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(54) **METHOD OF PREPARING AN ELECTRODE FOR A CAPACITIVE DEIONIZATION DEVICE, AN ELECTRODE FOR A CAPACITIVE DEIONIZATION DEVICE, AND A CAPACITIVE DEIONIZATION DEVICE HAVING THE ELECTRODE**

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977/742; 977/842

(57) **ABSTRACT**

A method of preparing an oxidized electrode for a capacitive deionization device, the method including electrochemically oxidizing an electrode including a hydrophobic active material to produce the oxidized electrode.

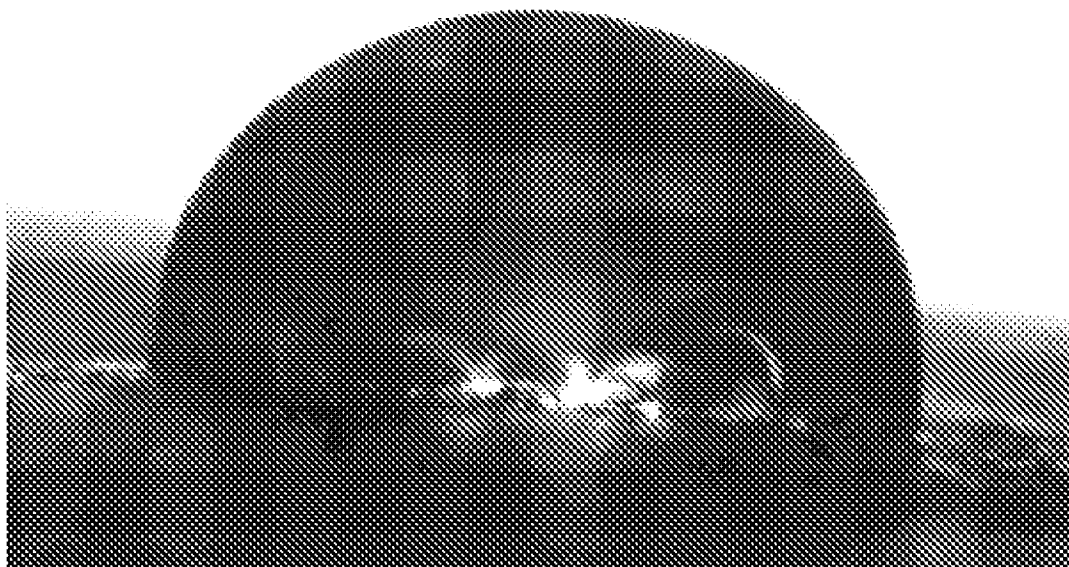


FIG. 1

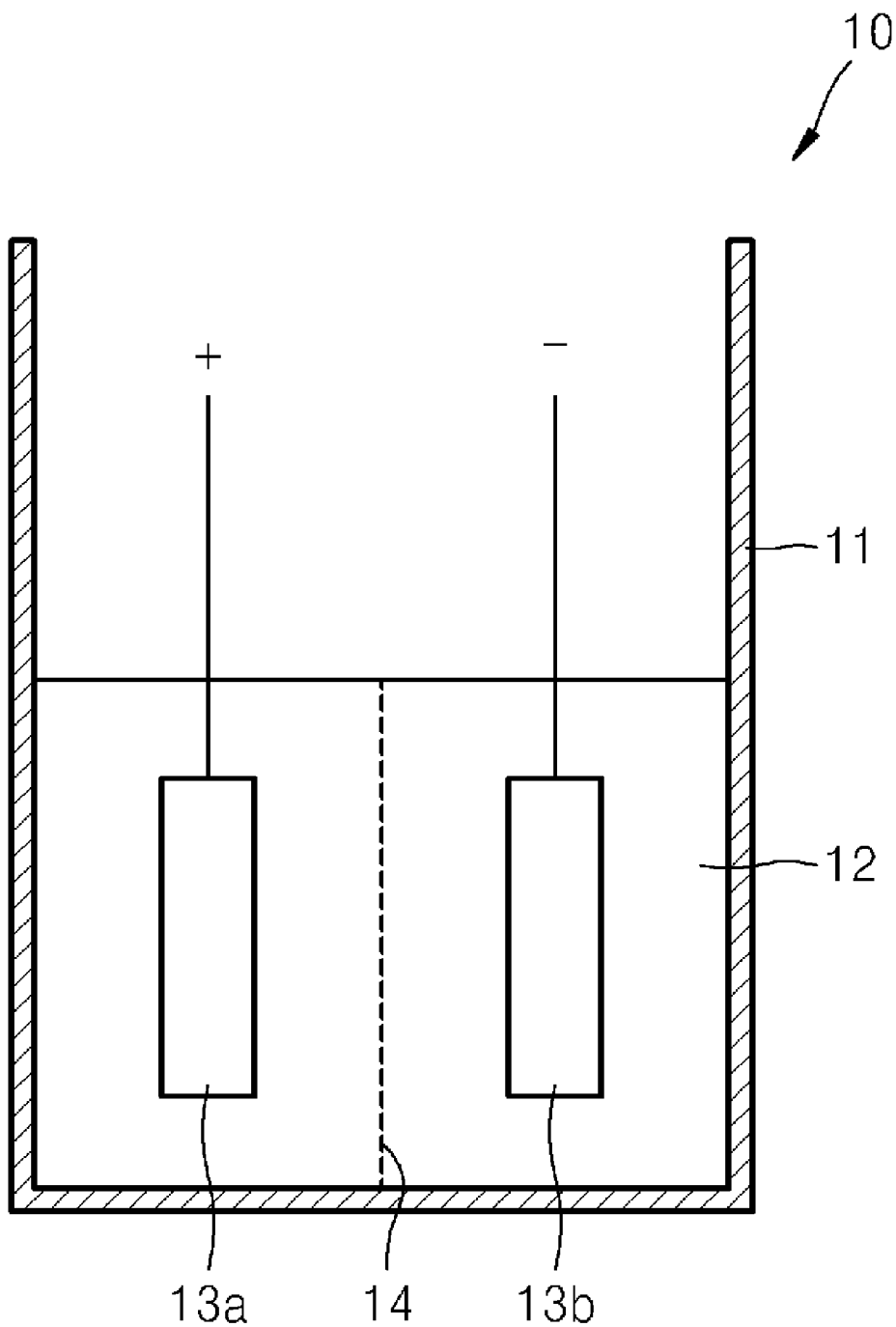


FIG. 2

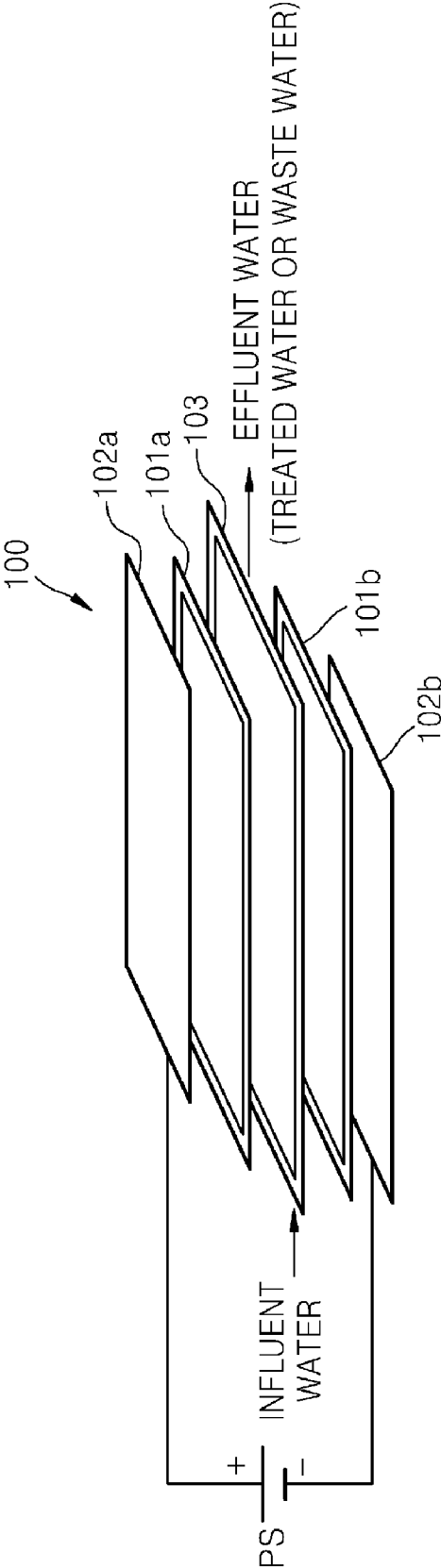


FIG. 3A

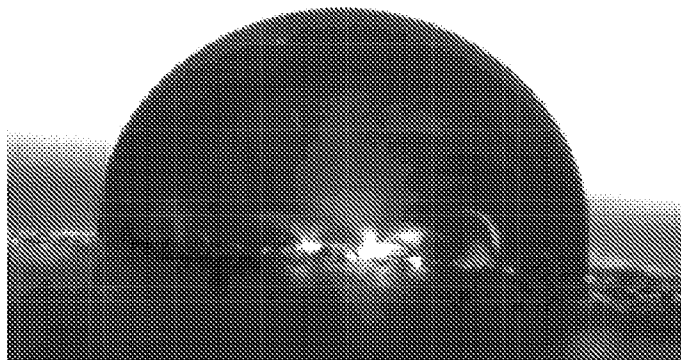


FIG. 3B

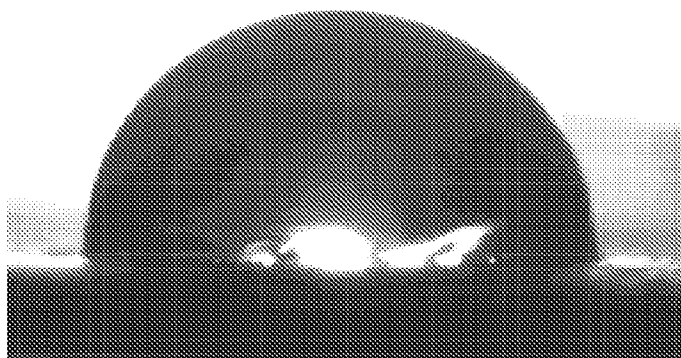


FIG. 3C



FIG. 4

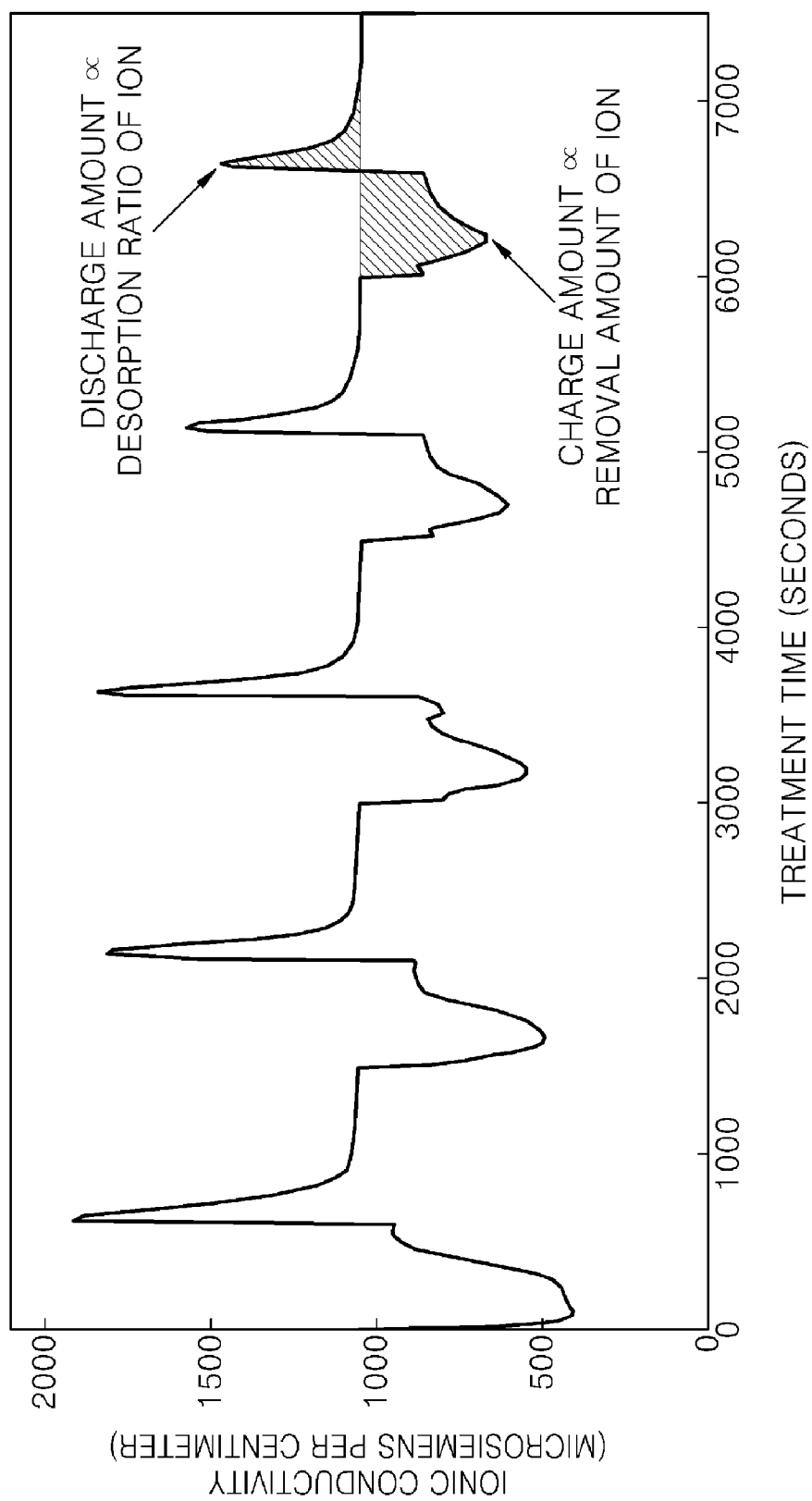


FIG. 5A

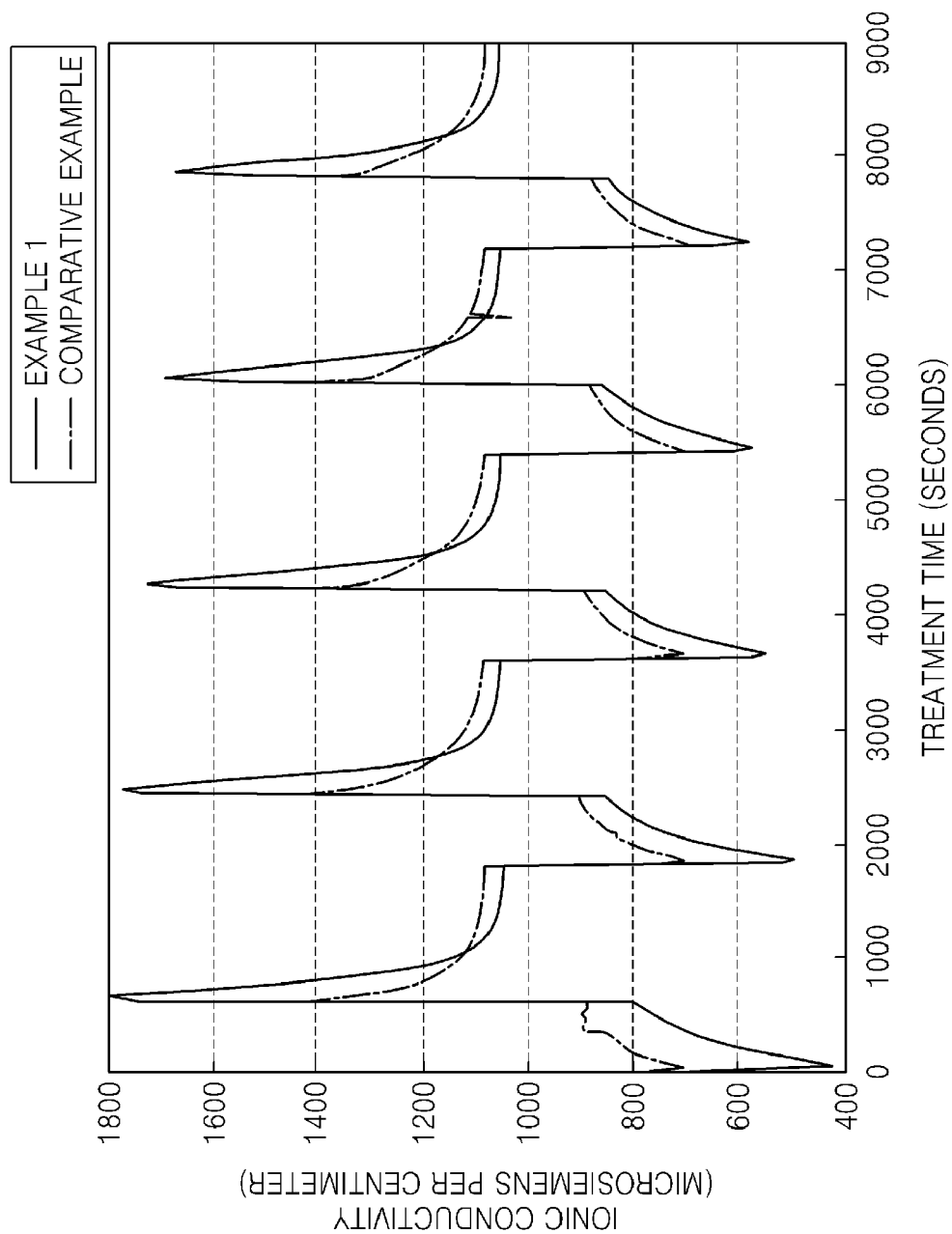


FIG. 5B

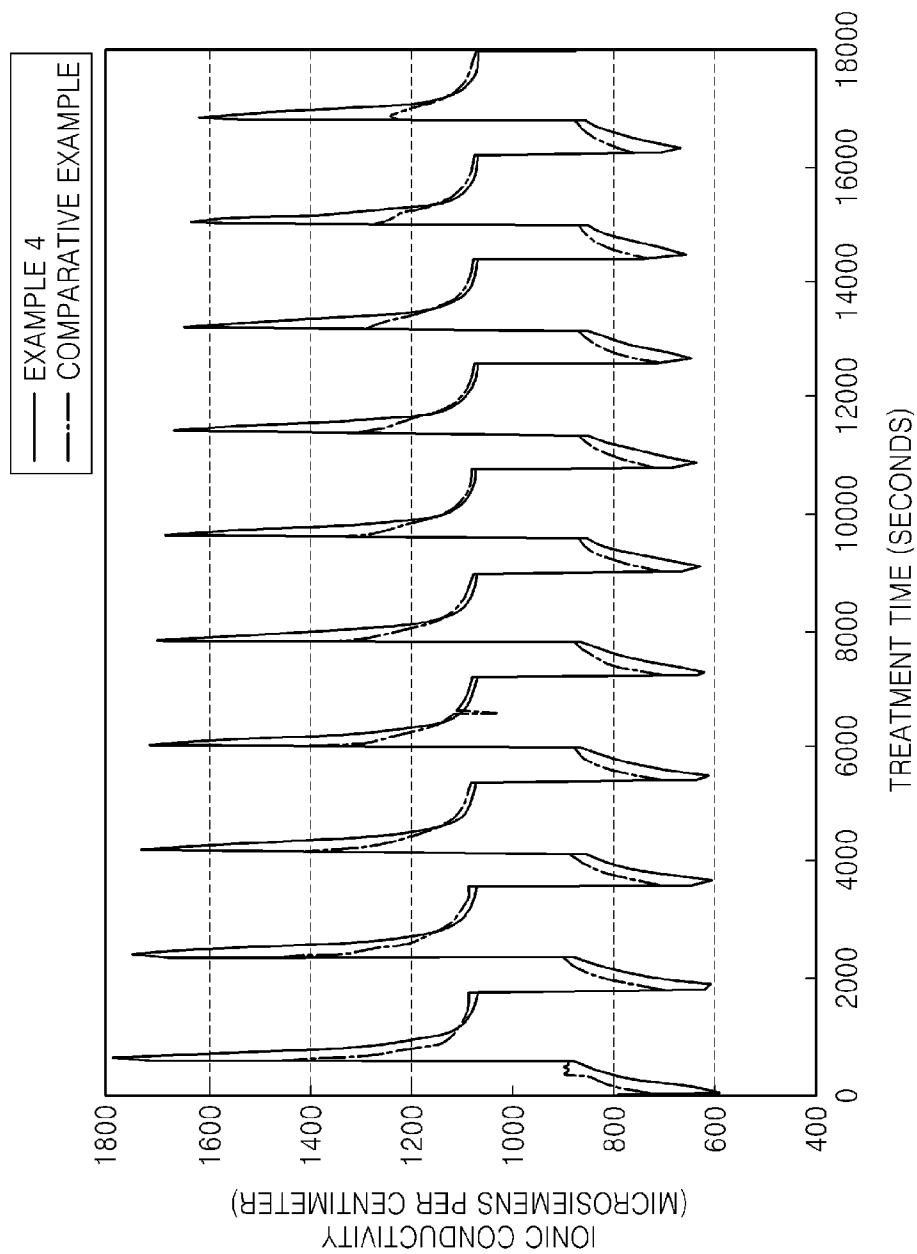


FIG. 6A

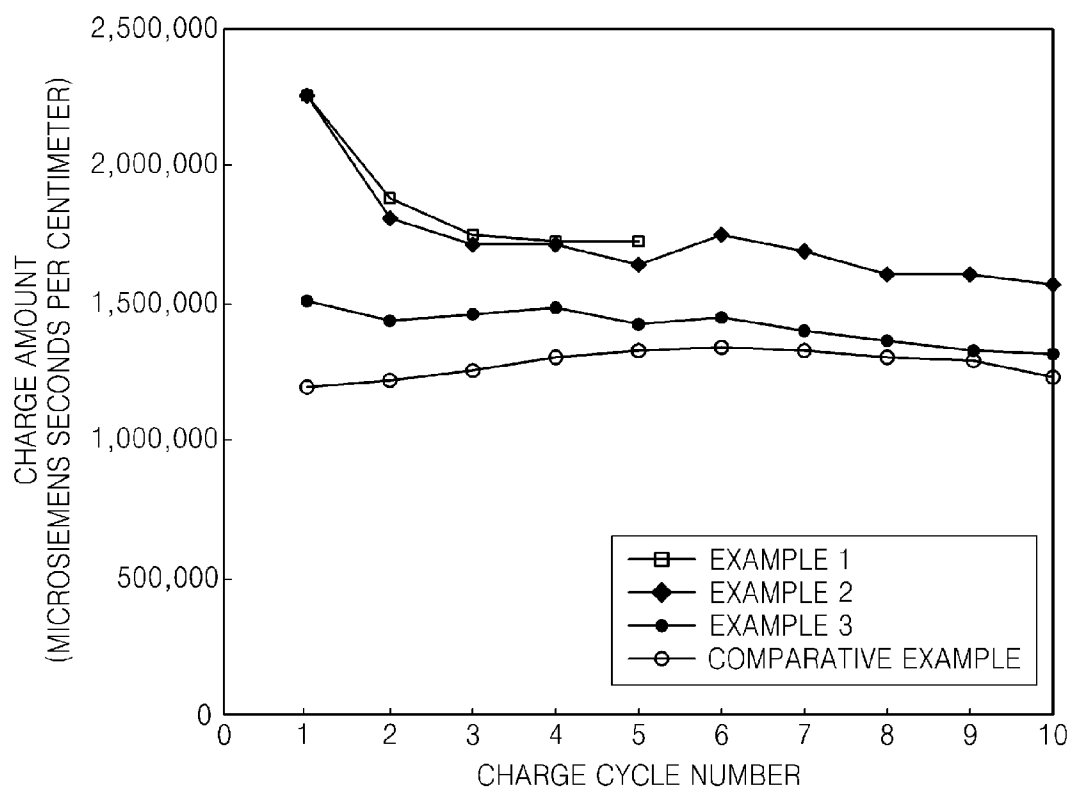


FIG. 6B

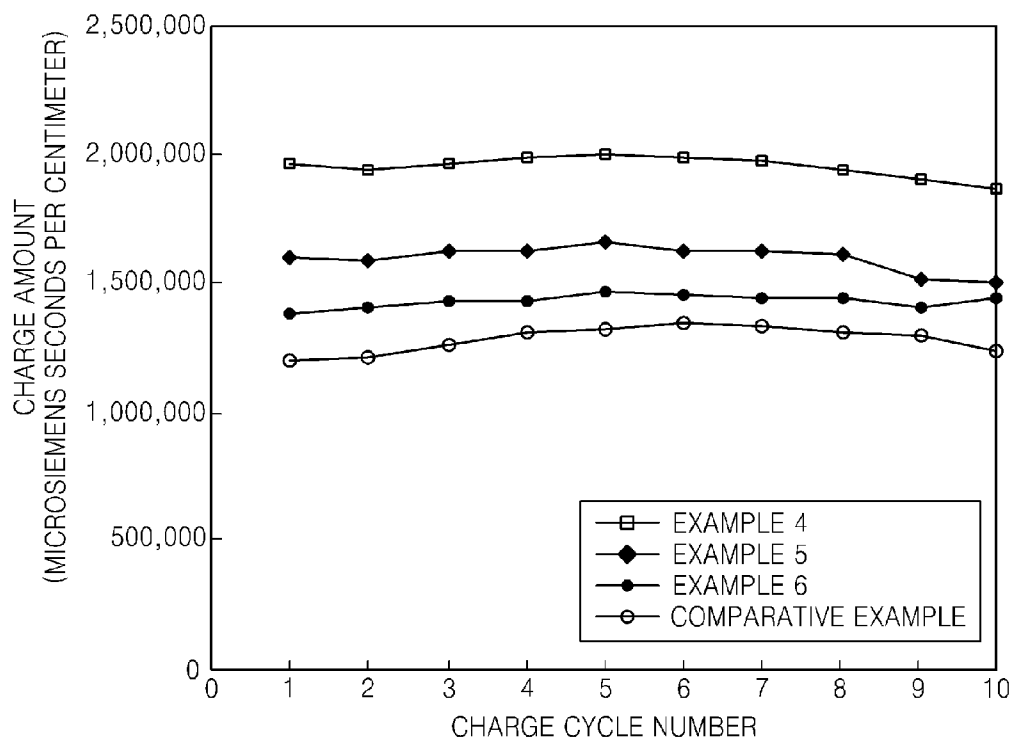


FIG. 7A

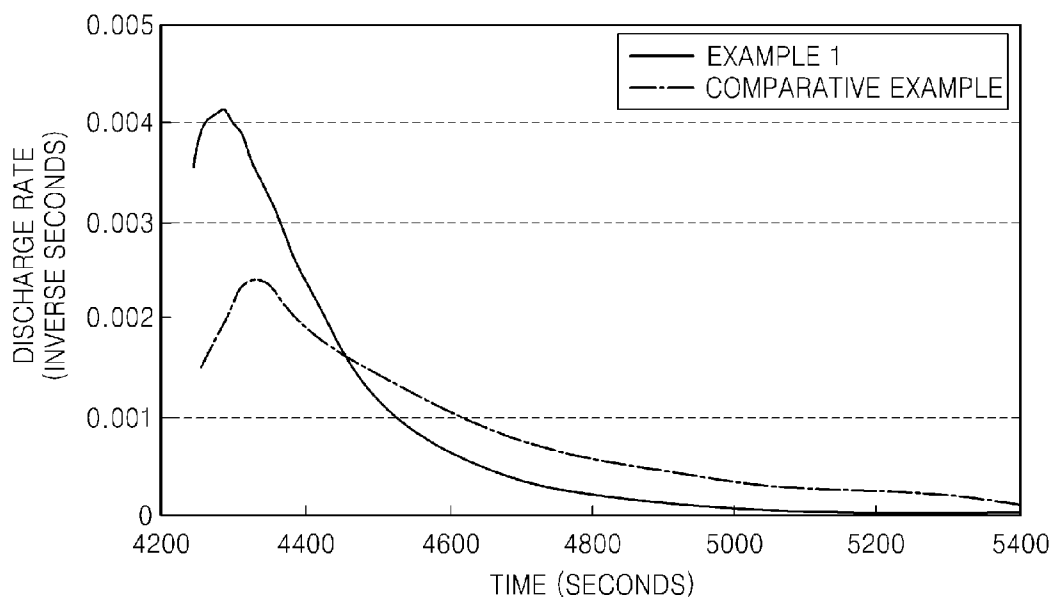
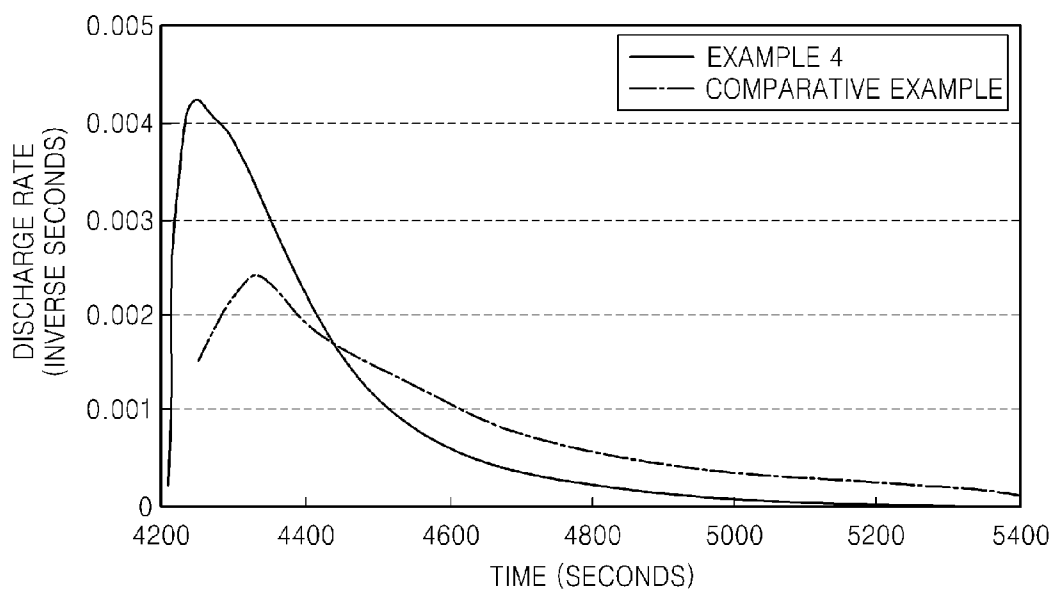


FIG. 7B



**METHOD OF PREPARING AN ELECTRODE
FOR A CAPACITIVE DEIONIZATION
DEVICE, AN ELECTRODE FOR A
CAPACITIVE DEIONIZATION DEVICE, AND
A CAPACITIVE DEIONIZATION DEVICE
