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⑤④ **An electrode structure for electrolyser cells.**

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CH-A- 331 199
DE-A-2 632 073
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Description

This invention relates to an electrode structure for electrolyser cells, more particularly of the unipolar type.

It is well known that the voltage of an electrolytic cell is the sum of three major components: the thermodynamic potential required for the overall cell reaction; the electrode overvoltages which result from kinetic limitations; and a resistive contribution to cell voltage. For a particular desired process, the major avenues open for reduction of energy requirements are electrode activation to reduce the overvoltages for the desired reactions, and design improvement to reduce resistive losses.

Resistive losses are of two types: ionic, reflecting a resistance to the passage of current in the electrolyte; and electronic, reflecting the resistance to the passage of current in current-carrying metallic components of the electrolyser. In bipolar electrolyser designs, the ionic resistance contribution is of overwhelming importance, since current paths through metallic elements are normally very short in length. In equipment of the unipolar design, however, electronic resistance losses can become substantial, as the electronic current is normally removed from each electrode to a current-removal structure.

In designing to control ionic resistance of an electrolyser, two considerations are particularly important: minimization of the distance between the anodic and cathodic electrode elements; and minimization of the quantity of evolved gases which is retained between the electrodes, increasing the effective electrolyte resistivity. This latter requirement can be particularly important in cells having gas separating elements or diaphragms, where gas may accumulate in the separator or on its surface, thus increasing its resistance.

A design approach directed at satisfying these two requirements for minimizing ionic resistance, which has come into widespread use, is to use a porous pre-electrode structure on which the gas evolves, and which allows passage of the product gases through the structure to a rear area where they can be removed. Typical pre-electrode forms are perforated plates, expanded-metal sheet, and woven metal cloth. Any suitably-porous structure can be envisaged, including grooved sheets on foam metal.

A number of designs make use of porous pre-electrodes of this type which are fabricated from material which is sufficiently strong to be used without support, and which can be attached directly to a current-removal structure at the periphery of the electrode. An example is Canadian Patent No. 822,662, issued September 9, 1969. However, these pre-electrodes do not have the current removal capacity which is required for industrial unipolar electrolyser cells.

Several inventors have recognized the desirability of using a supporting structure as part of the electrode, in order to accomplish desirable

mechanical objectives. For example, Canadian Patent 1,002,476 issued December 28, 1976, discloses the use of a thin corrugated structure, internal to the pre-electrode, to provide a spring effect and improve the compression of anode/separator/cathode array while allowing for flexibility during cell assembly. Canadian Patent 1,086,256, issued September 23, 1980, features the use of a similar internal structure for the purpose of providing support to the pre-electrode when a diaphragm material is being deposited on the electrode surfaces under vacuum. However, the internal support structure of these electrodes is not connected to current removal structures and, more importantly, not designed to carry currents in the order of 1000 to 10,000 amperes or more, such as required in industrial unipolar electrolyser cells.

The pre-electrode elements are often attached to central current-collector structures, for example rods or an equivalent fabricated structure in the unipolar design as disclosed in Canadian Patent 1,041,040, issued October 24, 1978, or a formed bipolar plate in bipolar electrolyser equipment, as disclosed in U.S. Patent 3,379,634, issued April 23, 1968. These electrode designs are, however, not adequate for electrolyser cells because they do not allow efficient removal of gases up the electrode. U.S. Patent 4,008,143 discloses an electrode structure comprising two spaced porous pre-electrodes and a plurality of current conductive rods separately attached to each porous pre-electrode and positioned in the space between the porous pre-electrodes in such a way as to leave space for electrolyte to flow upwardly between the porous pre-electrodes. However, electrolyser cells would require a large number of current conductive rods in order for the pre-electrodes to carry currents in the order of 1000 to 10,000 amperes and more, and this would unduly restrict gas circulation between the porous pre-electrodes.

Other prior art proposals include the following.

