

Method for improving the performance of nickel electrodes

Related Applications

0001 This application claims benefit to German Patent Application No. 10 2007 003 554.5, filed January 24, 2007 which is incorporated by reference in its entirety for all useful purposes.

0002 **1. Field of the Invention**

0003 The invention relates to a method for improving the performance of nickel electrodes in alkali chloride electrolysis.

0004 **2. Background of the Invention**

0005 In sodium chloride electrolysis, hydrogen is evolved from an alkaline solution. Conventionally, the cathodes in the process are made of iron, copper, steel, or nickel. Nickel electrodes can be either solid nickel or nickel plated.

0006 As mentioned in Offenlegungsschrift EP 298 055 A1, nickel electrodes can be coated with a metal from sub-group VIII, especially the platinum metals (*inter alia* Pt, Ru, Rh, Os, Ir, or Pd), of the periodic system of the elements or with an oxide of such a metal or with mixtures thereof. After a calcination process, the corresponding noble metal oxides are then usually present on the surface.

0007 The electrode so produced can be used, for example, in sodium chloride electrolysis as the cathode for hydrogen development. Many coating variants are known, because the coating of metal oxides can be modified in very different ways so that different compositions form on the surface of the nickel electrode. According to US-A-5 035 789, the cathode used is, for example, a ruthenium-oxide-based coating on nickel substrates.

0008 Once in operation, the plating on the nickel electrode degrades and causes the cell voltage to increase, making necessary to re-coat the electrode. This is technically complex, because the electrolysis must be stopped and the electrodes must be removed from the electrolytic cells. An object of the invention is, therefore, to find a simpler method for increasing or restoring performance.

0009 ELTECH has published and offered a technique with which a voltage reduction of from 200 to 300 mV as compared with untreated nickel electrodes can be achieved. In this technique, a noble-metal-containing solution of unnamed composition and constituents is applied *in situ*, i.e. during operation of the electrolysis, to the cathode side of the sodium chloride electrolysis in membrane cells. The solution is to be added during operation of the cell and is to lower the cell voltage.

00010 According to the teaching of patent specification US-A-4 555 317, iron compounds or finely divided iron is added to the catolyte in order to lower the cell voltage during sodium chloride electrolysis. The ELTECH publication contradicts this teaching, however, because, according to the information from ELTECH, coating the cathodes with iron is said to interfere with the electrolysis and to increase the cell voltage.

00011 According to the further known Offenlegungsschrift EP 1 487 747 A1, a 0.1 to 10 wt.% platinum-containing compound is added to sodium chloride electrolysis. The solution of the platinum-containing compound is added to the water that forms the catolyte, from 0.1 to 2 litres of the aqueous solution of the platinum-compound-containing solution being added per litre of water.

00012 According to JP 1011988 A, the activity of a deactivated cathode based on a Raney nickel structure with low hydrogen overvoltage is restored

by adding, into the catolyte, a soluble compound of a metal of the platinum group to the sodium hydroxide solution during operation of the sodium chloride electrolysis. For example, a sodium chloride electrolytic cell with 32 wt.% sodium hydroxide solution, a salt concentration of 200 g/l of sodium chloride is operated at 90°C and with a current density of 2.35 kA/m². The cathode is subjected to currentless nickelling for pretreatment and then nickel-plated in a nickel bath. Platinum chlorate, for example, was metered into the catolyte as the active compound, which resulted in a reduction in the cell voltage by 100 mV.

00013 According to US-A-4 105 516, metal compounds which are to lower the hydrogen overvoltage and accordingly reduce the cell voltage are added to the catolyte during the electrolysis of alkali metal chlorides. The examples given in US-A-4 105 516 in turn describe the metering and effects that arise by addition of an iron compound added to the catolyte of a sodium chloride diaphragm laboratory cell. The cell has an anode, consisting of expanded titanium metal, which is coated with ruthenium oxide and titanium oxide. The cathode consists of iron in the form of extended metal. The examples show the use of cobalt solution or iron solution at the iron cathode. Reference has already been made above to the disadvantages of iron compounds in the treatment of coated nickel electrodes.

