



(11)

EP 4 105 361 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

21.12.2022 Bulletin 2022/51

(21) Application number: **21179861.6**

(22) Date of filing: **16.06.2021**

(51) International Patent Classification (IPC):

C25B 1/21 (2006.01) **C25B 11/03** (2021.01)
C25B 11/052 (2021.01) **C25B 11/056** (2021.01)
C25B 11/063 (2021.01) **C25B 11/081** (2021.01)
C23C 18/24 (2006.01) **C23F 1/46** (2006.01)

(52) Cooperative Patent Classification (CPC):

C25B 1/21; C23C 18/24; C25B 11/03;
C25B 11/052; C25B 11/056; C25B 11/063;
C25B 11/081; C23F 1/46

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

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

(57) The present invention relates to a method for oxidizing manganese species in a treatment device, the method comprising the steps

(A) providing in the treatment device a manganese species having a first oxidation number,

(B) providing in the treatment device one or more than one anode and at least one cathode,

(C) applying a current to said anode and said cathode

such that at least a portion of the manganese species having the first oxidation number is anodically oxidized to a manganese species having a second oxidation number which is higher than the first oxidation number, characterized in that at least one of said one or more than one anode has a surface density of 6 m²/L or more, based on the total volume of said at least one anode.

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Description

Field of the Invention

[0001] The present invention relates to a method for oxidizing manganese species in a treatment device, the method comprising the steps

(A) providing in the treatment device a manganese species having a first oxidation number,

(B) providing in the treatment device one or more than one anode and at least one cathode,

(C) applying a current to said anode and said cathode such that at least a portion of the manganese species having the first oxidation number is anodically oxidized to a manganese species having a second oxidation number which is higher than the first oxidation number,

characterized in that at least one of said one or more than one anode has a surface density of 6 m²/L or more, based on the total volume of said at least one anode.

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 elec-

trical current. Respective regeneration methods and devices 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] The efficiency of regeneration typically depends on the current invested into a respective treatment device and how this current is interacting with the respective manganese species.

[0011] There is an ongoing demand to further increase the efficiency of respective regeneration methods and devices.

Objective of the present Invention

[0012] It is therefore the objective of the present invention to provide a method for oxidizing manganese species in a treatment device with high efficiency, thus, allowing a compact design of respective treatment devices. Most preferably it is the objective to provide a method which is in particular suitable for treating (i.e. recycling) acidic manganese-based etching compositions, in particular comprising permanganate, with increased efficiency.

Summary of the Invention

[0013] Above mentioned objectives are solved by a method for oxidizing manganese species in a treatment device, the method comprising the steps

(A) providing in the treatment device a manganese species having a first oxidation number,

(B) providing in the treatment device one or more than one anode and at least one cathode,

(C) applying a current to said anode and said cathode such that at least a portion of the manganese species having the first oxidation number is anodically oxidized to a manganese species having a second oxidation number which is higher than the first oxidation number,

characterized in that at least one of said one or more than one anode has a surface density of 6 m²/L or more, based on the total volume of said at least one anode.

[0014] The method of the present invention allows a

very effective oxidation (preferably regeneration) of manganese species because it particularly utilizes at least one anode with specifically a surface density of 6 m²/L or more, based on the total volume of said at least one anode. In other words, such an anode provides an exceptionally large effective surface area in already at least one single anode. In turn such a large effective surface area per litre provides a correspondingly large area for contacting the manganese species having the first oxidation number. As a result, this manganese species is efficiently oxidized at said anode to provide a manganese species with said second oxidation number.

[0015] However, in common methods typically conventional anodes are used having a typically low surface density, most typically below 6 m²/L. This can be also seen in comparatively low surface factors of such conventional anodes; a parameter typically used for electrodes with a primarily two-dimensional design (such as plates, meshes, etc.). For example, expended metal lattice anodes (metal laths; Streckmetall) at best provide a surface factor between 2 and 2.5, which is already considered as high. However, new manufacturing techniques, for example 3D-printing, allow production of anodes with a significantly higher surface area per volume compared to conventional anode designs. Furthermore, they can be designed in various geometries, in particular in all three dimensions. All this allows to reduce the size of a respective treatment device and to increase efficiency thereof. Furthermore, stacking of conventional anodes to a layer stack to mimic an anode with a high surface area per volume can be prevented if for some reason such a stacking is not desired. Instead, specific geometries can be intentionally formed to serve even sophisticated requirements and utilization of such anodes becomes more flexible.

