

PATENT SPECIFICATION

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(54) ELECTROLYTIC PROCESS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an electrochemical cell having a porous diaphragm.

More particularly, the invention relates to an electrochemical cell containing a porous diaphragm based on tetrafluoroethylene polymer. Such diaphragms are especially suitable for use in electrochemical cells for the electrolysis of alkali metal chloride solutions.

In the specification of our U.K. Patent No. 1,081,046 there is described a method of manufacturing porous diaphragms which comprises forming an aqueous slurry or dispersion of polytetrafluoroethylene and a solid particulate additive, for example starch, adding an organic coagulating agent, for example acetone, to said dispersion and then drying the coagulated dispersion. An organic lubricant, for example petroleum ether, is then added to the dried coagulated material to serve as a processing aid when the material is being rolled into a sheet. On completion of the rolling operation the starch is removed to give the desired porous diaphragm. The lubricant may also be removed if required. The use of organic lubricants, however, makes it difficult to obtain porous polytetrafluoroethylene diaphragms with a high degree of reproducibility.

An improved method of manufacturing porous diaphragms in which the organic lubricant is replaced by water as the lubricant is described in our U.K. Patent No. 1,424,804. This method comprises preparing an aqueous slurry or dispersion comprising polytetrafluoroethylene and a removable solid particulate additive, for

example starch, thickening said aqueous slurry or dispersion to effect agglomeration of the solid particles therein, forming from the thickened slurry or dispersion a dough-like material containing sufficient water to serve as lubricant in a subsequent sheet forming operation, forming a sheet of desired thickness from said dough, and removing solid particulate additive from the sheet to obtain the desired porosity.

As aforesaid, suitable removable solid particulate additives include starch, for example maize starch and/or potato starch, or a water-insoluble inorganic base or carbonate, for example calcium carbonate. If desired, these solid particulate additives may be removed from the diaphragm prior to introducing the diaphragm into the cell, for example, by soaking the diaphragm in an acid, preferably a mineral acid, e.g. hydrochloric acid. The diaphragm may then be washed with water to remove the acid and assembled, whilst wet, into a cell. It is necessary to keep the diaphragm wet during assembly in order to prevent collapse of the pores and this leads to considerable difficulties in handling since the diaphragm is both extremely wet and extremely slippery (the latter being due to the inherent properties of the polytetrafluoroethylene). Further disadvantages arising from the use of pre-extracted diaphragms, include the difficulty of ensuring adequate tautness of the wet diaphragm whilst assembling in the cell, and the possibility of leakages occurring at the sealing gasket mounted along the wet edges of the diaphragm. Alternatively, the solid particulate additives may be removed from the diaphragm *in situ* in the cell, for example as described in our U.K. Patent No. 1,468,355, wherein the removal is carried out by filling the cell with working electrolyte, e.g. an alkali metal chloride brine, and electrolysis the said electrolyte. This procedure avoids the aforesaid disadvantages associated with pre-extracted diaphragms, but can lead to con-

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tamination of the cell liquor by oxidation products.

We have now found that the aforesaid disadvantages associated with the preparation, handling, or use of porous diaphragms may be obviated or mitigated by the use of diaphragm materials based on porous polytetrafluoroethylene prepared in a particular way.

According to the present invention there is provided an electrochemical cell having an anode and a cathode separated by a diaphragm wherein the diaphragm comprises a porous polymeric material containing units derived from tetrafluoroethylene, said material having a microstructure characterised by nodes interconnected by fibrils.

The electrochemical cell is advantageously an electrolytic diaphragm cell for the electrolysis of an aqueous alkali metal chloride solution to give chlorine and an alkali metal hydroxide, e.g. chlorine and sodium hydroxide from sodium chloride brine.

According to another aspect of the present invention we provide a process for the electrolysis of aqueous solutions of ionisable chemical compounds in an electrochemical cell fitted with a diaphragm comprising the aforesaid porous polymeric material.

