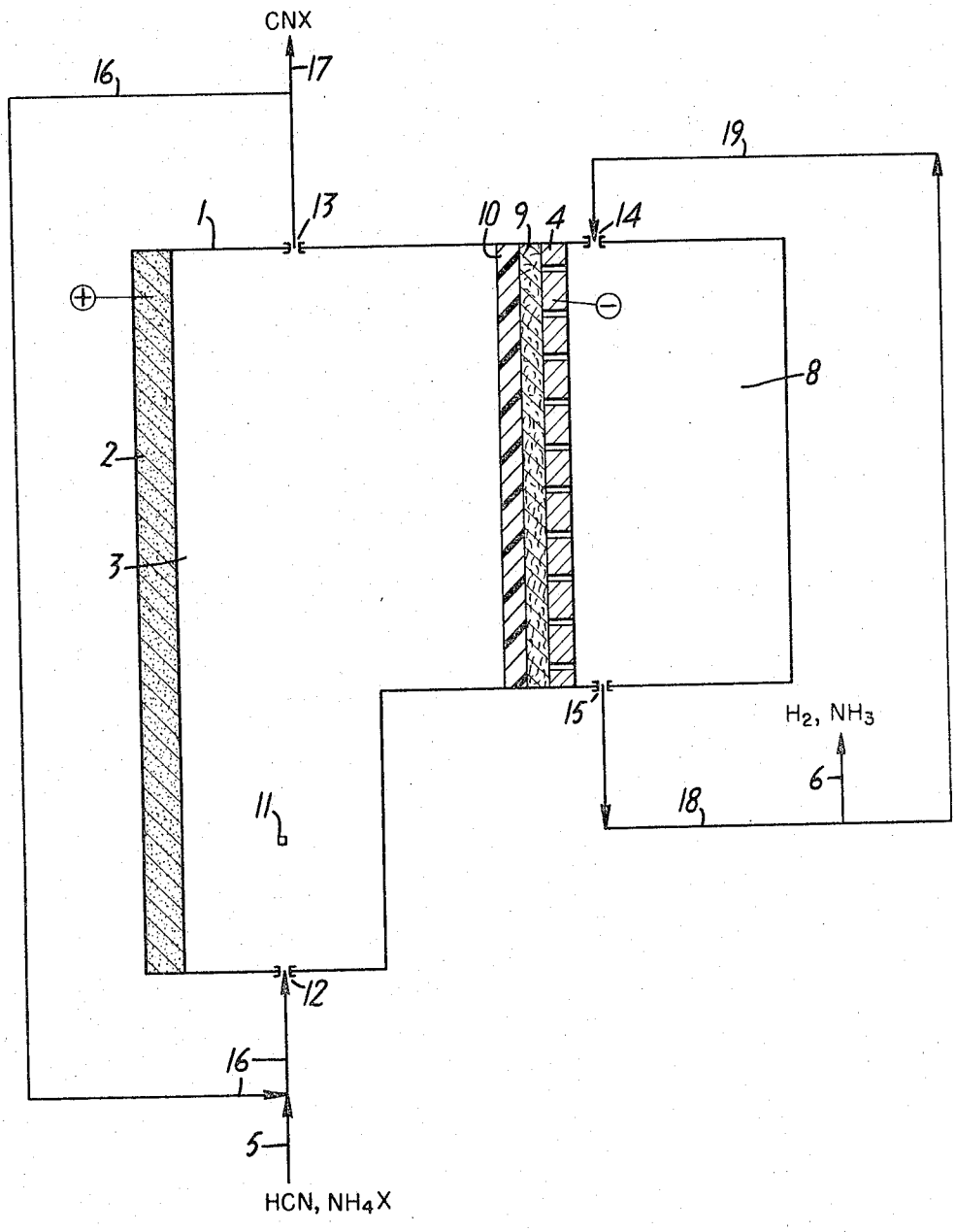
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PROCESS FOR THE PRODUCTION OF CYANOGEN HALIDE AND APPARATUS FOR USE THEREWITH

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PROCESS FOR THE PRODUCTION OF CYANOGEN HALIDE AND APPARATUS FOR USE THEREWITH

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This invention relates to a process for the production of a cyanogen halide and to an apparatus for use therewith. More particularly, the present invention relates to a process for the production of a cyanogen halide by the electrochemical reaction of an ammonium halide with hydrogen cyanide and to an improved electrochemical cell in which said process can be conducted.

