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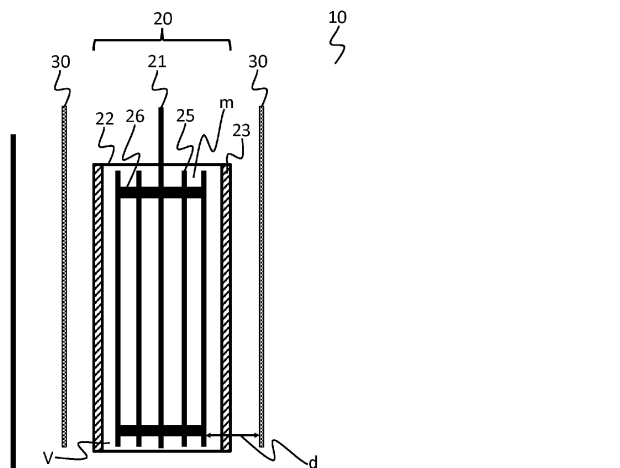
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(54) **METHOD FOR OXIDIZING MANGANESE SPECIES IN A TREATMENT DEVICE AND TREATMENT DEVICE**

(57) The present invention relates to a method for oxidizing manganese species in a treatment device (10) comprising at least one anode unit (20) and at least one cathode (30), wherein said unit comprises at least one anode (21) and is confined by a housing (22), the housing defining a free inner volume (V), wherein (i) the housing comprises at least one permeable barrier (23) and the at least one cathode is located outside the anode unit, or

(ii) the at least one anode unit comprises at least partly the at least one cathode, wherein the housing does not comprise a permeable barrier, characterized in that in (i) and (ii) the at least one anode and the at least one cathode have a distance (d) ranging from 0.5 mm to 100 mm. The invention furthermore refers to a respective treatment device (10).

Fig. 1



Description

Field of the Invention

[0001] The present invention relates to a method for oxidizing manganese species in a treatment device (10) comprising at least one anode unit (20) and at least one cathode (30), wherein said unit comprises at least one anode (21) and is confined by a housing (22), the housing defining a free inner volume (V), wherein (i) the housing comprises at least one permeable barrier (23) and the at least one cathode is located outside the anode unit, or (ii) the at least one anode unit comprises at least partly the at least one cathode, wherein the housing does not comprise a permeable barrier, characterized in that in (i) and (ii) the at least one anode and the at least one cathode have a distance (d) ranging from 0.5 mm to 100 mm. The invention furthermore refers to a respective treatment device (10).

Background of the Invention

[0002] Metallizing non-metallic substrates such as plastic substrates has a long history in modern technology. Typical applications are found in automotive industry as well as for sanitary articles.

[0003] However, making a non-metallic/non-conductive substrate receptive for a metal layer is demanding. Typically, a respective method starts with a surface modification of the substrate's surface, typically known as etching. Usually, a sensitive balance is required in order to ensure a sufficient surface roughening without causing too strong defects.

[0004] Many methods and etching compositions are known, including compositions comprising environmentally questionable chromium species, such as hexavalent chromium species (e.g. chromic acid). Although these compositions usually provide very strong and acceptable etching results, environmentally friendly alternatives are more and more demanded and to a certain extent already provided in the art. In many cases manganese-based etching compositions are utilized instead.

[0005] Typically, manganese-based etching compositions are either acidic or alkaline. However, acidic manganese-based etching compositions are inherently more susceptible to degradation, in particular permanganate-based etching compositions. As a result thereof, such etching compositions require a constant and comparatively high level of replenishment of active manganese species. Preferably, such etching compositions are continually recycled to maintain a comparatively constant level of active manganese species. This is typically either achieved by chemical oxidation or by applying an electrical current. Respective regeneration methods and devices, respectively, are known in the art.

[0006] CN 109628948 A refers to a regeneration device comprising a ceramic diaphragm for recycling a permanganate ion solution.

[0007] CN 1498291 A refers to an electrolytic regeneration treatment device for regenerating an etching treatment solution.

[0008] WO 2013/030098 A1 refers to a device for an at least partial regeneration of a treatment solution comprising permanganate, which is used for treatment and/or etching of plastic parts.

[0009] WO 01/90442 A1 refers to a cathode for an electrochemical arrangement for regeneration of permanganate etching solutions and a device for electrolytically regenerating permanganate etching solutions.

[0010] However, there is an ongoing demand to further increase the efficiency of respective regeneration methods and to provide more compact devices.

Objective of the present Invention

[0011] It is therefore the objective of the present invention to provide a method for oxidizing manganese species in a treatment device with high efficiency and a respective treatment device with a compact design. Most preferably it is the objective to provide a method and device, respectively, which are in particular suitable for treating (i.e. recycling) acidic manganese-based etching compositions, in particular comprising permanganate, with excellent efficiency.

Summary of the Invention

[0012] Above mentioned objectives are solved by a method for oxidizing manganese species in a treatment device (10), the method comprising the steps

(A) providing in the treatment device in a liquid at least one manganese species having an oxidation number below +7,

(B) providing in the treatment device at least one anode unit (20) and at least one cathode (30), wherein said unit comprises at least one anode (21) and is confined by a housing (22), the housing defining a free inner volume (V),

(C) applying a current to the at least one anode and the at least one cathode such that at least a portion of said at least one manganese species is anodically oxidized to a manganese species having the oxidation number +7, wherein

(i) the housing comprises at least one permeable barrier (23) and the at least one cathode is located outside the anode unit, or

(ii) the at least one anode unit comprises at least partly the at least one cathode, wherein the housing does not comprise a permeable barrier,

characterized in that in (i) and (ii) the at least one anode and the at least one cathode have a distance (d) ranging from 0.5 mm to 100 mm.

[0013] In the present invention, the treatment device (10) allows a very efficient anodic oxidation of manganese species having an oxidation number below +7. Furthermore, the at least one anode unit (20) allows a very compact design, which is the basis for the improved efficiency. As a result thereof, the present invention is very suitable for efficiently treating acidic manganese-based etching compositions because the volume needed in the treatment device is relatively low compared to the volume of a corresponding etching composition. For example, in commonly used techniques a volume in a respective treatment device is about identical to the volume of the utilized etching composition. In contrast, in the method of the present invention, the volume treated in the treatment device is significantly lower than the volume of the etching composition. Thus, the so-called dead volume has been significantly reduced compared to common methods and devices.

[0014] Preferred is a method of the present invention, wherein the liquid provided in step (A) has a volume of 50 vol.-% or less of a total liquid utilizing said liquid provided in step (A), preferably 40 vol.-% or less, most preferably 30 vol.-% or less.

[0015] In the context of the present invention it is essential that the at least one cathode is either outside the anode unit or comprised in the housing. In each case it denotes that the at least one cathode is (at least mainly) built around (in a sense of surrounding) the at least one anode. In other words, the at least one cathode at least mainly encircles or circulates the at least one anode, wherein this wording does not limit the ensemble to a circular shape. This essential anode/cathode arrangement can also be described as follows: referenced to the center point in the anode unit, the distance of the at least one anode to the center point is shorter than the corresponding distance of the corresponding at least one cathode. Thus, preferred is a method of the present invention, wherein the at least one anode is located more towards the center of the anode unit than the corresponding at least one cathode, preferably the at least one anode is centered in the anode unit.

Brief description of the Figures

[0016] All figures are schematic drawings of a treatment device (10) utilized in the method of the present invention, showing the principle of the present invention. They do not necessarily represent real size dimensions and ratios. A flow scheme as well as pipes and valves are not shown and omitted for the sake of simplicity.

Figure 1 shows a treatment device according to embodiment (i), wherein the at least one anode (21) and the at least one cathode (30) are vertically oriented and separated by at least one permeable barrier (23)

in the housing (22).

Figure 2 shows a treatment device according to embodiment (i), wherein the at least one anode (21) is horizontally oriented and separated by at least one permeable barrier (23) in the housing (22) from the at least one cathode (30).

Figure 3 shows a treatment device according to embodiment (ii), wherein the at least one anode (21) and the at least one cathode (30) are vertically oriented to each other and not separated by a permeable barrier (23). Instead, housing (22) at least partly comprises the at least one cathode (30) and forming a plurality of cathode spots (31) comprising a first set of cathode spots (32) and a second set of cathode spots (33).

Detailed Description of the Invention

[0017] In the method of the present invention, two alternative embodiments are present, (i) and (ii), wherein embodiment (i) comprises at least one permeable barrier and embodiment (ii) is free thereof. In embodiment (i), due to the presence of the at least one permeable barrier, a catholyte is formed/present around the at least one cathode and an anolyte around the at least one anode, respectively. They are permeably separated from each other by the at least one permeable barrier.

