March 22, 1966 O. DE NORA ET AL 3,242,065

CELL FOR ELECTROLYSIS OF HYDROCHLORIC ACID

Filed Dec. 21, 1960 2 Sheets-Sheet 1

Fig. 1

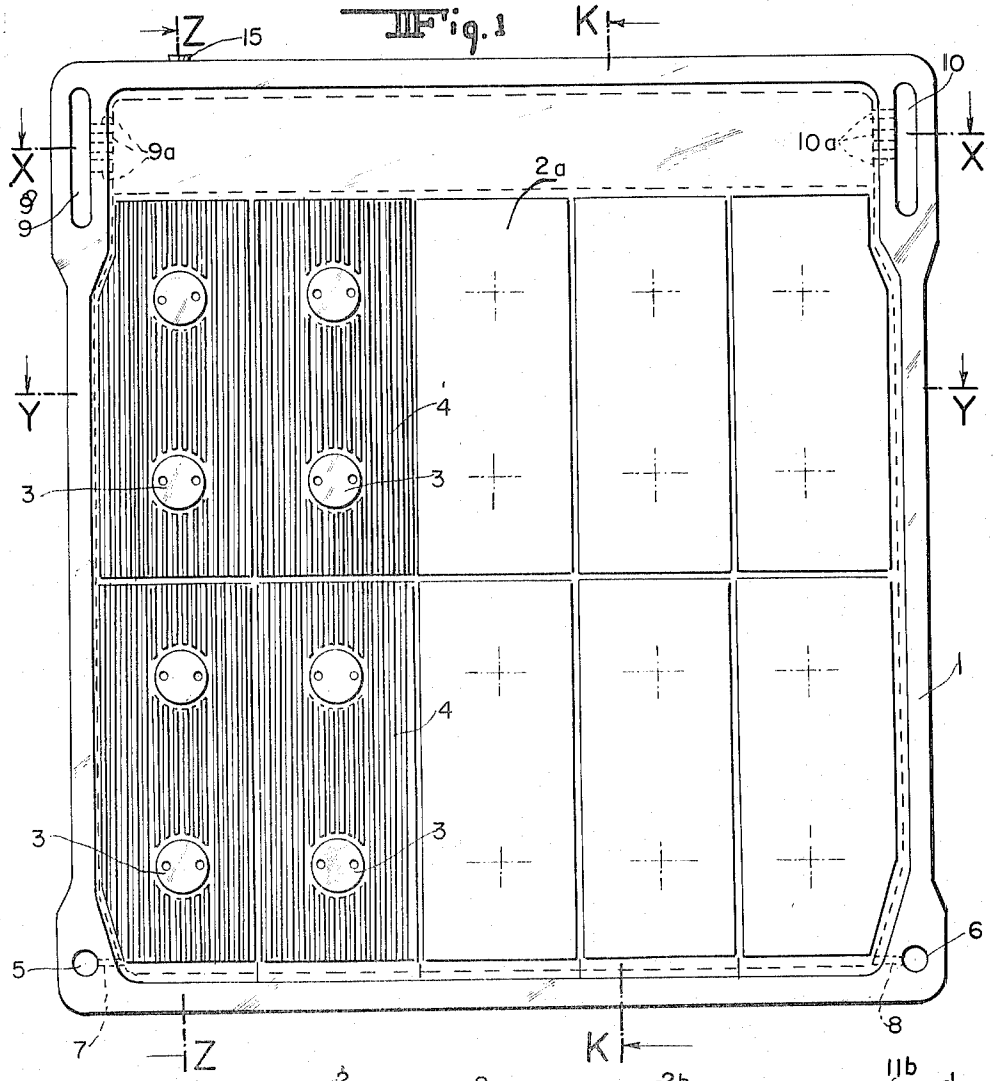


Fig. 2

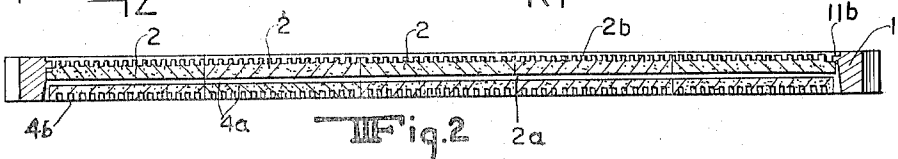
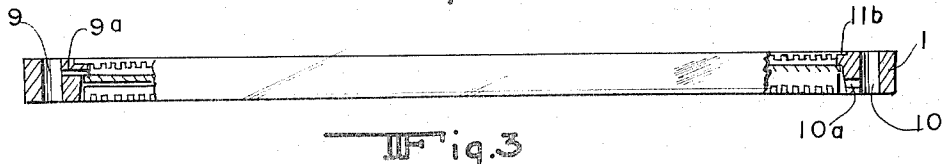