[0016] In some cases, a method of the present invention is preferred, wherein the one or more than one anode is a single anode and is at the same time the at least one anode having a surface density of 6 m²/L or more. However, in other cases, a method of the present invention is preferred, wherein more than one anode is provided in step (B), wherein at least one thereof has a surface density of 6 m²/L or more, preferably all thereof have a surface density of 6 m²/L or more.

Detailed Description of the Invention

[0017] As mentioned above, the method of the present invention anodically oxidizes a manganese species having a first oxidation number to a manganese species having a second oxidation number, wherein the second oxidation number is higher than the first oxidation number.

[0018] Preferred is a method of the present invention, wherein the first oxidation number is +4 or below.

[0019] More preferred is a method of the present invention, wherein the first oxidation number comprises +4, +3, and/or +2.

[0020] Preferred is a method of the present invention,

wherein the manganese species having the first oxidation number comprises Mn²⁺ ions and/or Mn³⁺ ions.

[0021] Preferred is a method of the present invention, wherein the manganese species having the first oxidation number comprises manganese particles (preferably oxides thereof), preferably colloidal manganese particles (preferably oxides thereof), most preferably colloidal MnO₂ particles. This preferably includes optional agglomerates thereof.

[0022] Preferred is a method of the present invention, wherein the second oxidation number is above +4, preferably is +7 (preferably comprises +7). However, this does not necessarily exclude manganese species having an oxidation number of +5 or +6.

[0023] Most preferably, the manganese species having the second oxidation number comprises permanganate ions.

[0024] Preferred is a method of the present invention, wherein the manganese species having the first oxidation number are comprised in a liquid, preferably in an acidic liquid. In fact, the method of the present invention is most preferably effective in treating such an acidic liquid. Preferably, the liquid is a treatment composition for treating, preferably etching, non-metallic substrates in an etching compartment, preferably plastic substrates. Most preferably, prior to step (A), the liquid was in contact with a plastic substrate. In other words, it is preferred that the manganese species having the first oxidation number were in contact with a non-metallic substrate, preferably a plastic substrate, prior to step (A).

[0025] More preferred is a method of the present invention, wherein the liquid comprises an acid, preferably an inorganic acid, most preferably phosphoric acid.

[0026] Preferred is a method of the present invention, wherein the manganese species having the second oxidation number is returned into the etching compartment. Most preferably, the manganese species having the second oxidation number is re-used for treating, preferably etching, a non-metallic substrate, preferably a plastic substrate. Thus, most preferably, the method of the present invention is a recycling method for manganese species. In this context "recycling" refers to a re-oxidation of (preferably already utilized) manganese species with subsequent re-utilization thereof. A method of the present invention is preferred, wherein the method is carried out continually or at least semi-continually. Continually preferably denotes that at least steps (A) and (C) of the method of the present invention are carried out continually, i.e. without interruptions. In contrast, semi-continually preferably denotes that step (A) and/or step (C) is interrupted from time to time for at least a little while. Such an interruption might be necessary for maintenance or to stabilize a concentration of one of the species present during the method of the present invention. However, a continual utilization is preferred.

[0027] Typically, etching a plastic substrate with e.g. permanganate chemically reduces permanganate to manganese species with lower oxidation numbers while

the material of the plastic is at least partly oxidized.

[0028] In some cases, a method of the present invention is preferred, wherein the treatment device utilized in the method of the present invention 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 utilized in the method of the present invention is at least partly integrated into the etching compartment. This preferably means that the treatment device is internal relative to the etching compartment.

[0029] Preferred is a method of the present invention, wherein the non-metallic substrate, preferably the plastic substrate, comprises acrylonitrile butadiene styrene (ABS), acrylonitrile butadiene styrene - polycarbonate (ABS-PC), polypropylene (PP), polyamide (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 often used in decorative applications such as automotive parts, in particular ABS and ABS-PC.

[0030] In order to maintain an efficient and energy-optimized method of the present invention, the one or more than one anode and the at least one cathode preferably have a comparatively low distance to each other. Preferred is a method of the present invention, wherein the one or more than one anode and the at least one cathode have a distance to each other ranging from 1 mm to 100 mm, preferably from 2 mm to 90 mm, more preferably from 3 mm to 80 mm, even more preferably from 4 mm to 70 mm, most preferably from 5 mm to 60 mm. Typically, the shorter the distance the less voltage and, thus, energy consumption, is needed. Therefore, in some cases a method of the present invention is preferred, wherein the one or more than one anode and the at least one cathode have a distance to each other 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. This most preferably applies to the at least one anode having a surface density of 6 m²/L or more.