French Patent No. 2,433,592 describes a brine cell using a flexible ion-permeable diaphragm pressed between anode and cathode units, the actual anodes and cathodes being prebonded to the respective sides of the diaphragm. Current is supplied to and removed from the tops of the units which in Fig. 3 comprise a corrugated metal sheet having a metal screen applied to each side thereof.

Swiss Patent No. 331199 describes bipolar electrode structures for filter press cells having a deformed metal plate carrying wire mesh electrodes on each side. Although this patent acknowledges that such plates having vertical ribs have been proposed, it prefers a dimpled structure for the plates.

British Patent Application No. 2,001,347 describes a lead anode for an electrowinning cell, having a horizontal hanger bar along its top edge through which the current flows to the electrode.

US Patent No. 4,124,482 describes a lead anode for use in the electrowinning of copper, having a

copper hanger bar extending along the top thereof, through which current flows to the electrode.

West German Patent Application No. 2,632,073 describes an accumulator, particularly a cadmium-nickel accumulator, and is concerned with the problem of making an electrical connection to an electrode which consists of a porous mass cut from a large sheet. A metal coating is flame-sprayed onto the electrode and a current collector is spot-welded to it. The coating and the collector are shown at the side of the electrode in the drawing.

It is an aim of at least the preferred embodiments of the present invention to provide an electrode for electrolyser cells which has the following characteristics:

a) Allows efficient removal of gases formed on the outer faces of the electrode surface to the interior of the electrode structure and up the electrode structure under the influence of their natural buoyancy in the electrolyte, thus reducing the ionic contribution to electrolyser voltage.

b) Allows current to be removed from each electrode while minimizing electronic resistance losses.

c) Is amenable to fabrication by low-cost techniques such as rolling, stamping and welding, thus providing an economic electrode.

d) Allow use of low-cost materials of construction having regular surfaces which can be reliably and economically protected from corrosion in the electrolyte by the electroplating of nickel or other corrosion-resistant coatings.

e) Has a thin profile, to be consistent with an electrolyser design for minimum size per unit of production capacity.

Generally, the invention provides an electrode structure for unipolar electrolyser cells, comprising a current collector provided by a generally rectangular formed metal plate having vertically orientated corrugations, a conductor or conductors for removing current from, or supplying current to, one vertical edge of said plate, said conductor(s) being attached along said vertical edge either by a continuous connection or by connections at a plurality of points, and a porous pre-electrode secured to the crests of said corrugations on at least one side thereof so as to form an essentially planar pre-electrode surface, the depths of the corrugations being from 0.1 to 3 cm, the electrode structure being designed to carry a current of at least 1000 amps. Such an electrode provides an unimpeded rise of the evolved gases to the top of the electrode.

The invention will now be described, by way of example with reference to the accompanying drawings in which:

Figure 1 is a perspective view of an electrode structure in accordance with the invention;

Figure 2 is a plan view of a portion of the electrode structure of Figure 1; and

Figures 3 and 4 illustrate typical optimization curves for an electrode structure from which current is being removed uniformly at the side.

Referring to Figures 1 and 2 of the drawings, there is shown a gas evolving electrode structure 10 (anode or cathode) which comprises a central current collector 12 to each side of which is attached a pre-electrode 14. Ionic current flow from the adjacent electrode structure or structures of opposite polarity would flow to the electrode structure perpendicular to the pre-electrodes, as shown by arrows A, and current is removed from the pre-electrodes by the current collector 12, as indicated by arrow B.

The pre-electrodes are normally woven screen, expanded metal, or perforated plate but can be of any perforated or porous geometry which allows for gas passage to the interior of the electrode structure.

The central current collector is a substantially rectangular solid, formed metal plate having vertically orientated corrugations and which allows for unimpeded rise of the evolved gases to the top of the electrode structure.

The pre-electrode is attached to the central current collector at the high points thereof so as to form an essentially-planar pre-electrode surface. The attachment may be by a weld, by screws or other mechanical fasteners, or by pressure which is exerted by the composite electrode/separator mass.

