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54 Method for manufacturing an electrode, and electrode thus manufactured.

57 A catalytic covering layer containing at least Ni and S is electro-deposited on an electrical-conducting, electrolytically-formed perforated nickel plate by polarizing said nickel plate as cathode inside an electrolysis cell with a soluble nickel plate as anode and with a bath which contains a sulfur-releasing component, a salt from transition metal other than nickel such as a cobalt salt and preferably also a nickel salt.

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"Method for manufacturing an electrode, and electrode thus manufactured".

The invention relates to a method for manufacturing an electrode, more particularly for preparing H_2 and O_2 in alkaline media, which comprises electro-depositing a catalytic coating layer which contains at least Ni and S, on an electrical-conducting support.

A method of this kind is known from BE-A-864,275.

According to said known method, a cathode is manufactured by first forming on a support, a thin layer of Ni and thereafter subjecting the electrode to an electrolysis inside a tank which contains nickel sulfate and thio-urea.

There is known from BE-A-865,396, a similar method for manufacturing an anode. A support is first coated by electroplating with an amount of Ni, whereafter the formed electrode is activated by electrolysis in a bath wherein nickel sulfate and thio-urea are dissolved. During the electrolysis, a portion of the nickel coating dissolves while sulfur is absorbed in the remaining portion of said coating.

The above-mentioned known methods pertain to manufacturing either an anode or a cathode.

The invention has for object to provide a method whereby an electrode is obtained which can work as well as anode as cathode inside a cell.

For this purpose, the support material is polarized as cathode inside an electrolysis cell with has as an anode, a soluble nickel plate and with a bath which contains a sulfur-releasing component and a salt from transition metal other than nickel.

Nickel from the anode dissolves and is deposited together with the other transition metal and sulfur on the support, in such a way that an electrode is formed with a thin catalytic layer which contains nickel, another transition metal and sulfur.

By acting on the proportion of the nickel and the other transition metal in the catalytic layer, the electrode can be made better suitable as anode, or better suitable as cathode.

Preparing the anode and the cathode can occur with a single equipment.

In a particular embodiment of the invention, use is made of an electrolysis cell with a bath which contains, besides a sulfur-releasing component and a salt from another transition metal than nickel, a nickel salt.

In a remarkable embodiment of the invention, use is made of an electrolysis cell with a bath which contains as salt from another transition metal than nickel, a cobalt salt.

The thin catalytic layer comprises nickel, cobalt and sulfur. The more nickel it does contain, the better the electrode is suitable as cathode. The more cobalt it does contain, the better the electrode is suitable as anode.

In another particular embodiment of the invention, use is made as support material of an electrolytically-formed perforated nickel plate.

In an advantageous embodiment of the invention, the support is first roughened, de-greased and then etched in boiling acid.

In a useful embodiment of the invention a thin layer of nickel is first deposited on the support before the latter is polarized as cathode.

In another useful embodiment of the invention, the electrolysis bath pH is maintained approximately at 3.

In another useful embodiment of the invention, the bath is retained during electrolysis, at a temperature of about 60°C.

The invention further pertains to an electrode manufactured by the method according to one of the above embodiments.

Other features and advantages of the invention will stand out from the following description of a method for manufacturing an electrode and of a thus manufactured electrode, according to the invention; this description is only given by way of example and does limit the invention.

To manufacture an electrode according to the invention, an electrical-conducting support is coated by electrolysis with a Ni-Co-S layer.

Use is made as support, of an electrolytically-formed Ni plate, which is perforated for about 50% of the surface area thereof with conically-shaped holes with a mean diameter of about 1 mm.

The plate is roughened by means of a carborundum brush, it is de-greased with acetone and it is etched during 30 seconds in boiling HCl - (15%).

The plate is brought thereafter in a bath which has the following composition :

240 g/l $NiCl_2$

120 g/l HCl.

The bath temperature is kept at 20°C.

The plate is first polarized as anode during 20 seconds and thereafter as cathode during 40 seconds.

Both said polarizing steps are performed with a current density of 60 mA.cm⁻² and with a Ni counter-electrode.

The thus pre-treated plate is arranged directly inside an electrolysis cell the bath whereof has the following composition : 60 g/l $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$

80 g/l $\text{Cs}(\text{NH}_2)_2$

1 ml/l concentrated H_2SO_4

4.5 g/l CH_3COOH

2 g/l NaOH .

The bath pH is 3. The bath temperature is kept at 60°C and the bath is stirred and filtered continuously.

The plate is polarized as cathode.

Use is made as anode for the electrolysis cell, of a soluble nickel electrode which is arranged five centimeters away from the plate. The soluble nickel electrode is shielded with a bag of porous synthetic material.

The electrolysis is performed during 76 hours with a current density of 6mA/cm².

Nickel from the anode is dissolved and is deposited together with Co and S on the cathode.

After the electrolysis, the plate is rinsed with water, whereafter it is blown dry with pressurized air.

Due to this electrolysis, there is obtained on the perforated nickel support, a thin layer with a 40µm thickness with as composition :

15 atom-% Co

40 atom-% S

45 atom-% Ni.

In another embodiment of the invention, one proceeds as above-described, with the exception that use is made of an electrolysis cell bath which contains, besides a sulfur-releasing component and a cobalt salt, also a nickel salt.

