

Electrolytic Cell for the Production of Oxidising Solutions

SUMMARY OF THE INVENTION

The invention relates to a three compartment electrolytic cell for the production of
5 oxidising solutions with disinfecting power containing active chlorine.

BACKGROUND OF THE INVENTION

The use of mildly acidic solutions containing active chlorine, mostly in the form of hypochlorous acid, is known in various disinfection processes pertaining to several
10 industrial fields including healthcare and sanitary applications; in food industry for instance, this kind of solutions are employed for the elimination of pathogenic bacteria such as Salmonella or Escherichia coli from the manufacturing cycle of foods of various kinds. The continuous production of solutions containing free active chlorine at appropriate concentration (e.g. 50-100 ppm) may be carried out electrolytically in
15 unseparated or in two-compartment cells, i.e. in cells partitioned by a semipermeable diaphragm or cation-exchange membrane and fed with alkali chloride brine; in the latter case, the desired solution is generated in the anodic compartment, while at the corresponding cathodic compartment an alkaline solution with good cleansing properties is obtained. In such systems, however, the salinity of the resulting anodic
20 product is too high to be suitable for use in many of the typical fields of application (food industry, hospitals, agriculture). An anodic product of superior quality can be obtained with an electrolytic cell equipped with three compartments, with a circulation of concentrated brine in an intermediate compartment, separated from the cathodic compartment by a cation-exchange membrane and from the anodic compartment by an
25 anion-exchange membrane. The above selection of separators allows the selective migration of sodium ions to the cathodic compartment, where a diluted alkali solution is generated (e.g. 50-100 ppm of caustic soda when the brine consists of sodium chloride) and of chloride ions to the anodic compartment, where chlorine is generated. None of the commercially available anionic membranes, however, is capable of resisting the
30 attack of chlorine-containing acidic solutions for more than a few tens of hours, despite their alleged resistance to oxidants; maintenance costs for the replacement of anionic membranes in three-compartment cells have hence proven not well suited to the needs of industry.

It was thus identified the need to provide an electrolytic cell for the production of acidic solutions containing active chlorine overcoming the drawbacks of the prior art, especially in terms of durability of the components.

5 SUMMARY OF THE INVENTION

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

Under one aspect, the invention relates to an electrolytic cell for the production of oxidising solutions with disinfectant properties comprising an anodic compartment and a cathodic compartment with an intermediate compartment interposed therebetween
10 delimited by an anodic separator and a cathodic separator; the cathodic separator, which separates the cathodic compartment from the intermediate compartment, consists of a cation-exchange membrane, while the anodic separator, which separates the anodic compartment from the intermediate compartment, comprises a diaphragm consisting of a network of fibres of organic polymer mechanically bound to particles of
15 ceramic material. In one embodiment, the diaphragm used as the anodic separator is applied to or otherwise arranged in intimate contact with an anion-exchange membrane. In one embodiment, the diaphragm consists of a composite tape of perfluorinated polymer and zirconium oxide with a thickness ranging between 0.1 and 1 mm, for example similarly to the product commercialised by Industrie De Nora as Polyramix®
20 Tape. This type of material has the advantage of being suitable for being arranged in multiple superposed layers until the desired thickness is obtained; additionally, it can act directly as the separator or it may be directly applied either to both sides of an anion-exchange membrane or to a single side thereof, which in one embodiment is the one facing the anodic compartment. Diaphragms of this kind may be obtained by deposition
25 into thin sheets of suspended polymeric fibres whereupon ceramic particles are previously impacted by mechanical means, with subsequent sintering and hydration. The deposition can take place according to procedures typical of the paper industry (for instance, by filtration on a suitable porous matrix). These diaphragms have proven surprisingly suitable for imparting high chemical resistance characteristics to the
30 commonest anion-exchange membranes, meanwhile enhancing their selectivity. In one embodiment, the anodic compartment is provided with means for feeding softened water, for example water of hardness not exceeding 7°f, and with means for extracting the mildly acidic oxidising solution, for example at a pH between 4 and 6.9, containing

free active chlorine; the cathodic compartment is provided with means for feeding softened water similarly to the anodic compartment and with means for extracting an alkaline catholyte, for example a caustic soda solution at a pH between 9 and 11; the intermediate compartment is provided with means for recycling an alkali chloride brine, for example a saturated sodium chloride brine.

