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NICKEL IMPREGNATED POROUS CATHODE AND METHOD OF MAKING SAME

Filed June 11, 1962

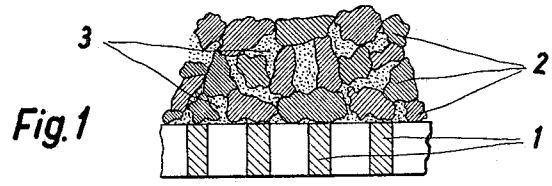


Fig. 1

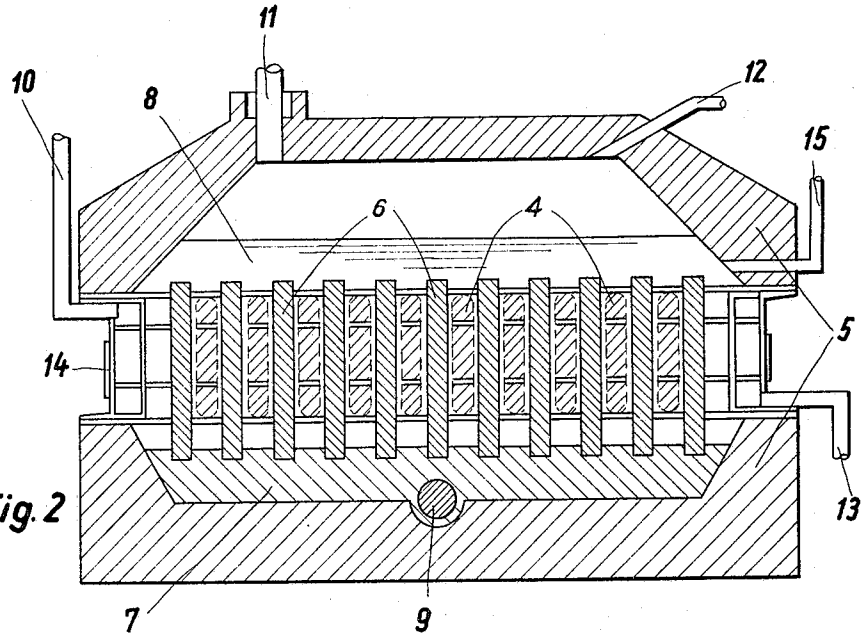


Fig. 2

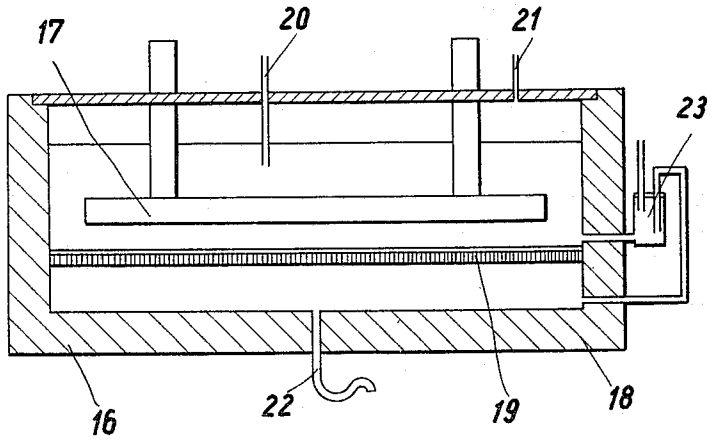


Fig. 3

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NICKEL IMPREGNATED POROUS CATHODE AND METHOD OF MAKING SAME

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4 Claims. (Cl. 204—37)

For the production of chlorine, alkaline liquor and hydrogen by electrolytic decomposition of alkali metal chloride solution (NaCl, KCl) diaphragm cells have been known for a long time where gaseous chlorine is produced at the anodes—usually made of graphite—and gaseous hydrogen at the cathodes—usually made of iron or nickel —with OH-ions being formed within the electrolyte. The most expedient manner of separating the anode area from the cathode area is by means of a diaphragm. Cells of this type operate at voltages which range from 3 to 4 volts, depending on current density and temperature even though in theory the decomposition voltage of alkali metal chloride is approximately 2.3 volts. The excess in voltage is required because of the ohmic resistance within the electrolyte and especially because of the so-called overvoltage at the electrodes.

It is the aim of the invention to produce a cathode which, even in case of great cathode loads, will have a minimum of overvoltage so that it becomes possible to attain the electrolysis of alkali metal chlorides at a cell voltage which is lower than needed for cathodes presently utilized for this process, for the purpose of attaining a saving in energy.

It is a well known fact that the hydrogen overvoltage depends, in the case of a constant current density, on the type and surface condition of the electrode material used. The overvoltage is particularly high in case of smooth surfaces.

U.S. Patent 2,970,095 of Kandler and Vogt describes a process for the electrical utilization of the decomposition energy of amalgams in case of the electrolysis of alkali metal chlorides by the amalgamation process. A cathode is employed in the amalgam decomposition cell which generates hydrogen and which is composed of porously sintered nickel or iron powder or mixtures thereof, preferably nickel powder. The hydrogen overvoltage at electrodes of this type is substantially smaller than at smooth electrodes. Therefore they are usable also with advantageous results as cathodes for diaphragm cells.