00014 According to the further known patent specification US-A-4 555 317, it is known that sodium chloride electrolysis can be started with a nickel-coated copper cathode. An initial metering under electrolysis conditions of the cell was carried out with hexachloroplatinic acid in three steps. In the first step, 2 mg of platinum were metered in per 102 cm², i.e. 0.02 mg/cm², in the second step about 0.03 mg/cm² and in the third step about 0.2 mg/cm². The cell voltage was lowered by a total of about 157 mV.

00015 According to US-A-4 160 704, metal ions having a low hydrogen overvoltage can be added to catolytes of a membrane electrolytic cell for sodium chloride electrolysis in order to coat the cathode. The addition takes place during the electrolysis. However, the only example given is the addition of platinum oxide in order to improve an iron or copper cathode.

00016 Sodium chloride electrolysis according to the membrane process is known in the prior art. The process is carried out as follows: a sodium-chloride-containing solution is fed to an anode chamber having an anode, and a sodium hydroxide solution is fed to a cathode chamber having a cathode. The two chambers are separated by an ion-exchange membrane. Joining multiple anode and cathode chambers forms an electrolyser. The product streams from the anode chamber include chlorine and a less concentrated sodium-chloride-containing solution. The product stream from the cathode chamber includes hydrogen, and a more highly concentrated sodium hydroxide solution than was fed thereto. The volume flow of sodium hydroxide solution fed to the cathode chamber is dependent on the current density and the cell design. At a current density of, for example, 4 kA/m^2 and with the cell design of UHDE, Version BM 3.0, the volume flow of lye to the cathode chamber is, for example, between from 100 to 300 l/h, with a concentration of the sodium hydroxide solution that comes off of from 30 to 33 wt.%. The geometrically projected cathode area is 2.71 m^2 , this corresponds to the membrane area. The cathode is made of specially coated extended nickel metal provided with a special coating (manufacturer e.g. DENORA) in order to lower the hydrogen overvoltage.

00017 The cathode coatings in sodium chloride electrolysis conventionally consist of platinum metals, platinum metal oxides or mixtures thereof, such as, for example, a ruthenium/ruthenium oxide mixture. As is described in EP 129 374, the platinum metals that can be used include ruthenium, iridium, platinum, palladium and rhodium. The cathode coating does not have long-

term stability, in particular not under conditions in which electrolysis does not occur or during interruptions in the electrolysis, during which pole reversal processes, for example, can occur. Accordingly, more or less pronounced damage occurs to the coating over the operating time of the electrolyser. Likewise, impurities which pass, for example, from the brine into the lye, such as, for example, iron ions, can become deposited on the cathode or especially on the active centres of the noble-metal-containing coating and as a result can deactivate the coating. The consequence is that the cell voltage rises, with the result that the energy consumption for the production of chlorine, hydrogen and sodium hydroxide solution increases and the economy of the process is markedly impaired.

00018 It is likewise possible for only individual elements to exhibit damage to the cathode coating, and it is not always economical to stop the entire electrolyser therefor and remove the element with the damaged coating, because this is associated with considerable production losses and costs.

00019 Methods for improving nickel electrodes for sodium chloride electrolysis which are coated with elements of the platinum metals (sub-group VIII of the periodic system), referred to hereinbelow as platinum metals, their oxides or mixtures thereof, have not hitherto been directly known from the prior art.

00020 SUMMARY OF THE INVENTION

00021 The object of the invention is, therefore, to develop a specific method for improving nickel electrodes coated with platinum metals, platinum metal oxides or mixtures thereof, for use as cathodes in the electrolysis of sodium chloride, which process can be used while electrolysis operation continues and avoids a prolonged interruption in electrode operation to restore cathode activity.

00022 The invention relates to a method for improving the performance of nickel electrodes that are used in a membrane sodium chloride electrolytic process comprising:

(a) preparing a water-soluble or alkali-soluble platinum solution comprising:

(i) a solvent and

(ii) a soluble platinum compound

and

00023 (b) adding the solution to the catolyte.

00024 The invention provides a method for improving the performance of nickel electrodes having a coating based on platinum metals, platinum metal oxides or mixtures of platinum metals and platinum metal oxides, for sodium chloride electrolysis according to the membrane process, characterised in that, in the electrolysis of sodium chloride, a water-soluble or alkali-soluble platinum compound, in particular hexachloroplatinic acid or especially preferably an alkali platinate, particularly preferably sodium hexachloroplatinate (Na_2PtCl_6) and/or sodium hexahydroxyplatinate ($\text{Na}_2\text{Pt}(\text{OH})_6$), is added to the catolyte.