Fig. 3



INVENTOR
GEORG MESSNER
BY ORONZIO DE NORA
Hammond & Littell
ATTORNEY

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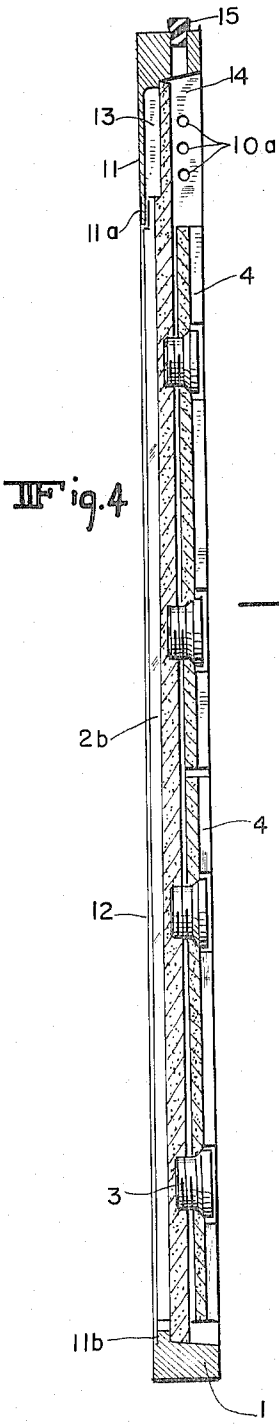