Yet another aspect of the present invention is a diaphragm for use in an electrochemical cell which diaphragm comprises the aforesaid porous polymeric material and which further comprises a non-removable filler which is chemically resistant to the liquors in the cell and which is incorporated into said porous polymeric material at a stage subsequent to the preparation of the porous polymeric material.

The present invention however is applicable to other types of electrochemical cell, for example olefin oxidation cells, fuel cells and batteries.

The porous polymeric material comprising the diaphragm for use according to the present invention may be a material as described and claimed in U.K. Patent No. 1,355,373, that is a porous polymeric material containing units derived from tetrafluoroethylene, the material having a microstructure characterised by nodes interconnected by fibrils, the material having a matrix tensile strength (as hereinafter defined) of at least 7300 psi. The "matrix tensile strength" is defined herein, and in the aforementioned U.K. Patent No. 1,355,373, as the product of the maximum tensile strength of the material (generally the longitudinal tensile strength) and the ratio of the specific gravity of the solid

polymer divided by the specific gravity of the expanded porous product.

Porous polymeric material for use in the diaphragm of the electrochemical cell of the invention may be prepared by a process which comprises forming a shaped article of a tetrafluoroethylene polymer by extruding a paste of the polymer and expanding the said shaped article after removal of lubricant therefrom by stretching it in one or more directions at a rate exceeding 10% per second of its original length and at an elevated temperature, preferably at a temperature in the range 35°C to 327°C. After stretching the resultant porous polymeric material is preferably heated while in its stretched condition to a temperature above the melting point of the polymer, and the porous material is maintained in its stretched condition while cooling. The porosity that is produced by expansion is retained for there is little or no coalescence or shrinkage on releasing the final cooled material. The optimum temperature for heating the porous polymeric material in its stretched condition is in the range of 350°C to 370°C and the heating periods may range, for example, from about 5 seconds to one hour.

The stretching may be effected biaxially.

The porosity of the porous polymeric material may be varied by introducing slight modifications into the manufacturing process; in particular an increase in stretch ratio gives rise to a material of high porosity. In addition, the temperature of heat treatment of the material is another important parameter as it is possible to enhance the strength of material if it is heat-treated to 327°C or greater. Since the porosity of the polymeric material may be varied by varying the processing conditions, diaphragms of different brine permeabilities may be obtained so that the porosity and therefore permeability of the diaphragm may be chosen according to diaphragm cell size and shape in order to gain efficient alkali halide conversion.

The porous polymeric material, for example the material described in U.K. Patent No. 1,355,373, may also incorporate fillers, for example asbestos, carbon black, pigments, mica, silica, titanium dioxide, glass or potassium titanate. The fillers may be mixed with the tetrafluoroethylene polymer paste prior to extruding the polymer into a shaped article.

In the present invention the porous polymeric material is used in sheet form and we have found that good results may be obtained by treating the sheets of porous polymeric material with a filler subsequent to their preparation by the stretching and heating technique described above. The

filler to be used in accordance with the present invention is one which is non-removable, chemically resistant to the liquors in the cell and is preferably one which renders the porous polymeric material wettable.

One method of incorporating the filler into the sheet of porous polymeric material is to immerse the sheet in a constantly agitated suspension of the filler in an organic liquid, for example in an aliphatic alcohol, e.g. in iso-propyl alcohol.

An alternative method of incorporating the filler into the sheet of porous polymeric material is to impregnate the sheet with a hydrolysable precursor of the filler and then hydrolyse the precursor *in situ* in the sheet by the action of water or alkaline solution. The filler is obtained in hydrated form by this technique.

The filler may be an organic material which renders the sheet wettable but it is preferred to use an inorganic material, for example an inorganic oxide. The use of titanium dioxide or zirconium oxide is especially preferred.

The filler is selected so that its particle size is less than the largest pore size of the porous polymeric material.