The central current collector must be attached to the conductor removing current from the electrode. This attachment may be continuous, through a welded, bolted, or riveted contact, or it may be at several points through connections to suitable conductors. In this latter case, additional current-conducting material may be included in the structure, as indicated by bar 16, to assist current equalization in the vertical direction, to further minimize resistive losses.

In any particular electrolyser design, the parameters of the electrode structure of this invention are established by an optimization which considers the resistive losses in the structure, the cost of the material of construction, and the physical constraints imposed by the detailed electrolyser design on maximum and minimum electrode structure thickness. It has been surprisingly found that a depth of the corrugations C (Figure 2) as low as 0.16 cm is satisfactory for electrode structure heights as great as 75 cm, with gas evolution at current densities to 1,000 mA/cm²; no increase in the ionic-resistance factor of the electrolyser was detectable with increasing current density, suggesting that the product gas is being effectively removed to the interior of the electrode structure. However, the depth of corrugations would likely not be less than 0.1 cm. The maximum depth of corrugation would be established by practical constraints on electrolyser size; it would be unlikely that a depth of corrugation greater than 3 cm would be desirable.

The thickness D (Figure 2) of the current collector material may be between .04 and 1.5 cm depending on the amount of current to be removed from the electrode. The wavelength E (Figure 2) of the corrugation waves, will be the

minimum consistent with economic forming of the current-collector material. This is necessary to minimize resistance losses in the pre-electrode. The wavelength of corrugation might be between 0.7 and 15 cm for a current-collector material having a thickness of between 0.04 and 1.5 cm.

Other dimensions of the current-collector structure can be established through a detailed optimization to minimize total operating cost, including capital amortization. Each of the major electrode structure parameters can be optimized in this way: thickness of the material from which the current collector is formed, width of the electrode structure, and, depending on the detailed method being used for current removal, dimensions of the current equalization or removal bar 16 and the electrode height.

Figures 3 and 4 illustrate a typical optimization for an electrode structure from which current is being removed uniformly at the side. The anode and cathode are assumed to be of similar design. The contribution to cell voltage due to electronic resistance of the current-collector structure (Fig. 3) diminishes as the thickness of the current-collector material is increased, or as the width of the electrode is reduced. Such voltage contributions can be calculated unambiguously by the method described by R. O. Loutfy and R. L. LeRoy in the *Journal of Applied Electrochemistry* 8 (1978) pages 549—555. The results presented assume that the material of construction is mild steel at 70°C, and that the current density on the projected pre-electrode is 240 mA/cm².

Figure 4 shows a typical optimization, in this case assuming a current price of mild steel and a power cost of \$0.03/kWh. The optimum electrode structure thickness is seen to increase with increasing electrode structure width. Of course the optimum values indicated by calculations such as these will have to be modified based on other considerations related to the overall dimensions of the electrolyser, the method of current removal, etc. The electrode structures of this invention are designed to carry currents of 1,000 to 10,000 amperes and more, and precise specification of the current-removal provisions is essential to achieve an economic result. Similarly, the massive quantities of gas evolved at such current loadings must be free to move unimpeded up the electrode structures to escape at the top.

Claims

1. An electrode structure for unipolar electrolyser cells, comprising a current collector provided by a generally rectangular formed metal plate having vertically orientated corrugations, a conductor or conductors for removing current from, or supplying current to, one vertical edge of said plate, said conductor(s) being attached along said vertical edge either by a continuous connection or by connections at a plurality of points, and a porous pre-electrode secured to the crests of said corrugations on at least one side thereof so as to

form an essentially planar pre-electrode surface, the depths of the corrugations being from 0.1 to 3 cm, the electrode structure being designed to carry a current of at least 1000 amps.

2. An electrode structure as claimed in claim 1, wherein a bar is secured to said vertical edge for current equalization when said attachment is at a plurality of points along the height of the electrode structure.

3. An electrode structure as claimed in claims 1 or 2, wherein the thickness of said plate is between 0.04 and 1.5 cm.

4. An electrode structure as claimed in claim 3, wherein the distance between the crests of said corrugations is between 0.7 and 15 cm.

