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COMPOUND ELECTRODE ASSEMBLY, AND MEASURING DEVICE WITH THE ASSEMBLY FOR PROCESSING WASTE SOLUTION

This invention relates to a compound electrode assembly which can achieve a pH measurement and an oxidation-reduction potential measurement simultaneously.

In processing a waste solution containing harmful material such as cyanide or hexavalent chromium so that it becomes harmless, it is essential to carry out a pH measurement and an oxidation-reduction potential measurement.

In order to make cyanide harmless, in general the following method is employed: while the pH value of the waste solution is maintained in an alkaline range of around 10, an oxidizing agent such as sodium hypochlorite is added thereto, to decompose the cyanide. In order to make hexavalent chromium harmless, in general, while the pH value is maintained in an acidic range of around 2, a reducer such as sodium bisulfite is added to reduce the hexavalent chromium into harmless trivalent chromium. In both cases, the pH measurement and the oxidation-reduction potential measurement for confirming the completion of oxidation or reduction reaction must be carried out in a reaction bath. For this purpose, heretofore, a pH measuring glass electrode and an oxidation-

reduction potential measuring electrode are inserted in the waste solution in the reaction bath and are connected respectively to a pH meter and an oxidation-reduction potential meter, to measure the pH value and oxidation-reduction potential thereof. In order to improve the measurement accuracy, a reference electrode which has an internal solution such as a 4-mol potassium chloride solution is set around the pH measuring glass electrode, and similarly a reference electrode having an internal solution is set around the oxidation-reduction potential measuring electrode.

The pH measuring glass electrode and the oxidation-reduction potential measuring electrode are built in glass tubes which are liable to be readily damaged. Therefore, when it is required to use the two electrodes at the same time, the electrodes must be set apart from each other, which gives rise to a problem that it is forced to perform the pH measurement and the oxidation-reduction potential measurement at different positions which should be carried out at one and the same position. Furthermore, the conventional method is not convenient in that two electrodes must be handled with great care.

SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide a compound electrode assembly in which the above-described difficulties accompanying a conventional method of measuring the pH value and oxidation-reduction potential of

harmful waste solution have been eliminated, and the pH value and the oxidation-reduction potential can be readily measured at one and the same point in the waste solution.

The foregoing object and other objects of the invention have been achieved by the provision of a compound electrode assembly for measuring the pH value and the oxidation-reduction potential of a waste solution, comprising:

an outer tube;

an inner tube located within said outer tube and having a first solution sealed therein;

a pH measuring glass film formed at one end of said inner tube and exposed to the exterior of said outer tube;

said outer tube, inner tube and glass film being integral;

an electrode located within said inner tube and in contact with said first solution;

a reference electrode located between said inner tube and said outer tube;

a space provided between said outer tube and said inner tube to contain a second solution in contact with said reference electrode there being a solution path between said space and the exterior of said outer tube;

a glass tube integral with said outer tube;

a wire of a noble metal located within said glass tube; and

an oxidation-reduction potential measuring electrode located adjacent said glass film so as to be exposed to the exterior of said outer tube, said measuring electrode being connected to one end of said wire.

The invention also provides a measuring device for measuring the pH value and the oxidation-reduction potential of a waste solution, comprising:

a compound electrode assembly including a pH measuring glass electrode, an oxidation-reduction potential

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measuring metal electrode and a common reference electrode;

a measuring section including a pH measuring operational amplifier connected to said glass electrode and said reference electrode to convert the output obtained between these two electrodes into a pH value, an oxidation-reduction potential measuring operational amplifier connected to said oxidation-reduction potential measuring electrode and said reference electrode to convert the output obtained between these two electrodes into an oxidation-reduction potential, and an indication circuit connected to both said amplifiers to indicate said pH value or said oxidation-reduction potential alternatively.

The nature, utility and principle of the invention will become more apparent from the following detailed description when read in conjunction with the accompanying drawings.

Brief description of the drawings

In the accompanying drawings:

Figure 1 is a longitudinal sectional view of one example of a compound electrode assembly according to this invention;

FIG. 2 is a cross sectional view taken along line II-II in FIG. 1;

FIG. 3 is a longitudinal sectional view of another example of the compound electrode assembly according to the invention;

FIG. 4 is a cross sectional view taken along line IV-IV in FIG. 3; and

FIG. 5 is a block diagram showing the arrangement of a measuring device for processing waste solution according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

A first example of a compound electrode assembly according to this invention is as shown in FIGS. 1 and 2. In these figures, reference numeral 1 designates an inner tube for a glass electrode, and the inner tube 1 has an end portion of glass film 2 for pH measurement. A solution 3 such as a 1/100-mol potassium chloride solution is sealed in the inner tube 1, and electrode 4 is built in the inner tube 1. An outer tube 5 for a reference electrode is fixedly secured to the outer wall of the inner tube 1. A solution 6 such as a 4 mol-potassium chloride solution is sealed in the outer tube 5, and a reference electrode 7 is built in the outer tube 5.

