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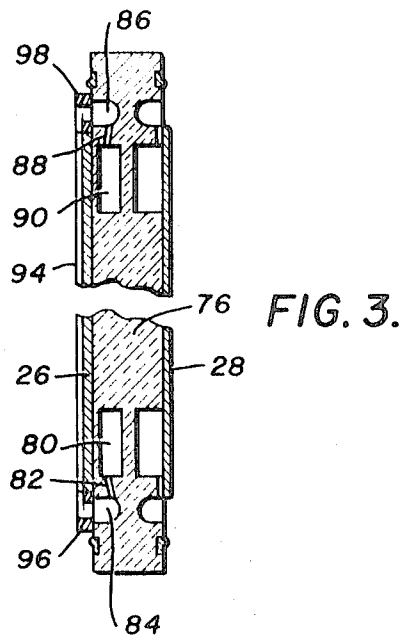
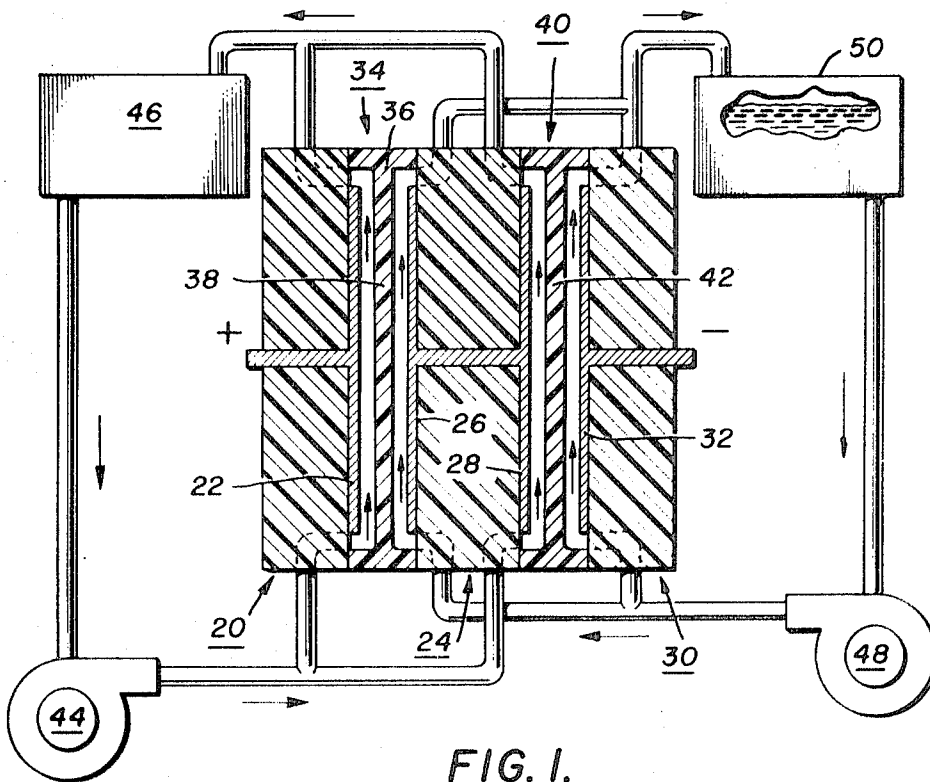
D. E. DANLY ET AL