The invention relates to an electrochemical cell of the diveded type, wherein an ion-permeable and gas-permeable membrane is employed to divide the cell into two compartments, a cathode compartment and an anode compartment. The invention is most particularly related to a cell of the divided type and to an electrochemical process conducted in said cell wherein a cyanogen halide is produced in the anode compartment by the reaction of hydrogen cyanide and an ammonium halide, which may be either the bromide or the chloride. In such a process and apparatus, gaseous ammonia and gaseous hydrogen are both formed in the cathode compartment and free bromine or chlorine is formed, as a side product, in solution in the anode compartment.

This invention is an improvement in both the process and the apparatus which are set forth in my copending application, Serial No. 162,333, now Patent No. 3,168,458, filed December 27, 1961, inasmuch as that application applies to the production of a cyanogen halide.

In my copending application Serial No. 162,333 as it relates to the present invention, an electrochemical cell of the divided type is set forth in which a perforated cathode, adapted to transfer liquid from one side of the cathode to the other, is in combination with electrolyte absorbing means disposed on one side, which means is gas permeable and at the same time capable of maintaining an interfacial contact between the perforated cathode and the electrolyte and which provides a continuous internal circuit for the transport of ions through both compartments of the cell. Briefly, such a cell includes a perforated cathode, preferably of regular geometric configuration, having opposed marginal boundaries and forming one wall of a cathode compartment. At one marginal boundary there is provided means for supplying catholyte to one surface of the cathode, and at an opposing marginal boundary there is provided means for collecting catholyte which has been replaced by fresh catholyte, as well as any excess catholyte in the cathode compartment. Thus, the catholyte in the cathode compartment is restricted to the surface of the cathode and the bottom of the cell from the cathode to the outlet. The perforated cathode serves as one wall of the cathode compartment and it and the gas-permeable, electrolyte absorbing means adjacent thereto, divide the cathode compartment from the anode compartment of the cell. One wall of the anode compartment comprises an impervious anode. Catholyte and anolyte are kept separate by an ion-permeable membrane, which also is a part of the divider, and can be located adjacent the electrolyte absorbing means. Such a cell is particularly well adapted for electrochemical conversions in which one or more gases is evolved and, thus, has been employed for the synthesis of cyanogen bromide or cyanogen chloride from hydrogen cyanide and ammonium bromide or ammonium chloride. Such a reaction is illustrated by the following equation:

$$HCN + NH_4X + 2F \xrightarrow[\text{cell}]{\text{divided}} CNX + H_2\uparrow + NH_3\uparrow$$

wherein X is Br or Cl. When the reaction illustrated above is conducted in a cell of the divided type, both the anode compartment and the cathode compartment contain NH_4Br or NH_4Cl as the electrolyte. HCN and NH_4Br or NH_4Cl and water are fed to the anode compartment. CNBr or CNCl is is produced in the anode compartment and is recovered therefrom. H_2 gas and NH_3 gas are produced in the cathode compartment, where there is ample reserve space to receive them, and are recovered therefrom. In addition, the use of a gas-permeable electrolyte absorbing separator between the perforated cathode and the ion-permeable membrane, results in prolonged membrane life and improved conductivity.

The invention provides a cell wherein the electrolyte in the anode compartment can be maintained at a pressure substantially in excess of the pressure of electrolyte in the cathode compartment. This type of cell has the following advantages: It requires reduced operating voltage; it provides high conductivity, and it results in high conversion rates.

Such a cell and process have demonstrated that excellent yields and long electrolyte life can be obtained employing commercially available ion-permselective membranes to divide the cell. However, in certain instances it has been observed that a degradation of the lower portion of such membranes occurs.

It is believed that this is due to chemical reactions within the membrane of halogen gas, formed as a result of a side reaction in the anode compartment. Halogen gas can enter the membrane. Ammonia which is formed in the cathode compartment may also be present in the membrance. The resulting reactions are probably complex reactions involving bromine (or chlorine), ammonia (if present) and the materials of which the membrane itself is composed (for example, quaternary ammonium groups). These reactions result in deterioration of the membrane.

The present invention comprises a novel process and an improved electrochemical cell, particularly adapted for the synthesis of cyanogen bromide or cyanogen chloride from hydrogen cyanide and ammonium bromide or ammonium chloride.

