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(71) **Demandeur/Applicant:**
INDUSTRIE DE NORA S.P.A., IT
(72) **Inventeurs/Inventors:**
OTTAVIANI, ANGELO, IT;
CARRETTIN, LEONELLO, IT;
DI FRANCO, DINO FLORIANO, US;
MOJANA, CORRADO, IT;
PEREGO, MICHELE, IT
(74) **Agent:** MACRAE & CO.

(54) **Titre :** ELECTRODE POUR DES CELLULES D'ELECTROLYSE A MEMBRANE
(54) **Title:** ELECTRODE FOR MEMBRANE ELECTROLYSIS CELLS

(57) **Abrégé/Abstract:**

The invention relates to an electrode for membrane electrolysis cells comprising a grooved metal support favouring the gas release and the electrolyte renewal on its surface. The grooved geometry of the support may be obtained by erosion of a metal sheet with abrasive media in a continuous process.

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(71) Applicant *(for all designated States except US)*: **INDUSTRIE DE NORA S.P.A.** [IT/IT]; Via Bistolfi 35, I-20134 Milan (IT).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **OTTAVIANI, Angelo** [IT/IT]; Via Pierlombardo 5, I-20135 Milan (IT). **CARRETTIN, Leonello** [IT/IT]; Via Soderini 55, I-20146 Milan (IT). **DI FRANCO, Dino Floriano** [US/US]; 553 Zorn Lane, Mayfield Village, Ohio 44143 (US). **MOJANA, Corrado** [IT/IT]; Via Campogrande 66, I-23868 Valmadrera (IT). **PEREGO, Michele** [IT/IT]; Via Pierlombardo 16, I-20135 Milan (IT).

(74) Agent: REITSTÖTTER KINZEBACH; Sternwartstr. 4, 81679 München (DE).

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(54) Title: ELECTRODE FOR MEMBRANE ELECTROLYSIS CELLS

(57) Abstract: The invention relates to an electrode for membrane electrolysis cells comprising a grooved metal support favouring the gas release and the electrolyte renewal on its surface. The grooved geometry of the support may be obtained by erosion of a metal sheet with abrasive media in a continuous process.

ELECTRODE FOR MEMBRANE ELECTROLYSIS CELLS

BACKGROUND

The invention relates to an electrode for electrochemical applications, in particular to an electrode for membrane electrolysis cells made on a metal support.
Electrolytic processes carried out in cells separated by ion-exchange membranes are among the most relevant industrial electrochemical applications. Some examples of such applications are the electrolysis of alkali chloride brines (chlor-alkali electrolysis), with particular reference to the electrolysis of sodium chloride brine for the production of chlorine and caustic soda, and the electrolysis of hydrochloric acid solutions.

In the following description, reference will be made to sodium chloride electrolysis as the most representative example in terms of overall production, but the present invention shall not be understood as limited to such application.

In membrane chlor-alkali electrolysis, the anodic compartment of the electrolysis cell is separated from the cathodic compartment by means of an ion-exchange membrane. The anodic compartment of the cell is fed with a sodium chloride brine, for instance at a concentration of about 300 g/l; chlorine evolution takes place on the anode surface, at a current density usually not above 4 kA/m^2, while brine is consequently depleted down to an outlet concentration usually comprised between 200 and 220 g/l. Sodium ions are transported by the electric field across the membrane to the cathodic compartment, where the caustic product is generated at a concentration usually not higher than 33% by weight. The caustic product is then extracted and concentrated by evaporation outside the cell. Hydrogen evolution also takes place on the cathode surface. The need of decreasing the capital investment has led to the design of plants operating at higher current density: in fact, while older plants usually work at 3 kA/m^2, those of newer construction operate at about 5 kA/m^2. The current trend in plant design is to further increase such values up to 6 kA/m^2 or more. The evolution of gas in form of bubbles, whose flow-rate increases at increasing current densities, may cause pressure fluctuations potentially dangerous for the mechanical integrity of the membrane: for this reason, the pressure differential across the two compartments is usually controlled in an accurate fashion and maintained below 3000 Pa, which complicates the cell operation. Moreover, the product gas has the tendency to build-up between the membrane and the electrode surfaces facing the same, increasing the ohmic drop in the contact zone and locally depleting the chloride-ion concentration due to poor electrolyte renewal. Brine dilution favours the local evolution of oxygen with consequent acidification. The combination of these different aspects (chlorine build-up, oxygen build-up, depletion of trapped brine, acidification) accounts for the early deterioration of the membranes, particularly in form of blister generation especially in correspondence of interstitial zones between anode and membrane, leading to voltage increase and electrolysis efficiency decrease. A similar deterioration may also take place in the interstitial zones between membrane and cathode: in this case, liquid stagnation leads to an increase in the caustic product concentration, which may reach a value up to 40-45%. Such a high alkalinity can damage the membrane chemical structure, with consequent voltage increase going along with the onset of localised blistering, as described for the anode side.