3,660,259

ELECTROLYTIC CELL

Original Filed May 31, 1966

2 Sheets-Sheet 1



INVENTORS
DONALD E. DANLY
ROBERT W. McWHORTER

Kelly O. Cooney
ATTORNEY

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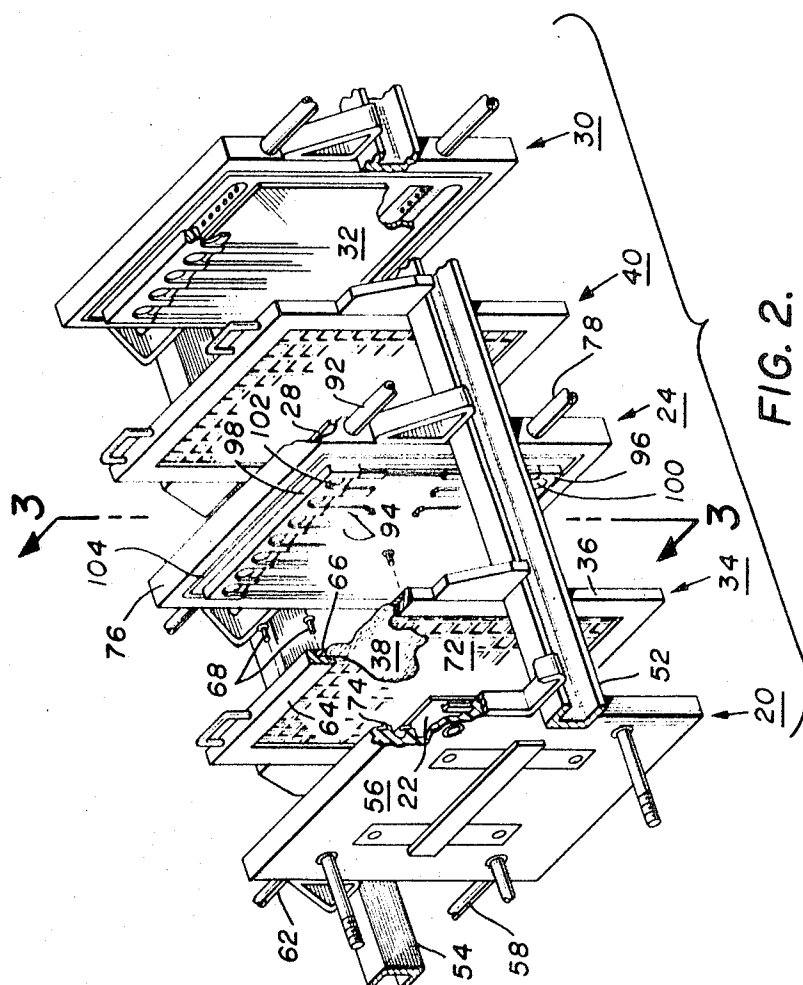


FIG. 2:

INVENTORS
DONALD E. DANLY
ROBERT W. McWHORTER

Kelly O. Corley
ATTORNEY

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3,660,259

ELECTROLYTIC CELL

Donald E. Danly and Robert W. McWhorter, Pensacola, Fla., assignors to Monsanto Company, St. Louis, Mo.
Original application May 31, 1966, Ser. No. 553,851.
Divided and this application Mar. 25, 1969, Ser. No. 810,123

Int. Cl. C07b 29/06; C07c 121/26; B01k 1/00
U.S. Cl. 204—73 A 3 Claims

ABSTRACT OF THE DISCLOSURE

An ion exchange membrane divides an electrolytic cell into separate anolyte and catholyte compartments. Spacer strips between the membrane and cathode define smooth-walled catholyte passages between the membrane and cathode. The spacer strips are parallel to catholyte flow. Anolyte pressure is slightly higher than catholyte pressure. The dimensions of the membrane frame are chosen to seal against the anode and cathode blocks without distorting the electrodes.

This application is a division of our co-pending application Ser. No. 553,851, filed May 31, 1966, now abandoned.

This invention relates to an electrolytic cell suitable for carrying out electrolytic reductive coupling and similar organic syntheses, and to a method for using the cell. More particularly, the invention relates to a cell suitable for electrohydrodimerizing acrylonitrile to produce adiponitrile.

There have recently been disclosed processes for electrolytic reductive coupling of organic compounds, as disclosed in U.S. Pats. 3,193,475 to 3,193,484, inclusive, the disclosures of which are incorporated herein by reference. A practical cell for performing such processes on a commercial scale was not previously available, since, as more fully discussed below, many practical requirements must be satisfied. The general requirements such as current concentrations, suitable electrolytes, etc., are disclosed in Pat. No. 3,193,480. Briefly, it has been discovered that such a cell should provide an ion exchange membrane separating the anode and cathode compartments, and means for spacing the membrane a small uniform distance from the cathode electrode. The cell must also provide a flow of catholyte at a controlled pressure and a uniform high velocity over the cathode surface. Known electrolytic cells are not designed for and are incapable of effectively carrying out the electrolytic reductive coupling (ERC) reaction.