[0018] It is an additional advantage of the method of the present invention to have a high measure of flexibility. The treatment device utilized in the method of the present invention can be used for both embodiments without investing high efforts to switch between embodiment (i) and (ii).

[0019] According to embodiment (i), the housing comprises at least one permeable barrier and the at least one cathode is located outside the anode unit. This embodiment is preferably also referred to as the membrane-approach (if the at least one permeable barrier comprises a membrane). It denotes that the at least one cathode is not directly part of the anode unit or its housing but is located (i.e. positioned, arranged) outside the anode unit (but within the treatment device). However, by means of the permeable barrier the current can flow despite the housing such that anodically the at least one manganese species is oxidized to a manganese species having the oxidation number +7. Preferably, the liquid is (i.e. corresponds to) the anolyte.

[0020] In embodiment (ii) no distinction between a catholyte and an anolyte is present or can be made due to the absence of a respective permeable barrier and due to the fact that the housing comprises at least partly the at least one cathode.

[0021] Generally, the maximum volume of the liquid (i.e. preferably the anolyte present in embodiment (i)) basically corresponds to the free inner volume (V). Most preferably, the liquid is an etching composition, i.e. pref-

erably means is provided as an utilized etching composition in step (A) and returned as refreshed/recycled etching composition after step (C).

[0022] Preferably (irrespective of embodiment (i) or (ii)), the free inner volume (V) corresponds to the total inner housing volume subtracted by at least the volume (i.e. the tare volume) of the at least one anode (including e.g. its parts for installation) which is located inside the housing and, thus, is reducing the total inner housing volume. In other words, the free inner volume (V) is more preferably the volume that the liquid can maximally occupy within the at least one anode unit.

[0023] Preferred is a method of the present invention, wherein the catholyte comprises an inorganic acid, preferably phosphoric acid, more preferably 20 wt.-% to 90 wt.-% phosphoric acid, even more preferably 30 wt.-% to 80 wt.-%, most preferably 40 wt.-% to 70 wt.-% phosphoric acid.

[0024] In embodiment (i) all manganese species are preferably separated from the at least one cathode. This preferably means that the permeable barrier is basically not permeable for negatively charged or neutral manganese species.

[0025] Preferred is a method of the present invention, wherein the at least one permeable barrier is an ion-selective permeable barrier, preferably an ion-selective permeable membrane.

[0026] Preferred is a method of the present invention, wherein the at least one permeable barrier is a cation-selective permeable barrier, preferably a cation-selective permeable membrane. Thus, most preferably only cations are permeable.

[0027] Preferred is a method of the present invention, wherein the at least one permeable barrier is not mineral. Preferred is a method of the present invention, wherein the at least one permeable barrier is essentially free of, preferably does not comprise, a ceramic.

[0028] More preferred is a method of the present invention, wherein the at least one permeable barrier is organic. More preferred is a method of the present invention, wherein the at least one permeable barrier is organic and comprises fluorine (preferably is fluorinated), most preferably is organic and perfluorinated. Most preferred, the at least one permeable barrier is a Nafion-type-membrane, although the at last one membrane is not particularly limited to this particular brand. Thus, the aforementioned preferably applies likewise to the preferred ion-selective (preferably cation-selective) permeable barrier, preferably the ion-selective (preferably cation-selective) permeable membrane. Membranes, preferably said organic membranes, are very thin and therefore positively contribute to the comparatively short distance (d), and, thus, to the compact design of the at least one anode unit.

[0029] In the context of the present invention, it is an advantage that the total area of permeable barrier can be kept comparatively low due to the very compact design.

[0030] In step (C) of the method of the present invention a current is applied, preferably an electrical current. This current and the electrical field related thereto typically affect the migration direction of the respective ions present in the liquid. As a result, negatively charged manganese species are forced to migrate to the at least one anode.

[0031] The permeable barrier, present in embodiment (i), in combination with said current typically brings about that negatively charged manganese species are even more fully prevented from contacting the at least one cathode. In the absence of the current, the permeable barrier preferably significantly suppresses/reduces the mixing of anolyte and catholyte with each other (preferably a transport of anions into the catholyte). This preferably means that the permeable barrier, most preferably the cation-selective permeable membrane, suppresses/avoids an anion transport from the anolyte into the catholyte. As a result, the transport of negatively charged manganese species, e.g. MnO_4^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- is significantly suppressed, without and even more with the current. Furthermore, also a transport of particulate, non-charged MnO_2 is preferably avoided or at least significantly suppressed. In contrast, the permeable barrier freely and primarily allows transport/migration of water molecules, preferably of water and hydrogen ions.

[0032] Preferred is a method of the present invention, wherein in (ii) the at least one cathode is at least partly integrated in the housing, preferably is at least partly penetrating the housing from the outside into the inside towards the at least one anode.

[0033] According to embodiment (ii), the housing comprises (preferably integrates) at least partly the at least one cathode, wherein the housing does not comprise (i.e. is free of) a permeable barrier. This embodiment is preferably also referred to as the membrane-free approach. Preferably, the entire housing does not comprise a permeable barrier. In this embodiment, the at least one cathode is, preferably at least partly, integrated in the housing. This also means that the at least one cathode (preferably at least partly) is preferably itself part of the housing and is therefore (preferably at least partly) preferably confining the at least one anode unit as part of the housing. In addition, the at least one cathode (preferably at least partly) is comprised (preferably integrated) in the housing and preferably at least partly exposes cathodic areas into the inside of the housing. As already mentioned, in this embodiment preferably no distinct catholyte and anolyte are formed but rather only the liquid. In this embodiment, preferably all manganese species are basically in contact with the at least one anode and the at least one cathode. Thus, preferred is a method of the present invention according to embodiment (ii), wherein in step (C) each manganese species is at least partly in direct contact with the at least one cathode. However, this is less preferred from the perspective of current efficiency. Own experiments have shown that, compared to a method utilizing a per-

meable barrier (i.e. embodiment (i)) a lower current efficiency was obtained due to a basic level of undesired cathodic side reactions leading to an undesired breakdown of the manganese species having the oxidation number +7. However, own experiments have also shown that embodiment (ii) provides a great advantage if the liquid comprises besides manganese species further metal ions such as silver ions. In this embodiment an undesired cathodic silver deposition can be prevented or at least reversed such that silver (or possibly other metal ions besides manganese) remains permanently dissolved or is re-dissolved at least in certain time intervals.

[0034] Preferred is a method of the present invention, wherein (d) is ranging from 1 mm to 90 mm, preferably from 2 mm to 80 mm, more preferably from 3 mm to 70 mm, even more preferably from 4 mm to 60 mm, most preferably from 5 mm to 50 mm.

[0035] The aforementioned regarding (d) is generally preferred in the method of the present invention.

[0036] Generally preferred is a method of the present invention, wherein the distance (d) is defined as the shortest distance between the at least one anode and the closest (preferably corresponding) at least one cathode. In other words, the distance (d) is preferably the shortest outer distance between the at least one anode and the closest (preferably corresponding) at least one cathode. The term "outer" preferably refers to the outermost of the at least one anode directly facing towards the outermost of the closest at least one cathode. Most preferred, the distance (d) is the shortest average outer distance between the at least one anode and the closest (preferably corresponding) at least one cathode. This is preferably the case if the at least one anode and the at least one cathode have a parallel alignment towards each other. For a supportive understanding, reference is made to Fig. 1 to 3.

[0037] Particularly in embodiment (i), a method of the present invention is preferred, wherein (d) is ranging from 9 mm to 70 mm, preferably from 10 mm to 60 mm, more preferably from 11 mm to 50 mm, even more preferably from 12 mm to 30 mm, most preferably from 13 mm to 20 mm. In this embodiment the minimum of distance (d) is typically larger compared to embodiment (ii) because the at least one cathode is located outside the anode unit (i.e. outside the housing) such that the housing is in between the at least one cathode and the at least one anode. Thus, preferred is a method of the present invention, wherein the distance (d) has a minimum distance with the proviso that the minimum distance in (i) is higher compared to the minimum distance (d) in embodiment (ii). Furthermore, in embodiment (i), the at least one permeable barrier is between the at least one anode and the at least one cathode without getting in direct contact to said anode and cathode. However, the thickness of the permeable barrier is preferably neglectable and therefore does not substantially contribute to the distance (d).

