



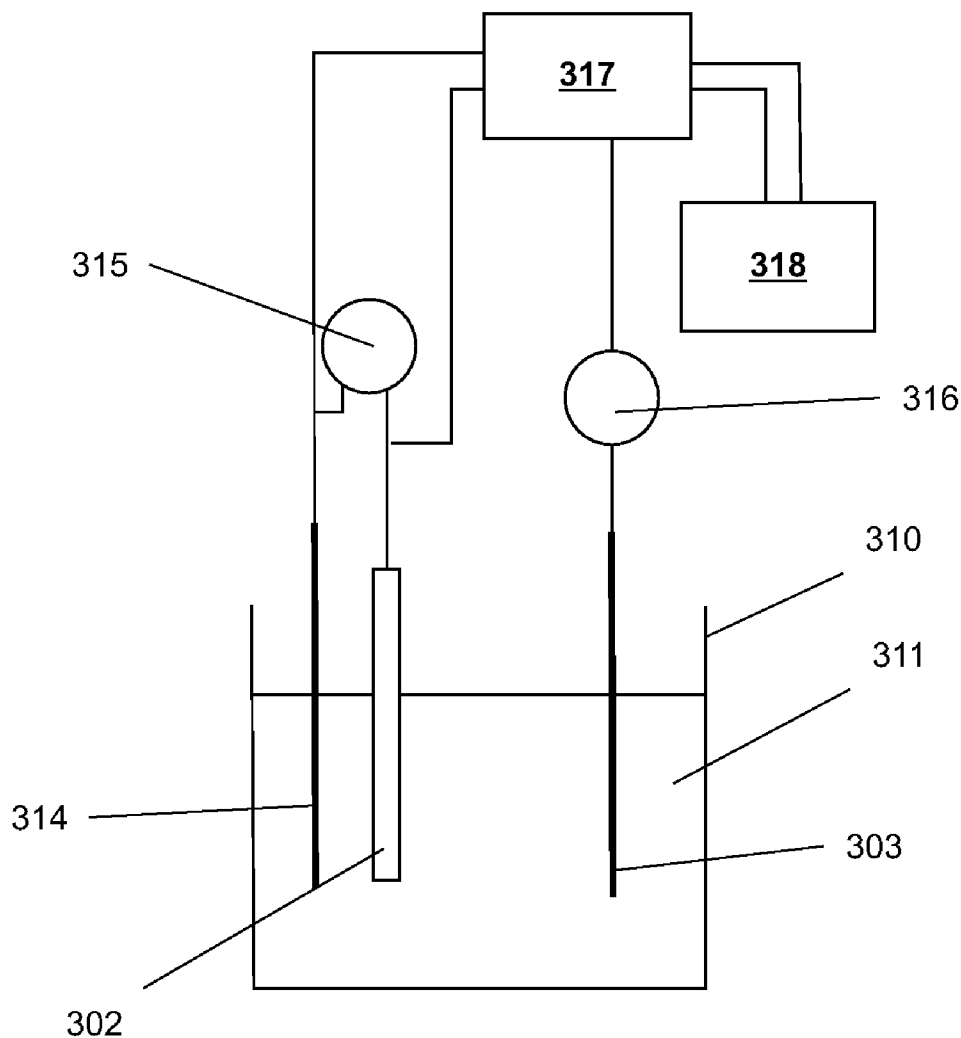
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(19) **United States**(12) **Patent Application Publication**  
**Zizek**(10) **Pub. No.: US 2009/0159462 A1**(43) **Pub. Date: Jun. 25, 2009**(54) **METHOD OF REGENERATING  
AMPEROMETRIC SENSORS****Publication Classification**(75) Inventor: **Claus Zizek**, Dietikon (CH)Correspondence Address:  
**STANDLEY LAW GROUP LLP**  
**6300 Riverside Drive**  
**Dublin, OH 43017 (US)**(73) Assignee: **Mettler-Toledo AG**, Greifensee  
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(51) **Int. Cl.****C25F 1/00** (2006.01)**C25F 7/00** (2006.01)(52) **U.S. Cl.** ..... **205/766; 204/242**(57) **ABSTRACT**

A method for regenerating an amperometric sensor involves bringing the electrodes of the sensor into contact with an active, complex-forming regenerating solution and connecting the electrodes into an adjustable electric circuit. This forms an electrochemical cell. Then, at least one negative and/or positive voltage pulse is applied to the electrochemical cell to either oxidize or reduce deposits on at least one of the electrodes into a deposit product, which is dissolved into the regenerating solution. The electrodes are removed from the regenerating solution and from the electric circuit, rinsed with a rinsing solution, and dried. After this, the electrodes are brought into contact with the sensor electrolyte and their functionality is verified. A device for performing this method is also provided.