[0031] Generally preferred is a method of the present invention, wherein the distance is defined as the shortest distance between the one or more than one anode and the closest (preferably corresponding) at least one cathode. In other words, the distance is preferably the shortest outer distance between the one or more than one anode and the closest (preferably corresponding) at least one cathode. The term "outer" preferably refers to the outermost of the one or more than one anode directly facing towards the outermost of the closest at least one cathode.

[0032] Preferred is a method of the present invention,

wherein the at least one cathode is (at least mainly) built around (in a sense of surrounding) the one or more than one anode, in particular around the at least one anode having the surface density of 6 m²/L or more. In other words, the at least one cathode at least mainly encircles or circulates the one or more than one anode, preferably the at least one anode having the surface density of 6 m²/L or more, wherein this wording does not limit the ensemble to a circular shape. However, this anode/cathode arrangement is not necessarily mandatory in the context of the present invention.

[0033] In some cases, a method of the present invention is preferred, wherein the one or more than one anode and the at least one cathode are separated from each other by a permeable barrier, preferably a permeable membrane. In such an embodiment an anolyte and a catholyte is preferably formed. Most preferably, the anolyte comprises the manganese species having the first oxidation number. Thus, preferably the anolyte is said liquid as described above. The catholyte preferably comprises an inorganic acid, more preferably sulfuric acid and/or phosphoric acid, most preferably (preferably only) phosphoric acid.

[0034] Despite the permeable barrier, the current applied in step (C) can flow such that at least a portion of the manganese species having the first oxidation number is anodically oxidized to the manganese species having said second oxidation number.

[0035] Preferably, if such a permeable barrier is utilized, substantially all manganese species are 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.

[0036] Preferred is a method of the present invention, wherein the permeable barrier is an ion-selective permeable barrier, preferably an ion-selective permeable membrane.

[0037] Preferred is a method of the present invention, wherein the permeable barrier is a cation-selective permeable barrier, preferably a cation-selective permeable membrane. Thus, most preferably only cations are permeable.

[0038] In some cases, preferred is a method of the present invention, wherein the permeable barrier is not mineral. In contrast, in other cases it is preferred that the permeable barrier is mineral, preferably comprises a ceramic. However, in some other cases, preferred is a method of the present invention, wherein the permeable barrier is essentially free of, preferably does not comprise, a ceramic.

[0039] More preferred is a method of the present invention, wherein the permeable barrier is organic. More preferred is a method of the present invention, wherein the permeable barrier is organic and comprises fluorine (preferably is fluorinated), most preferably is organic and perfluorinated. Most preferably, the at least one permeable barrier is a Nafion-type-membrane, although the membrane is not particularly limited to this particular

brand. Membranes, preferably said organic membranes, are very thin and therefore positively contribute to a comparatively short distance, and, thus, to a compact design. In contrast, a method of the present invention is also preferred, wherein the one or more than one anode and the at least one cathode are not separated from each other by a permeable membrane, preferably a permeable barrier.

[0040] In the context of the present invention it is essential that the at least one anode has a surface density of $6 \text{ m}^2/\text{L}$ or more. Preferred is a method of the present invention, wherein the surface density is $8 \text{ m}^2/\text{L}$ or more, preferably $10 \text{ m}^2/\text{L}$ or more, more preferably $14 \text{ m}^2/\text{L}$ or more, even more preferably $16 \text{ m}^2/\text{L}$ or more, most preferably $20 \text{ m}^2/\text{L}$ or more. In general, the higher the surface density the more efficient the method can potentially be, provided that a sufficient mass transport through the at least one anode is guaranteed. With the newly found techniques, production of anodes with said surface densities become more and more available. It was surprising to see that both, a very good mass transport as well as efficiency can be obtained. This was surprising because it was so far assumed that anodes having a huge effective surface area on comparatively small volume are affected by a detrimental shielding effect, meaning that the electrical field has only a very little penetration depth. In the context of the present invention it was surprising that said at least one anode provides a sufficiently high current efficiency/turnover despite the compact design. Although a shielding effect indeed occurs, the effect is surprisingly low and can be tolerated in favor of the great benefit to create a comparatively huge total effective anode surface area. It was surprising although said at least one anode provides a Faraday cage-like barrier. In other words, said anode surprisingly allows an extremely compact and dense anode architecture and still a high efficiency despite shielding effects.