[0038] Particularly in embodiment (ii), a method of the present invention is preferred, wherein (d) is ranging from

1 mm to 70 mm, preferably from 2 mm to 60 mm, more preferably from 3 mm to 50 mm, even more preferably from 4 mm to 30 mm, most preferably from 5 mm to 20 mm. In this embodiment typically a comparatively low distance (d) is maintained because the housing comprises at least partly the at least one cathode. Thus, the minimum of distance (d) is comparatively low. This has the advantage that less voltage is needed compared to embodiment (i), which preferably has a higher minimum of distance (d).

[0039] Preferred is a method of the present invention, wherein the at least one anode comprises a layer stack (25) of anode layers, preferably of 3 or more than 3 anode layers, more preferably the layer stack comprises 3 to 300 anode layers, even more preferably 4 to 200 anode layers, yet even more preferably 6 to 100 anode layers, most preferably 8 to 60 anode layers, even most preferably 9 to 30 anode layers.

[0040] In the context of the present invention it was very surprising to see that an anode having a very compact design, e.g. designed as a layer stack of multiple anode layers, provides a sufficiently high current efficiency/turnover, most preferably if the space between individual anode segments is very small; for example if the number of individual anode layers in a layer stack is comparatively high and therefore the space between them comparatively small. It was commonly believed that under such circumstances a very high and detrimental shielding effect occurs, e.g. in particular the more individual anode segments are consecutively placed towards the at least one cathode. However, although such a shielding effect indeed occurs, the effect is surprisingly low and can be surprisingly tolerated in favor of the great benefit to create a comparatively large total effective anode surface area. It was surprising that the electrical field has a penetration depth causing sufficient efficiency and turnover although such an anode is assumed to provide a Faraday cage-like barrier. In other words, such anodes surprisingly allow an extremely compact and dense anode architecture and therefore comparatively small treatment devices. This in turn allows to minimize the free inner volume (V).

[0041] In such a preferred layer stack, the layer stack preferably comprises at least one inner anode layer and at least one outer anode layer. The at least one inner anode layer is either facing another inner anode layer or at least on one side the at least one outer layer. However, if the layer stack comprises exactly two anode layers, they are at the same time the at least one outer anode layer. This likewise applies if the at least one anode comprises or is a single anode layer.

[0042] In some cases a method of the present invention is preferred, wherein the at least one anode comprises or is a single anode layer providing also a huge total effective anode surface area, preferably equivalent to the huge total effective anode surface area obtained by means of the preferred layer stack.

[0043] As already mentioned, preferred is a method of

the present invention, wherein the distance (d) is defined as the shortest distance between the at least one anode and the closest (preferably corresponding) at least one cathode. More preferred is a method of the present invention, wherein the distance (d) is defined as the shortest distance between an outermost anode layer of a layer stack and the closest (preferably corresponding) at least one cathode.

[0044] Generally preferred, distance (d) is a constant distance. This preferably means, (d) denotes a distance between the at least one anode and the at least one cathode, which are aligned to each other in parallel.

[0045] In the method of the present invention the at least one anode is preferably oriented horizontally or vertically (compare Fig. 1 and 2). More preferred is a method of the present invention, wherein the at least one anode is vertically oriented (compare Fig. 1). This most preferably applies to the anode layers of a layer stack (25). However, in some other cases a method of the present invention is preferred, wherein the at least one anode is horizontally oriented (compare Fig. 2). This most preferably also applies to the anode layers in a layer stack (25). Own experiments have shown that a vertical orientation provides in many cases an improved current efficiency and is therefore preferred. It is assumed that in such a case the liquid has an improved perfusion through the at least one anode unit and formed gas can easily escape without adsorbing on an anode surface. Furthermore, this approach is also related to lower costs.

[0046] Preferred is a method of the present invention, wherein in embodiment (i) the at least one anode comprises a layer stack (25) of 2 to 100 anode layers, preferably of 3 to 80 anode layers, more preferably of 4 to 60 anode layers, even more preferably of 5 to 40 anode layers, most preferably of 6 to 30 anode layers.

[0047] Preferred is a method of the present invention, wherein in embodiment (ii) the at least one anode comprises a layer stack (25) of 2 to 300 anode layers, preferably of 5 to 260 anode layers, more preferably of 7 to 220 anode layers, even more preferably of 9 to 170 anode layers, most preferably of 12 to 130 anode layers. However, in many cases the number of anode layers is preferably as defined above for embodiment (i).

[0048] Preferred is a method of the present invention, wherein in the layer stack the anode layers have a distance (m) to each other ranging from 0.5 mm to 20 mm, preferably from 1 mm to 15 mm, more preferably from 2 mm to 12 mm, even more preferably from 3 mm to 10 mm, most preferably from 4 mm to 9 mm.

[0049] Preferably, the distance (m) is fixed by means of a spacer (26). More preferably, (m) is (essentially) constant, most preferably is (essentially) constant between all anode layers in the layer stack.

[0050] In some cases, a very preferred distance (m) is ranging from 1 mm to 6 mm, preferably from 1.5 mm to 4 mm.

[0051] Preferred is a method of the present invention, wherein the at least one anode, preferably the layer stack,

comprises a sheet, a mesh, a woven web, and/or an expanded metal (i.e. a metal lath).

[0052] In the context of the present invention it is generally preferred to provide the at least one anode with a comparatively high total effective anode surface area. The aforementioned forms of the at least one anode (most preferably the layer stack) preferably fulfill this very desired and preferred characteristic. In many cases a method of the present invention is preferred, wherein the at least one anode comprises an expanded metal (metal laths; also called "Streckmetall"). Most preferably, the layer stack (25) comprises expanded metal as anode layers.

[0053] Preferred is a method of the present invention, wherein the at least one anode, preferably the individual anode layer in the layer stack, has a surface factor of 1 or more, preferably of 1.4 or more, even more preferably of 1.7 or more, yet even more preferably of 2 or more, most preferably of 2.1 or more, even most preferably of 2.2 or more.

[0054] In the context of the present invention, the surface factor denotes a parameter defining the total effective surface area per geometric area.

[0055] For example, a plate, i.e. a surface, geometrically of 1 m² typically has a surface factor of 2 (for the sake of simplicity, the area of the cutting edges is neglected), which results in a total effective surface area of 2 m² (including front side and back side). As a result, the surface factor is without any dimensions/units. A surface factor below or even above 2 is typically obtained if e.g. a plate has holes and a mesh has openings, respectively, in a defined number and with defined dimensions. However, the surface factor of commercially available meshes today is typically not exceeding 2.5.

[0056] In the method of the present invention it is in many cases preferred to obtain a comparatively high effective anode surface area, preferably by utilizing a layer stack. On the other hand, a shielding effect needs to be as low as possible to achieve the best possible efficiency.

[0057] In the context of the present invention, the surface factor as defined above most preferably applies to the individual anode layers in a layer stack.

[0058] Also preferred is a method of the present invention, wherein the at least one anode is, preferably additionally to anodes mentioned already above, selected from the group consisting of 3D-printed anodes, woven fabric anodes, foam anodes, and packed bed anodes. Typically, such anodes have a comparatively high effective surface area per volume, most preferably of 6 m²/L or more, based on the total volume of the at least one anode. This is also known as surface density, which denotes the total effective surface area per geometric volume.

[0059] Preferred is a method of the present invention, wherein the surface density is in a range from 6 m²/L to 100 m²/L, preferably from 8 m²/L to 70 m²/L, more preferably from 10 m²/L to 50 m²/L, even more preferably from 12 m²/L to 40 m²/L, yet even more preferably from

14 m²/L to 30 m²/L, most preferably from 16 m²/L to 22 m²/L.

[0060] Preferred is a method of the present invention, wherein the woven fabric anodes comprise woven metallic wires and/or woven metallized filaments.

[0061] Preferred is a method of the present invention, wherein the woven fabric anodes comprise flat woven fabric anodes and/or pile fabric anodes.

[0062] Preferred is a method of the present invention, wherein the 3D-printed anodes comprise 3D-printed lattice anodes and/or 3D-printed lamella anodes.

[0063] Preferred is a method of the present invention, wherein the foam anodes comprise a sponge anode.

[0064] Preferred is a method of the present invention, wherein the packed bed anodes comprise a package compartment selected from the group consisting of raschig ring, lessing ring, pall ring, bialecki ring, dixon ring, net balls, and Hex-X compartments.