When the filler is incorporated in the form of a hydrolysable precursor suitable precursors include tetra butyl titanate, titanium tetrachloride and zirconium oxychloride.

The introduction of fillers into the porous polymeric material gives rise to the formation of regularly shaped holes which is especially advantageous since the electrolytic process becomes more efficient due, partly, to the smooth and efficient disengagement of product gases i.e. chlorine and hydrogen from the face of the diaphragm, under operating conditions. In addition the presence of fillers modifies the strength characteristics of the diaphragm in that the dimensional stability of the diaphragm is improved under cell operating conditions so that the performance of the diaphragm remains constant for a longer period of time under cell conditions.

The diaphragms used in the electrochemical cells of the invention are highly porous, dimensionally stable, and are chemically resistant to the liquors in the cell.

The use of the diaphragms is especially advantageous in cells for the electrolysis of alkali metal chloride solutions since unlike more conventional polytetrafluoroethylene diaphragms, the highly porous fibrillated diaphragm material may be "amorphously locked", as defined in U.K. Patent No. 1,355,373. The porous polymeric material can also be joined to itself or to other materials, for example to metals used as

anodes and cathodes, e.g. titanium or iron, and to metals or cements used in cell bases, for example aluminium, by the application of pressure and heat or by the use of either inorganic or organic binder resins, for example epoxy or polyester resins, or polymethyl methacrylate. The ease with which complicated diaphragm shapes can be made therefore ensures the widespread adaptability of the diaphragm to numerous cells of different design.

Embodiments of the invention will now be described simply by way of example.

Example 1

A 12.6 cm x 9.6 cm x 1 mm piece of porous polytetrafluoroethylene "GORE-TEX" Grade L10213 sheet (manufactured by W. L. Gore and Associates, Inc., U.S.A. in accordance with the process described in British Patent No. 1,355,373) was successively treated with a 10% w/w aqueous solution of sodium hydroxide at ambient temperature for 2 hours, a 10% w/w aqueous solution of hydrochloric acid at ambient temperature for 2 hours, and a 10% w/w aqueous solution of sodium dihydrogen phosphate at the boiling point of the solution (about 100°C) for 1 hour.

The polytetrafluoroethylene sheet was mounted in a vertical diaphragm cell for the electrolysis of sodium chloride. The cell was fitted with a mild steel mesh cathode and had an anode/cathode gap of 9 mm. Brine was passed through the cell at a rate of 245 ml/hr from a head 9.5 cm high. This corresponded to a permeability of 0.215/hr. Applying current at 2 kA/m² gave rise to a voltage of 4.03 volts. The cell operated at a current efficiency of 95.2% corresponding to a salt conversion of 51%.

Example 2

A 12.6 cm x 9.6 cm x 1 mm piece of porous polytetrafluoroethylene "GORE-TEX" Grade L10213 sheet (manufactured by W. L. Gore and Associates, Inc., U.S.A. in accordance with the process described in British Patent No. 1,355,373) was successively treated with a 10% w/w aqueous solution of sodium hydroxide at ambient temperature for 2 hours, a 10% w/w aqueous solution of hydrochloric acid at ambient temperature for 2 hours, a 10% w/w aqueous solution of sodium dihydrogen phosphate at the boiling point of the solution (about 100°C) for 1 hour, and finally immersed in a constantly agitated 10% w/w suspension of titanium dioxide (of average particle size 0.2 micron) in isopropyl alcohol for 5 hours.

The polytetrafluoroethylene sheet impregnated with titanium dioxide was removed, washed with isopropyl alcohol to remove excess solid and then mounted in a

vertical diaphragm cell for the electrolysis of sodium chloride. The cell was fitted with a mild steel mesh cathode and had an anode/cathode gap of 9 mm. Brine was passed through the cell at a rate of 315 ml/hr from a head 12.0 cm high. This corresponded to a permeability of 0.218/hr. Applying current at 2 kA/m² gave rise to a voltage of 3.26 volts. The cell operated at a current efficiency of 95.9% corresponding to a salt conversion of 48.5%.

