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OF HIGH VALUE ALCOHOLS FROM SUGARS
AND SUGARY SUBSTANCES
Filed May 31, 1939

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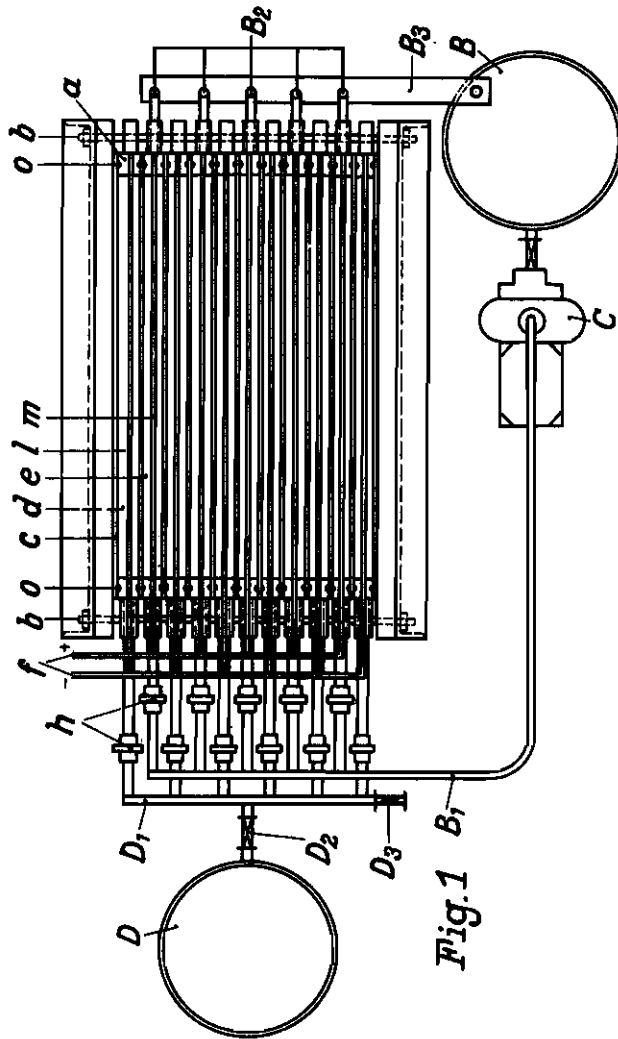


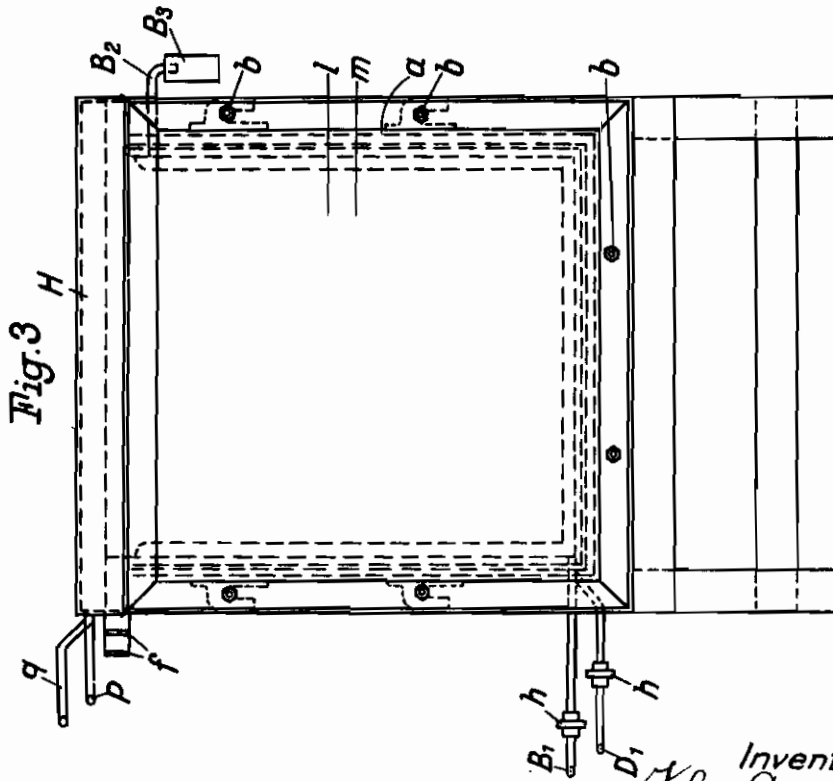
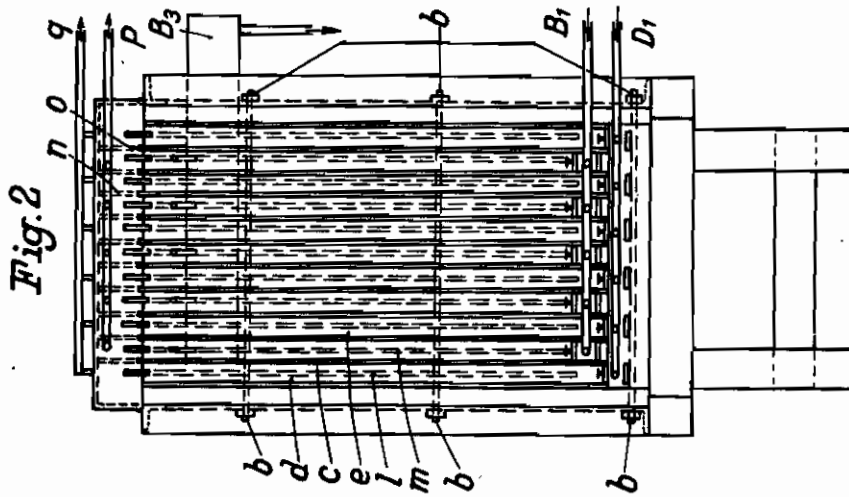
Fig. 1