00025 For purposes of the specification, the term “Group VIII metals” includes all metals listed in sub-Group VIII of the Periodic Table, their metal oxides, and any mixtures of the metals and metal oxides.

00026 The term “nickel cathode” includes electrodes used as cathodes that are solid nickel or nickel plated, regardless of any additional metal coatings on the electrode.

00027 The term “platinum solution” includes an alkali or water based solution containing at least platinum and the solvent.

00028 DETAILED DESCRIPTION OF THE INVENTION

00029 In this method it is possible in particular either to meter in the sodium hexachloroplatinate in the form of an aqueous solution or in alkaline solution, or the hexachloroplatinic acid is metered directly into the catolyte, in particular the sodium hydroxide solution, a reaction then taking place with the lye to form the chloroplatinate.

00030 The addition of the platinum compound is effected in particular while the electrolysis is taking place, under normal electrolysis conditions, at a current density of from 0.1 to 10 kA/m^2 , particularly preferably at a current density of from 0.5 to 8 kA/m^2 .

00031 In a further preferred form of the platinum addition, the electrolytic voltage is varied, after the addition of the platinum compound, in particular in a pulsed manner, in the range from 0 to 5 V in order to deposit platinum in a more finely divided form on the cathode. The voltage here describes the voltage between the anode and the cathode.

00032 To that end it can be sufficient, depending on the rectifier used to produce the electrolytic direct voltage, to lower the cell voltage in order to use the residual ripple of the rectifier therefor. In an alternating voltage in the mentioned voltage range, the residual ripple of the rectifier can result with an amplitude of from 0.5 to 500 mV. Modern rectifiers scarcely possess any residual ripple, but it is possible to produce a residual ripple artificially. The residual ripple is between 20 and 100 Hz, for example.

00033 If the amplitude is likewise regulated, it can be +100 or -100 mV around the resting potential for the time of the noble metal metering. The resting potential is the voltage at which no further current flows. That potential is normally about 2.1 to 2.3 V, depending on the cell technology

and membrane used. However, it is also possible in particular to carry out the noble metal metering when the cell voltage is 0 V, in which case the amplitude must be chosen greater than the resting potential.

00034 Higher modulated amplitudes are likewise conceivable.

00035 Platinum metals that can be present in metal or metal oxide form as the electrode coating on the nickel within the scope of the invention are in particular ruthenium, iridium, palladium, platinum, rhodium and osmium.

00036 In a further preferred form of the novel method, in addition to the platinum compound, at least one other further soluble compounds of sub-group 8 of the periodic system of the elements, in particular compounds of palladium, iridium, rhodium, osmium or ruthenium, can additionally be added. Such compounds are used in particular in the form of water-soluble salts or complex acids.

00037 After deactivation has been detected, the addition in the case of first-time metering is preferably carried out as follows: a platinum compound is added to the catholyte, in the feed to the cathode chamber, at a cathode area of 2.71 m^2 , from 0.02 to 11 g Pt per cathode element, corresponding to from 0.007 g/m^2 to 4 g/m^2 , at a current density of from 1 to 8 kA/m^2 . The area used as the basis is the geometrically projected cathode area, which also corresponds to the membrane area. The rate of metering can be such that the platinum-containing solution, based on the platinum content per m^2 of cathode area, is metered at a rate of from $0.001 \text{ g Pt/(hm}^2\text{)}$ to $1 \text{ g Pt/(hm}^2\text{)}$.

00038 The addition can take place at a current density preferably under normal operating conditions, or alternatively at a higher or lower current density. For example, the addition can take place at a current density of in particular from 0.1 to 10 kA/m^2 .

00039 The temperature at which the metering of the platinum compound preferably takes place is from 70 to 90°C. The metering can also take place at a lower temperature, however.

00040 If a further voltage increase is observed when metering is complete, this can immediately be offset by metering again. This metering requires a markedly smaller amount of noble metal in order to restore the original voltage. Depending on the quality of the brine, the lye or on stoppages, a further, but smaller addition of platinum may be necessary within a period of from 1 to 3 weeks. The addition of the platinum compound to the catholyte can likewise take place in the feed to the cathodes. The required amounts of platinum are to be calculated according to the scale of the damage. In the case of relatively considerable damage, corresponding to a high voltage increase, more platinum must be metered in, while correspondingly less platinum must be metered in in the case of slight damage, corresponding to a slight voltage increase. Overdosing with platinum does not result in any further improvement or lowering of the cell voltage, however.