It has been established however that it is possible to attain a substantial saving in energy in the case of the electrolysis of alkali metal chlorides in diaphragm cells even in comparison with the above mentioned electrode made of sintered nickel powder if porous frames are used as cathodes and metallic hydroxides, for example nickel or iron hydroxide, preferably nickel hydroxide, are inserted in these pores by electrolytic or chemical methods, and if these hydroxides are then reduced to metal. If desired platinum or palladium can subsequently be deposited on the metal obtained through the reduction process by impregnating the frame with platinum or palladium brine. The preferred cathodes of the invention consist of nickel sintered frames with very finely distributed nickel inserted in the pores. Iron is not quite so suitable a material for the cathodes of the invention due to its lesser corrosion resistance.

The insertion of metallic oxides or metallic hydroxides into the pores of frames is accomplished preferably electro-chemically in the following manner: Between a soluble or insoluble anode and an electrically conducting frame as the cathode an electrolysis is accomplished in an acid electrolyte containing the metallic ions which are to be separated in the form of oxides or hydroxides, and containing in addition thereto reducable ions, their reduction ("REDOX") potential being more positive than the separation potential of the metallic ions. Within the electrolyte area, outside the cathode, a pH value of the electrolyte is maintained that will not permit any metallic hydroxide precipitation within the electrolyte. In this manner oxides or hydroxides are deposited in the pores of the frame in an extraordinary fine distribution. The reducable ions are preferably nitrate ions but perchlorate ions, chlorate ions, chromate ions or permanganate ions can be employed likewise. The electrolyte is acidified preferably by nitric acid or hydrochloric acid but any other acid of sufficient strength can be used also.

When the metallic oxides or hydroxides—produced according to the above described process and fixed in finely divided form in the pores of the porous frame are converted to metallic form by reduction, preferably by a flow of hydrogen at high temperature, preferably at 200 to 300° C. the metals present within the pores of the frame will retain their fine distribution. It is possible in addition, as already mentioned above, to deposit more noble metals on the finely distributed metals obtained by the above described process, for example by impregnating the frame, in a manner known per se, with a platinum or palladium salt solution.

The porous frame, filled according to the invention with finely distributed metal, can be placed on a solid support, which may be perforated, made of nickel or iron, or foil-thin porous bodies can be used and placed on a solid support, which may be perforated, by spot welding or like manner, or foil-thin porous bodies can be used unsupported or supported by a wire grid. In this case the gases will be generated partly at the rear side due to the porous structure.

The new cathodes of the invention can be used in any commercial diaphragm cell for the electrolysis of alkaline metal halides, for example in cells with a vertical arrangement of the electrodes as well as in cells with a horizontal arrangement of the electrodes.

In order to provide a better understanding of the present invention reference is made to the accompanying drawing:

FIGURE 1 is a sectional view of a cathode according to the invention with a wire grid as a support on an enlarged scale.

FIGURE 2 shows a section through a diaphragm cell for the electrolysis of alkali metal chlorides with a vertical arrangement of the electrodes, generally called a "Hooker Cell."

FIGURE 3 shows a section through a diaphragm cell for the electrolysis of alkali metal chlorides with a horizonal arrangement of the electrodes generally called a "Siemens-Billiter-Cell."

In FIGURE 1 a nickel wire grid 1 is shown on which a layer of sintered nickel grain 2 is sintered. The pores of this structure of sintered nickel powder are filled with very finely divided nickel powder 3 produced as described in the examples.

The Hooker-Cell shown in FIGURE 2 is a typical representative of a diaphragm cell with a vertical arrangement of the electrodes in which the cathodes according to the invention can be used. The cathodes 4 which have the form of hollow bodies are prepared by the following method: A layer of sintered nickel powder is sintered on a nickel wire grid, which has the form of a hollow body, and the pores of this structure are filled with nickel metal as described in the following examples. The thus obtained cathode is immersed in a slurry of asbestos fibres. By the application of reduced pressure these fibres are caused to form a porous layer on the outside of the hollow body, which layer serves as the diaphragm to separate the cathode region from

the anode region. The cathodes are facing graphite anodes **6** embedded in a layer of lead **7** in the bottom portion of the casing **5** of the cell consisting for example of concrete. The space above the lead layer and between the cathodes and anodes is filled with the aqueous alkaline metal chloride solution **8** to be electrolyzed which is introduced through line **12** in the upper portion of the casing **5**. Current is supplied to the anodes by copper supplies **9** and **14** to the anodes and cathodes respectively. Hydrogen, chlorine and alkaline metal hydroxide solution produced by the electrolysis are withdrawn through lines **10, 11** and **13** respectively. The level of the electrolyte solution can be controlled with the aid of a transparent tube **15**.