[0041] In the context of the present invention, the surface density denotes a parameter defining the total effective surface area per geometric volume.

[0042] For example, a plate geometrically of 1 m^2 and having a thickness of 1 mm typically has a total effective surface area of 2.004 m^2 including front and rear side as well as the area of the cutting edges. The geometric volume of such a plate is $1 \text{ m} \times 1 \text{ m} \times 10^{-3} \text{ m} = 10^{-3} \text{ m}^3 = 1 \text{ liter}$. As a result, the surface density of this plate is $2.004 \text{ m}^2/\text{L}$, i.e. roughly $2 \text{ m}^2/\text{L}$. This also harmonizes with a common parameter named "surface factor" (total effective surface area per geometric area), which in this case is about 2 for such a primarily two-dimensional plate.

[0043] Typically, a surface density above 2 is obtained if e.g. a plate has holes and a mesh has openings, respectively, in a defined number and with defined dimensions. The same applies to the surface factor. However, the surface factor of commercially available meshes today is typically not exceeding 2.5. Furthermore, the surface factor does not sufficiently define electrodes having a significant third dimension. Contrary to the surface fac-

tor, which is without dimensions, the surface density in the context of the present invention is defined as m^2 per liter of the respective anode.

[0044] Preferred is a method of the present invention, wherein the at least one anode having a surface density of $6 \text{ m}^2/\text{L}$ or more comprises, most preferably in the inside of said anode, a random structural pattern, a uniform structural pattern, or a regularly recurring structural pattern. Most preferred is a uniform structural pattern and/or a regularly recurring structural pattern, most preferably in 3D-printed anodes, woven fabric anodes, permanently fixed stacked single-layer anodes (preferably permanently fixed by welding, gluing, and/or riveting), separable stacked single-layer anodes (preferably separable by unscrewing and/or unclamping), and packed bed anodes with a defined package. In the context of the present invention a random, i.e. a chaotic and without long-range order, structural pattern is slightly less preferred but typical e.g. for so called packed bed anodes with loosely filled materials, knot anodes, foam anodes, and 3D-printed anodes with a random structural pattern. Typically, a uniform and regularly recurring structural pattern ensures a homogeneous penetration depth of the electrical field into the interior of said anode, which is assumed to be an advantage over a random structural pattern. Preferably, a structural pattern comprises caverns and/or holes inside said anode, which are materially accessible from the outer surface and preferably cause the comparatively large total effective surface area. On the other hand, random structural patterns are easy to obtain and, as for packed bed anodes, comparatively low in price.

[0045] In general, preferred single-layer anodes comprise meshes and/or plates, preferably expanded metals (i.e. expanded laths).

[0046] Preferred is a method of the present invention, wherein the at least one anode having a surface density of $6 \text{ m}^2/\text{L}$ or more comprises (preferably is) a single-segment anode or a separable multi-segment anode. In the context of the present invention, single segment anode denotes an anode which consists of one piece and can be separated/dismantled only by destruction. In other words, such kind of anode is not designed for dismantling. Preferred single-segment anodes comprise 3D-printed anodes, woven fabric anodes, permanently fixed stacked single-layer anodes (preferably permanently fixed by welding, gluing, and/or riveting), knot anodes, packed bed anodes with a sintered, welded, and/or compressed anode material, and/or foam anodes.

[0047] In contrast, a separable multi-segment anode consists of at least two, preferably multiple, individual joint segments which are designed for non-destructive dismantling. A preferred separable multi-segment anode comprises separable stacked single-layer anodes (preferably separable by unscrewing and/or unclamping), packed bed anodes with a defined package, and/or packed bed anodes with loosely filled materials.

[0048] Generally 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.

[0049] Such particular surface densities are most preferably obtained with the following anodes:

Preferred is a method of the present invention, wherein the at least one anode having a surface density of 6 m²/L or more is selected from the group consisting of 3D-printed anodes, woven fabric anodes, foam anodes, stacked single-layer anodes, and packed bed anodes. More preferably, preferred anodes thereof are as defined above.

In some cases, preferred is a method of the present invention, wherein the providing in step (B) includes

- manufacturing the one or more than one anode (preferably said at least one anode having a surface density of 6 m²/L or more), preferably the 3D-printed anodes, woven fabric anodes, foam anodes, and packed bed anodes, most preferably the 3D-printed anodes and the woven fabric anodes.