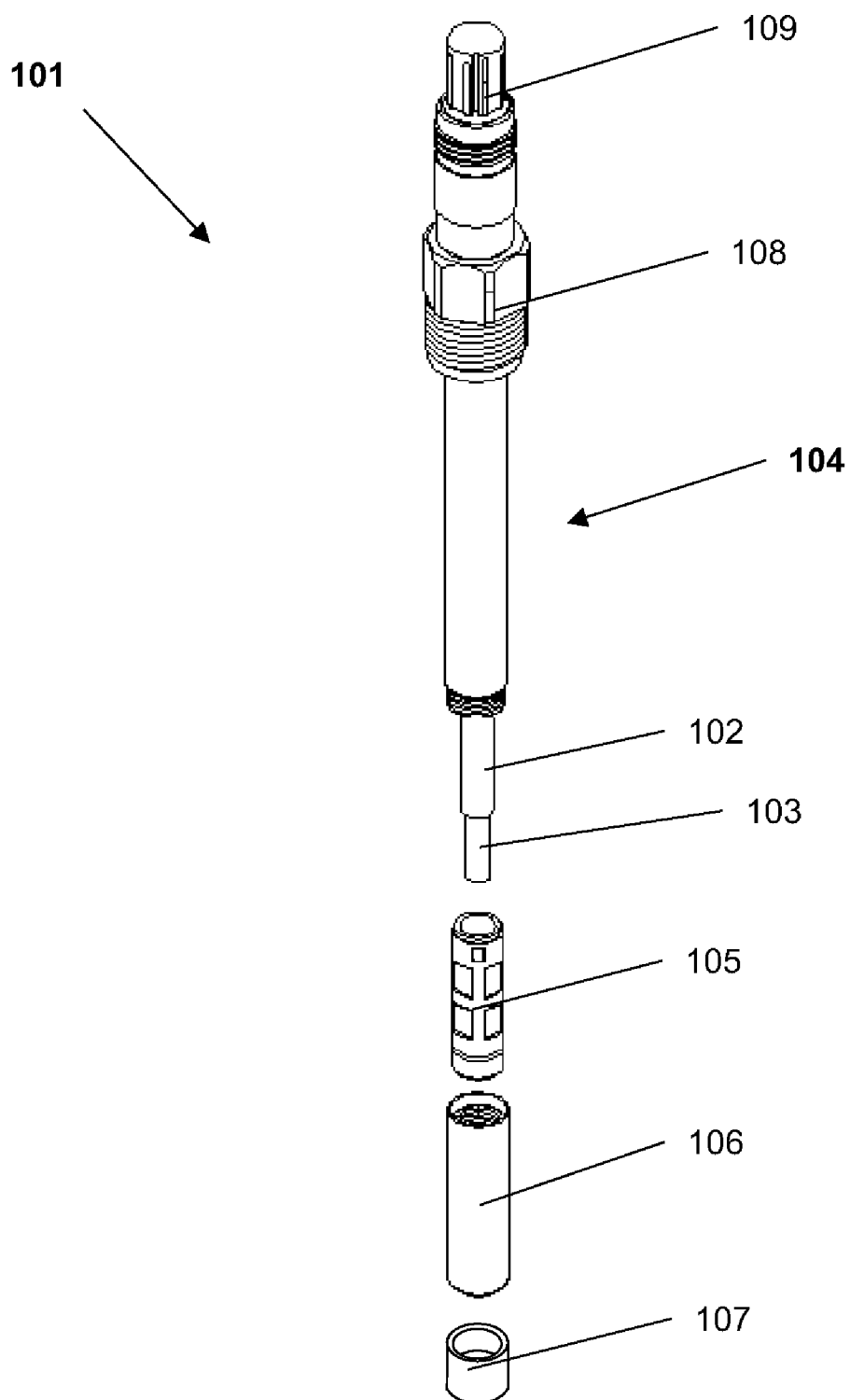


Fig. 1

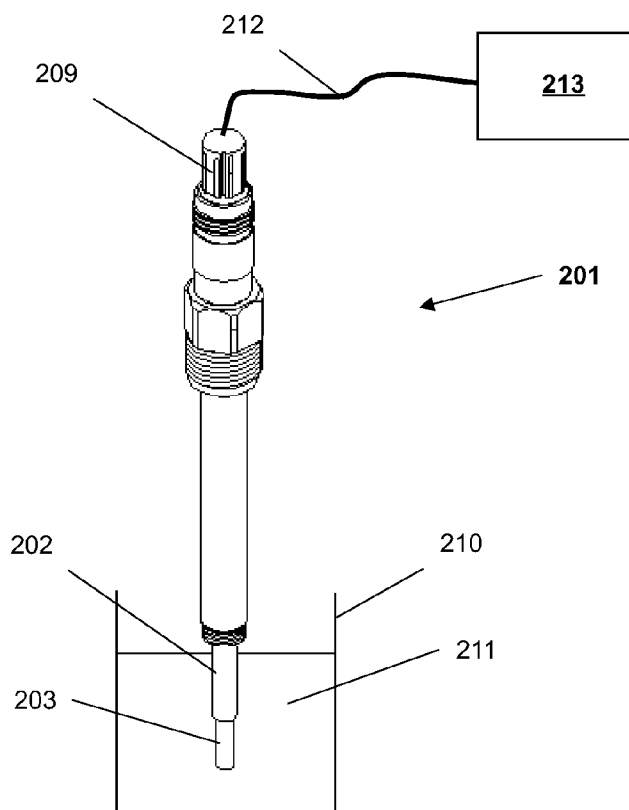


Fig. 2

Fig. 3

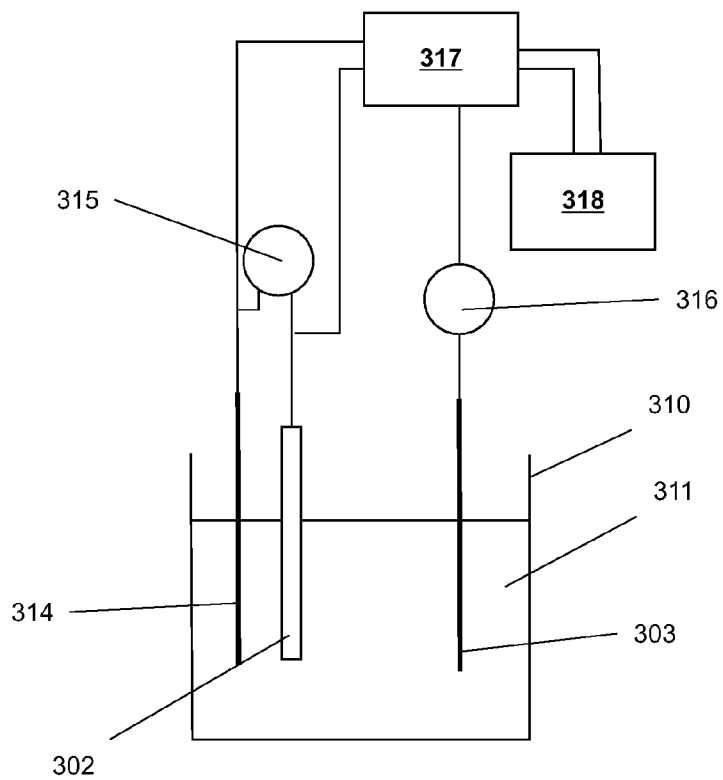


Fig. 4a

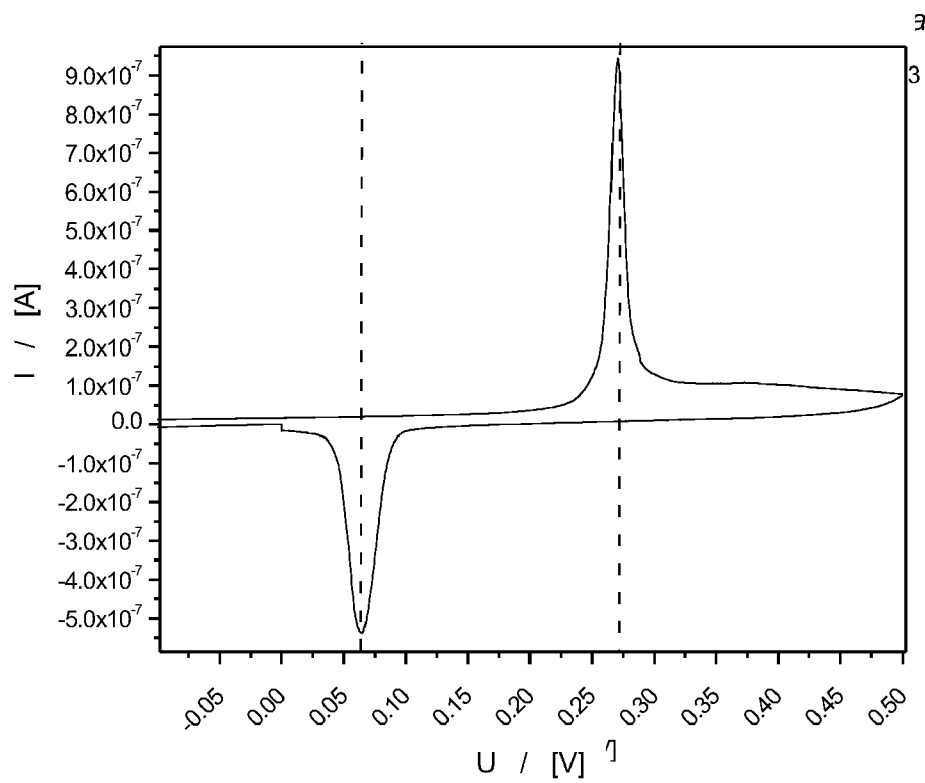
