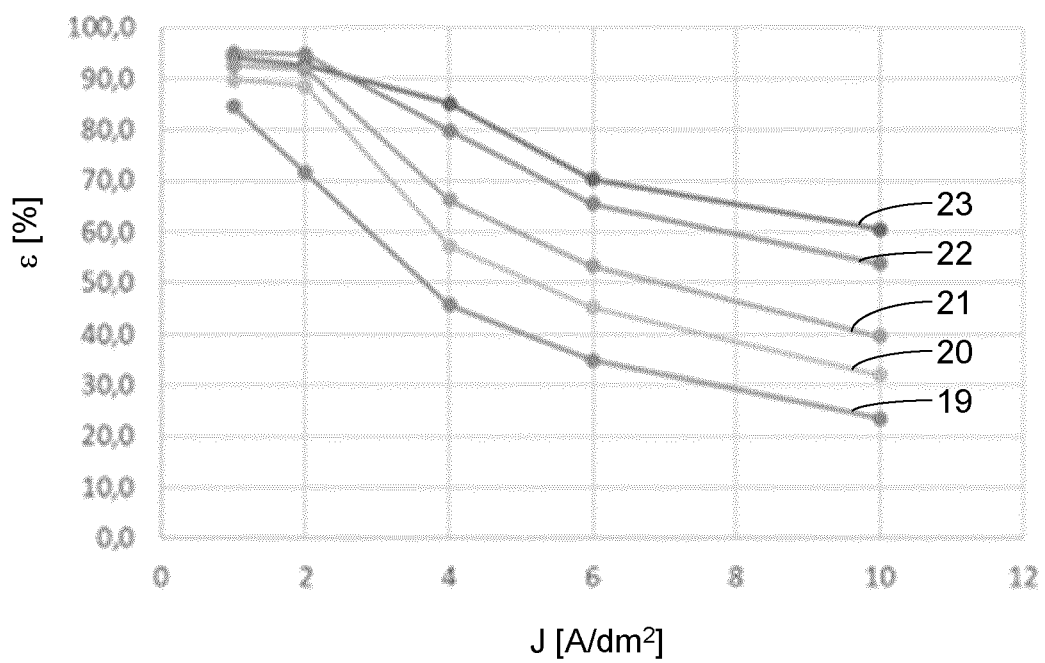


Fig. 4

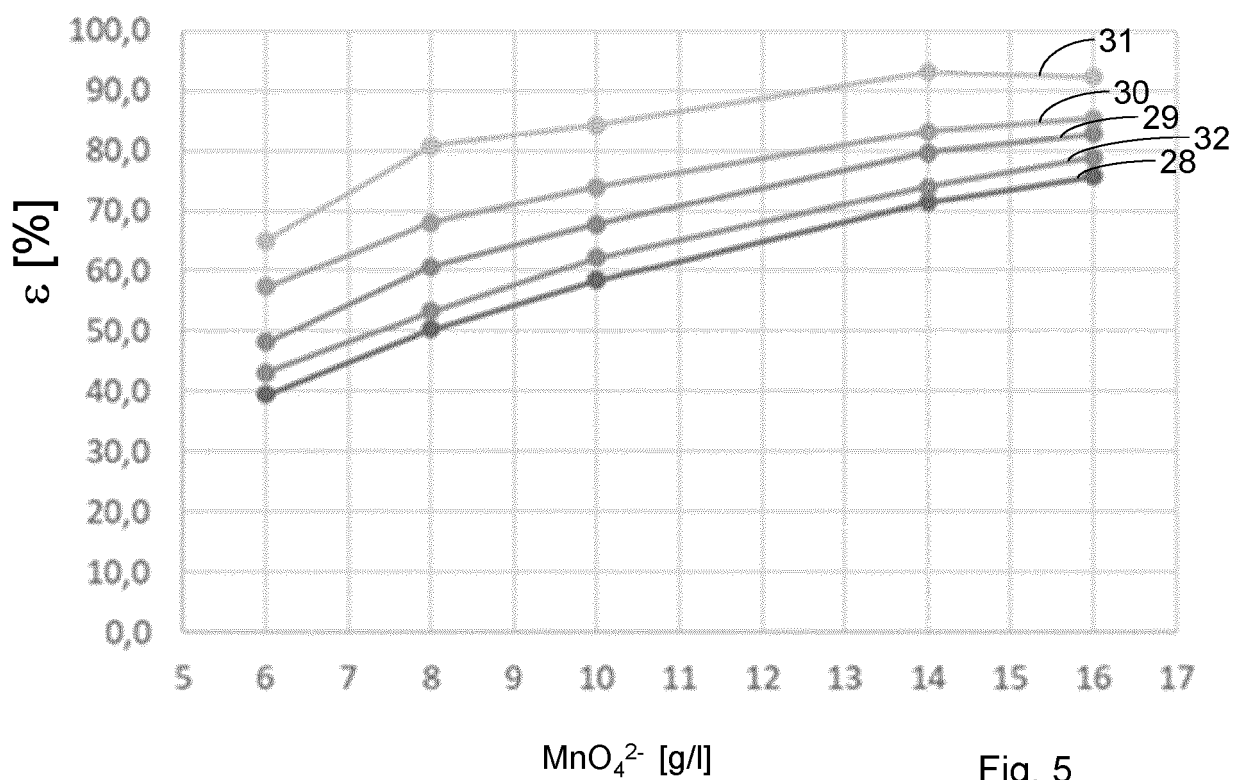


Fig. 5

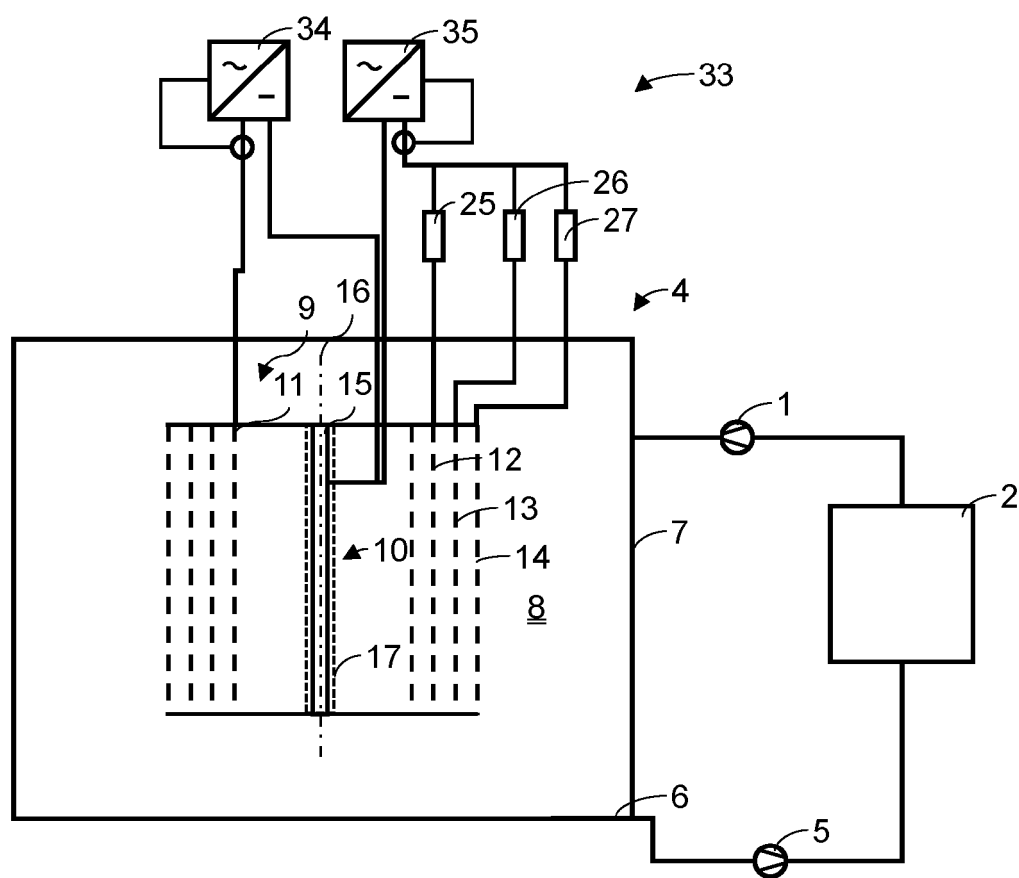


Fig. 6



EUROPEAN SEARCH REPORT

Application Number

EP 25 16 8470

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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Date of completion of the search			
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