The bath has the following composition :

60 g/l $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$

60 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

80 g/l $\text{Cs}(\text{NH}_2)_2$

4.5 g/l CH_3COOH

2 g/l NaOH

1 ml/l concentrated H_2SO_4 .

The ratio 60 g CoSO_4 /60 g NiSO_4 gives a compromise proportion between both transition metals in the thin catalytic layer of the electrode, which makes said electrode suitable both as anode and as cathode.

Still another embodiment of the invention differs from the preceding one by making use of an electrolysis cell bath which contains instead of a cobalt salt, a salt from another transition metal. The bath has the following composition :

60 g/l $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$

60 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

80 g/l $\text{Cs}(\text{NH}_2)_2$

2 g/l NaOH

4.5 g/l CH_3COOH .

In a variant of this latter embodiment, use is made as iron salt of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ instead of $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$.

The thus obtained electrodes have been tested as anode and as cathode in an electrolysis cell for water in alkaline media.

The over-voltages measured at 120°C and with a current density of 1 A/cm² did lie markedly lower than with uncatalysed pure nickel electrodes.

Various electrodes prepared according to the above-described way, have been tested in alkaline media, some of them during a time period up to 10,000 hours.

Depending on the composition of the catalytic layer of the electrode, there has been measured an anode potential lying between approximately + 0.50 V and + 0.60 V relative to a Hg/HgO reference electrode which was at room temperature.

Under the same conditions, cathode potentials have been measured lying between approximately -1.05 V and -1.15 V relative to a Hg/HgO reference electrode which was at room temperature.

The electrode prepared in the above-described way has for advantage that when being used as anode inside an electrolysis cell of bipolar type, it is stable with current interruptions, which is not the case with many other anodes which are manufactured from oxide material, when said latter ones are coupled with electrodes which can contain hydrogen.

The conically-shaped openings in the support material make possible a smooth discharge of the H_2 or O_2 bubbles.

The invention is in no way limited to the above-described embodiments and within the scope of the patent application, many changes might be brought to the described embodiments, notably as regards the shape, the composition, the arrangement and the number of the components which are being used to embody the invention.

Claims

1. Method for manufacturing an electrode, more particularly for preparing H_2 and O_2 in alkaline media, which comprises electro-depositing a catalytic covering layer which contains at least Ni and S, on an electrical-conducting support, characterized in that the support is polarized as cathode in an electrolysis cell with as anode, a soluble nickel plate and with a bath which contains a sulfur-releasing component and a salt from a transition metal other than nickel.

2. Method according to claim 1, characterized in that use is made of an electrolysis cell with a bath which contains, besides a sulfur-releasing component and a salt from transition metal other than nickel, a nickel salt.

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3. Method according to either one of claims 1 and 2, characterized in that use is made of an electrolysis cell with a bath which contains as salt from transition metal other than nickel, a cobalt salt.

4. Method according to any one of claims 1 to 3, characterized in that use is made as support, of an electrolytically-formed perforated nickel plate.

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5. Method according to claim 4, characterized in that use is made as support, of a nickel plate which is provided over approximately 50% of the surface area thereof, with conically-shaped openings.

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6. Method according to any one of claims 1 to 5, characterized in that the support is first roughened, de-greased and thereafter etched in boiling acid.

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7. Method according to any one of claims 1 to 5, characterized in that a thin layer of nickel is deposited onto the support before the latter is polarized as cathode.

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8. Method according to any one of claims 1 to 7, characterized in that the electrolysis bath pH is retained at about 3.

9. Method according to any one of claims 1 to 8, characterized in that the temperature of the electrolysis bath is retained at about 60°C during the electrolysis.

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10. Method according to any one of claims 1 to 9, characterized in that the electrolysis is performed with a current density of about 6 mA/cm².

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11. Method for manufacturing an electrode as described hereinabove.

12. Electrode, manufactured by the method according to any one of the preceding claims.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	US-A-4 422 920 (J. STACHURSKI) * Column 4, lines 49-56; column 6, claims 1-7; example *	1,2,6, 7,11, 12	C 25 B 11/04
Y	--- SOVIET INVENTIONS ILLUSTRATED, Section Chemical, week b30, abstract no. 55951, 5th September 1979, Derwent Publications Ltd, London, GB; & SU-A-627 183 (MOSC POWER INST) 04-09-1978 * Abstract *	1,3	
Y	--- CHEMICAL ABSTRACTS, vol. 103, no. 14, October 1985, page 491, abstract no. 112236h, Columbus, Ohio, US; & US-A-1 162 878 (INSTITUTE OF ELECTROCHEMISTRY, ACADEMY OF SCIENCES, U.S.S.R.) 23-06-1985 * Abstract *	1,3	TECHNICAL FIELDS SEARCHED (Int. Cl. 4) C 25 B 11
X	--- PATENT ABSTRACTS OF JAPAN, vol. 9, no. 130 (C-284)[1853], 5th June 1985; & JP-A-60 17 096 (TOYO SODA KOGYO K.K.) 28-01-1985 * Abstract *	1,2,9	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05-06-1987	Examiner GROSEILLER PH.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			