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ALIEN PROPERTY CUSTODIAN

PROCESS AND APPARATUS FOR THE PRODUCTION OF HIGH VALUE ALCOHOLS FROM SUGARS AND SUGARY SUBSTANCES

Felix Grandel, Emmerich am Rhein, Germany;
vested in the Alien Property Custodian

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This invention is for improvements in or relating to the production of high value alcohols from sugars and sugary substances.

It is known to reduce sugars and sugary substances by means of electrolysis in an electrolytic cell divided by a ceramic diaphragm into separate cathode and anode chambers, using a mercury-lead cathode and an aqueous electrolyte containing a sulphate of an alkali metal or of an alkaline earth metal, the sugar or sugary substance being contained in the cathode chamber.

With this known method, when a current is passed through the electrolyte, free alkali metal or alkaline earth metal is formed at the cathode and this forms with the mercury an alkali- or an alkaline earth amalgam. The hydrogen liberated reduces the sugar to its corresponding alcohol.

Due to the continuous formation of amalgam and conversion of the amalgam with water—assisted by the SO_4 ion movement from the catholyte through the ceramic diaphragm to the anode or the anode chamber—the alkali- or alkaline earth hydroxide concentration continually increases, until the catholyte contains only alkali- or alkaline earth hydroxide and the anolyte only sulphuric acid.

In the process, the diaphragm used is generally made of clay and it is found that due to the strong hydrolytic effects of the OH ions in the catholyte and the H ions in the anolyte, corrosion tends to occur of the diaphragm when working for long periods, with the result that the sugar-tightness of the diaphragm becomes impaired and in consequence sugar tends to pass into the anode chamber where it easily oxidises at the anode into undesirable carboxylic acids.

Another disadvantage of the known process is that, due to the continual increase of the OH concentration in the catholyte during the process of electrolysis, the alkali hydroxide tends to exercise a prejudicial effect on the sugar. For this reason, the pH concentration of the catholyte has to be carefully controlled and adjusted to certain pH intervals at a certain temperature by constant addition of sulphuric acid, and even in spite of this there is always the danger that the catholyte may become darkly coloured, with the result that the alcohol produced is correspondingly darkly coloured and requires an extensive after-treatment to work it up to the quality of a standard pure product.

Thus, the newly formed alkali or alkaline earth salt formed as the result of neutralisation with sulphuric acid during the process of electrolysis

has to be carefully separated from the high value sugar alcohol to be obtained by a series of crystallisations of the final electrolyte followed by the addition of a precipitating dissolving means such, for example, as ethyl alcohol. Even then moreover, a complete separation of the electrolyte salts can never be obtained with this process, the purest final product obtainable with it still containing generally about 1.5% of residual sodium sulphate together with about 0.82% of residual glucose.