[0065] Preferred is a method of the present invention, wherein the at least one anode comprises platinum, titanium, niobium, lead, gold, alloys comprising at least one thereof, oxides thereof, and/or mixtures thereof; preferably at least one of platinum, titanium, and gold.

[0066] As a matter of fact, not all anode materials are suitable for the purpose achieved with the method of the present invention. Since the liquid is preferably highly acidic and because of the strong oxidizing character of manganese species, the at least one anode (and its respective material) must be carefully selected. A minimum requirement is that a respective material is (electro-)chemically inert towards the liquid. Typically, the aforementioned anodes are resistant, at least for a certain time. Very preferred is a method of the present invention, wherein the at least one anode comprises a platinized anode and/or a platinum anode, preferably a platinized titanium anode, and/or a platinized niobium anode.

[0067] In some cases, a method of the present invention is preferred, wherein the at least one anode comprises lead and/or lead alloys. Preferred lead alloys comprise tin and/or silver as alloying elements. However, own experiments have shown that an excellent efficiency is obtained with at least one anode comprising platinum, preferably the at least one anode comprises a platinized anode and/or a platinum anode. This preferably applies likewise to embodiment (i) and (ii), respectively.

[0068] Generally preferred is a method of the present invention, wherein the at least one cathode comprises titanium, platinum, niobium, lead, alloys comprising at least one thereof, oxides thereof, stainless steel, and/or mixtures thereof. Typically preferred is a method of the present invention, wherein the at least one cathode is of a wide variety of materials as long as a respective material is preferably acid resistant, sufficiently stable against hydrogen embrittlement, and/or chemically resistant to the liquid (depending on the utilized embodiment). In some cases, a method of the present invention is preferred, wherein the at least one cathode is identical to the at least one anode, preferably in embodiment (ii).

However, in other cases, preferably, the at least one cathode is different from the at least one anode, preferably in embodiment (i) but also in cases of embodiment (ii).

[0069] Preferred is a method of the present invention, wherein in embodiment (i) the at least one cathode comprises platinum, titanium, lead, nickel, alloys comprising at least one thereof, oxides thereof, stainless steel, and/or mixtures thereof. Most preferred is stainless steel; it shows a very desired resistance in phosphoric acid, which is the most preferred catholyte in this embodiment. Furthermore, own experiments have shown that the cathodic current protects the at least one cathode such that even less resistant materials can be utilized. This general principle of cathodic protection preferably also applies to embodiment (ii).

[0070] However, in embodiment (ii) preferably an electro-chemically very inert cathode material is needed. In such a case it is preferred that the at least one cathode comprises titanium, platinum, niobium, lead, alloys comprising at least one thereof, oxides thereof, stainless steel, and/or mixtures thereof. In some cases, a method of the present invention is preferred, wherein the at least one cathode comprises a platinized cathode and/or a platinum cathode, preferably a platinized titanium cathode, and/or a platinized niobium cathode. In other cases, a method of the present invention is preferred, wherein the at least one cathode comprise stainless steel. Stainless steel is in some cases preferably used due to the cathodic protection and therefore can be used in embodiment (ii) according to the method of the present invention.

[0071] Generally preferred is a method of the present invention, wherein the at least one cathode comprises one cathode layer or a layer stack of two, three or more than three cathode layers, preferably of two cathode layers. A cathode layer stack, preferably of two cathode layers, is more preferred in embodiment (ii) of the method of the present invention.

[0072] More preferred is a method of the present invention, wherein the cathode layers in the layer stack are electrically separated from each other. This preferably allows that each cathode layer has a distinct current source.

[0073] Generally preferred is a method of the present invention, wherein the at least one cathode comprises a sheet, a mesh, a woven web, and/or an expanded metal. This most preferably applies to embodiment (i).

[0074] More preferred is a method of the present invention, wherein the at least one cathode and the at least one anode are vertically oriented, preferably vertically oriented and in parallel to each other.

[0075] Preferred is a method of the present invention, wherein the at least one anode provides a total effective anode surface area A_1 and the at least one cathode a total effective cathode surface area A_2 , wherein A_1 is larger than A_2 .

[0076] In the context of the present invention, "total effective surface area" refers to the area available for

participation in electrochemical redox-reactions.

[0077] Preferred is a method of the present invention, wherein in embodiment (ii) the at least one cathode is at least partly (preferably partly) penetrating the housing from the outside into the inside such that a plurality of cathode spots (31) are exposed into the inside towards the at least one anode and A_2 is formed by said spots. Such spots effectively minimize the total effective cathode surface area if only these spots are exposed into the anode unit towards the at least one anode.

[0078] Preferably, the spots are equally distributed over at least a part of the housing. In this way, the A_2 is homogeneously distributed within the anode unit.

[0079] In some cases, a method of the present invention is preferred, wherein the plurality of cathode spots is planar with the inside of the housing.

[0080] More preferred is a method of the present invention, wherein the at least one cathode, which is at least partly (preferably partly) penetrating the housing from the outside into the inside towards the at least one anode comprises a layer stack of at least two cathode layers (compare Fig. 3).

[0081] Most preferred is a method of the present invention, wherein the plurality of cathode spots is forming a first and a second set of cathode spots (32 and 33, respectively, compare Fig. 3), each set preferably having its own current. This preferably means that the first and second set are electrically separated from each other. This preferably furthermore allows to temporarily switch off one of the sets, to run both with different currents, or to reverse the current in one of the sets compared to the other set. Own experiments have shown that this is of great benefit to avoid deposition of e.g. metallic silver if silver ions are utilized in the liquid.

[0082] Preferred is a method of the present invention, wherein $A_1 : A_2$ is ranging from 5:1 to 100:1, preferably from 10:1 to 85:1, more preferably from 15:1 to 70:1, even more preferably from 20:1 to 60:1, most preferably from 30:1 to 50:1.

[0083] This is generally preferred in the method of the present invention.

[0084] More preferably, in particular in embodiment (i), a particular consideration to a certain ratio is not necessarily needed as long as A_1 is larger than A_2 . Preferably, $A_1 : A_2$ is ranging from 5:1 to 30:1, preferably from 6:1 to 25:1, more preferably from 7:1 to 20:1.

[0085] However, in embodiment (ii) a method of the present invention is preferred, wherein $A_1 : A_2$ is at least 10:1, preferably at least 20:1, more preferably at least 30:1, most preferably at least 40:1. Preferred is a method of the present invention, wherein $A_1 : A_2$ is ranging from 10:1 to 100:1, preferably from 20:1 to 70:1, more preferably from 30:1 to 50:1, most preferably from 35:1 to 45:1. This is preferably required to perform embodiment (ii) with a preferably high current efficiency and to sufficiently suppress undesired cathodic side-reactions breaking down desired manganese species. Furthermore, an optimal balance between current efficiency and energy consumption is provided.

sumption is provided.

[0086] Preferred is a method of the present invention, wherein A_1 is ranging from 10 dm²/dm³ to 100 dm²/dm³, based on the free inner volume (V), preferably from 15 dm²/dm³ to 85 dm²/dm³, more preferably from 20 dm²/dm³ to 70 dm²/dm³, even more preferably from 25 dm²/dm³ to 60 dm²/dm³, most preferably from 30 dm²/dm³ to 50 dm²/dm³.

[0087] In the context of the present invention the aforementioned parameter denotes an anode density (i.e. total effective anode surface area per dm³ of the free inner volume of the at least one anode unit). In the method of the present invention it is desired to achieve comparatively high anode densities to efficiently oxidize the manganese species having an oxidation number below +7. In fact, the aforementioned anode densities, in particular the preferred and most preferred ones, are typically considered as high. It is a parameter to characterize the compact and dense packing of the at least one anode in the at least one anode unit. This principle preferably applies to embodiment (i) as well as to embodiment (ii).

[0088] Preferred is a method of the present invention, wherein the treatment device and/or the at least one anode unit (preferably the at least one anode unit) has at least one inner surface comprising or consisting of a fluorinated plastic, preferably polyvinylidene fluoride (PVDF) and/or polytetrafluoroethylene (PTFE).

[0089] Own experiments have shown that such materials have the needed chemical resistance to prevent harm and damage (e.g. by means of dissolution and/or etching) to the treatment device and the at least one anode unit, respectively, coming from the harsh conditions of the liquid.

[0090] As mentioned above, in step (A) the at least one manganese species having an oxidation number below +7 is provided in a liquid.

[0091] Preferred is a method of the present invention, wherein in step (A) the liquid is obtained from an etching compartment for etching a non-metallic substrate, preferably a plastic substrate. As mentioned above, the liquid is preferably an etching composition, most preferably after being in contact with a non-metallic substrate, preferably a plastic substrate.