[0050] However, within the context of the present invention it is not relevant whether the method of the present invention includes a manufacturing of a respective anode or whether the anode is simply provided but manufactured at a different place and subsequently relocated to be utilized in the method of the present invention.

[0051] Preferred is a method of the present invention, wherein the woven fabric anodes comprise woven metallic wires and/or woven metallized filaments. Typically, the thickness of such wires and filaments define the maximum surface density. For example, for filaments and wires having a thickness of 0.2 mm the maximum surface density is preferably ranging from 18 m²/L to 22 m²/L, based on the total volume of said anode, preferably about 20 m²/L. For filaments and wires having a thickness of 0.1 mm the maximum surface density is preferably ranging from 30 m²/L to 42 m²/L, based on the total volume of said anode, preferably from 35 m²/L to 40 m²/L.

[0052] Preferred is a method of the present invention, wherein the woven fabric anodes comprise flat woven fabric anodes and/or pile fabric anodes.

[0053] Preferred is a method of the present invention, wherein the 3D-printed anodes comprise 3D-printed lattice anodes and/or 3D-printed lamella anodes. Typically, the printing resolution in 3D-printing defines the maximum surface density. For example, 3D-printed spots with a minimum dimension of about 50 μm preferably result in a 3D-printed anode having a surface density ranging from at least 60 m²/L up to 100 m²/L, based on the total

volume of said anode, preferably from 70 m²/L to 90 m²/L.

[0054] Preferred is a method of the present invention, wherein the foam anodes comprise a solid and/or flexible foam anode.

[0055] 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.

[0056] In the method of the present invention most preferably the at least one anode having a surface density of 6 m²/L or more comprises 3D-printed anodes and/or woven fabric anodes.

[0057] 3D-printed anodes for example, as already mentioned above, can theoretically manufactured with a potentially very high surface density. Very preferably, the surface density is 100 m²/L or below for such kind of anodes, based on the total volume of said anode, preferably ranging from 30 m²/L to 80 m²/L, preferably from 40 m²/L to 50 m²/L.

[0058] Most preferably, woven fabric anodes have a surface density ranging from 10 m²/L to 40 m²/L, based on the total volume of said anode, preferably from 15 m²/L to 30 m²/L.

[0059] In some cases, a method of the present invention is preferred, wherein the one or more than one anode does not comprise stacked single-layer anode layers (preferably as defined above as being preferred) having an individual surface density of 3 m²/L or below. Most preferably, the one or more than one anode does not comprise stacked single-layer anodes having an individual surface factor of 3 or below. In some cases, a method of the present invention is even preferred, wherein the one or more than one anode, preferably the at least one anode having the surface density of 6 m²/L or more, does not comprise stacked single-layer anodes at all. Although stacked single-layer anodes are basically possible and desired to be used in the context of the present invention, they typically need to be assembled compared to other preferred anodes which are manufactured in basically automated manufacturing methods.

[0060] Preferred is a method of the present invention, wherein the at least one anode having a surface density of 6 m²/L or more comprises a material selected from the group consisting of platinum, titanium, niobium, lead, gold, alloys comprising at least one thereof, oxides thereof, and mixtures thereof.

[0061] More preferred is a method of the present invention, wherein the one or more than one anode comprises a material selected from the group consisting of platinum, titanium, niobium, lead, gold, alloys comprising at least one thereof, oxides thereof, and mixtures thereof. This preferably means that it applies to all anodes.

[0062] As already said, the manganese species having the first oxidation number is preferably provided/comprised in a liquid. Since the liquid is preferably highly acidic and because of the strong oxidizing character of certain manganese species, the material of the one or more than

one anode is preferably carefully selected. A preferred minimum requirement is that a respective material is (electro-)chemically inert towards the liquid. Typically, the aforementioned materials are resistant, at least for a certain time. Very preferred is a method of the present invention, wherein the one or more than one anode comprises a platinized anode and/or a platinum anode, preferably a platinized titanium anode, and/or a platinized niobium anode. Such anode material is highly resistant, even over longer times. This most preferably applies to the at least one anode having a surface density of $6 \text{ m}^2/\text{L}$ or more.