The object of the present invention is to provide an improved process which will avoid these difficulties, as hereinafter set forth.

According to the invention, a process for the production of high value alcohol from sugar or a sugar substance by electrolysis in a cell divided by a diaphragm or diaphragms into one or more anode chambers and one or more corresponding cathode chambers is characterised in that the sugar or sugary substance is subjected to direct cathodic reduction in an aqueous solution of an ammonium salt.

The aqueous solution of a salt of ammonia may, if desired, contain a proportion of ammonia dissolved in it.

Further according to the invention, the cathode used in the process is preferably a cathode composed of pure lead and/or cadmium and/or a lead-cadmium alloy, instead of the usual mercury cathode.

Preferably, moreover, the process is operated with a relatively large total cathode surface, and similarly a relatively large total anode surface in immersion in the electrolyte.

Further according to the invention, the diaphragm which separates the cathode chamber from the anode chamber of the electrolytic cell is preferably composed of a non-ceramic material, for example a micro-porous hard rubber or vulcanised fibre material.

It is to be understood that the terms "sugar" and "sugary substance" as employed herein include all the monosaccharides and the non-hydrolysed and entirely or only partly hydrolysed disaccharides as well as the oligosaccharides.

In order to provide a relatively large total cathode surface, thereby increasing the reducing capacity of the surfaces per electrolysis unit, the use of lead plates with vertical reinforcements (which, at the same time, with large plates, stiffens the surface) or the use of accumulator plates (which, for example, have eight times the surface per unit of superficial area of the surface) have proved specially satisfactory.

By "accumulator plates" is meant plate-shaped formations consisting of ribs, the hollow spaces between which are filled with lead oxides, for example PbO, PbO₂ and Pb₂O₄ or mixtures thereof. When such electrodes are connected up as cathodes in the electrolytic cell, a fine film of pure lead forms on their surfaces. This lead film may be effectively mixed with the lead oxides of the electrode or inserted. For the most advantageous anode-cathode ratio (1:1) for the electrolysis accumulator plates having a large area are also used for the anode.

As chemically pure lead, according to the quality of the surface, has an electric over-voltage of between 0.35 and 0.64 volt, cadmium an over-voltage of 0.48 volt, while mercury, however, has a much higher over-voltage of between 0.78 and 0.5 volt, the reduction of the sugar takes place under extremely difficult conditions, with the result that its direct reduction in the process to high value alcohol was not to be expected.

By using a non-mercury cathode in accordance with the invention, the electrolytic process according thereto is considerably cheapened on account of the saving of mercury, and in addition the working up of the final electrolyte is simplified and a non-poisonous product is, moreover, obtainable.

The ammonium salt of the electrolyte may conveniently be ammonium sulphate. Other ammonium salts may be used, however, including, for example ammonium nitrate, ammonium carbonate, ammonium bicarbonate, ammonium bisulphate, ammonium metaborate and ammonium chloride.

The oxygen separated by the electrolysis in the process and to a smaller extent the released hydrogen may be collected in suitably constructed closed vessels and used for other technical purposes.

It is an important feature and further advantage of the process according to the present invention that a neutralisation and control of the pH value of the catholyte in the process is not required as the pH value of ammonium hydroxide does not rise above the limiting value of 10.8 and, what is more important, ammonium hydroxide has no disturbing and colouring influence on the various sugars and sugary substances which may be treated in the process or on the alcohols which may be formed therefrom. Thus, whereas an 8% sodium hydroxide solution containing 15% of pure glucose has a yellow-brown colour after only 10 hours of treatment, an 8% ammonium hydroxide solution containing 15% of pure glucose at 25° C. is as clear as water after 24 hours of treatment.

A further advantage of the improved process according to the invention is the simplicity with which the ammonium hydroxide containing electrolyte may be worked up for the recovery of the alcohol contained in it, namely by simply distilling off the superfluous ammonia so as to effect a concentration of the alcohol content and a separation of the ammonia therefrom. The difficult and expensive operation, therefore, necessary in the known process of separating alkali- or alkaline earth sulphates from the final electrolyte by the addition thereto of precipitating dissolving agents is eliminated. In addition, in the known process, care has to be taken to evaporate to complete neutralisation the final electrolyte (slightly acid and slightly alkali sugar and high value alcohol solutions immediately become darkened in the evaporation process),

whereas with the improved process according to the present invention, any excess of ammonium hydroxide on evaporation of the final electrolyte plays no part in the sense of deleteriously affecting the alcohol, as ammonium hydroxide does not change either the sugar or the high value alcohol in the given concentrations.