5. A unipolar electrolyser cell including an electrode structure as claimed in any preceding claim.

6. A method of operating a cell as claimed in claim 5, wherein a current of at least 1,000 amperes is employed.

Patentansprüche

1. Elektrodenaufbau für unipolare Elektrolysezellen, enthaltend einen Stromsammler, der durch eine im allgemeinen rechteckig ausgebildete Metallplatte mit senkrecht angeordneten Wellungen gebildet wird, einen Leiter oder mehrere Leiter für die Abführung von Strom von oder die Zufuhr von Strom zu einer senkrechten Kante dieser Platte, wobei der oder die Leiter entlang dieser senkrechten Kante entweder durch eine kontinuierliche Verbindung oder durch Verbindungen an einer Mehrzahl von Punkten befestigt ist bzw. sind, und eine poröse Vorelektrode, die an den Rücken dieser Wellungen an zumindest einer Seite derselben so befestigt ist, daß sie eine im wesentlichen ebene Vorelektrodenoberfläche bildet, wobei die Tiefen der Wellungen 0,1 bis 3 cm sind und der Elektrodenaufbau für eine Strombelastung von wenigstens 1000 A ausgelegt ist.

2. Elektrodenaufbau nach Anspruch 1, dadurch gekennzeichnet, daß ein Stab an dieser senkrechten Kante befestigt ist, um den Strom auszugleichen, wenn die Verbindung an einer Mehrzahl von Punkten entlang der Höhe des Elektrodenaufbaus erfolgt.

3. Elektrodenaufbau nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Dicke der Platte zwischen 0,04 und 1,5 cm ist.

4. Elektrodenaufbau nach Anspruch 3, dadurch gekennzeichnet, daß der Abstand zwischen den Rücken der Wellungen zwischen 0,7 und 15 cm beträgt.

5. Unipolare Elektrolysezelle, enthaltend einen Elektrodenaufbau nach einem der vorhergehenden Ansprüche.

6. Verfahren zum Betrieb einer Zelle nach Anspruch 5, dadurch gekennzeichnet, daß ein Strom von wenigstens 1000 A angewandt wird.

Revendications

1. Une structure d'électrode pour cellules

d'électrolyseurs unipolaires, comprenant un collecteur de courant muni d'une plaque en métal généralement mise sous forme de rectangle ayant des ondulations orientées verticalement, un conducteur ou des conducteurs pour enlever le courant de, ou alimenter le courant à, un bord vertical de ladite plaque, le(s)dit(s) conducteur(s) étant fixé(s) le long dudit bord vertical soit par un raccordement continu soit par des raccordements situés en plusieurs points, et une pré-électrode poreuse fixée aux crêtes desdites ondulations sur au moins un de ses côtés de façon à former une surface de pré-électrode pratiquement plane, les profondeurs des ondulations étant de 0,1 à 3 cm, la structure de l'électrode étant conçue pour transporter un courant d'au moins 1000 ampères.

2. Une structure d'électrode selon la revendication 1, dans laquelle un barreau est fixé audit bord

vertical pour égaliser le courant quand ladite fixation est effectuée en plusieurs points le long de la hauteur de la structure d'électrode.

5 3. Une structure d'électrode selon l'une des revendications 1 et 2, dans laquelle l'épaisseur de ladite plaque est comprise entre 0,04 et 1,5 cm.

10 4. Une structure d'électrode selon la revendication 3, dans laquelle la distance entre les crêtes desdites ondulations est comprise entre 0,7 et 15 cm.

15 5. Une cellule d'électrolyseur unipolaire comprenant une structure d'électrode telle que revendiquée dans l'une quelconque des revendications 1 à 4.

6. Un procédé de fonctionnement d'une cellule selon la revendication 5, dans laquelle on emploie un courant d'au moins 1000 ampères.