00041 The amount, based on the platinum, of the further soluble compounds from sub-group 8 in the solution to be added is particularly preferably from 1 to 50 wt.%.

00042 In a preferred embodiment, the variation in the electrolytic voltage can be effected by superimposing an alternating voltage on the electrolytic voltage. The frequency of the superimposed alternating voltage is in particular from 10 to 100 Hz. The amplitude can then be from 10 to 200 mV.

00043 By means of the method according to the invention it is possible for the first time to effect a voltage reduction by up to 200 mV in the case of

damaged nickel electrodes coated with ruthenium and/or ruthenium oxides or mixtures thereof.

00044 The preparation of the alkali platinate can be carried out by reaction of hexachloroplatinic acid with lye. This can be carried out separately or directly *in situ* if, for example, hexachloroplatinic acid is metered directly into the sodium hydroxide supply to the elements or to the electrolyser. The hexachloroplatinic acid is particularly preferably metered directly into the feed to the elements.

00045 Examples

00046 Example 1

00047 A commercial electrolyser having 144 elements whose nickel cathodes were provided with a coating based on ruthenium/ruthenium oxide from Denora was operated at a mean voltage of 3.12 V. Of these 144 elements, one exhibited a voltage increased by more than 100 mV as compared with the mean value. The following treatment cycle was begun: 65.88 litres of a hexachloroplatinate solution (1.19 g Pt/l) was metered at a rate of 10.98 l/h, during operation, into the sodium hydroxide solution (conc. 31.5%) of a membrane electrolyser at a current density of 4.18 kA/m^2 over a period of 6 hours. 78.25 g of platinum thus reached the surface of 144 cathodes (surface area of a cathode: 2.71 m^2). This corresponds to an amount of platinum of 0.21 g Pt/m^2 . The cell voltage fell on average to 3.08 V, the current consumption rose to 4.57 kA/m^2 . Converted to 4 kA/m^2 , this corresponds to a reduction in the voltage by 80 mV, accordingly from 3.09 to 3.01. Elements having a markedly higher voltage were no longer present. On the following day, a further 16.44 litres of the same solution, corresponding to 0.05 g Pt/m^2 , were metered in. The cell voltage did not improve further as a result.

00048 After 9 days, the mean voltage rose to 3.02 V (based on 4 kA/m^2), so that further metering of platinum in the form of hexachloroplatinic acid was carried out. 4.12 litres of the hexachloroplatinate solution (1.19 g Pt/l) were thereby metered in uniformly in the course of 2 hours, so that 4.9 g of platinum reached the surface of 144 cathodes (0.012 g Pt/m^2). The electrolysis was continued during the metering, the mean voltage thereafter was 3.01 V.

00049 The cell voltage at a current density of 4 kA/m^2 was on average 3.09 V before the metering and 3.01 V after the metering, which corresponds to a voltage reduction of 80 mV.

00050 Example 2

00051 A laboratory electrolytic cell was operated as described in Example 1 at a current density of 4 kA/m^2 at a cell voltage of 3.05 V with a standard cathode coating from Denora on the nickel cathode. After shutting down the cell without applying a protective potential, damage to the cathode coating occurred. A protective potential is conventionally applied during a shut-down in order to protect the coating of the cathode from damage. After re-starting, the cell voltage was 3.17 V.

00052 A solution of hexachloroplatinate having a platinum content of 1250 mg/l Pt was metered into the catolyte while the cell was operating. After metering the solution for 2 hours with a metered amount of 5 ml/h, the voltage fell to 3.04 V. A total of 12.5 mg of platinum (12.5 mg/100 cm^2) was added.

00053 Example 3

00054 The test of Example 2 was repeated, but a solution having a platinum concentration of 250 mg/l was metered in (same metering time and same feed capacity). Addition here 2.5 mg Pt/100 cm^2 . The voltage fell from 3.16 V to 3.07 V, i.e. by 90 mV.