Example 3

A piece of porous polytetrafluoroethylene "GORE-TEX" sheet manufactured according to British Patent No. 1,355,373 was presoaked in isopropyl alcohol for approximately thirty minutes. The sheet was then treated with a solution of tetra butyl titanate in iso-propyl alcohol (15% v/v) for thirty minutes. The sheet was rolled and agitated intermittently during this period to ensure homogeneous diffusion of the tetra butyl titanate. Hydrolysis of the tetra butyl titanate to hydrated titania was effected by immersing the sheet in water for thirty minutes. The filled sheet next was treated with a 20% w/w solution of sodium hydroxide for thirty minutes. Finally, the sheet was soaked in iso-propyl alcohol prior to mounting in an electrolytic cell.

The cell was on load conditions for a period of 84 days and the following results were typical. For a 120 cm² cell at 2 kA/m² — cell voltage was 3.20 volts; permeability 0.385 h⁻¹; sodium hydroxide in catholyte 98.4 gl⁻¹; sodium chloride 181.4 gl⁻¹; current efficient 94.5% corresponding to a salt conversion of 44.7%.

Example 4

A piece of porous polytetrafluoroethylene "GORE-TEX" sheet manufactured according to British Patent No. 1,355,373 was presoaked in iso-propyl alcohol. The sheet was then treated for 30 minutes in a solution comprising 100 parts of titanium tetrachloride to which was slowly added 100 parts of ammonium hydroxide solution in an ice bath, (0.88 v/v NH₄OH was used). The sheet then was washed and soaked in isopropyl alcohol prior to mounting in an electrolytic diaphragm cell.

The cell was on load conditions for a period of 14 days and the following results were typical. For a 120 cm² cell at 2 kA/m² — cell voltage was 3.55 volts; permeability 0.57 h⁻¹; sodium hydroxide in catholyte 111 gl⁻¹; sodium chloride 157 gl⁻¹; current efficiency was 90.3% corresponding to a salt conversion of 50.8%.

Example 5

A piece of porous polytetra-

fluoroethylene "GORE-TEX" sheet manufactured according to British Patent No. 1,355,373 was presoaked in iso-propyl alcohol. The sheet then was treated for 30 minutes in a 15% w/v solution of zirconium oxychloride in 40 ml of water and 160 ml of iso-propyl alcohol. Hydrolysis of the zirconium oxychloride and washing with water was effected over a period of thirty minutes. Finally, the sheet was soaked in isopropyl alcohol for thirty minutes prior to mounting in an electrolytic diaphragm cell.

The cell was put on load for 15 days. For a 120 cm² cell at 2 kA/m² a cell voltage of 3.60 volts and a permeability of 0.202 h⁻¹ were obtained.

WHAT WE CLAIM IS:—

1. An electrochemical cell having an anode and a cathode separated by a diaphragm wherein the diaphragm comprises a porous polymeric material containing units derived from tetrafluoroethylene, said material having a microstructure characterised by nodes interconnected by fibrils.

2. An electrochemical cell as claimed in Claim 1 for the production of chlorine and an alkali metal hydroxide by electrolysis of an aqueous alkali metal chloride solution.

3. An electrochemical cell as claimed in Claim 1 or Claim 2 for the production of chlorine and sodium hydroxide by electrolysis of a sodium chloride brine.

4. An electrochemical cell as claimed in any one of the preceding claims, wherein the diaphragm comprises a porous polymeric material containing units derived from tetrafluoroethylene, said material having a microstructure characterised by nodes interconnected by fibrils and a matrix tensile strength (as hereinbefore defined) of at least 7300 psi.

5. An electrochemical cell as claimed in any one of the preceding claims, wherein the diaphragm further comprises a non-removable filler which is chemically resistant to the liquors in the cell.