Accordingly, a primary object of this invention is to provide an electrolytic cell for carrying out ERC reactions. A further object is to provide an electrolytic cell including means for accurately spacing an ion exchange membrane from an electrode. A still further object is to provide a cell of the above character having means for pumping a catholyte at a controlled pressure and at a substantially uniform high velocity over the cathode surface. Other objects of the invention will in part be obvious and will in part appear hereinafter.

For a more complete understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings, in which:

FIG. 1 is a schematic vertical sectional view of a system of electrolytic cells;

FIG. 2 is an exploded perspective view, partly broken away, of the preferred embodiment of electrolytic cell, and

FIG. 3 is a vertical sectional view along line 3—3 in FIG. 2.

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FIG. 1 schematically illustrates a system of cells wherein electric current is passed through the cells in series while the anolyte and catholyte fluids are passed through the cells in parallel. The system includes an assembly of appropriate leaves which are assembled together and clamped under sufficient pressure to prevent fluid leakage. The FIG. 1 system includes an anode end leaf 20 having anode 22 mounted thereon, an intermediate leaf 24 having cathode 26 on its leftmost side as viewed in FIG. 1, electrically connected to an anode 28 on its rightmost side, and a cathode end leaf 30 including cathode 32. Membrane leaf 34 includes a peripheral frame 36 sealingly engaging the peripheral portions of the opposed surfaces of leaves 20 and 24, to define therewith a first cell. Membrane 38, supported by peripheral frame 36, divides the first cell into an anode compartment surrounding anode 22, and into a cathode compartment surrounding cathode 26. A second membrane leaf 40 with its membrane 42 similarly defines with the opposed surfaces of leaves 24 and 30 a second cell having anode and cathode compartments surrounding anode 28 and cathode 32 respectively. By addition of further intermediate leaves and membrane leaves between end leaves 20 and 30, the number of cells can be increased to any desired number.

Anolyte is pumped by anolyte pump 44 from surge tank 46 and is distributed for parallel circulation through the several anode compartments. Similarly, catholyte is pumped by catholyte pump 48 from surge tank 50 for parallel circulation through the several cathode compartments.

FIG. 2, which is drawn substantially to scale, shows the components of the preferred embodiment of the invention, wherein the individual leaf assemblies are slidably suspended from horizontal side rails 52 and 54 of a filter press node leaf 20 includes an electrically insulating block 56, which may be made for example of polypropylene. Anode 22 is mounted on the inner planar face of block 56, and is connected by a plurality of large conductors extending through block 56 to external conductors for connection to the positive terminal of the power supply. An anolyte inlet tube 58 near the bottom of block 56 permits introduction of anolyte into internal inlet plenum chambers laterally extending across the bottom of block 56, for distributing anolyte across the exposed anode 22. The anolyte fluid at the top of block 56 is collected in outlet plenum chambers and exits through outlet tube 62. The preferred anolyte plenum chambers are identical with those illustrated in FIG. 3, and will be described below.

Membrane leaf assembly 34 includes rectangular peripheral frame 36, which may be formed of polypropylene, for supporting membrane 38 and properly spacing the electrode leaves 20 and 24. Frame 36 has an L-shaped cross-section terminating in an inwardly directed flange 64 on the side adjacent end leaf 20. A rectangular membrane retainer 66 clamps membrane 38 to flange 64 by spaced screws 68. Suitable membranes are disclosed in Baizer et al., Pat. No. 3,193,480, the sulfonated styrene-divinyl polymer supported on glass fiber fabric being preferred. Suitable gaskets may be provided between membrane 38, flange 64, and retainer 66 to prevent fluid flow around the edge of the membrane from one chamber to the other.