A few measures have been proposed to improve brine circulation near the electrode surface in order to mitigate the problems associated with gas bubble stagnation: US 4,608,144 disclosed an anode surface equipped with vertical parallel channels alternatively directed to brine feed and withdrawal, and further equipped with horizontal channels of lower section reciprocally connecting the feed and withdrawal channels. In this way a forced brine circulation is achieved, somehow preventing the adhesion of chlorine bubbles. US 5,114,547 discloses an anode aimed at promoting brine circulation at the membrane-anode interface in order to obviate the increase in the electrical resistance associated with the depletion of stagnating brine at the interface by means of a structure consisting of vertical channels connected with slanted secondary channels disposed in a herringbone pattern. US 2006/0042935 addresses the same problem by providing an irregular anode surface obtained by sandblasting or acid etching in order to improve the brine supply to the anode.

While all of the proposed measures might contribute to some extent to prevent deterioration of ion-exchange membranes in the usual process conditions, they fail to guarantee an optimal functioning in the exasperated process conditions needed to meet the current market requirements aimed at a higher cell productivity.

It would therefore be desirable to have an electrode for membrane electrolytic cells overcoming the limitations of the prior art, particularly as regards the possibility to operate a membrane electrolysis cell with higher performances in terms of parameters such as membrane lifetime, higher applicable current density, operative voltage, concentration of the caustic product obtained in the cell, degree of brine utilisation or maximum applicable pressure differential.

SUMMARY

Various aspects of the invention are set out in the accompanying claims.

One embodiment provides an electrode obtained on a metal substrate having a multiplicity of locally parallel grooves with a depth of 0.005 to 0.02 mm and a pitch - defined as the distance between adjacent grooves - of 0.01 to 0.5 mm.

By locally parallel grooves it is hereby intended a multiplicity of grooves, of open or closed shape, running in parallel at least in part of their length; the path of the locally parallel grooves may assume a generally parallel trend across the whole electrode structure, in straight lines or with curvatures of any type. In one embodiment, the electrode surface presents locally parallel grooves having a closed shape and intersecting one another reciprocally.

The electrode as hereinbefore defined can be advantageous in any electrolytic application, especially for working in direct contact with an ion-exchange membrane; in the case of chlor-alkali electrolysis, the above electrode can be assembled with its grooved surface in direct contact with the membrane, with surprisingly advantageous results both used as the anode and/or as the cathode. The metal substrate may be made of different materials, including but not limited to titanium and titanium alloys for anode application and nickel, nickel alloys and stainless steels for cathode application. The substrate geometry can be of any type: as a non limiting example, the grooved surface can be provided on punched or expanded sheets, meshes and structures comprised of parallel strips optionally rotated along the horizontal axis, also called louvered electrodes.

The electrode substrate can be provided with a known catalytic coating on its grooved surface: for instance, when use as anode for chlorine evolution in chlor-alkali cells is intended, the electrode substrate may be provided with a coating based on noble metals or oxides thereof. Electrodes obtained on the substrate as hereinbefore defined can be particularly useful in chlor-alkali electrolysis cells, both as anodes for chlorine evolution and as cathodes for hydrogen evolution, especially when assembled with the grooved surface in direct contact with the membrane. In case of straight grooves running parallel across the whole structure, orienting the grooves in the vertical direction can provide an improved circulation of electrolyte and gas-bubble release from the surface. In the case of cells assembled according to the configuration known in the art as zero-gap, wherein both electrodes are in direct contact with the membrane, the inventors observed that manufacturing both the anode and the cathode on grooved substrates as defined made possible to operate at current densities largely exceeding 6 kA/m^2, up to 10 kA/m^2, with totally acceptable cell voltages. Life-tests were also carried out with excellent results at anolyte concentrations below 200 g/l (in particular down to 150 g/l), with caustic product concentrations above 33% (in particular up to 37%) and maintaining pressure differentials across the two compartments higher than 3000 Pa (in particular up to 10000 Pa), conditions which normally led to a quick deterioration of the membranes when prior art electrodes were employed.