Further in FIG. 1, reference numeral 8 designates a solution path near the lower end of the outer tube 5 for the reference electrode; 9, a solution supplying port provided in the upper portion of the outer tube 5; and

10, a thin glass tube integrally secured to the inner wall of the outer tube 5 for the reference electrode. A noble metal wire 11 such as a platinum or gold wire is built in the glass tube 10. An oxidation-reduction potential measuring electrode 12 is connected to one end of the noble metal wire 11 in such a manner that it is exposed outside of the glass film 2, and the end of the electrode 12 is, if required, connected to a disk of the same noble metal so as to increase the electrode area. Lead wires 13, 14 and 15 are connected to the glass electrode 4, the reference electrode 7, and the noble metal wire 11, respectively. The lead wires 13 and 14 are connected to a pH measuring unit through a cap 16 connected to the top of the outer tube 5, and the lead wires 14 and 15 are connected to an oxidation-reduction potential measuring unit. The cap 16 is filled with an insulating material 17 such as silicon rubber, so that the electrodes are insulated from one another.

The lower portion of the outer tube 5 is inserted into the waste solution in a reaction bath, which is to be subjected to oxidation-reduction potential measurement and pH measurement; that is, the oxidation-reduction potential measuring electrode 12, the pH measuring glass film 2, and the solution path 8 are inserted into the waste solution, so that a pH measurement is carried out with a pH measuring unit which is connected to the electrode 4 which is built in the inner tube 1 and

is confronted with the glass film 2 and to the reference electrode 7 which is provided between the inner tube 1 and the outer tube 5, while an oxidation-reduction potential measurement is carried out with an oxidation-reduction potential measuring unit which is connected to the reference electrode 7 and to the noble metal wire 11 which is built in the glass tube 10 and is connected to the oxidation-reduction potential measuring electrode 12. In this case, as the reference electrode 7 is commonly used in the pH measurement and in the oxidation-reduction potential measurement, the compound electrode assembly can be operated economically and readily. Thus, measurement can be achieved accurately even by an unskilled person.

Since the pH measuring electrode 4, the reference electrode 7 and the oxidation-reduction potential measuring electrode 12 are put together, the compound electrode assembly of the invention can be readily handled when compared with the conventional case where the operator inserts a plurality of electrodes into the waste solution while taking care not to contact them.

As the end portion of the oxidation-reduction potential measuring noble metal wire 11 is exposed to the side of the pH measuring glass film 2, the pH and oxidation-reduction potential measurements can be achieved substantially at the same position in the waste solution, which provides accurate reaction control. This is another

effect of the compound electrode assembly of the invention.

The noble metal wire 11 is built in the glass tube 10, which is integral with the outer tube 5, as described before. Therefore, the electrodes are sufficiently electrically insulated by the glass tubes, and accordingly no measurement error is caused. Since the compound electrode assembly is simply cylindrical, the outer surface thereof can be readily cleaned; in other words, if the outer surface becomes dirty, measurement error may be caused; however, such a trouble can be prevented because the outer surface can be readily cleaned. In these points, the compound electrode assembly of the invention is advantageous.

FIGS. 3 and 4 show a second example of the compound electrode assembly according to the invention.

In the second example, an oxidation-reduction potential difference measuring electrode 12a is arranged in a recess 5a which is formed in the end portion of the side wall of an outer tube 5 for a reference electrode. The surface of the electrode 12a is formed into a disk in order to increase the electrode area. A small space 18 is provided between the inner wall of the outer tube 5 for the reference electrode and an inner tube 10 for a metal electrode. The remaining components are similar to those in FIGS. 1 and 2, and are accordingly designated by the same reference numerals.

In the compound electrode assembly thus constructed, the oxidation-reduction potential measuring electrode 12a is not protruded out of the end of the outer tube 5. Therefore, the electrode 12a will never become an obstruction when the outer surface of the outer tube 5 is cleaned, or when the compound electrode assembly is handled. Thus, the compound electrode assembly is advantageous in that it is scarcely damaged and is durable for a long time. The noble metal wire 11 is built in the inner tube 10 for the metal electrode, and the inner tube 10 is fixedly secured to the outer tube 5 for the reference electrode with the aforementioned small space 18 therebetween. Accordingly, the electrodes are positively insulated from each other by the glass tube high in insulation and the small space 18, and therefore no measurement error is caused. Since the configuration of the entire compound electrode assembly is cylindrical, the assembly can be readily manufactured. Furthermore, as the outer surface of the assembly can be readily cleaned, similarly as in the first example, the measurement error due to the dirty outer surface can be prevented.

FIG. 5 shows a measuring device for processing a waste solution, which uses the above-described compound electrode assembly. In FIG. 5, reference numeral 21 designates the compound electrode assembly shown in FIGS. 1 and 2. The compound electrode assembly 21 may be replaced by one shown in FIGS. 3 and 4. Lead wires 24, 25 and 26 are connected to the glass electrode, the reference electrode and the metal electrode, respectively.