The process of the present invention makes it possible to prevent free gas which forms in solution in the anode compartment from entering and, thereafter, reacting in the membrane. This is accomplished by reacting free halogen in solution with hydrogen cyanide, and establishing a flow within the cell so as to withdraw free halogen for such reaction before it can diffuse into the membrane.

The reaction of hydrogen cyanide with bromine or chlorine results in the production of hydrogen bromide or chloride and cyanogen bromide or chloride. If an excess of hydrogen cyanide is introduced into the anolyte, more than that required to react with the halogen in the anolyte, and the anolyte then passed upwardly over the surface of the membrane, the hydrogen cyanide in the solution passing up over the membrane will react with any halogen which migrates toward the membrane, so that substantially no halogen reaches the membrane. Thus, introduction of a slight excess of hydrogen cyanide into the anolyte is preferred.

A modification of the present invention involves withdrawal of the halogen-rich phase from the base of the well, mixing it with fresh hydrogen cyanide-anolyte feed, whereby the halogen and hydrogen cyanide react to form hydrogen halide and ammonium halide, and returning the material to the cell at a point above the top of the well. This modification has the advantage that the well can be

made as small as possible to achieve minimum capital investment and/or to fit in a smaller working space.

Thus, the present invention comprises a process for the manufacture of a cyanogen halide comprising subjecting a solution of hydrogen cyanide and an ammonium halide selected from the group consisting of ammonium bromide and ammonium chloride to the action of a direct electric current in an electrolytic cell in which the cathode and anode compartments are divided by an ion-permeable membrane, withdrawing a halogen-rich phase from the anode compartment, admixing said phase with hydrogen cyanide in an amount at least sufficient to react with all of the halogen present in said phase, and returning the resulting solution to the anode compartment. Preferably, a slight excess of hydrogen cyanide is employed, and preferably the reaction with hydrogen cyanide is conducted in a well located immediately beneath the anode compartment. Furthermore, the solution resulting from the reaction of halogen with hydrogen cyanide is preferably passed up over the surface of the ion-permeable membrane, to serve as a supplemental barrier to diffusion of halogen therewithin.

In one embodiment of cell designed to carry out this process, a separate zone or well is provided at the bottom of the anode compartment of the cell, to take advantage of the increase in specific gravity of the ammonium halide solution after halide ion has been discharged at the surface of the anode. Therefore, a downward flow of highly concentrated aqueous ammonium halide solution containing free halogen runs along the face of the anode, and is collected in the well at the bottom of the cell where it is reacted with fresh hydrogen cyanide introduced at or near the bottom of the well.

The general structure of the cell of this invention is similar to that of Serial No. 162,333. The perforated cathode, as in that cell, preferably has guide portions coacting with the perforations. The guide portions may be of such configuration that they form scoops, either regularly or randomly disposed from the surface, to intercept liquid trickling down over the surface and to guide it from one surface to the opposite surface through the perforations thereof. The upper boundary of the cathode is provided with means which permit catholyte to be recycled after trickling down over the surface of the cathode.

While simple metal surfaces such as stainless steel, have been found quite satisfactory for use as the perforated cathode, the surface of metallic material which is in contact with the electrolyte absorbing separator may be activated by deposition thereon of reactive or catalytic materials and surface-multiplying agents such as platinum black, nickel black, and various metal oxides, etc. Metals of low hydrogen overvoltage are preferred.

A useful criterion in perforated electrode design is the ratio of the frontal electrode area excluding perforations, to the perforation diameter, which should be between about 10 and 25. The percent open area may range from about 10% to about 30% of the total area. These values are not critical, but are convenient guides in electrode design to achieve the lowest dynamic internal resistance.

As the perforated cathode there can be used a perforated metallic plate or a metallic screen which contains random or regularly spaced openings which will also provide means for transmitting the catholyte from one surface of the cathode to the opposite surface by means of the electrolyte-absorbing separator.

Disposed in contacting laminar relation with the perforated cathode is a gas- and liquid-permeable electrolyte-absorbing separator. This may be an inert highly porous material, for example a felt mat, and may be made of such materials as glass fibers, paper fibers, asbestos fibers, animal fibers, vegetable fibers, synthetic fibers or the like. The electrolyte-absorbing separator will soak up the electrolyte transmitted through the perforations of the cathode, and maintain the surface of the cathode opposite the cathode compartment saturated with electrolyte. At the same time, since it becomes saturated with electrolyte, it provides a continuous ion-containing and conducting medium.