In the preferred embodiment, leaf 34 further includes means to prevent membrane 38 from touching anode 22 in the event of pressure fluctuations within the cell, and means to reinforce frame 36 against outward distortion due to fluid pressure within the cell. Both these functions may be provided by a 1/4" x 1/4" mesh monofilament polypropylene cloth 72, which is fused or otherwise attached to the inner edge of flange 64. Other structures with large free openings and high tensile strength perpendicular to the frame sides may be used.

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As an important aspect of the invention, cloth 72 is attached to the edge of flange 64 near membrane 38, so that anode 22 may fit within the plane of flange 64. This permits sealing of the anode chamber, without exerting clamping pressure on anode 22, by a gasket 74 mounted between the opposed surfaces of flange 64 and block 56. This prevents distortion of anode 22 which might occur if it were attempted to seal against the anode itself.

Referring to FIGS. 2 and 3, intermediate leaf 24 includes an insulating block 76, which may be formed of polypropylene, supporting cathode 26 on a vertical planar face opposing membrane 38. In order to distribute the catholyte fluid uniformly across the exposed surface of cathode 26, the catholyte is introduced through a tube 78 into inlet plenum 30 extending horizontally inside block 76 substantially the width of cathode 26. Inlet plenum 80 is connected by a plurality of restricted apertures 82 with inlet auxiliary plenum 84 below the lower edge of cathode 26. At the upper end of block 76 the catholyte enters exit auxiliary plenum 86 and then flows through a similar series of restricted apertures 88 to exit plenum 90. The catholyte is then withdrawn through a tube 92 connected with outlet plenum 90.

A plurality of vertical parallel insulating membrane spacer strips 94, which may be formed of polypropylene, are attached to the exposed face of cathode 26, defining with the exposed cathode surface and membrane 38 parallel, vertical smooth-sided fluid passages for the catholyte flow. Slot shields 96 and 98 have thicknesses equal to the combined thickness of cathode 26 and strips 94, and are mounted at the upper and lower edges respectively of cathode 26. A series of apertures 100 extending through slot shield 96 connect auxiliary plenum 84 to the lower ends of the fluid passages between strips 94, while corresponding apertures 102 through slot shield 98 similarly connect outlet auxiliary plenum 86 to the upper ends of the fluid passages. Gasket 104 permits sealing frame 36 to block 76, to define therewith the cathode chamber, without exerting sealing pressure on cathode 26.

The anode side of block 26 is similar to the cathode side, except that no provision need be made for membrane spacer strips or slot shields, and therefore need not be described in detail. The plenum arrangements in anode end leaf 20 may be identical to the plenum arrangements for the intermediate leaves as illustrated in FIG. 3, although the requirements for uniformity of flow and pressure are not as stringent on the anode side as on the cathode side. Cathode 26 and anode 28 are electrically connected by a plurality of large conductors extending through block 76.

Membrane leaf 40 is identical in construction to membrane 34, and end leaf 30 is identical to the cathode side of intermediate leaf 24. Leaf 30 includes interior electrical connections extending from cathode 32 through the insulating block for connection to a negative power supply terminal.

With the apparatus as thus described, assembled by sliding the several leaves together on horizontal side rails 52 and 54, there are thus provided alternating anode and cathode chambers with the fluid seals between adjacent parts formed in the absence of sealing pressure on the anode and cathode electrodes. The anode electrodes may be formed of a lead-silver alloy containing about 1 percent silver. The various cathodes may be made of chemical lead (99.9% pure) since they are cathodically protected against corrosion.

In the typical ERC reaction, the anolyte fluid is composed of a dilute mineral acid, such as sulfuric acid, while the catholyte includes approximately 30-35 percent water, 35-40 percent quaternary ammonium salt, and the remainder being acrylonitrile, adiponitrile, and other organic reaction products, as is more fully described in the above-noted patent to Baizer et al., 3,193,480. The catholyte composition will thus have a lower electrical conductivity than the anolyte composition.