00055 Further additional metering did not bring about any further voltage reduction.

00056 Example 4 (comparison)

00057 A laboratory electrolytic cell was operated as described in Example 1 at a current density of 4 kA/m^2 at a cell voltage of 3.08 V with a standard cathode coating from Denora on nickel electrodes. After shutting down the cell without applying a protective potential, damage to the cathode coating occurred. A protective potential is conventionally applied during a shut-down in order to protect the coating of the cathode from damage. After re-starting, the cell voltage was 3.21 V.

00058 A solution of rhodium(III) chloride having a rhodium content of 125 mg/l was metered in over a period of 4 hours at 5 ml/h. Metering was then continued for a further 2 hours with a solution having a concentration of 1250 mg/l and at 5 ml/h, as a result of which a further 50 mV voltage reduction was achieved. The voltage reduction was only 60 mV.

00059 All the references described above are incorporated by reference in its entirety for all useful purposes.

00060 While there is shown and described certain specific structures embodying the invention, it will be manifest to those skilled in the art that various modifications and rearrangements of the parts may be made without departing from the spirit and scope of the underlying inventive concept and that the same is not limited to the particular forms herein shown and described.

We claim:

1. A method for improving the performance of nickel electrodes that are used in a membrane sodium chloride electrolytic process comprising:
 - (a) preparing a water-soluble or alkali-soluble platinum solution comprising:
 - (i) a solvent and
 - (ii) a soluble platinum compoundand
 - (b) adding the solution to the catolyteand thereby forming a coating on the nickel electrode.
2. The method according to Claim 1, wherein the platinum compound is a water-soluble salt or a complex acid.
3. The method according to Claim 1, wherein the platinum solution is hexachloroplatinic acid, or an alkali platinate, or a mixture thereof.
4. The method according to Claim 1, wherein the soluble platinum compound is Na_2PtCl_6 , or $\text{Na}_2\text{Pt}(\text{OH})_6$, or a mixture thereof.
5. The method according to Claim 1, wherein, after the addition of the platinum solution, the electrolytic voltage is varied in the range from 0V to 5V.
6. The method according to Claim 4, wherein, after the addition of the platinum solution, the electrolytic voltage is varied in the range from 0V to 5V.
7. The method according to Claim 5, wherein, after the addition of the platinum solution, the difference in the electrolytic voltage is from 0.5 to 500 mV.
8. The method according to Claim 6, wherein, after the addition of the platinum solution, the difference in the electrolytic voltage is from 0.5 to 500 mV.

9. The method according to Claim 5, wherein the voltage is varied by pulsing the voltage or by superimposing an alternating voltage on the electrolytic voltage, in the range from 0 to 5 V, and by a difference of from 0.5 to 500 mV.
10. The method according to Claim 8, wherein the voltage is varied by pulsing the voltage or by superimposing an alternating voltage on the electrolytic voltage, in the range from 0 to 5 V, and by a difference of from 0.5 to 500 mV.
11. The method according to Claim 10, which further comprises at least one additional water-soluble compound from Group VIII of the Periodic Table are added to the platinum solution.
12. The method according to Claim 1, which further comprises at least one additional water-soluble compound from selected from the group consisting of palladium, iridium, rhodium, osmium and ruthenium.
13. The method according to Claim 11, wherein, the additional water-soluble compound, based on the amount of platinum in the platinum compound, are present in a concentration of 1 wt. % to 50 wt. %.
14. The method according to Claim 12, wherein, the additional water-soluble compound, based on the amount of platinum in the platinum compound, are present in a concentration of 1 wt. % to 50 wt. %.
15. The method according to Claim 1, wherein the water soluble or alkali soluble platinum compound solution is metered at a rate of $0.001 \text{ g Pt}/(\text{h} \cdot \text{m}^2)$ to $\text{g Pt}/(\text{h} \cdot \text{m}^2)$.

16. The method according to Claim 14, wherein the water soluble or alkali soluble platinum compound solution is metered at a rate of 0.001 g Pt/(h*m²) to g Pt/(h*m²).
17. The method according to Claim 15, wherein the temperature at which the metering of the platinum solution is from 70 °C to 90 °C.
18. The method according to Claim 16, wherein the temperature at which the metering of the platinum solution is from 70 °C to 90 °C.
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19. The method according to Claim 15, wherein the metering of the platinum solution occurs during electrolysis and under a current density between 0.1 to 10 kA/m².
20. The method according to Claim 18, wherein the metering of the platinum solution occurs during electrolysis and under a current density between 0.1 to 10 kA/m².