The electrolyte-absorbing separator should be chemically stable and should preferably have a liquid permeability of at least about 100 gallons of water per minute per square foot per p.s.i.

The anode should be resistant to the reactants present in the anolyte, and to bromine or chlorine. A variety of materials are available which meet these requirements, such as graphite, carbon, platinum, titanium, stainless steel, etc.

Ion permeable membranes of the type which are employed to separate the anode and cathode compartments are conveniently those membranes which are electrically conductive and permeable to ions, but which are not permeable to molecules, such as the permselective membranes, i.e., those permeable to cations or anions but not both. Hence, they are referred to as cationic or anionic, as the case may be, and both types are useful in accordance with the present invention. An example of a specific ion-exchange resin membrane is as follows:

A mixture of about 95 parts by weight of styrene and about 5 parts by weight divinyl benzene was polymerized. The resulting polymer was comminuted to fine particles and 100 parts by weight of this finely-divided material was sulfonated by reaction with about 175 parts by weight of chlorosulfonic acid. The latter reaction was carried out by heating at reflux temperature for about 3 minutes and then maintaining the mixture at room temperature for 50 hours. The sulfonated product was then washed with a large excess of water to remove any remaining chlorosulfonic acids and any acid chlorides which were formed in the reaction. The sulfonated resin was then dried and 2 parts by weight of the dried resin were mixed with 1 part by weight of polyethylene and the resulting mixture was pressed into a sheet which then serves as the membrane.

The preparation and description of permselective membranes is well known in the art and there are numerous patents relating to such membranes. Examples of such membranes are described in U.S. Patents Nos. 2,636,851, 2,636,852, 2,861,319, 2,861,320, 2,702,272, 2,730,768, 2,731,403, 2,731,411, 2,731,425, 2,732,351, 2,756,202, 2,780,604, 2,800,445, 2,820,756, 2,827,426, 2,858,264, 2,860,096, 2,860,097, 2,867,575, 2,894,289, 2,903,406, and 2,957,206. Any of the membranes disclosed in the patents in the foregoing list may be employed in constructing the apparatus of the present invention.

As for the conditions under which the cell is conveniently operated, it has been found that currents in the range of from 10 to 1,000 amperes per square foot are satisfactory and the preferred range is 30 to 500 amps per square foot. The cell may be operated at voltages in the range of 2 to 6 volts, and the preferred voltage is in the range of from about 3 to about 4. In the electrochemical synthesis of cyanogen halide from hydrogen cyanide, the actual voltage will be determined by the current density.

The preferred temperature of operation is in the range of 20° to 75° C., it being understood that certain of the membranes employed as barriers are quite sensitive to temperature, and consequently the temperature at which the reaction is carried out will be below that at which the membrane is disadvantageously affected. Most membranes exhibit quite satisfactory physical stability at temperatures within the preferred range, namely, 20° to 75° C.

The product of the electrochemical reaction is found in the anolyte and may be removed by any convenient chemical or physical means, such as distillation.

The positive pressure exerted by the head of the anolyte in the anode compartment as a result of the essentially empty cathode compartment holds the membrane firmly

and evenly in place against the electrolyte-absorbing separator, which in turn is supported by the cathode. This prevents lateral motion of the membrane, and minimizes membrane wear. The pressure in the cathode compartment can be varied to adjust the pressure differential between the cathode and anode compartments. Vacuum may be applied to the cathode compartment in order to aid in gas removal. The decrease in pressure in going from the cathode to the anode compartment must be greater than the pressure drop of the gas going through the cathode. Generally, less than about two pounds per square inch differential is sufficient. Maximum pressure is limited by the strength of the cell barriers.

