ELECTRODE FOR MEMBRANE ELECTROLYSIS CELLS

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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

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation of PCT/EP2008/055887 filed May 14, 2008, that claims the benefit of the priority date of Italian Patent Application No. MI2007A000980 filed May 15, 2007, the contents of which are herein incorporated by reference in their entirety.

FIELD

[0002] The invention relates to an electrode for electrochemical applications, in particular to an electrode for membrane electrolysis cells made on a metal support.

BACKGROUND

[0003] 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.

[0004] In the following description, reference will be made to sodium chloride electrolysis as the most representative example in terms of overall production, but the invention shall not be understood as limited to such application.

[0005] 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/m², while brine is consequently deposed 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.

[0006] The need for 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/m², those of newer construction operate at about 5 kA/m². The current trend in plant design is to further increase such values up to 5 kA/m² or more. The evolution of gas in the 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 the 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.

[0007] 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. For instance, there has been 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. There has also been disclosed 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. The same problem has also been addressed by providing an irregular anode surface obtained by sandblasting or acid etching in order to improve the brine supply to the anode.

[0008] 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.

[0009] 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

[0010] This Summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Detailed Description. This Summary is not intended to identify key factors or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter.

[0011] As provided herein, the invention comprises an electrolysis cell having an ion-exchange membrane and at least one electrode in direct contact with the ion-exchange membrane, the electrode comprising a metal substrate having at least one surface equipped with a multiplicity of grooves, with the depth of the grooves ranging from 0.001 to 0.1 mm and the distance between adjacent grooves ranging from 0.1 to 0.5 mm.

[0012] To the accomplishment of the foregoing and related ends, the following description sets forth certain illustrative aspects and implementations. These are indicative of but a
few of the various ways in which one or more aspects may be employed. Other aspects, advantages, and novel features of the disclosure will become apparent from the following detailed description.

DESCRIPTION

In the following description, for purposes of explanation, numerous specific details are set forth in order to provide a thorough understanding of the claimed subject matter. It may be evident, however, that the claimed subject matter may be practiced without these specific details.

One or more implementations of the invention are hereinafter described. However, it will be appreciated by those skilled in the art that the invention is not limited to the exemplary implementations illustrated and described hereinafter.

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.

Locally parallel grooves, as defined herein, refers to 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 hereinafter 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 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 used as an anode for chlorine evolution in chloralkali cells as intended, the electrode substrate may be provided with a coating based on noble metals or oxides thereof. Electrodes obtained on the substrate as hereinafter 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 operation at current densities largely exceeding 6 kA/m², up to 10 kA/m², with 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.

The invention will be better understood by aid of the following examples, which shall not be intended as a limitation of the scope thereof.

Example 1

Six 1 mm thick and 600 mmx800 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 mmx5 mm diagonals and 1.6 mm displacement step. Upon completion of the expansion procedure, the grooves, as measured with a profilometer, displayed average depths as reported in Table 1:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Groove depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.003</td>
</tr>
<tr>
<td>A2</td>
<td>0.006</td>
</tr>
<tr>
<td>A3</td>
<td>0.01</td>
</tr>
<tr>
<td>A4</td>
<td>0.02</td>
</tr>
<tr>
<td>A5</td>
<td>0.05</td>
</tr>
<tr>
<td>A6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Similarly, three 1 mm thick and 600 mmx800 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, as measured with a profilometer, displayed average depths as reported in Table 2:

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Groove depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>0.004</td>
</tr>
<tr>
<td>B2</td>
<td>0.007</td>
</tr>
<tr>
<td>B3</td>
<td>0.015</td>
</tr>
<tr>
<td>B4</td>
<td>0.03</td>
</tr>
<tr>
<td>B5</td>
<td>0.06</td>
</tr>
<tr>
<td>B6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

[0101] These results evidence the suitability of the present invention compared to prior art electrodes.
TABLE 2

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Groove depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.002</td>
</tr>
<tr>
<td>C2</td>
<td>0.01</td>
</tr>
<tr>
<td>C3</td>
<td>0.05</td>
</tr>
</tbody>
</table>

[0026] One sheet of titanium and one of nickel, having the same size as the previous samples, identified as AO and CO 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.

[0027] 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

[0028] 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 chloralkali 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 non-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.