[0063] In some cases, a method of the present invention is preferred, wherein the material comprises lead and/or lead alloys. Preferred lead alloys comprise tin and/or silver as alloying elements. However, in most cases own experiments have shown that an excellent efficiency is obtained if the material comprise platinum, most preferably is platinized. Furthermore, lead is more and more an undesired material in terms of human and environmental hazards.

[0064] As mentioned above, in step (B) at least one cathode is provided.

[0065] Generally preferred is a method of the present invention, wherein the at least one cathode comprises a material selected from the group consisting of titanium, platinum, niobium, lead, alloys comprising at least one thereof, oxides thereof, stainless steel, and mixtures thereof. Typically preferred is a method of the present invention, wherein the at least one cathode preferably is of a wide variety of materials as long as a respective material is sufficiently acid resistant, sufficiently stable against hydrogen embrittlement, and/or chemically resistant to the liquid (if in contact with the liquid). In some cases, a method of the present invention is preferred, wherein the material of the at least one cathode is identical to the material of the at least one anode having a surface density of $6 \text{ m}^2/\text{L}$ or more, preferably to the material of the one or more than one anode. However, in other cases, preferably, the material of the at least one cathode is different from the material of the at least one anode having a surface density of $6 \text{ m}^2/\text{L}$ or more, preferably from the material of the one or more than one anode.

[0066] Own experiments have shown that in some cases the cathodic current protects the at least one cathode such that even less resistant materials can be utilized, preferably stainless steel. This most preferably applies, if a permeable barrier, preferably a permeable membrane is utilized in the method of the present invention, such that a catholyte is formed, preferably a catholyte comprising phosphoric acid, more preferably comprising as only mineral acid phosphoric acid, most preferably comprising as only acid phosphoric acid.

[0067] In some cases, preferred is a method of the present invention, wherein the at least one cathode comprises a sheet cathode, a mesh cathode, a woven web cathode, an expanded metal cathode, a 3D-printed cath-

ode, a woven fabric cathode, a foam cathode, and/or a packed bed cathode. Preferred is a sheet cathode and/or a mesh cathode.

[0068] Preferred is a method of the present invention, wherein the one or more than 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 . Preferably this applies to the at least one anode having the surface density of $6 \text{ m}^2/\text{L}$ or more.

[0069] In the context of the present invention, "total effective surface area" refers to the area available for participation in electrochemical redox-reactions. This is also used/included in the definition of the surface density.

[0070] In some cases, preferred is a method of the present invention, wherein 50% or more of A_1 are from the at least one anode having the surface density of $6 \text{ m}^2/\text{L}$ or more, preferably 60% or more, more preferably 70% or more, even more preferably 80% or more, yet even more preferably 90% or more, most preferably 95% or more, yet even most preferably 99% or more.

[0071] Generally 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.

[0072] In some cases, a method of the present invention is preferred, wherein $A_1 : A_2$ is ranging from 5:1 to 30:1, preferably from 6:1 to 25:1, more preferably from 7:1 to 20:1.

[0073] However, in other cases 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. More 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 in some cases most preferred, if no permeable barrier is utilized.

[0074] Generally preferred is a method of the present invention, wherein A_1 is ranging from $10 \text{ dm}^2/\text{dm}^3$ to $200 \text{ dm}^2/\text{dm}^3$, based on a total free inner volume in the treatment device, preferably from $15 \text{ dm}^2/\text{dm}^3$ to $175 \text{ dm}^2/\text{dm}^3$, more preferably from $20 \text{ dm}^2/\text{dm}^3$ to $150 \text{ dm}^2/\text{dm}^3$, even more preferably from $25 \text{ dm}^2/\text{dm}^3$ to $125 \text{ dm}^2/\text{dm}^3$, yet even more preferably from $30 \text{ dm}^2/\text{dm}^3$ to $100 \text{ dm}^2/\text{dm}^3$, most preferably from $35 \text{ dm}^2/\text{dm}^3$ to $75 \text{ dm}^2/\text{dm}^3$, yet even most preferably from $40 \text{ dm}^2/\text{dm}^3$ to $50 \text{ dm}^2/\text{dm}^3$.

[0075] In the context of the present invention, the total free inner volume corresponds to the total inner volume in the treatment device subtracted by at least the volume (i.e. the tare volume) of the one or more than one anode including e.g. its parts for installation and preferably all other installations inside the treatment device such as pipes, etc. In other words, the total free inner volume is more preferably the volume that the liquid can maximally occupy within the treatment device.