Operable pressures are dependent upon the degree of porosity and size of pores of the cathode and the current density, which controls the amount of gas produced at the cathode surface. The inter pore distances may be increased at the expense of an increased pressure differential. With small inter pore distances, there is more rapid gas clearance. The use of wire gauze as the cathode has been found to be particularly suitable from this standpoint, because of the rapid gas removal, its effective surface and sufficient contact. With too small a pore size there is an excessive rate of gas accumulation, and impractically high pressures across the cell barrier are required to force the gas through the perforations and out of the cell. The resultant effect of this cell structure creates high power efficiencies. With the use of the membrane, and electrolyte-absorbing separator, interelectrode distances less than those normally encountered may be utilized, so that advantage can be taken of the resulting decrease in cell voltage and in the overall size of the unit. Distances as short as 1/16 of an inch may be employed without danger form an internal short circuit. In addition, the pressure differential across the barrier to the gas producing electrode permits the accumulation of only a minimum amount of gas between the barrier and the perforated electrode. Since the operating voltage and the accumulation of gas in this space are in proportion, this effect too increases power efficiencies The overall effect of this cell structure provides the maximum conductivity path between the barrier and the electrode face or the minimum operating voltage at a given current density, electrolyte concentration and temperature.

When the anolyte is composed of an aqueous solution of hydrogen cyanide and ammonium bromide, and the catholyte is a saturated ammonium bromide solution, the products of the reaction at the cathode are ammonia gas and hydrogen, which are removed with the catholyte through the exit ports, and the product removed from the anolyte is cyanogen bromide. With these coacting electrolytes, in an electrochemical cell of the invention, under an impressed voltage of 3.2 volts at a current density of 100 amps per square foot, and an anolyte feed rate of 49 ml. per minute, an HCN conversion of 89% to cyanogen bromide and a current efficiency of 92% was obtained.

The figure is a schematic illustration of an improved electrochemical cell construction in accordance with one embodiment of the present invention.

The figure shows, in diagrammatic form, an electrochemical cell **1** in accordance with the present invention. The cell has an anode **2** as one wall of the anode compartment **3**. Cathode **4** is positioned vertically in the cell, at the boundary between the anode compartment **3** and cathode compartment **8**. Cathode **4** is in contact with the electrolyte-absorbing separator **9** which in this case is made of a sheet of wool felt, and this in turn is in contact with membrane **10**, which can be of permselective material. Well **11** is an extension of anode compartment **3**, into which the anode extends. Inlet port **12** and outlet port **13** are provided in anode compartment **3**, and inlet port **14** and outlet port **15** are provided in cathode compartment **8**. Anolyte is withdrawn through port **13** in recovery of cyanogen halide, and hydrogen cyanide together with fresh and recycle anolyte to replace that withdrawn at **13** are introduced into compartment **3** through port **12**, for reaction with halogen in the well **11**. Catholyte is withdrawn from cathode compartment **8** through port **15**, by means of line **18**, and is recycled to compartment **8** by means of line **19** through port **14**. Gas is removed from the cathode compartment **8** through port **15**, and through lines **18** and **6**.

In operation, anolyte circulates through anode compartment **3** entering the compartment from line **16** through port **12**, blending with anolyte passing downwardly over anode **2** into well **11**, and then passing upwardly past membrane **10** towards well **11**, at which a portion is bled out through port **13**, and line **17**. Anolyte from which cyanogen halide has been recovered is recycled through line **16** to the anode compartment, and HCN is introduced to it through line **5** before it enters the compartment.

Catholyte is introduced at the top of the cathode compartment **8** in such a manner that it trickles over cathode **4**. The catholyte is removed as fast as it collects at the bottom of the compartment through port **15** and line **18**. Gases formed in compartment **8** are also removed through port **15** and line **18**. The gases, hydrogen and ammonia are removed from line **18** through line **6**, and the catholyte is then recycled to the cathode compartment **8** through line **19** and port **14**.

The following examples in the opinion of the inventor represent preferred embodiments of the invention.

Examples 1 and 2

Two electrochemical reactions were carried out in the cell described in FIGURE 1. The reaction conditions and results of these reactions are presented in Table I. In each of these reactions, with the exceptions indicated below, hydrogen cyanide and ammonium bromide were electrochemically reacted to form cyanogen bromide. An aqueous solution of ammonium bromide and hydrogen cyanide was fed as anolyte into the anode compartment of the cell, in which cyanogen bromide was formed and from which it was recovered. Hydrogen and ammonia were formed and recovered from the cathode compartment and both anolyte and catholyte were recycled as described in connection with FIGURE 1.