[0092] Preferred is a method of the present invention, wherein in step (A) in said liquid the at least one manganese species having an oxidation number below +7 comprises manganese species having an oxidation number of +IV, preferably MnO₂. More preferably, manganese species having an oxidation number of +IV constitutes more than 50 mol-% of all manganese species in the liquid prior to step (C), preferably at least 75 mol-%. Preferably, the MnO₂ is particulate, preferably is present as colloidal particles. This preferably includes optional agglomerates thereof.

[0093] Preferred is a method of the present invention, wherein the plastic substrate comprises acrylonitrile butadiene styrene (ABS), acrylonitrile butadiene styrene - polycarbonate (ABS-PC), polypropylene (PP), poly-

amide (PA), polyurethane (PU), polyepoxide (PE), polyacrylate, polyetherimide (PEI), a polyetherketone (PEK), mixtures thereof, and/or composites thereof; preferably acrylonitrile butadiene styrene (ABS), acrylonitrile butadiene styrene - polycarbonate (ABS-PC), polyamide (PA), polyurethane (PU), polyepoxides (PE), polyacrylate, mixtures thereof, and/or composites thereof. Such plastic substrates are typically used in decorative applications such as automotive parts, in particular ABS and ABS-PC.

[0094] Preferred is a method of the present invention, wherein in step (C) the manganese species having the oxidation number +7 comprises permanganate ions, most preferably are permanganate ions. Typically, etching a plastic substrate with e.g. permanganate reduces permanganate to manganese species with lower oxidation numbers while the material of the plastic is at least partly oxidized.

[0095] Preferred is a method of the present invention, wherein in step (A) the at least one manganese species having an oxidation number below +7 have a total concentration ranging from 0.1 g/L to 4 g/L, based on the element manganese and the total volume of the liquid, preferably ranging from 0.2 g/L to 3 g/L, more preferably ranging from 0.3 g/L to 2 g/L, most preferably 0.4 g/L to 1.5 g/L.

[0096] In step (C) of the method of the present invention a current is applied to anodically oxidize at least a portion of manganese species having an oxidation number below +7.

[0097] Preferred is a method of the present invention, wherein at least a portion of the manganese species anodically oxidized in step (C) to a manganese species having the oxidation number +7 is transferred back into the etching compartment for etching a plastic substrate.

[0098] Most preferably, the method of the present invention is a recycling method for permanganate ions. In this context "recycling" refers to a re-oxidation of (preferably already utilized) manganese species to the oxidation number +7 with subsequent re-utilization thereof for etching. A method of the present invention is preferred, wherein the method is carried out continually.

[0099] In some cases, a method of the present invention is preferred, wherein the treatment device is external relative to the etching compartment. This means that the treatment device is outside the etching compartment. This is typically preferred. However, in other cases a method of the present invention is preferred, wherein the treatment device is at least partly integrated into the etching compartment. This preferably means that the treatment device is internal relative to the etching compartment.

[0100] Preferred is a method of the present invention, wherein in step (C) the current has a current density ranging from 0.1 A/dm² to 10 A/dm², preferably from 0.2 A/dm² to 8 A/dm², more preferably from 0.3 A/dm² to 6 A/dm², even more preferably from 0.4 A/dm² to 4 A/dm², yet even more preferably from 0.5 A/dm² to 2.8 A/dm²,

most preferably from 0.6 A/dm² to 1.5 A/dm². This is the anodic current density, preferably based on the effective anode surface area. Preferably, the anodic current density is comparatively low in order to avoid/reduce undesired anodic oxygen gas production, which in turn reduces the current efficiency.

[0101] Preferred is a method of the present invention, wherein in step (C) the at least one cathode has a cathodic current density ranging from 2 A/dm² to 70 A/dm², preferably from 3 A/dm² to 60 A/dm², more preferably from 4 A/dm² to 50 A/dm², even more preferably from 5 A/dm² to 40 A/dm², yet even more preferably from 6 A/dm² to 30 A/dm², most preferably from 7 A/dm² to 20 A/dm². This is the cathodic current density. In contrast to a comparatively low anodic current density it is desired to have a comparatively high cathodic current density. This typically leads to hydrogen gas production. Although this is generally not desired, in the context of the present invention, it suppresses undesired cathodic decomposition reactions of desired manganese species. This most preferably applies to embodiment (ii).

[0102] More preferred is a method of the present invention, wherein the cathodic current density in embodiment (ii) is higher than in embodiment (i).

[0103] In embodiment (i), a method of the present invention is preferred, wherein in step (C) the at least one cathode has a cathodic current density ranging from 2 A/dm² to 30 A/dm², preferably from 3 A/dm² to 25 A/dm², more preferably from 4 A/dm² to 20 A/dm², even more preferably from 5 A/dm² to 15 A/dm², most preferably from 6 A/dm² to 12 A/dm².

[0104] In embodiment (ii), a method of the present invention is preferred, wherein in step (C) the at least one cathode has a cathodic current density ranging from 10 A/dm² to 70 A/dm², preferably from 12 A/dm² to 65 A/dm², more preferably from 14 A/dm² to 60 A/dm², most preferably from 16 A/dm² to 50 A/dm². In some cases, a cathodic current density is preferred ranging from 18 A/dm² to 35 A/dm².

[0105] More preferred is a method of the present invention, wherein the liquid comprises an acid, preferably an inorganic acid, most preferably phosphoric acid.

[0106] Most preferred is a method of the present invention, wherein the liquid comprises, preferably after step (C),

(a) water,

(b) 0.0025 mol/L to 0.1 mol/L manganese species having the oxidation number +7, preferably permanganate ions,

(c) 7 mol/L to 12 mol/L phosphoric acid,

(d) 0 to 0.1 mol/L silver (I) ions, and

(e) 0 or less than 10 ppm manganese (II) ions.

[0107] The liquid utilized in the method of the present invention comprises water. Preferred is a method of the present invention, wherein (a), (b), (c), (d), and (e) form 90 wt.-% or more of the total weight of the liquid, preferably 92 wt.-% or more, more preferably 94 wt.-% or more, even more preferably 96 wt.-% or more, most preferably 98 wt.-% or more. Preferred is a method of the present invention, wherein in the liquid the balance is water.

[0108] Preferred is a method of the present invention, wherein in the liquid after step (C) the manganese species having the oxidation number +7, preferably the permanganate ions, have a concentration ranging from 0.004 mol/L to 0.09 mol/L, based on the total volume of the liquid, preferably from 0.005 mol/L to 0.075 mol/L, more preferably from 0.006 mol/L to 0.06 mol/L, even more preferably from 0.007 mol/L to 0.045 mol/L, yet even more preferably from 0.008 mol/L to 0.03 mol/L, most preferably from 0.009 mol/L to 0.019 mol/L.

[0109] Preferred is a method of the present invention, wherein in step (A) in the liquid all manganese species together have a total concentration ranging from 0.02 mol/L to 0.3 mol/L, based on the total volume of the liquid, preferably from 0.03 mol/L to 0.25 mol/L, most preferably from 0.035 mol/L to 0.2 mol/L. This includes residual amounts of manganese species having the oxidation number +7 (if present at all), preferably permanganate ions, and manganese species having an oxidation number below +7. This preferably applies to the liquid in step (A) as well as after step (C).

[0110] Preferred is a method of the present invention, wherein in the liquid the phosphoric acid has a concentration ranging from 7.4 mol/L to 11.8 mol/L, based on the total volume of the liquid, preferably from 7.8 mol/L to 11.5 mol/L, more preferably from 8.2 mol/L to 11.2 mol/L, even more preferably from 8.5 mol/L to 11 mol/L, most preferably from 8.7 mol/L to 10.8 mol/L.

[0111] Most preferred is a method of the present invention, wherein phosphoric acid is the only (mineral) acid in the liquid. It is in particular phosphoric acid and preferably the absence of other strong mineral acids that significantly slows down further reduction of manganese species having an oxidation number of +IV (such as MnO_2) to an oxidation number below +IV. This is very preferred. This is preferably also the reason that the liquid comprises comparatively low amounts of manganese (II) ions.

[0112] In some cases a method of the present invention is preferred, wherein in the liquid the phosphoric acid has a concentration ranging from 9.2 mol/L to 10.5 mol/L, based on the total volume of the liquid, preferably from 9.3 mol/L to 10.4 mol/L, more preferably from 9.4 mol/L to 10.3 mol/L.