6. An electrochemical cell as claimed in Claim 5, wherein the non-removable filler is mixed with tetrafluoroethylene polymeric paste prior to the formation of said porous polymeric material comprising the diaphragm.

7. An electrochemical cell as claimed in Claim 5, wherein the non-removable filler is incorporated at a stage subsequent to the formation of said porous polymeric material comprising the diaphragm.

8. An electrochemical cell as claimed in Claim 7, wherein the non-removable filler is incorporated by immersing the porous polymeric material comprising the diaphragm in a suspension of the filler in a liquid.



vertical diaphragm cell for the electrolysis of sodium chloride. The cell was fitted with a mild steel mesh cathode and had an anode/cathode gap of 9 mm. Brine was passed through the cell at a rate of 315 ml/hr from a head 12.0 cm high. This corresponded to a permeability of 0.218/hr. Applying current at 2 kA/m² gave rise to a voltage of 3.26 volts. The cell operated at a current efficiency of 95.9% corresponding to a salt conversion of 48.5%.

Example 3

A piece of porous polytetrafluoroethylene "GORE-TEX" sheet manufactured according to British Patent No. 1,355,373 was presoaked in iso-propyl alcohol for approximately thirty minutes. The sheet was then treated with a solution of tetra butyl titanate in iso-propyl alcohol (15% v/v) for thirty minutes. The sheet was rolled and agitated intermittently during this period to ensure homogeneous diffusion of the tetra butyl titanate. Hydrolysis of the tetra butyl titanate to hydrated titania was effected by immersing the sheet in water for thirty minutes. The filled sheet next was treated with a 20% w/w solution of sodium hydroxide for thirty minutes. Finally, the sheet was soaked in iso-propyl alcohol prior to mounting in an electrolytic cell.

The cell was on load conditions for a period of 84 days and the following results were typical. For a 120 cm² cell at 2 kA/m² — cell voltage was 3.20 volts; permeability 0.385 h⁻¹; sodium hydroxide in catholyte 98.4 gl⁻¹; sodium chloride 181.4 gl⁻¹; current efficient 94.5% corresponding to a salt conversion of 44.7%.

Example 4

A piece of porous polytetrafluoroethylene "GORE-TEX" sheet manufactured according to British Patent No. 1,355,373 was presoaked in iso-propyl alcohol. The sheet was then treated for 30 minutes in a solution comprising 100 parts of titanium tetrachloride to which was slowly added 100 parts of ammonium hydroxide solution in an ice bath, (0.88 v/v NH₄OH was used). The sheet then was washed and soaked in isopropyl alcohol prior to mounting in an electrolytic diaphragm cell.

The cell was on load conditions for a period of 14 days and the following results were typical. For a 120 cm² cell at 2 kA/m² — cell voltage was 3.55 volts; permeability 0.57 h⁻¹; sodium hydroxide in catholyte 111 gl⁻¹; sodium chloride 157 gl⁻¹; current efficiency was 90.3% corresponding to a salt conversion of 50.8%.

Example 5

A piece of porous polytetra-

fluoroethylene "GORE-TEX" sheet manufactured according to British Patent No. 1,355,373 was presoaked in iso-propyl alcohol. The sheet then was treated for 30 minutes in a 15% w/v solution of zirconium oxychloride in 40 ml of water and 160 ml of iso-propyl alcohol. Hydrolysis of the zirconium oxychloride and washing with water was effected over a period of thirty minutes. Finally, the sheet was soaked in isopropyl alcohol for thirty minutes prior to mounting in an electrolytic diaphragm cell.

The cell was put on load for 15 days. For a 120 cm² cell at 2 kA/m² a cell voltage of 3.60 volts and a permeability of 0.202 h⁻¹ were obtained.

WHAT WE CLAIM IS:—

1. An electrochemical cell having an anode and a cathode separated by a diaphragm wherein the diaphragm comprises a porous polymeric material containing units derived from tetrafluoroethylene, said material having a microstructure characterised by nodes interconnected by fibrils.