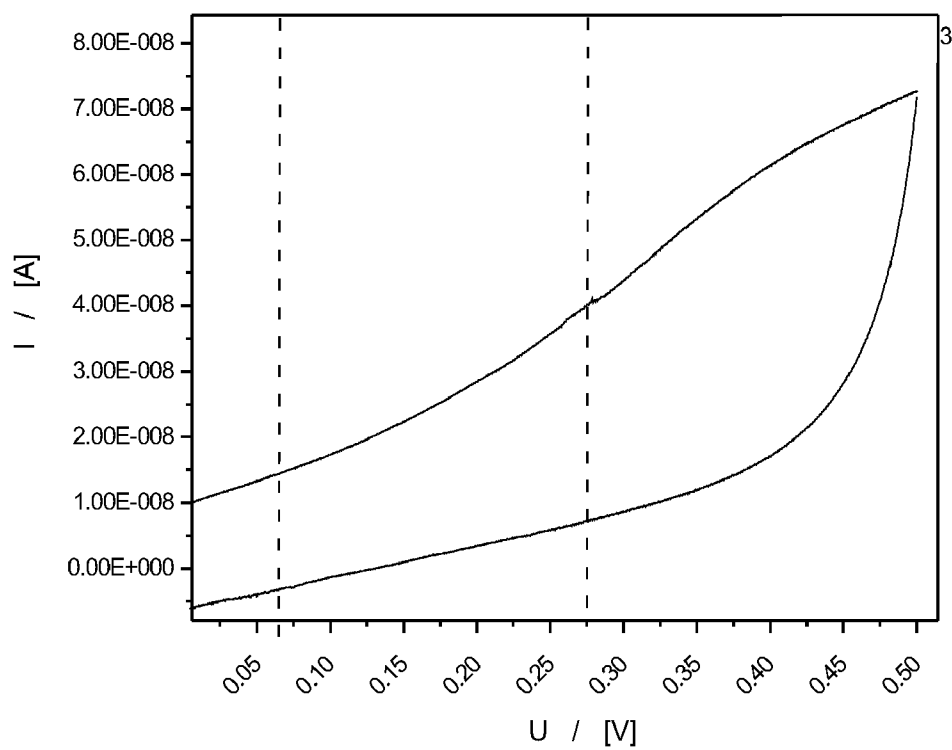


Fig. 4b



## METHOD OF REGENERATING AMPEROMETRIC SENSORS

### CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims a right of priority under 35 USC §119 from German patent application 10 2007 061806.0, filed 19 Dec. 2007, the content of which is incorporated by reference as if fully recited herein.