HAVING THE ELECTRODE**

**CROSS-REFERENCE TO RELATED
APPLICATIONS**

[0001] This application claims priority to Korean Patent Application No. 10-2010-0000577, filed on Jan. 5, 2010, and all benefits accruing therefrom under 35 U.S.C. §119, the content of which in its entirety is herein incorporated by reference.

BACKGROUND

[0002] 1. Field

[0003] The present disclosure relates to a method of preparing an electrode for a capacitive deionization device, an electrode for a capacitive deionization device, and a capacitive deionization device having the electrode.

[0004] 2. Description of the Related Art

[0005] Tap water supplied to homes contains hardness components, e.g., various water-hardening minerals such as calcium, although the contents thereof vary according to the region where the home is located. In particular, in Europe where large amounts of limestone components contact underground water, the hardness of tap water is significant.

[0006] Unwanted and undesirable scaling easily occurs in a heat exchanger of a home appliance or on an inner wall of a boiler when hard water, which contains high concentrations of hardness components, is used therein, and thus the energy efficiency of the device is significantly reduced due to the scaling. In addition, hard water is unsuitable for washing due to the difficulty of producing a lather with the hard water. Methods for overcoming such problems associated with the use of hard water include (i) removing the scaling with chemicals, and (ii) chemically softening hard water using ion exchange resins, wherein after use the contamination in the ion exchange resin may be removed using a large amount of high-concentration salt water, so that the ion exchange resin may be reused. However, such methods are inconvenient and cause environmental damage. Thus, there is a demand for a technology to more simply soften hard water in an environmentally friendly manner.

[0007] Capacitive deionization (“CDI”) is a technology for removing an ionic material from a medium by adsorbing the ionic material onto a surface of an electrode having nano-sized pores by applying a first voltage to the electrode. To regenerate the electrode, a second voltage opposite in polarity to the first voltage is applied to the electrode, which may be a carbon electrode, so as to remove the adsorbed ionic material, and the ionic material is discharged with water. CDI may operate without chemicals to regenerate the carbon electrode and may operate without an ion exchange resin, a filter, or a membrane. Also, CDI may improve capacitance of the medium, which may be water, without discharging hardness components, such as Ca^{2+} or Mg^{2+} , or harmful ions, such as Cr.

[0008] In CDI, when a direct current (“DC”) voltage having a low potential difference with respect to the medium is applied to a carbon electrode while a medium, i.e., an electrolyte solution containing dissolved ions, flows through a

flow path and contacts the carbon electrode, anions are absorbed and concentrated in a negative electrode, and cations are absorbed and concentrated in a positive electrode. Accordingly, when application of the DC voltage is stopped, the concentrated anions and cations are desorbed from the negative electrode and positive electrode.

[0009] The carbon electrode desirably has a low electrical resistance and a large specific surface area, and thus, the carbon electrode may be manufactured by binding an activated carbon with polytetrafluoroethylene (“PTFE”), or the carbon electrode may be manufactured by carbonizing a resorcinol formaldehyde resin and then performing a complicated drying process, thereby obtaining a carbon electrode having a plate-like shape.

[0010] Commercial electrodes for CDI are usually in the form of a sheet and are manufactured by binding an activated carbon with PTFE. The activated carbon has a large specific surface area and numerous pores, and thus, has high processing capacity when the activated carbon is used as an active material for a CDI electrode.