2. An electrochemical cell as claimed in Claim 1 for the production of chlorine and an alkali metal hydroxide by electrolysis of an aqueous alkali metal chloride solution.

3. An electrochemical cell as claimed in Claim 1 or Claim 2 for the production of chlorine and sodium hydroxide by electrolysis of a sodium chloride brine.

4. An electrochemical cell as claimed in any one of the preceding claims, wherein the diaphragm comprises a porous polymeric material containing units derived from tetrafluoroethylene, said material having a microstructure characterised by nodes interconnected by fibrils and a matrix tensile strength (as hereinbefore defined) of at least 7300 psi.

5. An electrochemical cell as claimed in any one of the preceding claims, wherein the diaphragm further comprises a non-removable filler which is chemically resistant to the liquors in the cell.

6. An electrochemical cell as claimed in Claim 5, wherein the non-removable filler is mixed with tetrafluoroethylene polymeric paste prior to the formation of said porous polymeric material comprising the diaphragm.

7. An electrochemical cell as claimed in Claim 5, wherein the non-removable filler is incorporated at a stage subsequent to the formation of said porous polymeric material comprising the diaphragm.

8. An electrochemical cell as claimed in Claim 7, wherein the non-removable filler is incorporated by immersing the porous polymeric material comprising the diaphragm in a suspension of the filler in a liquid.



9. An electrochemical cell as claimed in Claim 7, wherein the non-removable filler is incorporated by impregnating the porous polymeric material comprising the diaphragm with a hydrolysable precursor of the filler and then subjecting the precursor to hydrolysis by the action of water or an alkaline solution.

10. An electrochemical cell as claimed in any one of Claims 5 to 9, wherein the non-removable filler is one which renders the porous polymeric material wettable.

11. An electrochemical cell as claimed in Claim 9, wherein said precursor is titanium tetrachloride, tetra butyl titanate or zirconium oxychloride.

12. An electrochemical cell as claimed in any one of Claims 5 to 10, wherein the non-removable filler is an inorganic oxide.

13. An electrochemical cell as claimed in Claim 12, wherein the non-removable filler is titanium dioxide or zirconium oxide.

14. An electrochemical cell as hereinbefore described with reference to the Examples.

15. A process for the electrolysis of aqueous solutions of ionisable chemical compounds in an electrochemical cell as claimed in any one of Claims 1 to 14.

16. A diaphragm suitable for use in an electrochemical cell which diaphragm comprises a porous polymeric material containing units derived from tetrafluoroethylene, said material having a microstructure characterised by nodes interconnected by fibrils and which further comprises a non-removable filler which is chemically resistant to the liquors in the

cell and which is incorporated into the aforesaid porous polymeric material at a stage subsequent to the preparation of said porous polymeric material.

17. A diaphragm as claimed in Claim 16, wherein the non-removable filler is incorporated by immersing said porous polymeric material in a suspension of the filler in a liquid.

18. A diaphragm as claimed in Claim 16, wherein the non-removable filler is incorporated by impregnating said porous polymeric material with a hydrolysable precursor of the filler and then subjecting the precursor to hydrolysis by the action of water or an alkaline solution.

19. A diaphragm as claimed in any one of Claims 16 to 18, wherein the non-removable filler is one which renders the porous polymeric material wettable.

20. A diaphragm as claimed in Claim 18, wherein said precursor is titanium tetrachloride, tetra butyl titanate or zirconium oxychloride.

21. A diaphragm as claimed in any one of Claims 16 to 19, wherein the non-removable filler is an inorganic oxide.

22. A diaphragm as claimed in Claim 21, wherein the non-removable filler is titanium dioxide or zirconium oxide.

23. A diaphragm suitable for use in an electrochemical cell substantially as hereinbefore described with reference to the Examples.

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