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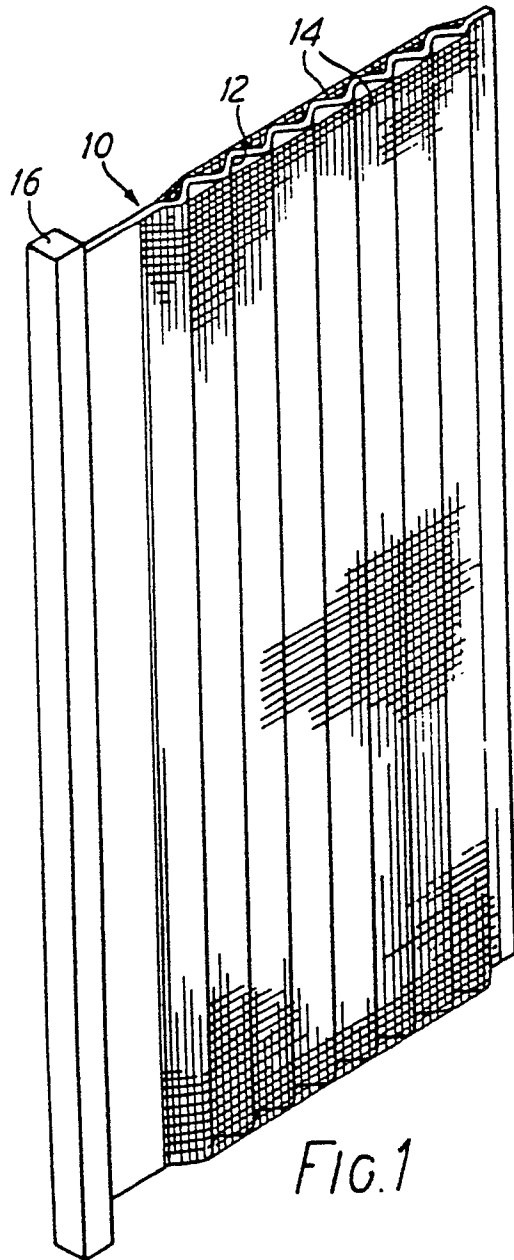