[0029] Process conditions were set as follows:

[0030] brine concentration at the anodic compartment outlet: 150 g/l
[0031] concentration by weight of product caustic soda: 37%
[0032] pressure differential across the two compartments: 5000 Pa
[0033] current density: 12 kA/m²
[0034] The results obtained are reported in Table 3:

TABLE 3-continued

<table>
<thead>
<tr>
<th>Test number</th>
<th>Anode</th>
<th>Cathode</th>
<th>Duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>A1</td>
<td>C2</td>
<td>887</td>
</tr>
<tr>
<td>16</td>
<td>A2</td>
<td>C2</td>
<td>959</td>
</tr>
<tr>
<td>17</td>
<td>A3</td>
<td>C2</td>
<td>1682</td>
</tr>
<tr>
<td>18</td>
<td>A4</td>
<td>C2</td>
<td>1704</td>
</tr>
<tr>
<td>19</td>
<td>A5</td>
<td>C2</td>
<td>1011</td>
</tr>
<tr>
<td>20</td>
<td>A6</td>
<td>C2</td>
<td>622</td>
</tr>
<tr>
<td>21</td>
<td>A3</td>
<td>C3</td>
<td>1088</td>
</tr>
<tr>
<td>22</td>
<td>A4</td>
<td>C3</td>
<td>1544</td>
</tr>
<tr>
<td>23</td>
<td>A3</td>
<td>C1</td>
<td>1305</td>
</tr>
<tr>
<td>24</td>
<td>A4</td>
<td>C1</td>
<td>1593</td>
</tr>
</tbody>
</table>

Example 3

[0035] 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 AO and a non-grooved cathode sample CO were subjected to a lifetime test at process conditions sensibly more severe than the common industrial practice.

[0036] Process conditions were set as follows:

[0037] brine concentration at the anodic compartment outlet: 180 g/l
[0038] concentration by weight of product caustic soda: 35%
[0039] pressure differential across the two compartments: 4000 Pa
[0040] current density: 10 kA/m²
[0041] After about 900 hours of testing, the cell equipped with electrode samples AO and CO 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.

[0042] 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.

[0043] Although the disclosure has been shown and described with respect to one or more embodiments and/or implementations, equivalent alterations and/or modifications will occur to others skilled in the art based upon a reading and understanding of this specification. The disclosure is intended to include all such modifications and alterations and is limited only by the scope of the following claims. In addition, while a particular feature may have been disclosed with respect to only one of several embodiments and/or implementations, such feature may be combined with one or more other features of the other embodiments and/or implementations as may be desired and/or advantageous for any given or particular application. Furthermore, to the extent that the terms “includes”, “having”, “has”, “with”, or variants thereof are used in either the detailed description or the claims, such terms are intended to be inclusive in a manner similar to the term “comprising.”

[0044] 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 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 invention before the priority date of each claim of this application.

What we claim is:

1. Electrolysis cell comprising an ion-exchange membrane and at least one electrode in direct contact with said ion-exchange membrane, the electrode comprising a metal substrate having at least one surface equipped with a multiplicity of grooves, the depth of the 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, the depth of the grooves ranging from 0.005 to 0.02 mm.

3. The electrolysis cell according to claim 1, the grooves being generally parallel along the whole surface.

4. The electrolysis cell according to claim 1, the locally parallel grooves intersecting one another.

5. The electrolysis cell according to claim 1, the material of the electrode substrate comprising one or more of titanium and alloys thereof, nickel and alloys thereof, or stainless steel.

6. The electrolysis cell according to claim 5, the electrode substrate having a geometry comprising one or more of punched or expanded sheets, meshes and louvered structures.

7. The electrolysis cell according to claim 1, further comprising a catalytic coating applied to the surface provided with grooves.

8. The electrolysis cell according to claim 7, the catalytic coating comprising noble metals or oxides thereof.

9. The electrolysis cell of claim 1, the at least one electrode assembled with the grooves generally parallel along the whole surface oriented in a mostly vertical direction.

10. Method for manufacturing an electrolysis cell according to claim 1 comprising the step of forming a multiplicity of grooves on the metal substrate of the electrode by continuous erosion.

11. The method according to claim 10, the erosion carried out continuously by means of at least one device comprising one or more of rollers of abrasive paper or fabric, grindstones or lamellar grinding wheels.

12. The method according to claim 10, the erosion 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 comprising an ion-exchange membrane and at least one electrode in direct contact with said ion-exchange membrane, the electrode comprising a metal substrate having at least one surface equipped with a multiplicity of grooves, the depth of the grooves ranging from 0.001 to 0.1 mm and the distance between adjacent grooves ranging from 0.1 to 0.5 mm, the process comprising evolving a gaseous product on the surface of the at least one electrode.

14. The process according to claim 13, the gaseous product comprising anodically-evolved chlorine or cathodically-evolved hydrogen.

15. The process according to claim 13, the density of the direct electric current being at least 5 kA/m².

16. The process according to claim 13, the pressure differential across the membrane of the electrolysis cell being at least 3000 Pa.

17. The process according to claim 13, the concentration of the brine at the anodic compartment outlet being at most 200 g/l.

18. The process according to claim 13, the caustic solution at a weight concentration of at least 33% is produced at the cathodic compartment.

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