A flat perforated carbon steel screen (1/16 inch d.) was used as the cathode. In each case, the electrolyte employed in both compartments was aqueous 4.2 N NH_4Br containing an equilibrium concentration of ammonia of 8 to 10 N, and the interelectrode distance was 7/16". The table shows the number of faradays required per mole of HCN (F/HCN), current density, the initial potential of the cell, the decay of the cell and the condition of the membrane.

TABLE

Example No.	F/HCN	Current Density (amp./ft.)	Initial Potential (volts)	Decay (volt/day)	Membrane Condition (after drying)
1	1.9	100	3.29	0.038	Only trace of polymer, and slight embrittlement, good condition.
2	1.8	200	4.40	0.057	Only trace of polymer, trace of bubbles, good condition.

Each of these electrochemical reactions was continued for over five days. At the end of this time, only a trace of brown polymeric material had accumulated in the membrane, and the membrane flexibility was largely retained.

This showed the effect of circulating anolyte so that the bromide was carried into the well and reacted with hydrogen cyanide there before it could reach the membrane.

A cell in which there was no well and in which anolyte was not circulated was operated under similar conditions as were employed in Examples 1 and 2. After five days of operation, the membrane in this cell had to be replaced, since it was found to be brittle and embedded in a polymeric honeycomb which prevented effective operation of the cell.

Obviously, the electrochemical cells of this invention can be employed in conjunction with other equipment. For example, in a commercial installation a multiplicity of such cells could be employed in series or parallel in general configurations which are well known in the art.

I claim:

1. A process for the electrochemical production of cyanogen halide using a cell comprising an anode compartment, a cathode compartment, an anode positioned vertically at one side of the anode compartment, and a membrane positioned vertically and separating the two compartments, and positioned at the opposite side of the anode compartment, comprising subjecting an aqueous solution of hydrogen cyanide and ammonium halide to the action of a direct current in the anode compartment so that at the anode halogen is discharged and cyanogen halide formed, flowing heavy halogen-rich anolyte downwardly by gravity at the anode to the bottom of the cell, adding hydrogen cyanide to the halogen-rich anolyte and lowering its specific gravity, flowing the lighter hydrogen cyanide-enriched anolyte upwardly across the anode side of the membrane and thereby preventing halogen in the halogen-rich anolyte from reaching and attacking the membrane, and reacting the halogen therein with hydrogen cyanide to form cyanogen halide, removing cyanogen halide from the anolyte, and recycling the anolyte for further electrochemical reaction.

2. A process in accordance with claim 1 in which hydrogen cyanide is added in excess of that required to react with the halogen in the halogen-rich anolyte.

3. The process of claim 1 in which the halogen-rich anolyte is withdrawn from the anode compartment for reaction with hydrogen cyanide and then recycled to the anode compartment.

4. The process of claim 1 in which the halogen is bromide.

5. The process of claim 1, in which the halogen is chlorine.

6. The process of claim 1 which includes diluting the heavy halogen-rich anolyte with a feed of fresh anolyte and hydrogen cyanide, and flowing the lighter feed-enriched anolyte upwardly across the anode side of the membrane.

7. An electrochemical cell comprising, in combination, an anode compartment and a cathode compartment, a perforated cathode in the cathode compartment, an electrolyte-absorbing separator in contact with the cathode, and a membrane in contact with the separator, separating the anode and cathode compartments, the membrane and separator being positioned vertically and defining one side wall of the anode compartment, an anode positioned vertically and defining another side wall of the anode compartment, a well therebetween at the bottom of the anode compartment, and a horizontally extending portion at one side of the anode compartment defining the top of the well, the membrane being positioned in the said portion as one wall thereof, and means for lowering the specific gravity of anolyte in the well, the space above the wall between the membrane and the anode being open and substantially unobstructed, permitting downward circulation of heavier anolyte at the anode into the well and upward circulation of lighter anolyte from the well across the membrane, thus providing gravity circulation of anolyte within the anode compartment.

8. An electrochemical cell in accordance with claim 7 in which the membrane is ion-permselective.

9. An electrochemical cell in accordance with claim 8 in which the membrane comprises an ion exchange resin.

10. An electrochemical cell in accordance with claim 7 in which the anode forms one wall of the anode compartment and extends into the well.

11. An electrochemical cell in accordance with claim 7 in which the well extends from adjacent the anode to adjacent the membrane.

12. An electrochemical cell in accordance with claim 7 in which the means for lowering the specific gravity comprises means for introducing hydrogen cyanide into the well.

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