The Siemens-Billiter-Cell shown in FIGURE 3 is a typical representative of a diaphragm cell with a horizontal arrangement of the electrodes in which the cathodes according to the invention can be used. A graphite anode **17** and a cathode **18** as above described in connection with the Hooker-Cell are horizontally arranged in a casing **16** with a diaphragm **19** between them. The diaphragm consists of a mixture of barium sulfate and asbestos fibres. The alkaline metal halide solution is supplied by line **20**, and chlorine and hydroxide solution produced by the electrolysis are withdrawn through lines **21** and **22** respectively. The device **23** serves for controlling the pressure below the diaphragm by which pressure the rate of flow of solution through the diaphargm can be controlled.

A more detailed description of the Hooker-Cell and the Siemens-Billiter-Cell is laid down in Billiter "Die technische Elektrolyse der Nichtmetalle," Wien (1954) pages 237 and 244 respectively.

The invention is further illustrated by the following examples. It should however be understood that the invention is not restricted to the specific embodiments described therein.

Example 1

A cathode for a diaphragm cell for the electrolysis of alkali metal chlorides was obtained in the following manner:

A frame formed of porous sintered nickel powder in the form of a foil of .7 mm. thickness was placed as the cathode in an aqueous solution of nickel nitrate containing nitric acid (100 g. $Ni(NO_3)_2 \cdot 6H_2O$ for each liter) with a nickel plate serving as anode. The electrolysis at a current density of .5 amp/dm.^{2} was carried on until the pores of the frame were filled from the inside to the outside with green bivalent nickel hydroxide (approximately six hours). The pH value of the electrolyte was checked throughout the duration of the electrolysis and restored, when necessary, to approximately 3 by the addition of nitric acid. The electrode was then rinsed with water and treated for eight hours at a temperature of 250° C. with a flow of hydrogen. The subsequent cooling off process was accomplished also under a hydrogen atmosphere.

The electrode prepared in said manner was then incorporated in an electrolytic cell for the decomposition of a NaCl solution, a graphite electrode serving as anode and the above described electrode as cathode. Anode and cathode areas were separated by a diaphragm made of asbestos. Utilization of the electrode prepared according to the invention makes possible a reduction in voltage within the NaCl decomposition cell by .4 volt at a current density of 20 amp/dm.^{2} when compared with a NaCl decomposition cell using a smooth Ni-plate as cathode. When compared with a NaCl decomposition cell where a nickel sintered element, as described by U.S. Patent 2,970,095, was used as cathode, the reduction in the voltage, at identical current density of 20 amp/dm.^{2}, mounted to .15 volt.

For use in technical electrolysis cells an electrode is employed which is manufactured in the manner described above and which is provided with a mechanical support, for example a reinforcement of perforated metal or a wire mesh made of nickel or iron. The reinforcement can be accomplished by sintering a foil-thin layer of sintered material onto the support and by subsequently impregnating this layer, or by connecting the previously impregnated frame with a solid support, for example by spot welding.

Example 2

A nickel cathode was prepared in the manner described in Example 1 but the electrolyte used for the the filling of the pores of the porous frame with oxide or hydroxide was acidified with hydrochloric acid in place of nitric acid.

The reduction in voltage attained by such cathode when compared with the known electrodes was the same as set forth in Example 1.

I claim:

1. Process for the manufacture of a cathode for the electrolysis of alkali metal chlorides in a diaphragm cell which comprises depositing a compound selected from the group consisting of nickel and iron oxides and hydroxides in the pores of a metallic electrically conducting porous frame by electrolysis between said frame as cathode and an anode in an acid electrolyte containing the ions of the metal of the compound to be deposited while maintaining the electrolyte outside the cathode at a pH value which will prevent the precipitation of said compound, said electrolyte containing also reducible ions the reduction potential of which is more positive than the separation potential of said metallic ions, removing said frame and deposited compound from said electrolyte and reducing the deposited compound to the metallic state.

2. A cathode for a diaphragm cell for the electrolysis of alkali metal chlorides consisting essentially of a metallic electrically conducting porous frame the pores of which contain a finely divided metal selected from the group consisting of iron and nickel made by the process defined in claim **1**.

3. Process for the manufacture of a cathode for the electrolysis of alkali metal chlorides in a diaphragm cell, which comprises electrolytically depositing a nickel compound selected from the group consisting of the oxide and hydroxide in the pores of a porous nickel sintered frame by carrying out an electrolysis between the nickel sintered frame as the cathode and a nickel anode in a nickel nitrate solution containing nitric acid as the electrolyte, and reducing the deposited nickel compound in a flow of hydrogen at a temperature between 200 and 300° C.

4. Process for the manufacture of a cathode for the electrolysis of alkali metal chlorides in a diaphragm cell, which comprises electrolytically depositing a nickel compound selected from the group consisting of oxide and hydroxide in the pores of a porous nickel sintered frame by carrying out an electrolysis between the nickel sintered frame as the cathode and a nickel anode in a nickel nitrate solution containing hydrochloric acid as the electrolyte, and reducing the deposited nickel compound in a flow of hydrogen at a temperature between 200 and 300° C.

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