[0113] In some cases, a method of the present invention is preferred, wherein the liquid comprises silver (I) ions. Silver ions are preferably needed in order to better catalyze the electrolytic re-oxidation.

[0114] Preferred is a method of the present invention, wherein in the liquid the silver (I) ions have a concentra-

tion ranging from 0.0001 mol/L to 0.09 mol/L, preferably from 0.0002 mol/L to 0.07 mol/L, more preferably from 0.0005 mol/L to 0.05 mol/L, even more preferably from 0.0007 mol/L to 0.03 mol/L, most preferably from 0.001 mol/L to 0.01 mol/L.

[0115] Preferred, in step (A) the liquid is substantially free of, preferably does not comprise, manganese (II) ions. In some cases, the concentration thereof is preferably comparatively low, most preferably not exceeding 10 ppm, based on the total volume of the liquid. This preferably applies generally to the liquid utilized in the method of the present invention.

[0116] Preferred is a method of the present invention, wherein the liquid comprises alkali ions, most preferably sodium ions, preferably in a total concentration ranging from 0.002 mol/L to 0.5 mol/L, based on the total volume of the liquid, preferably from 0.004 mol/L to 0.3 mol/L.

[0117] Preferred is a method of the present invention, wherein the liquid is substantially free of, preferably does not comprise, a methane sulfonic acid and salts thereof, preferably is substantially free of, preferably does not comprise, a C1 to C4 alkyl sulfonic acid and salts thereof, most preferably is substantially free of, preferably does not comprise, a C1 to C4 sulfonic acid and salts thereof.

[0118] Preferred is a method of the present invention, wherein the liquid is substantially free of, preferably does not comprise, bromide and iodide anions, preferably is substantially free of, preferably does not comprise, chloride, bromide, and iodide anions, most preferably is substantially free of, preferably does not comprise, halide anions.

[0119] Preferred is a method of the present invention, wherein the liquid is substantially free of, preferably does not comprise, trivalent chromium ions and hexavalent chromium compounds, preferably is substantially free of, preferably does not comprise, any compounds and ions comprising chromium.

[0120] Preferred is a method of the present invention, wherein the liquid is substantially free of, preferably does not comprise, sulfuric acid.

[0121] Preferred is a method of the present invention, wherein during step (C) the liquid has a temperature ranging from 20°C to 65°C, preferably from 30°C to 50°C.

[0122] Preferred is a method of the present invention, wherein the liquid in step (A) and after step (C) is acidic, preferably has a pH of 2 or below, more preferably of 1 or below, even more preferably of 0.5 or below.

[0123] Preferred is a method of the present invention, wherein in step (A) and after step (C) the liquid has a density in a range from 1.2 g/cm³ to 1.7 g/cm³, referenced to a temperature of 20°C, preferably from 1.3 g/cm³ to 1.6 g/cm³, more preferably from 1.4 g/cm³ to 1.6 g/cm³. This density is preferably the result of large amounts of phosphoric acid and particulate and/or colloidal MnO_2 .

[0124] The present invention furthermore refers to a respective treatment device, preferably for oxidizing manganese species having an oxidation number below +7 to a manganese species having the oxidation number

+7, the treatment device comprising at least one anode unit (20) and at least one cathode (30), wherein said unit comprises at least one anode (21) and the unit is confined by a housing (22), the housing defining a free inner volume (V), wherein

(i) the housing comprises at least one permeable barrier (23) and the at least one cathode is located outside the anode unit, or

(ii) the housing comprises at least partly the at least one cathode, wherein the housing does not comprise a permeable barrier,

characterized in that in (i) and (ii) the at least one anode and the at least one cathode have a distance (d) ranging from 0.5 mm to 100 mm.

[0125] Preferably, the aforementioned regarding the method of the present invention applies likewise to the treatment device of the present invention, most preferably features defined as preferred for the treatment device utilized in the method of the present invention apply likewise to the treatment device of the present invention.

[0126] The invention will now be further illustrated by reference to the figures and the following examples.

[0127] A liquid comprising approximately 9 to 10 mol/L phosphoric acid, approximately 10 mmol/L permanganate ions, and approximately 2 mmol/L silver (I) ions was used as etching composition for etching ABS and ABS-PC substrates at approximately 40°C. The etching time was approximately between 5 to 20 minutes. During etching, the amount of permanganate ions quickly decreased.

[0128] In order to establish an environmental and ecological favorable etching method, the etching composition was continually provided by actively pumping (not shown) as a liquid to a treatment device (10) for recycling.

[0129] In embodiment (i) according to Figure 1, the treatment device (10) was filled with a catholyte consisting of aqueous, concentrated phosphoric acid (70 wt.-%), wherein the liquid (i.e. the anolyte in this embodiment) was continually pumped through the at least one anode unit (20). The at least one anode unit (20) was a defined compartment comprising at least one anode (21) in the center of the at least one anode unit (20). The at least one anode (21) was provided as a vertically oriented layer stack comprising a plurality of 8 to 20 anode layers (25), which were expanded metals having an individual surface factor of slightly above 2. The at least one anode unit (20) provided a total effective anode surface area A_1 of about 40 dm²/dm³.

[0130] The at least one anode unit (20) was confined by a housing (22) comprising at least one permeable barrier (23), which was a Nafion-type membrane. Typically, two of them were used on opposite sides of the housing (22) as shown in Fig. 1. The distance (m) between the plurality of anode layers was fixed by spacers (26) and

was approximately 1 to 2 mm.

[0131] Typically, 1 to 5 anode units are utilized in the treatment device to constantly recycle permanganate ions with a performance of about 200 L etching composition recycled per anode unit. In a specific case, 5 anode units in one treatment device were utilized for about 600 to 1000 L etching composition. Typically, the volume of the liquid present in the at least one anode unit corresponds to the free inner volume (V) as defined above in the text.

[0132] Outside the at least one anode unit, at least one cathode (30) was provided, typically around the at least one anode unit (20) on opposite sides relative to the at least one anode unit (20). The at least one cathode (30) provided a total effective cathode surface area A_2 , wherein A_1 was significantly larger than A_2 . The distance (d) between the at least one anode (21) and the at least one cathode (30) was approximately 15 mm.

[0133] An electrical current was applied to said at least one anode (21) and said at least one cathode (30). The anodic current density was approximately 1 A/dm², wherein the cathodic current density was approximately 10 A/dm².

[0134] While flowing through the at least one anode unit (20), the liquid was in contact with the anode layers of layer stack (25) and manganese species having an oxidation number below +7 were continually re-oxidized to permanganate ions (i.e. a manganese species having the oxidation number +7).

[0135] In an alternative embodiment (i) according to Fig. 2, the layer stack of anode layers was provided horizontally. It was observed that the current efficiency was slightly below the current efficiency obtained with the vertically oriented anode layers.

[0136] In both variants of embodiment (i), silver (I) ions were replenished from time to time to compensate not only drag out but also an undesired minor precipitation.

[0137] In embodiment (ii) according to Figure 3, no permeable barriers (23) were used in housing (22). Instead, the at least one cathode was at least partly integrated in the housing (22) on opposite sides in such a way that the at least one cathode (30) partly penetrates the housing (22) into the inside towards the at least one anode (21). By doing so, a plurality of cathode spots (31) was formed, approximately 16 to 60 spots per side on two opposite inner sides of the housing (22) of the at least one anode unit (20). Furthermore, two cathodes (30) were utilized such that a first set (32) and a second set (33) of cathode spots (from said plurality of cathode spots) were present inside the at least one anode unit (20) towards the at least one anode (21). Both cathodes were electrical separated from each other. The electrical cathodic current was repeatedly reversed such that silver precipitation was dissolved and therefore basically avoided. Only a loss due to drag out was compensated in time intervals. As a result, significantly less silver was consumed.

[0138] No distinction between an anolyte and a

catholyte was present. The cathodic current density was approximately 50 A/dm² and thus, significantly higher than in embodiment (i). The distance (d) between the at least one anode (21) and the at least one cathode (30) was approximately 10 mm.

[0139] In each embodiment, the liquid comprising re-oxidized permanganate ions was returned as etching composition.

[0140] Furthermore, in each case a very compact anode unit was provided, allowing to constantly recycle respective manganese species in a strongly acidic environment.