Without wishing to be limited by any particular theory, it might be supposed that the electrode obtained on a grooved substrate as defined allows a particularly efficient release of the gas bubbles, also in comparison with grooved electrodes of the prior art, possibly because the densely packed and shallow grooves favour capillary transport phenomena as opposed to an electrolyte circulation.

The electrode as defined can be obtained by simple and cheap methods such as a superficial erosion carried out by means of abrasive paper or fabric - optionally in a continuous rolling process - lamellar grinding wheels or grindstones; other techniques include the use of draw-benches or rolling mills, besides more sophisticated technologies such as laser etching or lithographic techniques, according to the selected geometry. The erosion by grindstone for instance can be suitable for obtaining locally parallel grooves of closed shape and intersecting one another, while a lamellar grinding wheel, a draw-bench or a rolling mill can be more suitable for obtaining generally parallel grooves along the whole surface.

An electrode obtained with the above mentioned techniques can allow a sensible cost reduction compared to other grooved electrodes known in the art and characterised by a much higher groove depth, which cannot be obtained by simple abrasion.

EXAMPLE 1

Six 1 mm thick and 600 mm x 800 mm wide sheets of titanium grade 1 were degreased and subjected to an erosion treatment with a lamellar grinding wheel, obtaining grooves of 0.2 mm pitch on all samples at various depths; the sheets were expanded according to a known technique, obtaining a rhomboidal-mesh geometry of 10 mm x 5 mm diagonals and 1.6 mm displacement step. Upon completion of the expansion procedure, the grooves measured with a profilometer displayed average depths as reported in table 1:

TABLE 1

Sample ID	Groove depth (mm)
A1	0.003
A2	0.006
A3	0.01
A4	0.02
A5	0.05
A6	0.2

Similarly, three 1 mm thick and 600 mm x 800 mm wide sheets of nickel were degreased and subjected to the same erosion treatment and subsequent expansion, so as to obtain an identical geometry. Upon completion of the expansion procedure, the grooves measured with a profilometer displayed average depths as reported in table 2:

TABLE 2

Sample ID	Groove depth (mm)
C1	0.002
C2	0.01
C3	0.05

One sheet of titanium and one of nickel, having the same size as the previous samples, identified as A0 and C0 respectively, were subjected to the same expansion treatment as the above samples, after sandblasting with corundum and subsequent etching in HCl as known in the art; no additional abrasive treatment was effected on these samples.

All titanium samples were subsequently coated with a ruthenium and titanium oxide-based catalyst for anodic evolution of chlorine, with an overall catalyst loading of 12 g/m². A new check of the groove depth did not show any significant variation introduced by the coating step.

EXAMPLE 2

All samples prepared in the previous example were cut into 150 mm x 200 mm wide pieces and characterised, coupled in various combinations, in a multiple bench for chlor-alkali electrolysis accelerated lifetime tests. Each station of the multiple bench was equipped with one membrane electrolysis cell suitable for accommodating one anode and one cathode of 1 mm thickness in direct contact with a reference sulphonic/carboxylic double layer membrane (Nafion® 982 produced by DuPont, U.S.A.). The electrode samples of tables 1 and 2 were assembled with vertically oriented grooves. The lifetime test was carried out simultaneously starting-up all cells with the various combinations of anodes and cathodes at process conditions much more severe than the common industrial practice, determining the time of ion-exchange membrane decay, defined as the time required for the cell voltage to increase by 0.5 V with respect to the initial value at the process current density.

Process conditions were set as follows:

- brine concentration at the anodic compartment outlet: 150 g/l
- concentration by weight of product caustic soda: 37%
- pressure differential across the two compartments: 5000 Pa
- current density: 12 kA/m²

The results obtained are reported in table 3:

TABLE 3

Test number	Anode	Cathode	Duration (h)
1	A0	C0	514
2	A0	C0	562
3	A0	C2	580
4	A0	C3	565
5	A1	C0	729
6	A2	C0	904
7	A3	C0	1213
8	A4	C0	1417
9	A5	C0	866
10	A6	C0	578
11	A2	C1	940
12	A3	C1	1283
13	A4	C1	1646
14	A5	C1	1108
15	A1	C2	887
16	A2	C2	959
17	A3	C2	1682
18	A4	C2	1704
19	A5	C2	1011
20	A6	C2	622
21	A3	C3	1088
22	A4	C3	1544
23	A3	C1	1305
24	A4	C1	1593

EXAMPLE 3

An electrolysis cell as in example 2, equipped with an anode sample A4 and a cathode sample C2, and a second analogous electrolysis cell equipped with a non-grooved anode sample A0 and a non-grooved cathode sample C0 were subjected to a lifetime test at process conditions sensibly more severe than the common industrial practice.