[0011] In addition, high surface area graphite (“HSAG”) has a relatively large specific surface area and is inexpensive, and thus, may be applied to an active material in spite of a high degree of graphitization.

[0012] However, an electrode including the carbonaceous material has low hydrophilicity, and thus has low wettability in CDI influent water. Also, reduction of the wettability of the electrode is caused by repulsion between the hydrophobic carbonaceous material and the influent water, thereby decreasing the capacitance and deionization rates of the electrode. Thus there remains a need for an improved CDI electrode material.

SUMMARY

[0013] Provided is a method of preparing an electrode for a capacitive deionization device, the method including electrochemically oxidizing an electrode including a hydrophobic active material.

[0014] Provided is an electrode for a capacitive deionization device, the electrode including an electrochemically oxidized active material.

[0015] Provided is a capacitive deionization device including the electrode.

[0016] Additional aspects will be set forth in part in the description which follows and, in part, will be apparent from the description.

[0017] According to an aspect, a method of manufacturing an oxidized electrode for a capacitive deionization device includes: electrochemically oxidizing an electrode including a hydrophobic active material to produce the oxidized electrode.

[0018] The electrode may further include a binder and a conducting agent.

[0019] The method may further include disposing a powdered hydrophobic active material.

[0020] The hydrophobic active material may include a carbonaceous material.

[0021] The carbonaceous material may include at least one selected from the group consisting of activated carbon, carbon nanotube (“CNT”), mesoporous carbon, activated carbon fiber, graphite, and graphite oxide.

[0022] The graphite may include high surface area graphite (“HSAG”).

[0023] The electrochemical oxidization of the electrode may be performed in an electrochemical cell including the electrode, a counter electrode, an electrolyte solution in which the electrode and the counter electrode are immersed, and a separator which electrically insulates the electrode from the counter electrode, wherein the electrode is used as a positive electrode, and the counter electrode is used as a negative electrode in the electrochemical cell.

[0024] The electrode and the counter electrode may be the same or different from each other.

[0025] The electrolyte solution may be an acidic, alkaline, or neutral solution.

[0026] An amount of electric charge charged in the electrochemical cell during the electrochemically oxidizing the electrode may be in the range of about 20 to about 30,000 coulombs per gram, based on the weight of an active material of the electrode.

[0027] A contact angle between the electrode and a hydrophilic electrolyte solution may be decreased by the electrochemical oxidization of the electrode.

[0028] The method may further include washing the electrochemically oxidized electrode with a cleaning solution.

[0029] According to another aspect of the present invention, an electrode for a capacitive deionization device includes an electrochemically oxidized active material.

[0030] The electrode for a capacitive deionization device may further include an acidic functional group.

[0031] The amount of the acidic functional group per unit weight of the electrode may be about 0.7 to about 5 millimoles per gram.

[0032] The acidic functional group may include at least one selected from the group consisting of a carboxyl group ($-\text{COOH}$), a carboxylate group ($-\text{COO}^-$), and a phenol group.

[0033] According to another aspect of the present invention, a capacitive deionization device includes the electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0034] These and/or other aspects will become apparent and more readily appreciated from the following description of the embodiments, taken in conjunction with the accompanying drawings in which:

[0035] FIG. 1 is a schematic cross-sectional view of an exemplary embodiment of an electrochemical cell used in a method of preparing an electrode for a capacitive deionization device;

[0036] FIG. 2 is a schematic cross-sectional view of an exemplary embodiment of a capacitive deionization device including an electrode;

[0037] FIGS. 3A and 3B are photographs of exemplary embodiments of electrochemically oxidized electrodes which are prepared according to an embodiment and are in contact with hard water, and FIG. 3C is a photograph of an exemplary embodiment of an electrode which is not electrochemically oxidized and is in contact with hard water;

[0038] FIG. 4 is a graph illustrating ionic conductivity of effluent water (microsiemens per centimeter, $\mu\text{S}/\text{cm}$) versus treatment time (seconds, sec) when influent water is treated using a comparative capacitive deionization device, and describes how to calculate a charge amount and a discharge amount;

[0039] FIGS. 5A and 5B are graphs of ionic conductivity (microsiemens per centimeter, $\mu\text{S}/\text{cm}$) versus treatment time (seconds, sec) respectively showing ionic conductivity of

effluent water according to treatment time when deionization of influent water is conducted using an exemplary embodiment of a capacitive deionization device including an exemplary embodiment of an electrode or using a capacitive deionization device including a comparative electrode;

[0040] FIGS. 6A and 6B are graphs of charge amount (microsiemens seconds per centimeter, $\mu\text{m}\cdot\text{sec}/\text{cm}$) versus charge cycle number respectively showing charge amount with respect to number of charge cycles when deionization of influent water is conducted using a capacitive deionization device including an exemplary embodiment of an electrode or using a capacitive deionization device including a comparative electrode; and

[0041] FIGS. 7A and 7B are graphs respectively showing discharge rate (inverse seconds, sec^{-1}) versus time (seconds, sec) when deionization of influent water is conducted using an exemplary embodiment of a capacitive deionization device including an exemplary embodiment of an electrode or using a capacitive deionization device including a comparative electrode.

DETAILED DESCRIPTION

[0042] Reference will now be made in detail to embodiments, examples of which are illustrated in the accompanying drawings, wherein like reference numerals refer to the like elements throughout. In this regard, the present embodiments may have different forms and should not be construed as being limited to the descriptions set forth herein. Accordingly, the embodiments are merely described below by referring to the figures to explain aspects of the present description.

[0043] It will be understood that when an element is referred to as being “on” another element, it can be directly on the other element or intervening elements may be present therebetween. In contrast, when an element is referred to as being “directly on” another element, there are no intervening elements present. As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0044] It will be understood that, although the terms first, second, third etc. may be used herein to describe various elements, components, regions, layers and/or sections, these elements, components, regions, layers and/or sections should not be limited by these terms. These terms are only used to distinguish one element, component, region, layer, or section from another element, component, region, layer or section. Thus, a first element, component, region, layer, or section discussed below could be termed a second element, component, region, layer, or section without departing from the teachings of the present invention.

[0045] The terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting. As used herein, the singular forms “a,” “an” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms “comprises” and/or “comprising,” or “includes” and/or “including” when used in this specification, specify the presence of stated features, regions, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, regions, integers, steps, operations, elements, components, and/or groups thereof.

[0046] Furthermore, relative terms, such as “lower” or “bottom” and “upper” or “top,” may be used herein to

describe one element's relationship to another elements as illustrated in the Figures. It will be understood that relative terms are intended to encompass different orientations of the device in addition to the orientation depicted in the Figures. For example, if the device in one of the figures is turned over, elements described as being on the "lower" side of other elements would then be oriented on "upper" sides of the other elements. The exemplary term "lower," can therefore, encompass both an orientation of "lower" and "upper," depending on the particular orientation of the figure. Similarly, if the device in one of the figures is turned over, elements described as "below" or "beneath" other elements would then be oriented "above" the other elements. The exemplary terms "below" or "beneath" can, therefore, encompass both an orientation of above and below.

[0047] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and the present disclosure, and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

[0048] Exemplary embodiments are described herein with reference to cross section illustrations that are schematic illustrations of idealized embodiments. As such, variations from the shapes of the illustrations as a result, for example, of manufacturing techniques and/or tolerances, are to be expected. Thus, embodiments described herein should not be construed as limited to the particular shapes of regions as illustrated herein but are to include deviations in shapes that result, for example, from manufacturing. For example, a region illustrated or described as flat may, typically, have rough and/or nonlinear features. Moreover, sharp angles that are illustrated may be rounded. Thus, the regions illustrated in the figures are schematic in nature and their shapes are not intended to illustrate the precise shape of a region and are not intended to limit the scope of the present claims.

[0049] Hereinafter, a method of preparing an electrode for a capacitive deionization device, an electrode prepared using the method, and a capacitive deionization device including the electrode are described in further detail with reference to the accompanying drawings.

[0050] The method of preparing an electrode for a capacitive deionization device includes electrochemically oxidizing an electrode having a hydrophobic active material. By electrochemically oxidizing the electrode, the hydrophobicity of the hydrophobic active material contained in the electrode decreases and the hydrophilicity of the active material increases, which will be further described below.

[0051] The hydrophobic active material may include a carbonaceous material. The carbonaceous material may include at least one selected from the group consisting of activated carbon, carbon nanotube ("CNT"), mesoporous carbon, activated carbon fiber, graphite, and graphite oxide. In addition, the graphite may include high surface area graphite ("HSAG"). The term "HSAG" as used herein refers to graphite having a specific surface area equal to or greater than about 30 square meters per gram (m^2/g).