Under another aspect, the invention relates to a method for the production of an active chlorine-containing oxidising solution with disinfectant power in a cell as hereinbefore described, comprising feeding water, optionally softened water of hardness not exceeding 7°f, to the anodic compartment and optionally to the cathodic compartment,

recycling alkali chloride brine, optionally a saturated sodium chloride aqueous solution, through the intermediate compartment, feeding direct electric current between the anodic compartment - connected to the positive pole of a power supply unit - and the cathodic compartment, connected to the negative pole and extracting the product

oxidising solution from the anodic compartment. In one embodiment, the recycling of alkali chloride brine through the intermediate compartment is carried out through an external reservoir containing a decomposition catalyst, for example based on RuO_2 or Co_3O_4 . This can have the advantage of reducing the content of free chlorine in the intermediate compartment, contributing to the protection of the anionic membrane especially in the case where the polymer diaphragm is applied only to the side of the

membrane facing the anodic compartment. The RuO_2 or Co_3O_4 catalyst is particularly fit for this purpose because it can be introduced into the tank in form of a catalytic coating applied to appropriate components thereof, for instance to plates made of titanium or other suitable material inserted into the tank. Other decomposition catalysts capable of reducing the levels of free chlorine in the recycled brine can be used without departing

from the scope of the invention.

Some implementations exemplifying the invention will now be described with reference to the attached drawing, which has the sole purpose of illustrating the reciprocal arrangement of the different elements relatively to said particular implementations of the invention; in particular, drawings are not necessarily drawn to scale.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 shows a diagram of the electrolytic cell according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE DRAWING

Figure 1 shows a side view of an electrolytic cell **100** according to one embodiment of the invention, subdivided into three compartments respectively consisting of an anodic compartment **200** and a cathodic compartment **400** with an intermediate compartment **300** interposed therebetween. The anodic compartment **200** contains an anode **250** and is separated from intermediate compartment **300** by means of a polymer diaphragm **321** applied to a anion-exchange membrane **320** on the side facing anodic compartment **200**. Cathodic compartment **400** contains a cathode **450** and is separated from intermediate compartment **300** by means of a cation-exchange membrane **340**. The sealing between the various compartments is ensured by means of a gasketing system **600**. Within intermediate compartment **300** a saturated solution of sodium chloride or other type of alkali chloride brine **510** is recycled with the aid of tank **500**. Inside tank **500** a decomposition catalyst is optionally contained, for example, ruthenium dioxide applied as coating of a metallic component (not shown).

Anodic compartment **200** is supplied with softened water **210** through appropriate supply means (not shown); from the same compartment, product oxidising solution **220** containing free active chlorine at slightly acidic pH is extracted. Cathodic compartment **400** is also fed with softened water **410**; in one embodiment, softened water feed **210** and **410** to anodic compartment **200** (anolyte in the following) and to cathodic compartment **400** (catholyte in the following), respectively, are unified. In another embodiment, only anodic compartment **200** is supplied with softened water **210**. A dilute alkali solution with negligible salinity **420** is extracted from cathodic compartment **400**, suitable for use as a cleaning agent in many industrial applications.

The following examples are included to demonstrate particular embodiments of the invention, whose practicability has been largely verified in the claimed range of values. It should be appreciated by those of skill in the art that the compositions and techniques disclosed in the examples which follow represent compositions and techniques discovered by the inventors to function well in the practice of the invention; however, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the scope of the invention.