FIG. 1

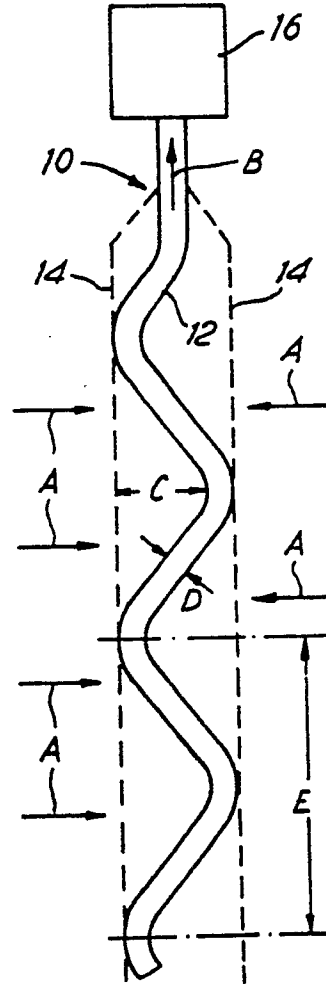


FIG. 2

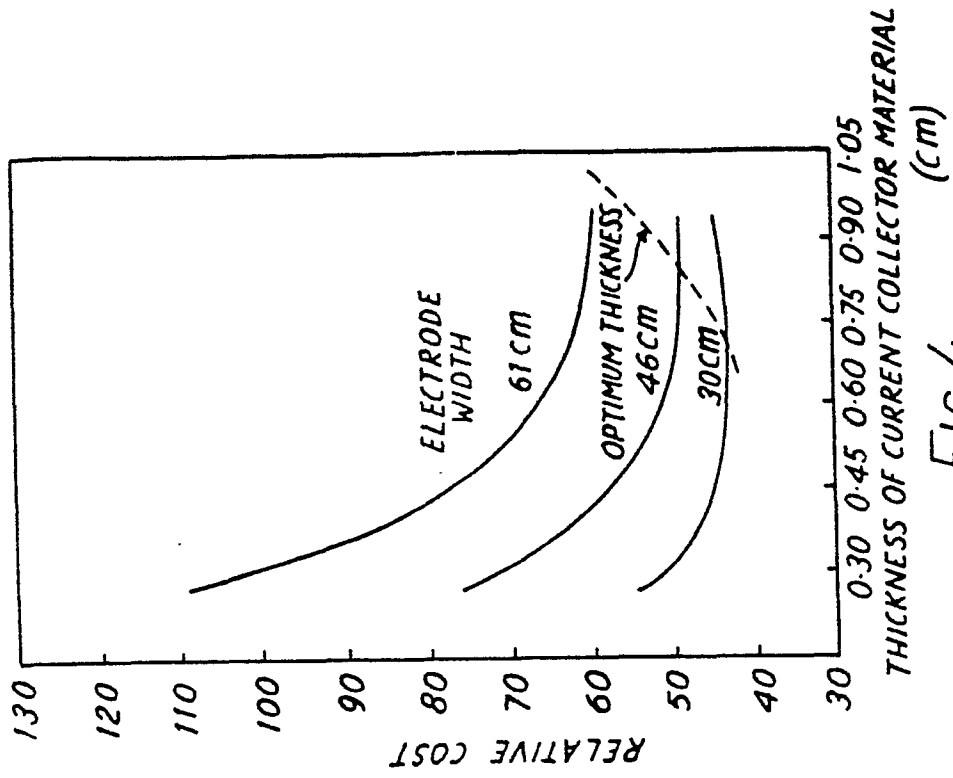


FIG. 4

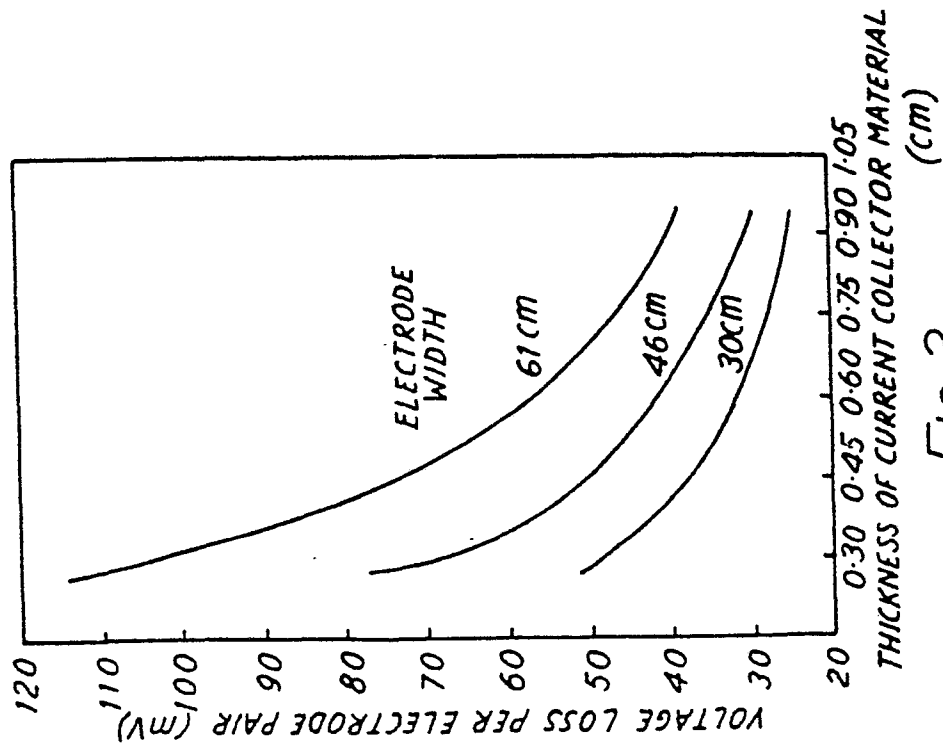


FIG. 3