[0052] The electrode may further include a binder and a conducting agent. In an embodiment, the electrode may be prepared using a powdered hydrophobic active material. For

example, the electrode may be prepared by adding a powdered hydrophobic active material and a conducting agent to a binder suspension, stirring the mixture, kneading the stirred mixture, and press molding the kneaded stirred mixture.

[0053] The binder may include styrene butadiene rubber ("SBR"), carboxymethylcellulose ("CMC"), polytetrafluoroethylene ("PTFE"), or the like, or a combination comprising at least one of the foregoing.

[0054] The conducting agent may include carbon black, vapor grown carbon fiber ("VGCF"), graphite, or the like, or a combination comprising at least one of the foregoing.

[0055] Hereinafter, the electrochemically oxidizing the electrode will be further described in detail with reference to FIG. 1.

[0056] FIG. 1 is a schematic cross-sectional view of an exemplary embodiment of an electrochemical cell 10 used in a method of preparing a working electrode 13a for a capacitive deionization device.

[0057] Referring to FIG. 1, the electrochemical cell 10 may include a reaction vessel 11, an electrolyte solution 12, a working electrode 13a, and a counter electrode 13b, which are immersed in the electrolyte solution 12, and a separator 14 which electrically insulates the working electrode 13a from the counter electrode 13b.

[0058] In the electrochemical cell 10, the working electrode 13a may be used as a positive electrode, and the counter electrode 13b may be used as a negative electrode. That is, if a positive (+) electrical potential is applied to the working electrode 13a and a negative (-) electrical potential is applied to the counter electrode 13b in the electrochemical cell 10, the working electrode 13a, which is a positive electrode, is electrochemically oxidized. In an embodiment, whether the working electrode 13a is electrochemically oxidized or not may be identified by stirring (e.g., contacting) the working electrode 13a with a cleaning solution, such as deionized water, to wash the working electrode 13a, and titrating the resulting deionized water solution with an alkaline solution, and/or measuring a contact angle between the working electrode 13a and a hydrophilic electrolyte solution (e.g., hard water). Thus, if the hydrophobic active material contained in the working electrode 13a is electrochemically oxidized, an acidic functional group, which may include oxygen, may be present on the surface of the active material, and the amount of the acidic functional group may be measured by titrating the solution collected after washing the working electrode 13a with an alkaline solution. Also, a contact angle between the working electrode 13a and the hydrophilic electrolyte solution may be smaller than a contact angle between the working electrode 13a and the hydrophilic electrolyte solution before the working electrode 13a is electrochemically oxidized. The term "contact angle" as used herein refers to an angle between a free surface of a liquid (e.g., a hydrophilic electrolyte solution such as hard water) and a tangent plane of a solid (e.g., an electrode) where the liquid meets the solid. The contact angle is determined by a cohesive force between liquid molecules and an adhesive force between the surface of the liquid and the surface of the solid. As such, while not wanting to be bound by theory, it is understood that if the amount of the acidic functional group formed on the surface of the working electrode 13a increases, the contact angle between the working electrode 13a and the hydrophilic electrolyte solution decreases, and thus the hydrophilicity of the surface of the working electrode 13a is improved and the wettability of the working electrode 13a to the hydrophilic

electrolyte solution (e.g., hard water) increases. In addition, the specific surface area of the working electrode **13a** is proportionate to the amount of the acidic functional group that exists on the surface of the working electrode **13a**, e.g., the amount of the alkaline solution used for titrating the acidic functional group (see, for example, Carbon 37 (1999), 85-96, C. U. Pittman et al).

[0059] The amount of the acidic functional group per unit weight of the electrochemically oxidized electrode may be about 0.7 to about 5 millimoles per gram (mmol/g), specifically 1 to 4 mmol/g, more specifically about 3 mmol/g. When the amount of the acidic functional group is within this range, the wettability of the electrode to the hydrophilic electrolyte solution may be improved.

[0060] The acidic functional group may include at least one oxygen-containing functional group selected from the group consisting of a carboxyl group ($-\text{COOH}$), a carboxylate group ($-\text{COO}^-$), and a phenol group.

[0061] The working electrode **13a** and the counter electrode **13b** may be the same or may be different from each other. For example, the working electrode **13a** and the counter electrode **13b** may each independently include activated carbon. For example, the working electrode **13a** may include HSAG and the counter electrode **13b** may include activated carbon.

[0062] The electrolyte solution may be an acidic solution such as an aqueous H_2SO_4 solution, an alkaline solution such as an aqueous KOH solution, or a neutral solution such as an aqueous KCl solution.

[0063] In addition, the amount of electric charge charged in the electrochemical cell **10** in the electrochemically oxidizing the electrode may be about 20 to about 30,000 coulombs per gram (C/g), specifically about 100 to about 10,000 C/g, more specifically about 1,000 to about 5,000 C/g, based on a weight of an active material of the electrode. If the amount of the electric charge is within the foregoing range, the hydrophilicity of the electrode may be improved with reduced energy costs and within a shortened period of time.

[0064] The working electrode **13a**, which is electrochemically oxidized as disclosed above, may be washed with a cleaning solution such as distilled water, and then may be used as a positive electrode, such as positive electrode **101a** of FIG. 2 and/or a negative electrode, such as negative electrode **101b** of the capacitive deionization device **100** of FIG. 2. In an embodiment, the electrochemically oxidized positive electrode **101a** and/or the negative electrode **101b** of FIG. 2 has high wettability to the hydrophilic electrolyte solution and high specific surface area, as further disclosed above. Accordingly, capacitance and life-span characteristics of the electrode are improved, and deionization rates of influent water, such as hard water, and regeneration rates of the electrode increase, thereby improving the performance of the capacitive deionization device **100** of FIG. 2.

[0065] The electrochemical oxidation of the electrode for a capacitive deionization device may be conducted using the electrochemical cell **10** of FIG. 1 and/or the capacitive deionization device **100** of FIG. 2 (see, for example, Examples 1 to 6).

[0066] FIG. 2 is a schematic cross-sectional view of an exemplary embodiment of a capacitive deionization device **100** including a positive electrode **101a** and/or negative electrode **101b**.

[0067] Referring to FIG. 2, the capacitive deionization device **100** may include a pair of electrodes, specifically a

positive electrode **101a** and a negative electrode **101b**, a pair of current collectors, specifically a positive current collector **102a** and a negative current collector **102b**, and a separator **103**. In an embodiment, the positive electrode **101a** and the negative electrode **101b** may respectively be disposed on opposite sides of the separator **103**, and each of the positive and negative current collectors **102a** and **102b** may respectively be disposed at a side of the positive electrode **101a** and the negative electrode **101b** which is opposite to the separator **103**.

[0068] At least one of the positive electrode **101a** and the negative electrode **101b** may be an electrode which is electrochemically oxidized according to the method disclosed above. For example, the positive electrode **101a** may include activated carbon which is not electrochemically oxidized, and the negative electrode **101b** may include electrochemically oxidized HSAG. Alternatively, the positive electrode **101a** and the negative electrode **101b** may respectively include an electrochemically oxidized activated carbon.

[0069] The influent water (e.g., hard water), which flows into the capacitive deionization device **100** at a first end of the separator **103**, is deionized while passing through the capacitive deionization device **100**, and thus is changed into treated water (e.g., soft water), which is discharged at a second end of the separator **103**.

[0070] A power supply ("PS") may be electrically connected to the positive and negative current collectors **102a** and **102b**, respectively. Thus, the positive and negative current collectors **102a** and **102b** may provide an electrical path to supply electric charge to the positive and negative electrodes **101a** and **101b** during charging, i.e., when the influent water is deionized, and to discharge the electric charge accumulated in the positive and negative electrodes **101a** and **101b** during discharging, i.e., when the positive and negative electrodes **101a** and **101b** are regenerated. The positive and negative current collectors **102a** and **102b** may be a carbon plate, a carbon paper, a metal plate, a metal mesh, a metal foam, or the like, and may include aluminum, nickel, copper, titanium, stainless steel, iron, or the like, or a combination comprising at least one of the foregoing.

[0071] The separator **103** provides a flow path between the pair of stacked positive and negative electrodes **101a** and **101b**, and blocks electrical contact between the positive and negative electrodes **101a** and **101b** and their corresponding current collectors, the positive and negative current collectors **102a** and **102b**, respectively. The separator **103** may include, for example, an acrylic fiber, a polyethylene film, a polypropylene film, or a combination comprising at least one of the foregoing.

[0072] Hereinafter, the operation and effects of the capacitive deionization device **100** are disclosed in further detail.

[0073] First, a process of deionizing influent water (also referred to as a charging process) is performed as follows. In an embodiment, the influent water is to be deionized and also functions as an electrolyte solution of the capacitive deionization device **100**.