EXAMPLE

An electrolytic cell according to the scheme shown in the figure was assembled using an anode **250** consisting of a 0.5 mm thick titanium mesh with an area of 113 mm x 53 mm, activated with a catalytic coating based on oxides of Ru, Ir and Ti; a cathode **450** consisting of a 0.5 mm thick titanium mesh with an area of 113 mm x 53 mm, activated with a catalytic coating based on Pt; a cation-exchange membrane **340** of Nafion[®] N115 type, produced by DuPont; an anodic separator comprising an anion-exchange membrane **320** of FAP-0 type, produced by Fumatec, with two layers of 0.5 mm thick polymer diaphragm tape **321** of the Polyramix[®] Tape type by Industrie De Nora superimposed thereto on the side facing anodic compartment **200**, consisting of a network of PTFE fibres modified with Zr particles obtained by deposition of a thin sheet from an aqueous suspension of fibres, drying at 100 °C, sintering at 345 °C for 90 minutes and conditioning for 60 minutes in dilute caustic soda at pH 11 containing 0.1% of Zonyl[®] surfactant at a temperature of 90 °C. Anodic compartment **200** and cathodic compartment **400** were fed respectively with anolyte and catholyte consisting of softened water at 4 °f. Intermediate compartment **300** was fed with a saturated brine **510** obtained out of 99% pure NaCl, coming from reservoir **500** containing a few titanium plates coated with a paint based on RuO₂; brine **510** at the outlet was recycled to tank **500**, as shown in the figure. Catholyte **410** was fed at a fixed flow rate of 1 l/min, while the flow rates of anolyte **210** and brine **510** were changed in the course of the various tests, all carried out upon feeding a 6 A direct current (corresponding to a current density of 1 kA/m²) after connecting the positive pole of a rectifier to anode **250** and the negative pole to cathode **450**. The best results in terms of efficiency of production of active chlorine were obtained with a flow-rate of anolyte **210** of 0.6 l/min and a flow rate of brine **510** of 0.7 l/min. In such conditions, it was possible to generate in continuous an oxidising solution **220** containing 65-70 ppm of free active chlorine at a pH just above 6. The test was continued for 650 hours with consistent performances. The build-up of active chlorine in recycled brine **510** was continuously monitored, obtaining a value consistently below 1 ppm/h. At the end of the test, the opening of the cell showed no visible decay in any of the components.

COUNTEREXAMPLE

An electrolytic cell was assembled similarly to the previous example except for the anodic separator, consisting in this case of anion-exchange membrane **320** of the FAP-0 type only, without any polymer diaphragm **321** interposed. The test was carried out at the same current density, with flow rates of 0.6 l/min of anolyte **210**, 1 l/min of catholyte and 0.7 l/min of brine **510**. In such conditions, it was possible to generate an oxidising solution **220** in continuous containing 80 ppm of free active chlorine at a pH of about 6. During the test, a build-up of active chlorine of about 2 ppm/h was observed within recycling brine **510**. The test was forcibly stopped after about 50 hours due to the sudden decay of the anionic membrane, detected through contamination by sodium ions of product solution **220**. The test was repeated with a different anionic membrane (Selemion[®], manufactured by Asahi Glass) with substantially similar results.

The previous description shall not be intended as limiting the invention, which may be used 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, components or additional process steps. 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. Electrolytic cell (100) for the production of oxidising solutions comprising an anodic compartment (200) containing an anode (250) and a cathodic compartment (400) containing a cathode (450) with an intermediate compartment (300) delimited by an anodic separator (320,321) and a cathodic separator (340) arranged therebetween, said cathodic separator (340) interposed between said cathodic compartment (400) and said intermediate compartment (300) comprising a cation-exchange membrane, said anodic separator (320,321) interposed between said anodic compartment (200) and said intermediate compartment (300) comprising a diaphragm (321) formed by a network of organic polymer fibres mechanically bound to ceramic material particles, said diaphragm (321) being arranged in one or more layers in intimate contact with an anion-exchange membrane (320), wherein said anodic separator (320,321) is oriented with a major surface consisting of said diaphragm (321) facing said anode (250).
2. The cell according to claim 1 wherein said diaphragm (321) of said anodic separator (320, 321) is made of a 0.1 to 1 mm thick composite tape of perfluorinated polymer and zirconium oxide.
3. The cell according to any one of the preceding claims, wherein said anodic compartment (200) is provided with means for supplying water and means for extraction of an oxidising solution, said cathodic compartment (400) is provided with means for supplying water and means for extraction of alkaline catholyte, said intermediate compartment is provided with means for recycling alkali chloride brine.
4. Method for the production of an oxidising solution containing active chlorine in a cell according to any one of the preceding claims, comprising the following simultaneous or successive steps:
 - supplying water to said anodic compartment and optionally to said cathodic compartment;
 - recycling alkali chloride brine through said intermediate compartment;
 - supplying direct electrical current between said anode and said cathode;
 - extracting the product oxidising solution from said anodic compartment.

5. The method according to claim 4 wherein said water supplied to said anodic and cathodic compartments has a hardness of not more than 7°f.
6. The method according to claim 5 wherein said oxidising solution extracted from said anodic compartment has a pH of 4 to 6.9.
7. The method according to claim 4 to 6 wherein said alkali chloride brine recycling is carried out through an external reservoir containing a decomposition catalyst optionally based on RuO_2 or Co_3O_4 .
8. The method according to any one of claims 4 to 7 where said alkali chloride brine is a saturated of sodium chloride brine.