The use as the electrolyte in the process of a solution of an ammonium salt, with or without a proportion of free ammonia dissolved in the solution, provides the possibility of using in conjunction with the process the process discovered by Lobry de Bruyn, of partial racemisation of monosaccharides without any substantial darkening of the reaction product by the use of aqueous ammonia (ammonium hydroxide solution) prior to the actual carrying out of the electrolytic reduction of the monosaccharide to the corresponding alcohol but as a step in direct connection therewith.

From α -glucose is formed, for example α -mannose which with cathodic reduction almost entirely changes over to α -mannitol, whilst without racemisation the glucose would be transformed by the cathodic reduction into a mixture of about 80% of sorbitol and about 20% of mannitol, the mixture being a syrup.

The completion of the reaction of the Lobry de Bruyn transformation takes place mostly, as has been determined, during the subsequent electrolysis.

As sugars and sugary substances, particularly those containing an aldehyde group in the molecule, are oxidised more readily than they are reduced, it is important that the dissolved sugar or sugary substance shall not come into contact with the anode or pass into the anode chamber of the electrolytic cell.

The known ceramic diaphragms of alundum have not been satisfactory from this point of view, as after a comparatively short period of use of the cell, they tend to permit the passage of sugar through them, on account of the corroding effect on the diaphragm at one side thereof of the acid of the anolyte and on the other side of the alkali of the catholyte. In addition, an alundum or like ceramic diaphragm has to be fired and is easily broken. It is for these reasons that, as hereinbefore stated, it is preferred according to a feature of the present invention, to employ a diaphragm composed of a non-ceramic or synthetic material such, for example, as microporous hard rubber with a 10 to 15% porosity or a vulcanised flexible fibre substance.

The invention will now be further described with reference to several examples of execution which illustrate how the invention may be carried into effect.

Example 1

In this example, the catholyte used was an aqueous solution containing 15% of glucose and 5% of ammonium sulphate and the anolyte employed was a 3% aqueous solution of ammonium sulphate. The electrolytic reduction was carried out at a temperature of 25 to 30°C. and with the use of a current density of 0.005 amps/cm² and a voltage of about 4 to 5 volts per bath.

The apparatus used consisted of an electroliser which could be externally cooled and in which was placed a cylinder, open at the top and closed at the bottom, of micro-porous hard rubber of about 5 mm. in thickness and having a porosity of 15%. This cylinder constituted the diaphragm of the cell and in place of micro-porous

hard rubber as the component material of the diaphragm, vulcanised flexible fibre or some other suitable non-ceramic natural or synthetic material could have been used. In the inner chamber of the cell thus formed were placed the cathode, the catholyte and a glass stirrer, while the outer chamber contained the anolyte and the anode.

The level of liquid in the anode chamber was a few millimeters higher than in the cathode chamber, as this is found to be preferable on account of the fact that it ensures against passage of the sugar solution into the anolyte in the anode chamber due to the presence of possible leaks in the diaphragm or to the perviousness thereof.

In this connection, it may be remarked further that, taking into account that the diaphragm material will develop osmotic forces, the electrolysis concentration of the anolyte should, as was the case in this example of execution of the invention, be less than that of the catholyte, whereby the osmotic balance shall be in the direction of anode to cathode and not in the reverse direction.

The cathode and anode used in the the example consisted of open-ended cylinders of chemically pure lead, although, as hereinbefore indicated, cadmium could have been used in place of lead. These cylinders were degreased with ether, rubbed with fine sand and several times sprayed carefully with distilled water, prior to their insertion in the respective chambers of the electrolytic cell, although it may be remarked that with cylinders which have already been used, a mere mechanical cleaning is generally sufficient. Then, following the cleaning treatment, the cathode and anode cylinders were submitted to an electro-chemical treatment in a 20% solution of sulphuric acid with the use of a current flow of 0.02 amp/cm², the treatment lasting for ½ an hour. The electrode which in this process of electro-chemical treatment of the electrode was subjected to anode oxidation was then inserted into the cathode chamber of the electrolytic cell while the other electrode was inserted into the anode chamber and the process of electrolysis was commenced. It will be understood that with the use of accumulator plate electrodes, the foregoing preparation of the electrodes would not have been necessary.