REFERENCE SIGNS

[0141]

1	liquid
10	treatment device
20	at least one anode unit
21	at least one anode
22	housing
23	at least one permeable barrier
25	layer stack of anode layers
26	spacer
30	at least one cathode
31	plurality of cathode spots
32	first set of cathode spots
33	second set of cathode spots
V	a free inner volume defined by the housing
d	distance between the at least one anode and the at least one cathode
m	distance of anode layers to each other in a layer stack

Claims

1. A method for oxidizing manganese species in a treatment device (10), the method comprising the steps
 - (A) providing in the treatment device in a liquid at least one manganese species having an oxidation number below +7,
 - (B) providing in the treatment device at least one anode unit (20) and at least one cathode (30), wherein said unit comprises at least one anode (21) and is confined by a housing (22), the housing defining a free inner volume (V),
 - (C) applying a current to the at least one anode and the at least one cathode such that at least a portion of said at least one manganese species is anodically oxidized to a manganese species having the oxidation number +7,
 wherein
 - (i) the housing comprises at least one permeable barrier (23) and the at least one

cathode is located outside the anode unit, or
 (ii) the at least one anode unit comprises at least partly the at least one cathode,

wherein the housing does not comprise a permeable barrier,

characterized in that in (i) and (ii) the at least one anode and the at least one cathode have a distance (d) ranging from 0.5 mm to 100 mm.

2. The method of claim 1, wherein the at least one permeable barrier is an ion-selective permeable barrier, preferably an ion-selective permeable membrane.
3. The method of claim 1, wherein in (ii) the at least one cathode is at least partly integrated in the housing, preferably is at least partly penetrating the housing from the outside into the inside towards the at least one anode.
4. The method of any of claims 1 to 3, wherein (d) is ranging from 1 mm to 90 mm, preferably from 2 mm to 80 mm, more preferably from 3 mm to 70 mm, even more preferably from 4 mm to 60 mm, most preferably from 5 mm to 50 mm.
5. The method of any of claims 1 to 4, wherein the at least one anode comprises a layer stack (25) of anode layers, preferably of 3 or more than 3 anode layers, more preferably the layer stack comprises 3 to 300 anode layers, even more preferably 4 to 200 anode layers, yet even more preferably 6 to 100 anode layers, most preferably 8 to 60 anode layers, even most preferably 9 to 30 anode layers.
6. The method of claim 5, wherein in the layer stack the anode layers have a distance (m) to each other ranging from 0.5 mm to 20 mm, preferably from 1 mm to 15 mm, more preferably from 2 mm to 12 mm, even more preferably from 3 mm to 10 mm, most preferably from 4 mm to 9 mm.
7. The method of any of claims 1 to 6, wherein the at least one anode comprises a sheet, a mesh, a woven web, and/or an expanded metal.
8. The method of any of claims 1 to 7, wherein the at least one anode has a surface factor of 1 or more, preferably of 1.4 or more, even more preferably of 1.7 or more, yet even more preferably of 2 or more, most preferably of 2.1 or more, even most preferably of 2.2 or more.
9. The method of any of claims 1 to 8, wherein the at least one anode comprises platinum, titanium, niobium, lead, gold, alloys comprising at least one there-

of, oxides thereof, and/or mixtures thereof.

10. The method of any of claims 1 to 9, wherein the at least one anode provides a total effective anode surface area A_1 and the at least one cathode a total effective cathode surface area A_2 , wherein A_1 is larger than A_2 . 5
11. The method of claim 10, wherein $A_1 : A_2$ is ranging from 5:1 to 100:1, preferably from 10:1 to 85:1, more preferably from 15:1 to 70:1, even more preferably from 20:1 to 60:1, most preferably from 30:1 to 50:1. 10
12. The method of claim 10 or 11, wherein A_1 is ranging from 10 dm²/dm³ to 100 dm²/dm³, based on the free inner volume (V), preferably from 15 dm²/dm³ to 85 dm²/dm³, more preferably from 20 dm²/dm³ to 70 dm²/dm³, even more preferably from 25 dm²/dm³ to 60 dm²/dm³, most preferably from 30 dm²/dm³ to 50 dm²/dm³. 15 20
13. The method of any of claims 1 to 12, wherein the treatment device and/or the at least one anode unit has at least one inner surface comprising or consisting of a fluorinated plastic, preferably polyvinylidene fluoride (PVDF) and/or polytetrafluoroethylene (PTFE). 25
14. A treatment device (10) comprising at least one anode unit (20) and at least one cathode (30), wherein said unit comprises at least one anode (21) and the unit is confined by a housing (22), the housing defining a free inner volume (V), wherein 30 35
 - (i) the housing comprises at least one permeable barrier (23) and the at least one cathode is located outside the anode unit,
 - or
 - (ii) the housing comprises at least partly the at least one cathode, wherein the housing does not comprise a permeable barrier, 40

characterized in that in (i) and (ii) the at least one anode and the at least one cathode have a distance (d) ranging from 0.5 mm to 100 mm. 45
15. The treatment device of claim 14 as defined in any one of claims 2 to 13. 50