The measuring device 27 comprises: a power source circuit 28; an indication circuit 29; an operational amplifier circuit 30a for pH measurement; and an operational amplifier circuit 30b for oxidation-reduction potential measurement. The lead wire 24 extended from the glass electrode 4 is connected to the pH measuring operational amplifier circuit 30a, and the lead wire 26 extended from the metal electrode 12 is connected to the oxidation-reduction potential measuring operational amplifier circuit 30b. The lead wire 25 from the reference electrode 7 is connected to both of the operational amplifier circuit 30a and 30b.

In operation, the compound electrode assembly 21 is inserted into the waste solution in a reaction bath 22, so that the pH measuring glass film 2, the solution path part 8 and the metal electrode 12 are at a measurement position. The pH value of the waste solution is measured by the glass electrode 4 confronted with the glass film 2 and the reference electrode 7, as a result of which the pH value thus measured is indicated by the indication circuit 29 through the operational amplifier circuit 30a for pH measurement. At the same time, the oxidation-reduction potential difference of the waste solution is measured by the metal electrode 12 and the reference electrode 7. The potential thus measured is applied to the operational amplifier circuit 30b. Therefore, the potential is indicated by the indication circuit 29 by switching the connection of the indication circuit

29 from the operational amplifier circuit 30a to the operational amplifier circuit 30b.

As was described above, according to the invention, the pH measuring glass electrode 4, the oxidation-reduction potential measuring metal electrode 12 and the common comparison electrode 7 are formed into one unit, i.e., the compound electrode assembly 21. Accordingly, the compound electrode assembly of the invention is advantageous in the following points: the electrodes can be readily handled when compared with the prior art in which different reference electrodes are provided for these measurements. Accordingly the measurement can be achieved accurately even by an unskilled person. Heretofore, a plurality of electrodes are inserted into the waste solution with care not to bring them into contact; however, such care is unnecessary for the compound electrode assembly of the invention. In addition, the pH measurement and the oxidation-reduction potential measurement can be achieved substantially at the same position in the waste solution, which contributes to correct reaction control.

The measuring device 27 comprises: the pH measuring operational amplifier circuit 30a; the oxidation-reduction potential measuring operational amplifier circuit 30b; the single power source circuit 28; and the indication circuit 29, as described before. Therefore, the outputs of the glass electrode 4 and the reference

electrode 7 in the compound electrode assembly 21 are converted into a pH value accurately by the operational amplifier circuit 30a, while the outputs of the metal electrode 12 and the reference electrode 7 are converted into an oxidation-reduction potential by the operational amplifier circuit 30b. Since the power source circuit 28 and the indication circuit 29 are used commonly for the two kinds of measurements in the measuring device 27, the construction is much simpler than that of a conventional measuring device in which the pH measuring section and the oxidation-reduction potential measuring section have substantially the same power source circuits and indication circuits, respectively.

In the invention, the two kinds of measurements are indicated by the common indication circuit, and therefore it is unnecessary to provide two measuring devices, and the operation is simplified as much.

In the invention, the electrode section and the metering section are compound respectively, and therefore they can be calibrated at the same time by inserting the compound electrode assembly into standard potential solutions which are prepared by adding quinhydrone to a pH 4 standard solution and a pH 7 standard solution.

CLAIMS:

1. A compound electrode assembly for measuring the pH value and the oxidation-reduction potential of a waste solution, comprising:

an outer tube;

an inner tube located within said outer tube and having a first solution sealed therein;

a pH measuring glass film formed at one end of said inner tube and exposed to the exterior of said outer tube; said outer tube, inner tube and glass film being integral;

an electrode located within said inner tube and in contact with said first solution;

a reference electrode located between said inner tube and said outer tube;

a space provided between said outer tube and said inner tube to contain a second solution in contact with said reference electrode there being a solution path between said space and the exterior of said outer tube;

a glass tube integral with said outer tube;

a wire of a noble metal located within said glass tube; and

an oxidation-reduction potential measuring electrode located adjacent said glass film so as to be exposed to the exterior of said outer tube, said measuring electrode being connected to one end of said wire.

2. A compound electrode assembly as claimed in claim 1, wherein said glass tube is located in spaced relationship between said inner tube and said outer tube, and said oxidation-reduction potential measuring electrode is exposed in a recess formed in the end portion of said outer tube.

3. A measuring device for measuring the pH value and the oxidation-reduction potential of a waste solution, comprising:

a compound electrode assembly including a pH measuring

glass electrode, an oxidation-reduction potential measuring metal electrode and a common reference electrode;

a measuring section including a pH measuring operational amplifier connected to said glass electrode and said reference electrode to convert the output obtained between these two electrodes into a pH value, an oxidation reduction potential measuring operational amplifier connected to said oxidation-reduction potential measuring electrode and said reference electrode to convert the output obtained between these two electrodes into an oxidation-reduction potential, and an indication circuit connected to both said amplifiers to indicate said pH value or said oxidation-reduction potential alternatively.