Process conditions were set as follows:

- brine concentration at the anodic compartment outlet: 180 g/l
- concentration by weight of product caustic soda: 35%
- pressure differential across the two compartments: 4000 Pa
- current density: 10 kA/m²

After about 900 hours of testing, the cell equipped with electrode samples A0 and C0 had to be shut down because the progressive deterioration of the membrane had caused a strong increase in the cell voltage, which attained high values strongly fluctuating in time. The cell disassembly evidenced a general formation of blisters on the surface, with a higher population in correspondence of the brine exhaust outlet nozzle, where an incipient local delamination of the two layers of the membrane could also be observed.

The cell equipped with anode A4 and cathode C2 was dismantled after 2400 hours of continuous testing at practically constant voltage. Upon disassembling the cell, no particular phenomenon of membrane deterioration was observed.

The previous description shall not be intended as limiting the invention, which may be practised according to different embodiments without departing from the scopes thereof, and whose extent is solely defined by the appended claims.

Throughout the description and claims of the present application, the term "comprise" and variations thereof such as "comprising" and "comprises" are not intended to exclude the presence of other elements or additives.

The discussion of documents, acts, materials, devices, articles and the like is included in this specification solely for the purpose of providing a context for the present invention. It is not suggested or represented that any or all of these matters formed part of the prior art base or were common general knowledge in the field relevant to the present invention before the priority date of each claim of this application.

CLAIMS

1. Electrolysis cell comprising an ion-exchange membrane and at least one electrode in direct contact with said ion-exchange membrane, said electrode comprising a metal substrate having at least one surface equipped with a multiplicity of locally parallel grooves; the depth of said grooves ranging from 0.001 to 0.1 mm and the distance between adjacent grooves ranging from 0.1 to 0.5 mm.

2. The electrolysis cell according to claim 1 wherein said depth of said grooves ranges from 0.005 to 0.02 mm.

3. The electrolysis cell according to claim 1 or 2 wherein said grooves are generally parallel along the whole surface.

4. The electrolysis cell according to claim 1 or 2 wherein said locally parallel grooves are intersecting one another.

5. The electrolysis cell according to any one of the preceding claims wherein the material of said electrode substrate is selected from the group consisting of titanium and alloys thereof, nickel and alloys thereof, stainless steel.

6. The electrolysis cell according to any one of the preceding claims wherein said electrode substrate has a geometry selected from the group consisting of punched or expanded sheets, meshes and louvered structures.

7. The electrolysis cell according to any one of the preceding claims wherein said electrode further comprises a catalytic coating applied to said surface provided with grooves.

8. The electrolysis cell according to claim 7 wherein said catalytic coating comprises noble metals or oxides thereof.

9. The electrolysis cell according to any one of the preceding claims wherein said at least one electrode is assembled with said grooves generally parallel along the whole surface oriented in a mostly vertical direction.

10. Method for manufacturing an electrolysis cell according to any one of claims 1 to 9 comprising the step of forming said multiplicity of grooves on said metal substrate of said electrode by continuous erosion.

11. The method according to claim 10 wherein said erosion is carried out continuously by means of at least one device selected from the group of rollers of abrasive paper or fabric, grindstones and lamellar grinding wheels.

12. The method according to claim 10 wherein said erosion is carried out by means of a draw-bench or a rolling mill.

13. Process of electrolysis of an alkali chloride brine carried out by applying direct electric current in a membrane electrolysis cell according to any one of claims 1 to 9 comprising the step of evolving a gaseous product on the surface of said at least one electrode.

14. The process according to claim 13 wherein said gaseous product is anodically-evolved chlorine or cathodically-evolved hydrogen.

15. The process according to any one of claims 13 to 14 wherein the density of said direct electric current is at least 5 kA/m^2.

16. The process according to any one of claims 13 to 15 wherein the pressure differential across the membrane of the electrolysis cell is at least 3000 Pa.

17. The process according to any one of claims 13 to 16 wherein the concentration of said brine at the anodic compartment outlet is at most 200 g/l.

18. The process according to any one of claims 13 to 17 wherein a caustic solution at a weight concentration of at least 33% is produced at the cathodic compartment.

19. Membrane electrolysis cells substantially as hereinbefore described with reference to the examples and the drawings.