The electrolytic cell having thus been prepared, a filtered solution containing, as above described, 15% of glucose and 5% of ammonium sulphate in distilled water was placed in the cathode chamber of the cell and an aqueous solution containing 3% of ammonium sulphate in the anode chamber, the temperature of the solutions being about 30° C. The electric current was then switched on.

The cathode and anode current densities were thus, as above indicated, namely 0.005 amps/cm² and the ratio of cathode surface to anode surface was 1:1.6. The cell voltage was, also as above indicated, 4 to 5 volts and the temperature maintained during the electrolysis was from 25 to 30° C.

During the electrolysis, the degree of reduction in the electrolyte was tested by determining the glucose content of the catholyte solution. When the glucose content had been reduced to 0.8 to 1.0%, the current was switched off and the solution was worked up for sorbitol and mannitol.

The ammonium hydroxide containing catholyte was for this purpose evaporated during the

concentration of the high value alcohol for the purpose of recovering the ammonia liquor, the recovered ammonia liquor being afterwards neutralised with a part of the final anolyte of sulphuric acid for regeneration of the used ammonium sulphate.

The current yield was about 70%, the current consumption 4 kilowatts per kilogram of sorbitol (mannitol mixture) and the chemical yield was about 80% of the theoretical yield.

Example 2

In this example, a catholyte consisting of 15% of pure xylose or a technical pentose product from beechwood extraction or saccharification with a corresponding pentose content, and 5% of ammonium sulphate dissolved in distilled water is used and is treated as in Example 1.

The final product, containing xylite and arabitol or a mixture of those pentites corresponding to the technical pentose-containing product used in the process, in the event of such a product having been used therein, is of good chemical and electro-chemical quality. With the use of pure xylose, the raw product is a clear syrup which on standing for a long time forms a crystalline mass and from which pure xylite can be obtained suitable, for example, for the production of xylite pentanitrate. With the use, on the other hand, of a technical pentose product, the syrupy pentite mixture obtained can be used as a substitute for glycerine in the paint and chemical industries.

Example 3

In this example a 15% cane sugar solution was heated with a 3.7% sulphuric acid solution to a temperature of 50 to 90° C. for one hour. After inversion thus, it was neutralised with ammonium hydroxide. An invert sugar solution was thus obtained containing about 15% of glucose and a similar percentage of fructose.

This invert sugar solution was then electrolysed as in Example 1. A mixture was obtained consisting of a relatively large proportion of mannitol and a correspondingly small proportion of sorbitol, as fructose is completely transformed into mannitol in the process.

Example 4

In this example, commercial water-clear strong syrup containing about 38-42% of glucose, 40-45% of dextrine (malt erythodextrine) and 15-18% of water was diluted with distilled water so as to obtain a 20% glucose-dextrine solution. 5% of ammonium sulphate was then added and the solution was subjected to cathodic reduction as in Example 1.

As the result, not only was the glucose contained in the syrup transformed into mannitol and sorbitol, but also the dextrines.

Example 5

In this example pentosane, which comprises, for example, 50% of syrup on the pre-extraction of wood saccharification, was treated in a low pressure autoclave composed of lead with a 3.7% aqueous sulphuric acid solution at a temperature of about 120° C. until by hydrolysis all of the pentoses in the syrup were released from the pentosane. The syrup was then neutralised with ammonium hydroxide and submitted to cathodic reduction in the manner described in Example 1.

The final product obtained was a mixture of tetrites and pentites.

Example 6

In this example, non-hydrolysed disaccharides, for example, maltose, lactose and cellobiose, are made up into a 15% aqueous solution which contains in addition to the disaccharides, 5% of ammonium sulphate. The resulting solution is then subjected to cathodic reduction in the manner described in Example 1.

There remains after evaporation of the resultant ammonia during the hydrolysis, a viscous to oily product which, after dissolving in alcohol of high concentration and then placing in a refrigerating chamber, crystallises into a soft powder, which by its fusing point, specific properties and hydrolytic decomposition, is identifiable as a mixture of maltite, lactite and cellobite corresponding to the disaccharides used in the process.