Fig. 4

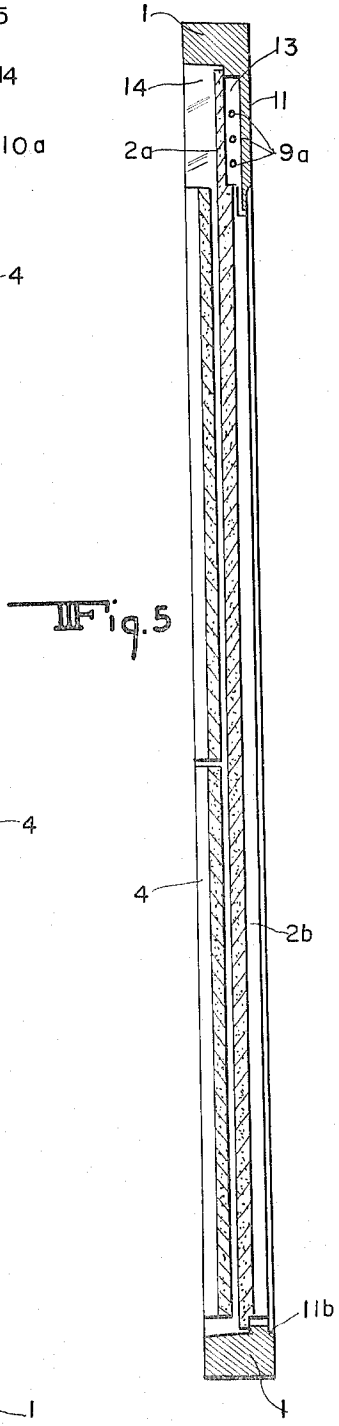


Fig. 5

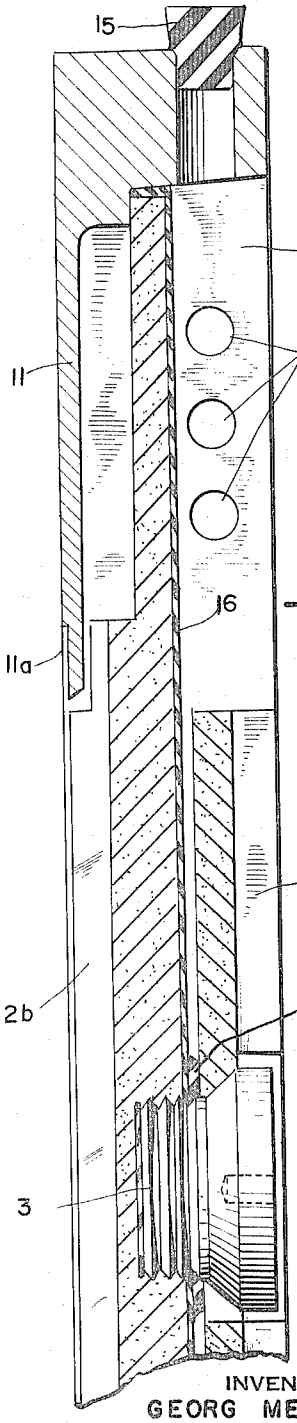


Fig. 6

INVENTOR
GEORG MESSNER
BY ORONZIO DE NORA

ATTORNEY

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3,242,065

CELL FOR ELECTROLYSIS OF HYDROCHLORIC ACID

Oronzio De Nora and Georg Messner, Milan, Italy, assignors to Oronzio De Nora Impianti Elettrochimici, Milan, Italy, a corporation of Italy

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5 Claims. (Cl. 204—256)

This invention relates to improvements in electrolytic cells for the production of chlorine by the electrolysis of hydrochloric acid.

In a number of chemical operations such as chlorination of organic compounds, hydrochloric acid is formed as a by-product. Since the need for hydrochloric acid at the place of its production is negligible and there is usually no immediate market for it, the hydrochloric acid presents a disposal problem. It can not be dumped in streams without neutralization because of stream pollution, and to neutralize the acid before dumping is prohibitive because of the cost.

It had been proposed to regenerate chlorine from the hydrochloric acid thereby eliminating the disposal problem and recovering the expensive chlorine otherwise lost as hydrochloric acid. The oxidation of the hydrochloric acid with oxygen in the presence of a catalyst or with nitrogen peroxide has been attempted but equipment and operations costs for these operations are too high with reference to the value of the chlorine recovered.

Therefore, industry has turned to the electrolysis of hydrochloric acid to form chlorine and hydrogen as a means of overcoming the problems. The equipment necessary for the operation is simple and the installation cost is low. Moreover, the process is flexible because the load of the electrolytic cells can be varied 25% above or below rated capacity to allow for change in amounts of hydrochloric acid produced as a by-product.

One of the better cells for the electrolytic process is described in the F.I.A.T. Final Report No. 832 issued by the Office of Military Government for Germany (U.S.) on June 16, 1946. This cell has a filter press type assembly and consists of a number of individual or unit cells clamped together to form a liquid tight assembly. Each unit cell consists of an outer Haveg frame which is covered with a corrosion-resistant material. Into this frame a bipolar graphite electrode is fastened. The bipolar electrode is grooved on the cathode side from bottom to top to allow easy passage of hydrogen gas to the top and is made smooth on the other side, and a diaphragm is placed over the grooves. When the frames are placed in the electrolytic cell assembly, there is a space between the smooth anode side of the bipolar graphite electrode and the diaphragm in the next frame, and this space is filled with graphite lumps. The lumps act as the anode and allow the free chlorine gas to rise to the top. Since the anode is consumed during the process, more graphite lumps can be added from holes in the top of the frame without disassembling the cells.

While the said cells function quite well, they have some defects due to the use of graphite lumps as anodic material. The electrical contact of the graphite lumps with the smooth side of the graphite plates is not complete due to the spaces between the lumps, and there is a voltage drop or loss in the unit cell. This loss of electrical energy raises the cell operating temperature to about 95° C. and makes the cell more susceptible to corrosion. The graphite lumps may also cause slight bowing or buckling of the diaphragm where the lumps contact the diaphragm and particularly near the bottom of the cell, due to the greater weight of the graphite lumps. Due to the deformation of the diaphragm, some lumps will be closer to the corresponding graphite cathode and will cause a

concentration of the current at those points. The current concentration causes local heating which further weakens the diaphragm which will eventually be destroyed.

An attempt to overcome the problems of the use of graphite lumps as an anode has been made in the German patent application No. 1,054,430, published April 9, 1959. In this cell there is a gas-tight and current-tight wall attached to the filter press frame members which separates the grooved graphite cathode and anode plates. The cathodes and anodes are attached by means of graphitic bolts passing through the separating wall. The graphite bolts hold the cathode and anode against each side of the separating wall and allow the current to pass through the cell from the anodes to the cathodes through the graphite bolts. Gaskets are used to separate the anode and cathode plates from the separating walls and to prevent passage of the electrolyte from the anode to the cathode compartments and separate diaphragms are held between each frame of the filter press assembly. The separating walls are made of cast iron or steel coated with a non-conducting material, and act as a mechanical support for the electrodes.