### TECHNICAL FIELD

[0002] The invention relates to a method and a device for regenerating at least one electrode of an amperometric sensor.

### BACKGROUND OF THE ART

[0003] Amperometric sensors are used in the laboratory and in the process field for the determination of a multitude of chemical substances such as the determination of dissolved gases and in particular the determination of oxygen or ozone. Amperometric sensors are known in the form of two-electrode systems or three-electrode systems which have a working electrode, a counter electrode and, optionally, a reference electrode. During operation, the electrodes are immersed in an electrolyte.

[0004] During operation of a sensor and in particular during continuous operation in a process system, it is possible that the measurement medium and in particular volatile components dissolved in the measurement medium penetrate and contaminate the electrolyte. In addition, deposits can accumulate over the course of time on the working electrode and/or the reference electrode, which can thereby become passivated. Both of these developments have a negative effect on the measurement result and the functionality of the sensor.

[0005] On metal electrodes, for example, deposits of insoluble salts or complexes will accumulate which occur as a result of oxidation or reduction of the electrolyte, the electrolyte contaminants or the electrode material, and/or as a result of a reaction between components of the electrolyte and a subsequent redox reaction.

[0006] In order to extend the lifetime and to maintain the functionality of an amperometric sensor, these deposits and/or contaminants should be removed from the electrolyte at certain time intervals. Conventional methods of regenerating amperometric sensors such as oxygen sensors involve for example exposing the electrodes and then manually regenerating them through a chemical and/or physical procedure, as well as exchanging the electrolyte.

[0007] It is known, for example, to remove the deposits mechanically by grinding or abrasion. While a removal of the deposits by grinding is certainly effective, it involves the risk, particularly when practiced repeatedly, that the geometry and/or the dimensions, and thus also the performance specifications, of the electrodes are changed, since not only deposits are being removed, but also electrode material. Especially when this removal of deposits is practiced repeatedly, it can thus have a negative effect on the functionality of the sensor and on the quality of the measurement results.

[0008] A further known practice is the chemical removal by cleaning the electrodes in highly concentrated acids, for example nitric acid or sulfuric acid. This procedure has on the one hand the disadvantage that the handling of such acids requires extraordinary care and special protective measures. Furthermore, these acids should be properly disposed. On the

other hand, electrodes of base metals such as for example zinc or silver can be attacked by acids, so that with this procedure, too, the dimensions of the electrodes are changed and the measurement results are negatively affected.

[0009] As an example, US 2005/0236280 A1 discloses a combination of electrical stripping of the electrodes by applying strong electric pulses and using sulfuric acid as electrolytic cleaning solution for the cleaning of the electrode surfaces in an electrochemical cell which is used for the precipitation of copper.

[0010] As has been found, the regenerating method with strong electrical pulses has only limited use for electrodes of amperometric sensors, in particular the working electrode and/or the reference electrode, because due to the formation of bubbles the accumulated deposits can be dissolved in the electrolyte only to a limited extent.

[0011] Therefore, it is the objective to develop a simple, user-friendly and environmentally compatible method of regenerating an amperometric sensor, wherein even a repeated use of the method has an insignificant effect or preferably no effect on the performance specifications of the sensor.

### SUMMARY

[0012] This objective is met by the method for regenerating an amperometric sensor and by a regenerating device for carrying out the method, as will be described hereinafter.