[0076] In the context of the present invention the afore-

mentioned parameter denotes an anode density (i.e. total effective anode surface area per dm^3 of said total free inner volume). In the method of the present invention it is desired to achieve comparatively high anode densities to very efficiently oxidize the manganese species having the first oxidation number, i.e. as much as possible and as quick as possible under the given circumstances. In fact, the aforementioned anode densities are typically considered as high. It is a parameter to characterize the compact and dense packing of the treatment device.

[0077] Preferred is a method of the present invention, wherein the treatment device has at least one inner surface comprising or consisting of a fluorinated plastic, preferably polyvinylidene fluoride (PVDF) and/or polytetrafluoroethylene (PTFE). 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.

[0078] In step (C) of the method of the present invention a current is applied, preferably an electrical current.

[0079] Preferred is a method of the present invention, wherein in step (C) the current has a current density ranging from 0.1 A/dm^2 to 10 A/dm^2 , preferably from 0.2 A/dm^2 to 8 A/dm^2 , more preferably from 0.3 A/dm^2 to 6 A/dm^2 , even more preferably from 0.4 A/dm^2 to 4 A/dm^2 , yet even more preferably from 0.5 A/dm^2 to 2.8 A/dm^2 , most preferably from 0.6 A/dm^2 to 1.5 A/dm^2 . 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 reduce undesired anodic oxygen gas production, which in turn reduces the current efficiency.

[0080] 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/dm^2 to 70 A/dm^2 , preferably from 3 A/dm^2 to 60 A/dm^2 , more preferably from 4 A/dm^2 to 50 A/dm^2 , even more preferably from 5 A/dm^2 to 40 A/dm^2 , yet even more preferably from 6 A/dm^2 to 30 A/dm^2 , most preferably from 7 A/dm^2 to 20 A/dm^2 . 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 may suppress undesired cathodic decomposition reactions of desired manganese species.

[0081] In some cases, 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/dm^2 to 30 A/dm^2 , preferably from 3 A/dm^2 to 25 A/dm^2 , more preferably from 4 A/dm^2 to 20 A/dm^2 , even more preferably from 5 A/dm^2 to 15 A/dm^2 , most preferably from 6 A/dm^2 to 12 A/dm^2 .

[0082] In other cases, 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/dm^2 to 70 A/dm^2 , preferably from 12 A/dm^2 to 65 A/dm^2 , more preferably from 14 A/dm^2 to 60 A/dm^2 , even more pref-

erably from 16 A/dm^2 to 50 A/dm^2 , most preferably from 18 A/dm^2 to 35 A/dm^2 .

[0083] As already mentioned above, preferred is a method of the present invention, wherein the manganese species having the first oxidation number are comprised in a liquid.

[0084] Preferred is a method of the present invention, wherein in step (A) in the liquid all manganese species together (i.e. including the manganese species having the first oxidation number) 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 preferably applies to the liquid in step (A) as well as after step (C).

[0085] Generally preferred is a method of the present invention, wherein the liquid comprises acids in a total concentration ranging from 5 mol/L to 13 mol/L , based on the total volume of the liquid, preferably from 6 mol/L to 12 mol/L , more preferably from 7 mol/L to 11.5 mol/L , most preferably from 8 mol/L to 11 mol/L . Most preferably this applies to inorganic acids.

[0086] More preferred is a method of the present invention, wherein the liquid comprises phosphoric acid, preferably in 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 .

[0087] Most preferred is a method of the present invention, wherein phosphoric acid is the only (mineral) acid in the liquid. Preferred is in some cases a method of the present invention, wherein the liquid is substantially free of, preferably does not comprise, sulfuric acid.

[0088] 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.

[0089] 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.

[0090] Only in a few cases a method of the present invention is preferred, wherein the liquid comprises iodine-comprising compounds.

[0091] 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.

[0092] Preferred is a method of the present invention, wherein the liquid comprises alkali metal 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.

[0093] 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.

[0094] Preferred is a method of the present invention, wherein the liquid in step (A) and preferably additional 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.

[0095] Preferred is a method of the present invention, wherein in step (A) and preferably additional 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.

[0096] Preferred is a method of the present invention, wherein in the liquid after step (C) the manganese species having the second oxidation number, 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.

[0097] Preferred is a method of the present invention, wherein the liquid comprises water, preferably water is balance.

[0098] The invention will now be further illustrated by the following example.