In order to replace the anode plate which is consumed in the process in the cells of the said German application, it is necessary to disassemble the cell units and also separately remove the diaphragm and the cathode plate which is not consumed in the operation of the cell and this complicates the disassembly and reassembly of the cell units. Moreover, the assembly and disassembly of the cell is further complicated by the gas separator and the diaphragm which are parts separate from the filter press construction of the cell. During the disassembly particularly the diaphragm is susceptible to damage when removing it. When assembling the cell, it is difficult to position the gas separator and diaphragm exactly in place so that there is no leakage between the gas collecting chambers or distortion of the diaphragm, and each section of the anode and cathode graphite plates and their corresponding gaskets must be separately assembled and held on each side of the separating walls while the graphite bolts which connect the anode and cathode plates are screwed into place.

It is an object of this invention to provide an electrolytic unit cell for the recovery of chlorine and hydrogen from hydrochloric acid which operates with low electrical consumption and at low temperatures.

It is another object of this invention to provide a simply constructed unit cell for the electrolysis of hydrochloric acid which will operate for a period of years without the necessity for replacement of the anode plates.

It is a further object of the invention to provide a unit cell for the electrolysis of hydrochloric acid wherein the anode is bolted to the cathode which is formed integral with graphite plates attached into the individual filter press frames for easy assembly and disassembly.

It is another object of this invention to provide a unit cell for electrolysis of hydrochloric acid in which the diaphragm and the grooved cathode plates do not have to be removed during assembly and disassembly.

These and other objects and advantages of this invention will become apparent from the following detailed description.

The prior art disadvantages are overcome by the unique construction of the unit cell of the present invention described herein. The need for a separating wall is eliminated by cementing grooved cathode plates directly to the frame. There is no need to remove the cathode as only the anodes are consumed during the operation of the cell. Therefore, assembly and disassembly of the cell is made easier by the novel construction described herein as only the anode need be removed. Also, since

the cathode need not be removed during the changing of the anode plates, the diaphragm covering the cathode plate is permanently cemented to the frame as it does not have to be removed. This prevents damage or distortion of the diaphragm. Moreover, the electrolytic cell is easily assembled because the gas separator is not a separate part, as in the said German application.

The grooved cathode plate may be made of graphite, coke or graphite coated with coke. If the cathode plate is graphite it should be activated to reduce the cathode potential about 0.1 to 0.2 volt. The grooved graphite plate may be activated simply by applying the electrical current to a complete electrolyser cell or installation in the wrong direction for a few hours. In this manner the final cathodes act as anodes for a short time and are slightly attacked by the temporary chlorine development. The slight attack of chlorine activates the graphite plates and reduces the cathode potential.

The grooved cathode plates are preferably made of coked carbon or graphite coated with coke. The use of a coke surface on the grooved cathode plates give a cathodic hydrogen overvoltage which is 0.2 to 0.3 volt lower than the use of a graphite surface. This lower overvoltage results in an electric energy saving of about 10%.

The coke surface may be applied to the grooved graphite cathode plates in any of the usual coking processes. For example, the graphite plate may be impregnated with a liquid organic material such as a resin, tar or solution of sugar in water and then the impregnated graphite plate heated at temperatures between 500° and 900° C.

Another method of forming a coke surface on the grooved graphite plate is to heat the said graphite plate at 500° C. for a few hours in an atmosphere containing carbon dioxide.

The use of graphite plates as the anode rather than graphite lumps provides a better electrical contact and a lower voltage drop is obtained across the cell. The normal loss in the graphite lump anode is about 400 millivolts while the usual loss in the cell of the present invention is about 25 to 30 millivolts. Also, the operating temperature is lower and corrosion is reduced in the cell described herein giving a longer life to the cell. The diaphragms have a longer life because there is no local over-heating at spots of higher current density due to stress on the diaphragm because of lumps pressing against the diaphragm.

While the present electrolytic cell has to be disassembled to replace the anode plates, the individual filter press units consisting of the outer frame, the grooved graphite separating and cathode plates and the diaphragm remain together and only the partially consumed anode plates need be removed and replaced by new anode plates, and because of better operating conditions, the anode plates will last for 5 to 6 years under normal operation. Any disadvantage caused by replacement of the anode plates every 5 to 6 years is more than off-set by the ability to operate the present cell at 30 to 35% higher current density.