[0013] The amperometric sensor includes a working electrode, a counter electrode and, optionally, a reference electrode which in their operative state are immersed in an electrolyte. The method for regenerating the sensor comprises several steps. First, the electrodes are brought into contact with a chemically active regenerating solution and are connected into an adjustable electric circuit, so that an electrochemical cell is formed. To cause an oxidation and/or reduction of deposits resulting in at least one deposit product, a negative and/or positive voltage pulse is applied to the electrochemical cell. The deposit product which results from reduction or oxidation of the deposits reacts with the regenerating solution, particularly with a complexing agent of the solution, and the reaction product is dissolved in the regenerating solution. The electrodes are removed from the regenerating solution and from the electric circuit and are subsequently rinsed with a preferably neutral rinsing solution and then thoroughly dried. For checking their functionality the electrodes are subsequently brought into contact with the electrolyte or with a new electrolyte and tested.

[0014] The regenerating solution used for this procedure is in addition distinguished by the fact that it is less harmful to the environment than the concentrated acids used in prior-art methods and that it can be used without major safety measures even by semiskilled workers.

[0015] The method can further include a step of removing a membrane body from the sensor before the electrodes are brought into contact with the regenerating solution. Prior to the function check, the membrane body is reinstalled. These steps are performed primarily with membrane-covered amperometric sensors.

[0016] The voltage pulse which is applied for the oxidation and/or reduction of the deposits lasts from about 15 sec to about 300 sec and its magnitude is about  $-3$  V to about  $+3$  V.

[0017] In a preferred embodiment the method can further include the polarizing and/or the recalibrating of the electrodes. The term "polarizing" in the context of oxygen- or

ozone sensors means the time it takes for a quasi-stationary reaction equilibrium to establish itself. The polarizing can occur either in operation through the transmitter or also before putting the sensor into operation.

[0018] To verify that the regenerated electrodes are functioning properly, one or more sensor-specific parameters can be examined by measuring them and comparing them to a specified limit value. Such parameters include for example the slope, a reference potential, the response behavior, or the stability of the measurement signal of the electrochemical cell.

[0019] It is particularly advantageous to use an aqueous sodium thiosulfate solution as regenerating solution, as the thiosulfate ion is a good complexing agent, and most thiosulfate compounds show good or even very good solubility in aqueous solutions. In addition, sodium thiosulfate is easy to use and does not require any further safety measures or safety precautions. Methods with this kind of regenerating solution are therefore also suitable for use with instruments for mobile applications in the field, i.e. with instruments that are used outside of a controlled laboratory environment.

[0020] A particularly suitable means for performing the regenerating method as described here is a regenerating device comprising an amperometric sensor with a working electrode, a counter electrode and, optionally, a reference electrode, wherein the electrodes in their operating state are immersed in an electrolyte. The regenerating device further includes an adjustable voltage source which serves to apply at least one kind of positive and/or negative voltage pulse to the electrodes, and a container which can be filled with a chemically active regenerating solution.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0021] An exemplary device according to the invention and the results that can be obtained with it in the process of regenerating amperometric sensors are exemplarily described by means of the following drawings, wherein

[0022] FIG. 1 is a schematic depiction of an embodiment of the amperometric sensor with exposed electrodes;

[0023] FIG. 2 is a simplified representation of a regenerating device for an amperometric sensor with two electrodes;

[0024] FIG. 3 is a schematic representation of a regenerating device for an amperometric sensor with three electrodes;

[0025] FIGS. 4a and 4b show current/voltage graphs for amperometric oxygen sensors of the type InPro6800 made by Mettler-Toledo, with FIG. 4a showing the situation prior to regeneration and with FIG. 4b showing the graph for the same sensor after regeneration with a voltage pulse of 1 V over 157 sec in 0.5% Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>.

#### DETAILED DESCRIPTION OF THE DRAWINGS

[0026] FIG. 1 shows an amperometric sensor 101 with exposed electrodes 102, 103 of the kind known for example as a state-of-the-art oxygen sensor. The sensor 101 has a sensor housing 104 at one end of which a working electrode 102 and a counter electrode 103 are arranged. Shown here is a two-electrode sensor, but three-electrode versions with an additional reference electrode also exist (see FIG. 3). In the operative state, the electrodes 102, 103 are covered by a membrane body 105 filled with an electrolyte and encased by a cover sleeve 106 which, as shown here, can be additionally covered by a protective cap 107. The electrodes 102, 103 are immersed in the electrolyte.