Example 7

In this example, a 15% aqueous solution having a specific rotation angle of $\alpha_D^{20} = +15.9$ was heated, with an addition of 2% of ammonia, at a temperature of 50° C. until, after about 12 hours, the specific rotation angle was reduced to $\alpha_D^{20} = +3.5$. This was the sign that a far reaching conversion had taken place from glucose to mannose according to the reaction discovered by Lobry de Bruyn. The solution, which was faintly coloured, was then electrolysed in the manner described in Example 1. During the electrolytic reduction, the solution cleared after a few hours, the specific rotation angle further falling to 1/1.5.

The final product obtained was a slightly stiff syrup which was capable of withstanding temperatures above 200° C. and which contained a large proportion of mannitol. Due to its special properties, the syrup was particularly suitable for esterification purposes instead of glycerine.

It has been found that for purposes of large scale effectuation of the process, it is advantageous to employ a form of apparatus constructed as shown in the accompanying drawings, which will now be described.

In these drawings,

Figure 1 is a plan view, and

Figures 2 and 3 are respectively an end and side elevation of the apparatus.

The apparatus shown consists of an electrolytic cell generally denoted with the letter A, a low lying collecting vessel B provided with cooling pipes, a centrifugal pump C and a raised storage vessel D for the anolyte to be used in the apparatus.

The catholyte is distributed by means of the distribution tube B₁ to a number of individual cathode chambers provided in the cell A and the supply of catholyte to the chambers is accurately regulated by means of cocks *h* disposed near the bottom of the cell. After passing through the cathode chambers, the catholyte is caused to flow through the tubes B₂ into a channel B₃ and from thence back into the collecting vessel B from which the solution has been pumped into the distribution tube B₁ by means of the pump C.

The anolyte is stored in the vessel D from which it flows through a distribution tube D₁

into a number of anode chambers provided in the cell in correspondence with the cathode chambers therein. These anode chambers have no overflow. The flow of anolyte to the anode chambers is accurately controlled by means of cocks *h*. Should it be desired to empty the anode chambers, the cock D₂ is closed and a valve D₃ is opened.

The cell is supplied with current by way of a negative current bar connected in common to all the cathodes of the cell and a positive current bar similarly connected to all of the anodes of the cell.

All parts of the apparatus which come into contact with the liquids therein are made of non-metallic material, for example earthenware, hard rubber or suitable forms of wood or other natural or synthetic materials.

The electrolytic cell A consists of eleven separate frames *a* of hard rubber or specially prepared non-swelling wood combined in the form of a filter press and held together by means of six tension bolts *b*. The diaphragms of the cell, which are marked *c*, are held between the frames and rubber packings may be inserted to ensure a tight fit therewith.

This arrangement enables a uniform distribution of the anode chambers, which are marked *d*, and the cathode chambers, which are marked *e*, to be obtained, together with almost a double utilisation of the electrode surfaces.

In the chambers of the cell, lead and/or cadmium electrodes *l*, *m* are suspended from aluminium current bars *f*, the arrangement being such that these bars which lie in wedges on the edge of the frame of the cell serve at the same time to carry the electrodes. Current flows through the aluminium bars *f* to the anodes *l* and the cathodes *m*.

On the same side of the apparatus as the current carrying bars *f* and arranged at the foot of the frame, are the two distributing tubes B₃ and D₃ and the cocks *h* for the regulation of the flow of electrolyte to the cathode and anode chambers.

In the cathode chambers, on the opposite side of the apparatus are the overflow tubes B₂ which conducts the catholyte into the channel B₃.

For collection of the hydrogen and oxygen, a hood H is fitted over the electrolyser, which hood is provided with internal walls *n* separating the anode and cathode chambers. These walls rest on rubber packings *o* on the diaphragms to enclose the cells in a gas-tight manner.

The gases are led off through tubes *p*, *q*.

Accumulator plates having large surfaces are preferably used as the cathodes and anodes of the cell.

In the use of an apparatus of the foregoing description, the hydrogen and oxygen generated can be recovered during the electrolysis. The apparatus also has the advantage that the U-shaped frames used are easy to make and a simple construction and extension to large batteries is made easily possible. Another advantage is the utilisation of both sides of the electrodes.

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