Referring now to the drawings which illustrate a preferred embodiment of the invention:

FIG. 1 is a front view of a unit cell of the filter press assembly from the anode side;

FIG. 2 is a sectional top view of a unit cell along the line Y—Y of FIG. 1;

FIG. 3 is a sectional top view of a unit cell along the line X—X of FIG. 1;

FIG. 4 is a sectional side view of a unit cell along the line Z—Z of FIG. 1;

FIG. 5 is a sectional side view of the unit cell along the line K—K of FIG. 1; and

FIG. 6 is an enlarged side view of the top of the unit cell as seen in FIG. 4.

As seen in FIGS. 1, 2 and 3, the unit cell consists of an outer frame **1** into which a plurality of grooved plates **2** are cemented to provide smooth surfaces **2***a* on the anodic side and grooved surfaces **2***b* on the cathodic side. To the smooth surface of the grooved plates **2**, which on the grooved side act as the cathode, there are bolted by means of graphite bolts **3** a number of smaller graphite plates **4** which act as anodes. The electrodes are spaced by an acid-resistant washer **3***a* made of plexiglas or polyvinyl chloride, for example. The graphite anode plates **4** have a smooth surface **4***a* on the inner side and a smooth or preferably grooved surface **4***b* on the anodic side. If both sides of the anode plate are smooth, a space of a few mm. should be left between surface **4***b* and the diaphragm to allow the gas bubbles formed to rise through the cell.

At the lower corners of frame **1** there are holes **5** and **6** through which the incoming hydrochloric acid passes around the length of the assembled cell. The passages **7** and **8** from the holes or openings **5** and **6** respectively to the interior of the unit cell allow the concentrated hydrochloric acid supply of the unit cell to be maintained by the incoming hydrochloric acid flowing in holes **5** and **6** while the spent acid flows from the top of each cell unit. One or both of holes **7** and **8** can be used for draining the cell liquid in the case of a shut down and disassembling of the cell.

At the upper corners, each frame **1** is provided with oblong openings **9** and **10** connected by passages **9***a* and **10***a* with the interior of the unit cell and which when the cell is assembled provide channels from end to end of the assembled cell for the passage of hydrogen and chlorine gases as well as spent electrolyte out of the cell.

If the incoming hydrochloric acid enters the cell unit in the anodic space, most of the spent electrolyte will leave with the chlorine gas. A small amount of acid will pass through the diaphragm to the cathodic space and will be removed as a mist or foam with the hydrogen gas. If the incoming hydrochloric acid enters the cell unit in the cathode space, most of the spent electrolyte will leave with the hydrogen gas and the small amount which passes through the diaphragm to the anodic space will be removed as foam with the chlorine gas.

As can be seen in FIGS. 4, 5 and 6, each frame **1** has an integral extension **11** extending into the cell on the cathodic side with a rabbeted edge **11***a*, a registering rabbeted groove **11***b* extends around the entire frame, and an acid-resistant diaphragm **12** is cemented in this rabbeted groove. The extension **11** acts as a gas separator to prevent intermingling of the hydrogen and chlorine gases and the diaphragms **12** permanently cemented on the cathode side of the plates **2** serve to separate the anode and cathode compartments. The hydrogen gas collects in the space **13** and the chlorine gas collects in the space **14** and are drawn off through passages **9***a* and **10***a*, respectively. The diaphragms **12** may be formed of woven polyvinyl chloride cloth as described in the F.I.A.T. Report No. 832 or any other suitable diaphragm material. In the frame **1** there is an opening closed by stopper **15**, through which control instruments such as a thermometer or a manometer may be inserted while the electrolytic cell is operating. The stopper **15** may be a tapered polyvinyl chloride plug and may be secured in place with polyvinyl chloride cement.

On the smooth side **2***a* of the cathode plates **2** and about the graphite bolts **3** there is a coating **16** of gas and liquid impermeable material such as a Bakelite varnish or resin. The coating **16** eliminates electrolytic conductivity through the pores of graphite plates **2** which would result in an appreciable loss of current yield. The coating is also applied to the base of the opening for the bolts **3** to further eliminate electrolytic conductivity. It is preferred to impregnate the cathode plates **2** by a series of partial impregnations to eliminate the electrolytic conductivity.

While we have described a preferred embodiment of the invention, various modifications of the apparatus of the present invention may be made without departing

from the scope or spirit thereof, and it is to be understood that the invention is limited only as defined in the appended claims.