[0027] To perform the regenerating process according to the inventive method, the membrane body 105, the electrolyte, the cover sleeve 106 and the protective cap 107 are

removed, and the exposed electrodes 102, 103 are brought into contact with an active regenerating solution (see FIGS. 2 and 3) and subjected to at least one voltage pulse. The other end of the sensor 101 has a connector element 108 and a connecting socket 109. The connector element 108 serves to fasten the sensor 101 to an armature, a container, or a conduit pipe, so that the sensor 101 can be brought into contact with a measurement medium. The connector element 108 as shown here is configured in the form of a threaded sleeve.

[0028] FIG. 2 shows an exemplary regenerating device. The exposed electrodes 202, 203 of the sensor 201 are immersed here in a container 210 that is filled with an active regenerating solution 211. Furthermore, the electrodes 202, 203 are connected by way of the connecting socket 209 and a suitable connection 212, in this case a cable, to a transmitter 213 which, among other elements, comprises or is connected to a potentiostat or an adjustable voltage source.

[0029] FIG. 3 shows a schematic diagram of a regenerating device for an amperometric sensor according to the invention. The sensor has a working electrode 302, a counter electrode 303 and a reference electrode 314, which are immersed in a chemically active regenerating solution 311 in a container 310. The counter electrode 303 is connected by way of an amperemeter 316 to a potentiostat 317. The working electrode 302 and the reference electrode 314 are likewise connected to the potentiostat 317. A voltmeter 315 which is arranged between the working electrode 302 and the reference electrode 314 serves to measure, when the arrangement is in a measurement mode, the voltage potential arising between the electrodes 302 and 314.

[0030] The potentiostat 317 is connected to an external adjustable voltage source 318 which supplies the working electrode 302 and/or the reference electrode 314 with the voltage pulses needed for the regenerating process.

[0031] With the devices illustrated in FIGS. 2 and 3, the regenerating method according to the invention can be performed on an amperometric sensor such as an oxygen sensor of the type InPro6800 of Mettler-Toledo. This sensor encompasses a three-electrode system which consists of an Ag/AgCl working electrode, a platinum wire as counter electrode, and a reference electrode, all of which are in this case arranged in an electrolyte that contains potassium chloride. The composition of this sensor corresponds in essence to the sensor shown in FIG. 1, except that it has three electrodes. During operation, the silver ions which are present in the electrolyte are at least partly oxidized at the working electrode and/or at the reference electrode into silver oxide which accumulates on the electrodes and passivates them.

[0032] To evaluate the optimal conditions for the regenerating method according to the invention, a statistically designed experiment was set up. The experimental conditions were not arbitrarily chosen but were selected so as to make optimal use of the multi-dimensional parameter space defined by the variable parameters of the experiment. The results obtained with the experiment according to this design are statistically relevant and represent a means for determining the optimal conditions and/or parameters for the method. According to the design of experiments, the sensor was in each case characterized before and after the regeneration. As a representative example, the result of one of these experiments, wherein the cyclic voltammetry method was used for the characterization, is shown in FIGS. 4a and 4b and will be explained in detail in the following.

[0033] To carry out the regenerating method according to the invention, the sensor was removed from the process and the sensor electrodes were exposed by removing the protective cap, the cover sleeve, the membrane body, and the elec-

trolyte. The exposed electrodes of the sensor were then brought into contact with a chemically active regenerating solution, in this case an aqueous sodium thiosulfate solution with a concentration of about 0 to 2%, and connected to a suitable voltage source, so that the electrodes together with the regenerating solution formed an electrochemical cell.

**[0034]** Next, the working electrode and/or the reference electrode were subjected to one or more voltage pulses, whereby the deposits on the electrode were oxidized or reduced into deposit products. These deposit products then reacted with the chemically active components of the regenerating solution resulting in ionic compounds and/or complex compounds preferably with a good solubility in the regenerating solution. In this manner, the deposits were transported into the regenerating solution.

**[0035]** In the case of the InPro6800 sensor which was used here, the accumulated silver oxide was reduced again into silver ions which then formed complexes with the sodium thiosulfate and were dissolved.