[0074] When the power supply PS applies a direct current ("DC") voltage to the positive and negative current collectors **102a** and **102b**, the influent water flows into the capacitive deionization device **100** at a first end of the separator **103**. The positive electrode **101a**, which is electrically connected to a positive (+) terminal of the power supplier PS via the positive current collector **102a**, is positively charged, and the negative electrode **101b**, which is electrically connected to a negative

(-) terminal of the power supplier PS via the negative current collector **102b**, is negatively charged. Thus the positive and negative electrodes are polarized. Referring to FIG. 2, the positive electrode **101a**, which is positively charged, and the negative electrode **101b**, which is negatively charged, face each other, and the separator **103** is disposed therebetween. Accordingly, anions, which may include harmful ions such as Cl^- and may be contained in the influent water, are adsorbed onto the positive electrode **101a**, which is positively charged, and cations, which may including hardness components such as Ca^{2+} and Mg^{2+} and may be contained in the influent water, are adsorbed onto the negative electrode **101b**, which is negatively charged. As the processing time passes, the anions and cations, which are dissolved in the influent water, are adsorbed and accumulated in the positive electrode **101a** and the negative electrode **101b**. Accordingly, the influent water, which passes through the capacitive deionization device **100**, is deionized and turned into treated water. Moreover, at least a portion of the harmful ions, which may be included in the influent water, are removed. However, after additional processing time, a surface of the active material included in the positive and negative electrodes **101a** and **101b** may be covered (e.g., saturated) with the adsorbed cations or anions, and thus, a deionizing efficiency of the influent water may gradually decrease. The deionizing efficiency may be determined by measuring the ionic conductivity of treated water (e.g., soft water) flowing out from the capacitive deionization device **100** over time. In other words, when the ionic conductivity of the treated water is low, the amount of removed cations and anions may be large, and thus, the deionizing efficiency may be high. On the contrary, when the ionic conductivity of the treated water is high, the amount of the removed cations and anions may be small, and thus, the deionizing efficiency may be low.

[0075] Thus, if the ionic conductivity of the treated water is equal to or greater than a selected value, it may be desirable to regenerate the positive and negative electrodes **101a** and **101b**. In an embodiment, when the power supplied to the capacitive deionization device **100** is stopped and the capacitive deionization device **100** is electrically shorted, so as to discharge the capacitive deionization device **100**, the positive and negative electrodes **101a** and **101b** may become unpolarized, and the ions which are adsorbed onto the active material of the positive and negative electrodes **101a** and **101b** may be desorbed. Thus, the active surfaces of the positive and negative electrodes **101a** and **101b** may be restored.

[0076] Although the capacitive deionization device **100** of FIG. 2 includes one separator, a pair of electrodes, and a pair of current collectors, the disclosed device is not limited thereto. For example, an exemplary embodiment of a capacitive deionization device may be any of the devices disclosed in Korean Patent Application Nos. 2008-0123154 and 2009-0077161, which are herein incorporated by reference in their entirety, further including at least one electrochemically oxidized electrode as disclosed above.

[0077] Hereinafter, one or more embodiments of the present disclosure will be disclosed in further detail with reference to the following examples. However, these examples are not intended to limit the purpose and scope of the one or more embodiments of the disclosure.

EXAMPLES

Examples 1 to 6

Preparation of Capacitive Deionization Cell Electrode Manufacture

[0078] Manufacture of Activated Carbon Electrode

[0079] A 45 gram (g) quantity of activated carbon (PC, available from Osaka Gas Co., Ltd.), 5 g of carbon black (Super P, available from Timcal), and 8.3 g of an aqueous suspension of 60% by weight of polytetrafluoroethylene ("PTFE"), and 100 g of polyvinyl alcohol were put into a stirring vessel, kneaded, and then press-molded. The resulting mixture was dried in an oven at 80° C. for 2 hours, at 120° C. for 1 hour, and at 200° C. for 1 hour to complete the manufacture of an activated carbon electrode, referred to below as a "PC electrode."

[0080] Manufacture of HSAG Electrode

[0081] A 45 g quantity of high surface area graphite (HSAG, available from Timcal), 5 g of carbon black (Super P, available from Timcal), and 8.33 g of an aqueous suspension of 60% by weight of polytetrafluoroethylene ("PTFE"), and 100 g of polyvinyl alcohol were put into a stirring vessel, kneaded, and then press-molded. Then, the resulting mixture was dried in an oven at 80° C. for 2 hours, at 120° C. for 1 hour, and at 200° C. for 1 hour to complete the manufacture of an HSAG electrode.

[0082] Electrochemically Oxidized HSAG Electrode Manufacture

[0083] First, each of the PC electrode and the HSAG electrode prepared above was cut to prepare 2 pieces, each having of the dimensions 10 centimeters (cm)×10 cm and an area of 100 square centimeters (cm²).

[0084] Second, the two pieces of the PC electrode and the two pieces of the HSAG electrode were put into distilled water and were vacuum-impregnated.

[0085] Third, an electrochemical cell was prepared by sequentially stacking a current collector (graphite foil), one piece of the two pieces of HSAG electrode prepared above, a separator (polyester fiber: manufactured by Sefar), one piece of the two pieces of PC electrode prepared above, and the current collector (graphite foil).

[0086] Fourth, an aqueous 0.5 M H₂SO₄ solution or an aqueous 0.5 M KCl solution was added to each electrochemical cell, as shown in Table 1 below, as the electrolyte solution, and each electrochemical cell was assembled.

[0087] Fifth, both electrodes of the electrochemical cells were charged using a constant current-constant voltage regime. Specifically the cells were charged using a constant current of 2 A applied to both electrodes until a voltage between the electrodes reached 3 V, and then the cells were charged by applying a constant voltage of 3 V to the electrodes, thereby charging the electrodes to have an electric charge of 200 to 3,000 C/g as shown in Table 1 below. During the charging, the HSAG electrode was used as a positive electrode, and the PC electrode was used as a negative electrode.

[0088] Sixth, the electrochemically oxidized HSAG electrode was washed with distilled water.

TABLE 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Electrolyte solution (0.5M aqueous solution)	H ₂ SO ₄	H ₂ SO ₄	H ₂ SO ₄	KCl	KCl	KCl
Amount of electric charge (C/g)	3,000	1,000	300	3,000	1,000	200

[0089] Capacitive Deionization Cell Manufacture

[0090] A capacitive deionization cell was prepared by sequentially stacking a current collector (graphite foil), the electrochemically oxidized HSAG electrodes prepared above, a separator (polyester fiber: manufactured by Sefar), the other piece of the PC electrodes prepared above, and a current collector (graphite foil). In the capacitive deionization cell, during the deionizing, the PC electrode was used as a positive electrode, and the HSAG electrode was used as a negative electrode.

Comparative Example

Preparation of Capacitive Deionization Cell

[0091] An HSAG electrode which was not electrochemically oxidized and a PC electrode were prepared in the same manner as in Examples 1 to 6, and then a capacitive deionization cell including the PC electrode as a positive electrode, and the HSAG electrode, which was not electrochemically oxidized, as a negative electrode during the deionizing, was prepared in the same manner as in Examples 1 to 6.

EVALUATION EXAMPLES

Evaluation Example 1

Evaluation of Degree of Oxidation of Electrochemically Oxidized HSAG Electrode

[0092] The electrochemically oxidized HSAG electrodes prepared according to Examples 1 and 4, and the HSAG electrode which was not electrochemically oxidized and prepared according to the Comparative Example, were each added to deionized water, and the deionized water stirred at 150 revolutions per minute ("rpm") for 4 days to desorb the functional groups attached on the surface of the HSAG electrodes. Then, the deionized water obtained after washing the HSAG electrodes was titrated using an aqueous 0.01 M NaOH solution. The amount of NaOH used in the titration is shown in Table 2 below.

TABLE 2

	Example 1	Example 4	Comparative Example
Amount of NaOH used in the titration (mmol/g)	2.213	1.105	0.383

[0093] Referring to Table 2, the electrochemically oxidized HSAG electrodes prepared according to Examples 1 and 4 had more acidic functional groups than the HSAG electrode which was not electrochemically oxidized and prepared

according to the Comparative Example, and thus it was determined that the electrochemically oxidized HSAG electrodes have higher hydrophilicity.

Evaluation Example 2

Evaluation of Contact Angle of Electrochemically Oxidized HSAG Electrode

[0094] The electrochemically oxidized HSAG electrodes prepared according to Examples 1 and 4 and the HSAG electrode which was not electrochemically oxidized and prepared according to the Comparative Example were contacted with hard water according to IEC 60734. FIGS. 3A to 3C are photographs of the flat HSAG electrodes in contact with a droplet-like hard water, and contact angles were measured using a contact angle measuring device (DSA 10, available from Kruss) and listed in Table 3 below.