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Fig. 1

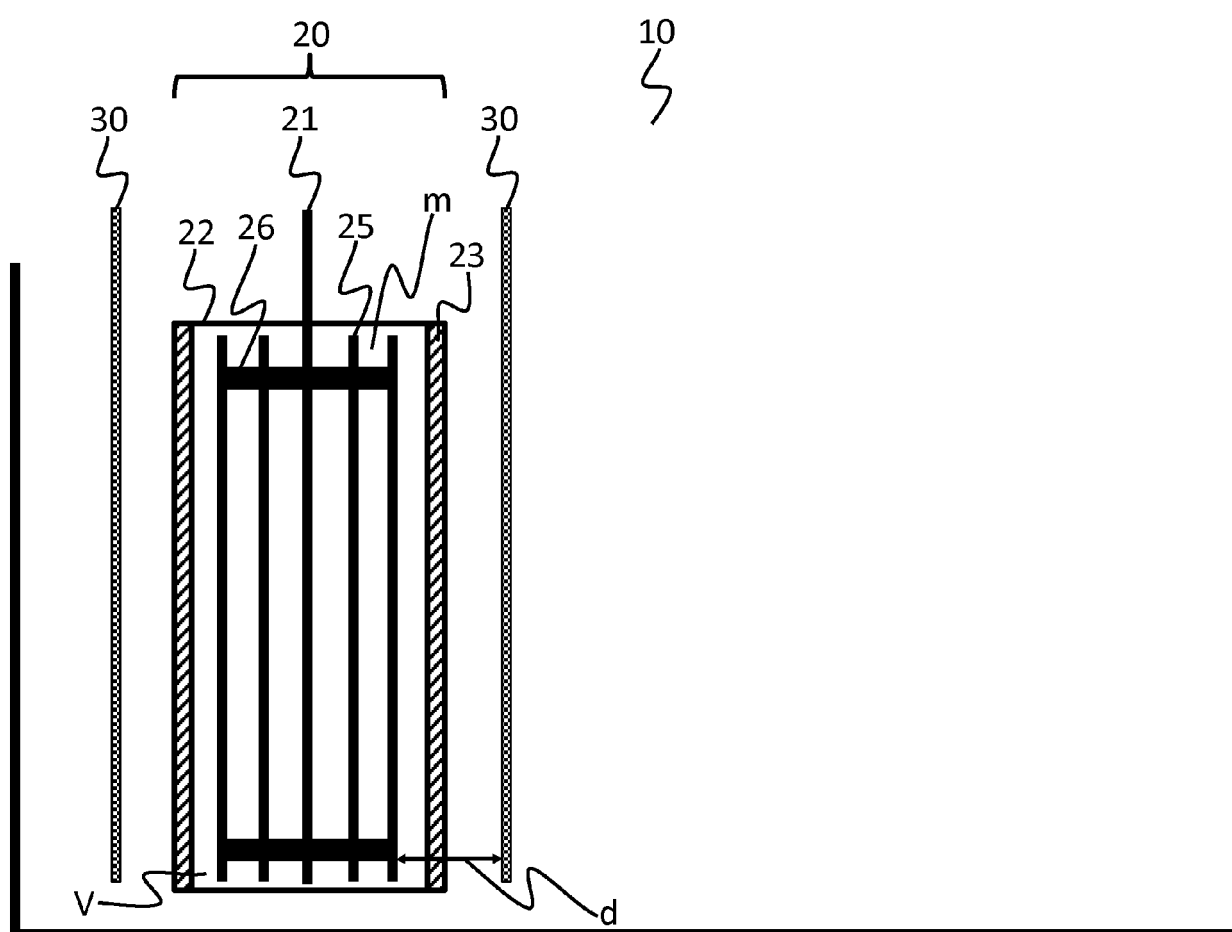


Fig. 2

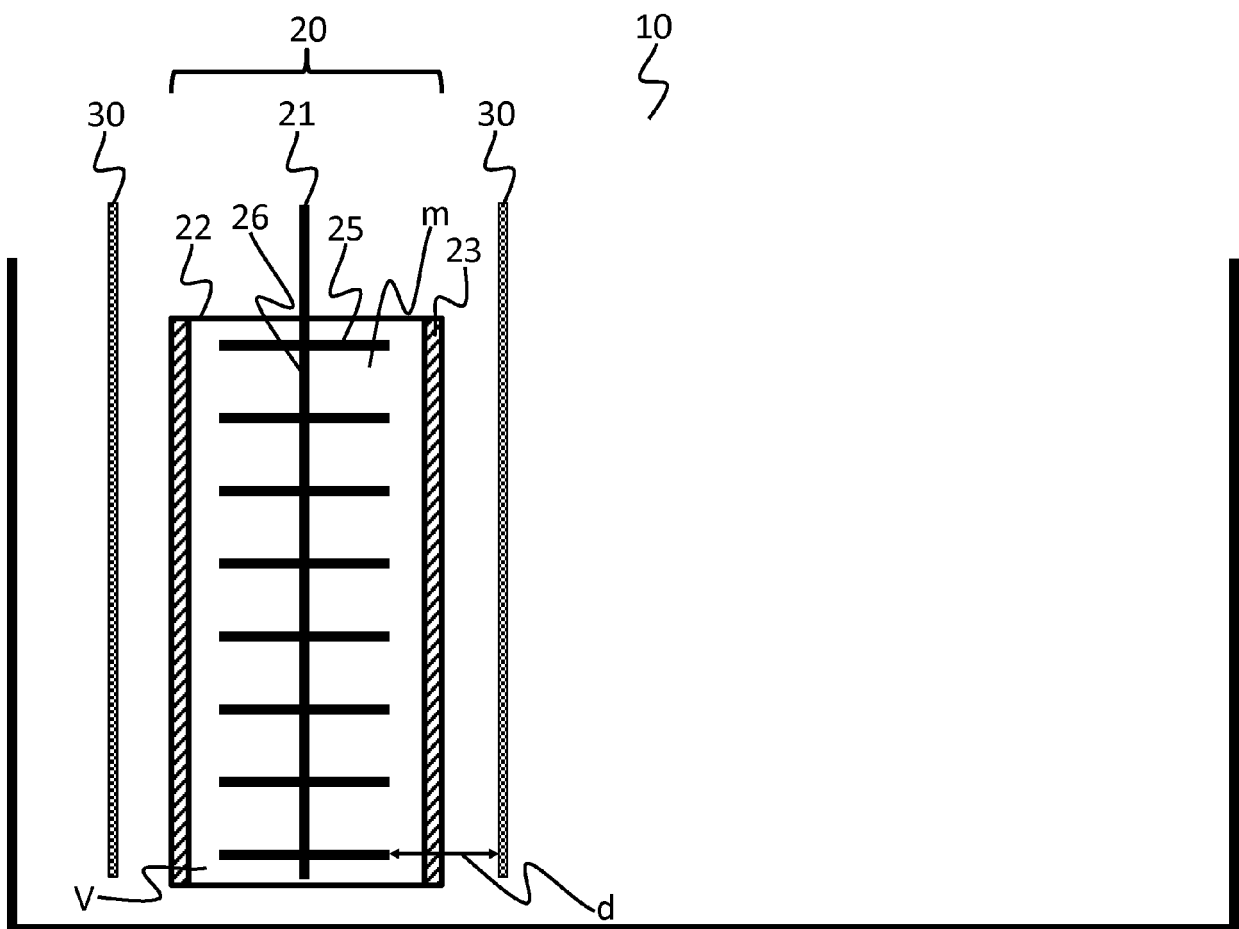
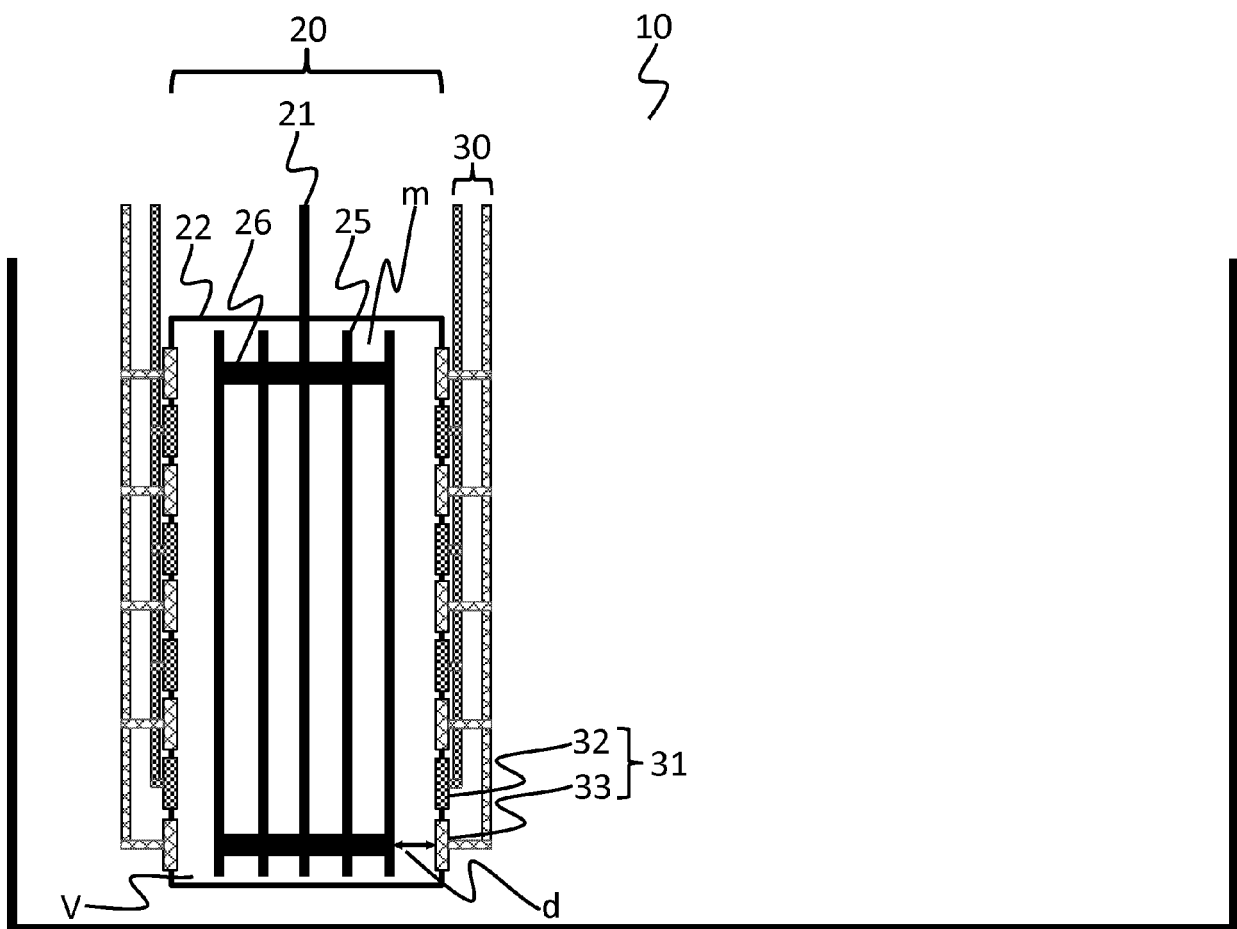


Fig. 3





PARTIAL EUROPEAN SEARCH REPORT

Application Number

under Rule 62a and/or 63 of the European Patent Convention.
This report shall be considered, for the purposes of
subsequent proceedings, as the European search report

EP 21 17 9866

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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Y	* the whole document *	5, 6	C25B C23C C23F
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INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC so that only a partial search (R.62a, 63) has been carried out.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:
see sheet C

Place of search
Munich

Date of completion of the search
31 January 2022

Examiner
Ritter, Thomas

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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O : non-written disclosure
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L : document cited for other reasons
& : member of the same patent family, corresponding document



**INCOMPLETE SEARCH
SHEET C**

Application Number

EP 21 17 9866

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Claim(s) completely searchable:
1-13

Claim(s) searched incompletely:
14, 15

Reason for the limitation of the search:

The reasons for the incomplete search are provided in the accompanying search opinion.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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31-01-2022

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