**[0036]** After the regeneration had been completed, the sensor was removed from the regenerating solution, rinsed with distilled water and dried with a lint-free cloth. The exposed electrodes of the sensor were then immersed again into new electrolyte and covered with the membrane body, the cover sleeve and the protective cap.

**[0037]** Finally, the functionality of the regenerated sensor was verified by measuring the slope, the reference potential, the response behavior and/or the stability of the measuring signal and by comparing the measurement to a base value which had been determined for example with the same sensor or a new sensor of the same kind or was specified by the manufacturer. To determine these parameters, in particular an oxygen sensor like the sensors of the InPro6800 Series of Mettler-Toledo should be polarized according to the manufacturer's specifications and also recalibrated if necessary.

**[0038]** FIG. 4a and 4b show plots of current/voltage which were recorded to monitor and verify the functionality of an amperometric oxygen sensor, in this case an InPro6800 made by Mettler-Toledo, before and after using the regenerating method according to the invention. An aqueous 0.5% sodium thiosulfate solution was used as chemically active regenerating solution.

**[0039]** FIG. 4a shows a cyclic voltammogram of a contaminated sensor which has been in use for about three months. The diagram shows prominent silver peaks in the forward scan and the return scan, whose position is indicated by the broken lines in FIGS. 4a and 4b. The peak of the forward scan lies at about 0.275 V, and the peak of the return scan at about 0.06 V. After regeneration with the method according to the invention, these peaks have in the case of FIG. 4b almost totally disappeared, noting that the scale on the axis for the current in ampere in FIG. 4b differs by a factor of 10 from FIG. 4a. The regeneration in the example of FIG. 4 was performed with a pulse of 1 V over a time period of 157 sec. This leads to the conclusion that the method according to the invention is very well suited for the regeneration of amperometric sensors and that the contaminants, particularly deposits of silver oxide, could be almost completely removed from the electrodes.

What is claimed is:

1. A method for regenerating an amperometric sensor comprising an electrolyte and at least one electrode immersed in the electrolyte during operation of the sensor, the at least one

electrode comprising at least one of: a working electrode, a counter electrode and a reference electrode, the method comprising the steps of:

contacting the electrodes with a chemically active regenerating solution and connecting the electrodes into an adjustable electric circuit, thereby forming an electrochemical cell, the regenerating solution comprising a complexing agent;

applying a voltage pulse, of either positive or negative voltage, to the electrochemical cell to either oxidize or reduce deposits on the electrodes into at least one deposit product;

reacting the at least one deposit product with the regenerating solution, resulting in dissolving the at least one deposit product in the regenerating solution;

removing the electrodes from both the regenerating solution and the electric circuit;

rinsing the electrodes with a rinsing solution and drying the electrodes; and

bringing the electrodes into contact with the operating electrolyte and verifying the overall functionality of the electrode.

2. The method of claim 1, further comprising the steps of: preparing the electrodes, prior to the contacting step, by removing a membrane body from the sensor, thereby exposing the electrodes; and reinstalling the removed membrane body after removing the electrodes from the regenerating solution.

3. The method of claim 2, wherein: the voltage pulse applying step lasts from about 15 to about 300 sec.

4. The method of claim 3, wherein: the voltage pulse has a magnitude in the range of from about -3 V to about +3 V.

5. The method of claim 1, wherein: the voltage pulse applying step lasts from about 15 to about 300 sec.

6. The method of claim 1, wherein: the voltage pulse has a magnitude in the range of from about -3 V to about +3 V.

7. The method of claim 1, further comprising the step of: polarizing and/or recalibrating the electrodes prior to and/or after verifying the functionality thereof.

8. The method of claim 1, wherein: the step of verifying the functionality of the electrodes comprises the substeps of determining at least one of: the slope, a reference potential, the response behavior and the stability of the measurement signal of the electrochemical cell.

9. The method of claim 1, wherein: the regenerating solution is an aqueous solution of sodium thiosulfate.

10. A device for regenerating an amperometric sensor using the method of claim 1, the device comprising:

a container adapted to be filled with a chemically active regenerating solution; and

a source of adjustable voltage for applying a voltage pulse to the electrodes, the voltage source arranged to be connected to the electrodes while the electrodes are immersed in the regenerating solution.

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