[0095] FIGS. 3A and 3B are photographs of the electrochemically oxidized electrodes which are prepared according to Examples 1 and 4 and are in contact with hard water, and FIG. 3C is a photograph of the HSAG electrode which is not electrochemically oxidized, prepared according to the Comparative Example and is in contact with hard water. The contact angles shown in FIGS. 3A to 3C are provided in Table 3.

TABLE 3

	Example 1	Example 4	Comparative Example
Contact angle (°)	96	94	122

[0096] Referring to FIGS. 3A to 3C, and Table 3, the electrochemically oxidized HSAG electrodes prepared according to Examples 1 and 4 had a smaller contact angle than the HSAG electrode which was not electrochemically oxidized and was prepared according to the Comparative Example. Thus it was determined that the electrochemically oxidized HSAG electrodes have higher hydrophilicity than the HSAG electrode which was not electrochemically oxidized.

Evaluation Example 3

Evaluation of Life-Span Characteristics of Cell Electrode

[0097] The capacitive deionization cells prepared according to Examples 1 to 6 and the Comparative Example were operated under the conditions disclosed below. Then, the ionic conductivity of the effluent water (i.e., treated water during charging or waste water during discharging) according to the treatment time (Examples 1 and 4, and Comparative Example), charge amount with respect to the number of

charge cycles (Examples 1 to 6, and Comparative Example), and discharge rates over time (Examples 1 and 4, and Comparative Example) thereof were measured, and the results are shown in FIGS. 5A and 5B, 6A and 6B, and 7A and 7B.

[0098] First, each cell was operated at room temperature while the electrodes were immersed in the electrolyte solution.

[0099] Second, hard water according to IEC 60734 was used as influent water, and the flow rate of hard water was adjusted to 30 milliliters per minute (mL/min).

[0100] Third, each cell was charged using a constant voltage of 2.0 V for 10 minutes (“min”), and then discharged for 20 minutes by electrically shorting the electrodes.

[0101] The charge amount may be calculated using Equation 1 below as shown in FIG. 4. FIG. 4 is a graph illustrating ionic conductivity of effluent water versus treatment time when influent water is treated using a comparative capacitive deionization device, and describes how to calculate a charge amount and a discharge amount. The charge amount is in proportion to the amount of ions in the influent water removed by the electrochemical cell.

$$Q_a = (\lambda_i t_c) - Q_c \tag{Equation 1}$$

In Equation 1, Q_a is the charge amount, λ_i is the ionic conductivity of the influent water measured before passing through the cell, t_c is the charging time, and Q_c is determined by integrating the ionic conductivity of the effluent water over the actual charging time.

charging and the ionic conductivity of the waste water more rapidly increased during the discharging in Examples 1 and 4 when compared to the Comparative Example. Based on these results, it is identified that a larger amount of ions are removed from the influent water, and faster deionization rates and faster electrode regeneration rates are obtained in Examples 1 and 4 than the Comparative Example.

[0105] FIGS. 6A and 6B are graphs respectively showing charge amount with respect to the number of charge cycles when deionization of influent water is conducted using an exemplary embodiment of a capacitive deionization device including an exemplary embodiment of an electrode or using a capacitive deionization device including a comparative electrode.

[0106] Referring to FIGS. 6A and 6B, each of the capacitive deionization devices prepared according to Examples 1 to 6 has a larger charge amount than the capacitive deionization device prepared according to the Comparative Example. As the charge amount increases, the deionization rate and the deionization amount increase. Furthermore, because the charge amount just slightly decreases as the number of charge cycle increases in the capacitive deionization devices prepared according to Examples 4 to 6, it is determined that the electrodes of Examples 4 to 6 have improved life-span characteristics.

[0107] The charge amount of the first charge cycle shown in FIGS. 6A and 6B is shown in Table 4 below.

TABLE 4

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example
Charge amount (uS · sec/cm)	2,257,000	2,257,000	1,512,000	1,967,000	1,595,000	1,381,000	1,199,000
Relative charge amount (%) (based on the charge amount of the Comparative Example)	188	188	126	164	133	115	100

[0102] In addition, the discharge amount may be calculated using Equation 2 below as shown in FIG. 4. The discharge amount is in proportion to the desorption ratio of ions from an electrode.

$$Q_b = Q_d - (\lambda_i t_d) \tag{Equation 2}$$

In Equation 2, Q_b is the discharge amount, Q_d is determined by integrating ionic conductivity of the effluent water over the actual discharging time, λ_i is the ionic conductivity of the influent water measured before passing through cell, and t_d is the discharging time.

[0103] FIGS. 5A and 5B are graphs respectively showing ionic conductivity of effluent water according to treatment time when deionization of influent water is conducted using an exemplary embodiment of a capacitive deionization device including an exemplary embodiment of an electrode or using a capacitive deionization device including a comparative electrode. In FIGS. 5A and 5B, the concave peaks represent charge peaks, and the convex peaks represent discharge peaks.

[0104] Referring to FIGS. 5A and 5B, the ionic conductivity of the treated water more rapidly decreased during the

[0108] Referring to Table 4, the charge amount of the first charge cycle in Examples 1 to 6 was about 1.15 to about 1.88 times of that in the Comparative Example.

[0109] FIGS. 7A and 7B are graphs respectively showing discharge rates versus time when deionization of influent water is conducted using an exemplary embodiment of a capacitive deionization device including an exemplary embodiment of an electrode or using a capacitive deionization device including a comparative electrode. In this regard, “discharge rate” as used herein refers to a value obtained by dividing a discharge amount per second by the total discharge amount.

[0110] Referring to FIGS. 7A and 7B, each of the capacitive deionization devices prepared according to Examples 1 and 4 has a faster discharge rate than the capacitive deionization device prepared according to the Comparative Example. As the discharge rate increases, the regeneration rate of the electrode increases, and the amount of the influent water consumed for the electrode regeneration process decreases.

[0111] It should be understood that the exemplary embodiments described herein should be considered in a descriptive sense only and not for purposes of limitation. Descriptions of

features or aspects within each embodiment should typically be considered as available for other similar features or aspects in other embodiments.

What is claimed is:

1. A method of manufacturing an oxidized electrode for a capacitive deionization device, the method comprising:

electrochemically oxidizing an electrode comprising a hydrophobic active material to produce the oxidized electrode.

2. The method of claim **1**, wherein the electrode further comprises a binder and a conducting agent.

3. The method of claim **2**, wherein the electrode is prepared using a powdered hydrophobic active material.

4. The method of claim **1**, wherein the hydrophobic active material comprises a carbonaceous material.

5. The method of claim **4**, wherein the carbonaceous material comprises at least one selected from the group consisting of activated carbon, carbon nanotube, mesoporous carbon, activated carbon fiber, graphite, and graphite oxide.

6. The method of claim **5**, wherein the graphite comprises high surface area graphite.

7. The method of claim **1**, wherein the electrochemical oxidization of the electrode is performed in an electrochemical cell comprising the electrode, a counter electrode, an electrolyte solution in which the electrode and the counter electrode are immersed, and a separator which electrically insulates the electrode from the counter electrode,

wherein the electrode is used as a positive electrode, and the counter electrode is used as a negative electrode in the electrochemical cell.

8. The method of claim **7**, wherein the electrode and the counter electrode are the same or different from each other.

9. The method of claim **7**, wherein the electrode and the counter electrode are the same.

10. The method of claim **7**, wherein the electrode and the counter electrode are different from each other.

11. The method of claim **7**, wherein the electrolyte solution is an acidic, alkaline, or neutral solution.

12. The method of claim **7**, wherein the electrolyte solution is an acidic solution.

13. The method of claim **7**, wherein the electrolyte solution is an alkaline solution.

14. The method of claim **7**, wherein the electrolyte solution is a neutral solution.

15. The method of claim **7**, wherein an amount of electric charge charged in the electrochemical cell during the electrochemically oxidizing the electrode is about 20 to about 30,000 coulombs per gram, based on a weight of an active material of the electrode.

16. The method of claim **7**, wherein a contact angle between the electrode and a hydrophilic electrolyte solution is decreased by the electrochemical oxidization of the electrode.

17. The method of claim **1**, further comprising washing the electrochemically oxidized electrode with a cleaning solution.

18. An electrode for a capacitive deionization device, the electrode comprising:
an electrochemically oxidized active material.

19. The electrode of claim **18**, further comprising an acidic functional group on the electrode.

20. The electrode of claim **19**, wherein the amount of the acidic functional group per unit weight of the electrode is about 0.7 to about 5 millimoles per gram.

21. The electrode of claim **19**, wherein the acidic functional group comprises at least one selected from the group consisting of a carboxyl group, a carboxylate group, and a phenol group.

22. A capacitive deionization device comprising the electrode of claim **18**.

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