We claim:

1. In an electrolytic cell of the filter press type for the production of Cl_2 and H_2 by the electrolysis of hydrochloric acid, filter press frame members of chlorine and acid resistant material, hydrochloric acid inlets into said frame members, Cl_2, H_2 and spent acid outlets in said frame members, the said inlets and outlets of one frame member communicating with similar inlets and outlets of adjacent frame members, cathode plate members secured in said frame members, said plate members having activated surfaces of a material selected from the group consisting of graphite and coke, integral grooves on one side of said plate members forming the cathode plates, the other side of said plates being substantially smooth, an impregnating material sealing the smooth side of said cathode plates, a diaphragm secured in said frame members on the grooved side of said cathode plates, and separate graphite anode plates on the smooth side of said cathode plates, and means securing said anode plates to said cathode plates in electrical conductive contact therewith.

2. In an electrolytic cell of the filter press type for the production of Cl_2 and H_2 by the electrolysis of hydrochloric acid, filter press frame members of chlorine and acid resistant material, hydrochloric acid inlets in said frame members, Cl_2, H_2 and spent acid outlets in said frame members, the said inlets and outlets of one frame member communicating with similar inlets and outlets of adjacent frame members, a projection of said frame members extending into the cell as a gas separating partition, cathode plate members secured in said frame members, said plate members having activated surfaces of a material selected from the group consisting of graphite and coke, integral grooves on one side of said plate members forming the cathode plates, the other side of said plates being substantially smooth, an impregnating material sealing the smooth side of said plates, a diaphragm secured in said frame members on the grooved side of said plates, and separate graphite anode plates on the smooth side of said cathode plates, and means removably securing said anode plates to said cathode plates in electrical conductive contact therewith.

3. In an electrolytic cell of the filter press type for the production of Cl_2 and H_2 by the electrolysis of hydrochloric acid, filter press frame members of chlorine and acid resistant material, hydrochloric acid inlets into said frame members, Cl_2, H_2 and spent acid outlets in said frame members, the said inlets and outlets of one frame member communicating with similar inlets and outlets of adjacent frame members, a projection of said frame members extending into the cell as a gas separating partition, cathode plate members secured in said frame members, said plate members having activated surfaces of a material selected from the group consisting of graphite and coke, integral grooves on one side of said plate members forming the cathode plates, the other side of said plates being substantially smooth, an impregnating material sealing the smooth side of said plates, a rabbet around the interior of said frame members and across the bottoms of said gas separating partitions, a diaphragm secured in said rabbet on the grooved side of said plates, and separate graphite anode plates on the smooth side of said cathode plates, and means securing said anode plates to said cathode plates in electrical conductive contact therewith.

4. In an electrolytic cell of the filter press type for the production of Cl_2 and H_2 by the electrolysis of hydrochloric acid, filter press frame members of chlorine and acid resistant material, hydrochloric acid inlets into said frame members, Cl_2, H_2 and spent acid outlets in said frame members, the said inlets and outlets of one frame member communicating with similar inlets and outlets of adjacent frame members, a projection of said frame members extending into the cell as a gas seperating partition, cathode plate members secured in said frame members, said plate members having activated surfaces of a material selected from the group consisting of graphite and coke, integral grooves on one side of said plate members forming the cathode plates, the other side of said plates being substantially smooth, an impregnating material sealing the smooth side of said plates, a diaphragm secured in said frame members on the grooved side of said plates, and separate grooved graphite anode plates on the smooth side of said cathode plates, and graphite bolts securing said anode plates to said cathode plates in electrical conductive contact therewith.

5. In an electrolytic cell of the filter press type for the production of Cl_2 and H_2 by the electrolysis of hydrochloric acid, filter press frame members of chlorine and acid resistant material, hydrochloric acid inlets into said frame members, Cl_2, H_2 and spent acid outlets in said frame members, the said inlets and outlets of one frame member communicating with similar inlets and outlets of adjacent frame members, a projection of said frame members extending into the cell as a gas separating partition, cathode plate members secured in said frame members, said plate members having activated surfaces of a material selected from the group consisting of graphite and coke, integral grooves on one side of said plate members forming the cathode plates, the other side of said plates being substantially smooth, an impregnating material sealing the smooth side of said plates, a diaphragm secured in said frame members on the grooved side of said plates, and separate smooth graphite anode plates on the smooth side of said cathode plates, and graphite bolts securing said anode plates to said cathode plates in electrical conductive contact therewith.

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JOHN H. MACK, *Primary Examiner.*