[0099] 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 prepared as etching composition. Due to a high degree of self-decomposition, the amount of permanganate ions quickly decreased. The volume of the liquid was about 0.5 L.

[0100] In order to establish an environmental and ecological favorable etching method, the etching composition was subjected to electrolytic re-oxidation as defined in the present invention in a treatment device for recycling. In the treatment device, the following different types of a single anode were tested:

(a) platinized titanium as woven fabric anode; surface density of about 10 m²/L (surface factor of about 10); geometrical surface area 0.2 dm²; tested with an anodic current density of 0.75 A/dm², 1 A/dm², and 1.3 A/dm²;

(b) platinized stainless steel as woven fabric anode; surface density of about 14 m²/L (surface factor of about 14); geometrical surface area 0.15 dm²; anodic current density 1 A/dm²

[0101] As cathode, a lead alloy cathode was used. The anode and the cathode were separated by a ceramic permeable barrier such that an anolyte and a catholyte were formed.

[0102] The treatment device was filled with a catholyte consisting of aqueous, concentrated phosphoric acid (70 wt.-%), wherein the liquid was the anolyte.

[0103] The distance between the anode and the cathode was approximately 20 mm.

[0104] The anodic current density was as mentioned above, wherein the cathodic current density was approximately 10 A/dm².

[0105] While in contact with the anode, the manganese species having the first oxidation number was continually re-oxidized to permanganate ions (i.e. the manganese species having the second oxidation number). The manganese species having the first oxidation number comprised particulate manganese oxide.

[0106] Due to the unusual high surface density, the constant recycling was very efficient and only a comparatively small anode was necessary. Nevertheless, the total concentration of permanganate ions was maintained.

Claims

1. A method for oxidizing manganese species in a treatment device, the method comprising the steps

- (A) providing in the treatment device a manganese species having a first oxidation number,
- (B) providing in the treatment device one or more than one anode and at least one cathode,
- (C) applying a current to said anode and said cathode such that at least a portion of the manganese species having the first oxidation number is anodically oxidized to a manganese species having a second oxidation number which is higher than the first oxidation number,

characterized in that at least one of said one or more than one anode has a surface density of 6 m²/L or more, based on the total volume of said at least one anode.

2. The method of claim 1, wherein the first oxidation number is +4 or below.

3. The method of claim 1 or 2, wherein the second oxidation number is above +4, preferably is +7.

4. The method of any of claims 1 to 3, wherein the one or more than one anode and the at least one cathode have a distance to each other ranging from 1 mm to 100 mm, preferably from 2 mm to 90 mm, more preferably from 3 mm to 80 mm, even more preferably from 4 mm to 70 mm, most preferably from 5 mm to

60 mm.

5. The method of any of claims 1 to 4, wherein the one or more than one anode and the at least one cathode are separated from each other by a permeable barrier, preferably a permeable membrane. 5
6. The method of any of claims 1 to 5, wherein the surface density is 8 m²/L or more, preferably 10 m²/L or more, more preferably 14 m²/L or more, even more preferably 16 m²/L or more, most preferably 20 m²/L or more. 10
7. The method of any of claims 1 to 6, 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. 15
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8. The method of any of claims 1 to 7, wherein the at least one anode having a surface density of 6 m²/L or more is selected from the group consisting of 3D-printed anodes, woven fabric anodes, foam anodes, stacked single-layer anodes, and packed bed anodes. 25
9. The method of claim 8, wherein the woven fabric anodes comprise woven metallic wires and/or woven metallized filaments. 30
10. The method of claim 8 or 9, wherein the woven fabric anodes comprise flat woven fabric anodes and/or pile fabric anodes. 35
11. The method of claim 8, wherein the 3D-printed anodes comprise 3D-printed lattice anodes and/or 3D-printed lamella anodes. 40
12. The method of claim 8, 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. 45
13. The method of any of claims 1 to 12, wherein the at least one anode having a surface density of 6 m²/L or more comprises a material selected from the group consisting of platinum, titanium, niobium, lead, gold, alloys comprising at least one thereof, oxides thereof, and mixtures thereof. 50
14. The method of any of claims 1 to 13, wherein the one or more than one anode provides a total effective anode surface area A₁ and the at least one cathode a total effective cathode surface area A₂, wherein A₁ is larger than A₂. 55

15. The method of any of claims 1 to 14, wherein A₁ : A₂ 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.



EUROPEAN SEARCH REPORT

Application Number
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