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It is therefore desirable to space membrane 38 near cathode 26, and thus reduce the length of the electrical path through the catholyte fluid, in order to reduce electrical power consumption during the ERC reaction, and in order to reduce the volume of fluid required to be pumped. This function is performed by the membrane spacer strips 94 in conjunction with a small pressure differential between anolyte and catholyte fluids, which presses the membrane on to the surface of the membrane spacer strips 94. A pressure differential of about 1 p.s.i. has been found to be satisfactory. The edges of strips 94 which contact membrane 38 should be slightly rounded to prevent cutting into the membrane. In addition to aiding membrane spacer strips 94 in spacing membrane 38 from cathode 26, the slightly higher pressure on the anode side aids in preventing oxidizable components of the catholyte from entering the anode chamber in the event of a leak in membrane 38. If these oxidizable components entered the anode chamber they would be oxidized at anode 22 to form corrosive compounds which would attack the anode. Therefore, the pressure differential helps prevent fluid flow through the membrane toward the anode.

In order to provide uniform flow across the entire exposed surface of cathode 26 the catholyte is fed into inlet plenum 80 and distributed across the entire width of block 76. Apertures 82 are so selected as to provide a pressure drop between chamber 80 and chamber 84 which is equal to at least one-half the total pressure drop from chamber 84 to chamber 86. This produces substantially uniform pressure in all portions of chamber 80, and establishes substantially equal flow rates at all portions of cathode 26.

For maximum yields, it is necessary to maintain the critical thickness of the stagnant catholyte film on the cathode at as low a level as practicable, meanwhile maintaining the cathode-to-membrane distance as short as practicable to keep down the electrical resistance of the cell. The critical film thickness on the cathode governs the concentration of desired reactants at the cathode: if the film becomes too thick at any given current density, the supply of desired reactant becomes depleted at the electrode because mass transport from the flowing stream through the stagnant film to the cathode cannot supply reactant as fast as it is consumed in the electrode reaction. When this condition occurs, the reaction will consume reactants other than the desired one, producing undesirable by-products and lowering the yield. The use of localized projections or turbulence-initiating sites projecting into the catholyte stream usually adversely affects yield, since this leads to localized deposits of matter on the cathode.

It has been discovered that mass transport can be more efficiently increased by properly proportioning the thickness of membrane spaced strips 94, in correlation with a minimum catholyte velocity. In the preferred embodiment of the invention, spacer strips 94 were nominally 1/8 inch thick by 3/16 inch wide in cross-section, and were laterally spaced on cathode 26 to provide catholyte channels 0.757 inch wide.

Using the acrylonitrile-containing catholyte solution described in the above noted patent to Baizer, U.S. 3,193,480, wherein the viscosity is about 1.8 centipoises and at the preferred fluid flow velocity of some six feet per second, produces a Reynolds Number Re of 5720 and results in excellent yields of adiponitrile. The Reynolds Number Re, as used in the specification and claims, equals the dimensionless group

$$\frac{4LV\rho}{\mu}$$

where L equals a characteristic length of the system (in this case the cross-sectional area of the catholyte passageway divided by the perimeter of the cross-section), V equals fluid velocity, ρ equals fluid density, and where

μ equals fluid viscosity. In this particular cell, a minimum Reynolds number as thus defined of at least about 2000, and preferably about 3000 or more, was required to reduce the critical stagnant film thickness to a sufficient low level for adequate depolarizing of the electrode and suppression of undesired side reactions.

The spacer strips should have a thickness in the direction of electrical current flow of between $\frac{1}{16}$ " and $\frac{3}{16}$ ". Spacer strips thinner than about $\frac{1}{16}$ " lead to excessively high frictional pressure drop from apertures 100 to apertures 102, while spacer strips thicker than about $\frac{3}{16}$ " require an excessive amount of fluid to be pumped, as well as increasing the electrical resistance of the cell undesirably.

With presently available membranes, the spacer strips should be laterally spaced between centers from about $\frac{1}{2}$ " to about $1\frac{1}{2}$ ", the selection requiring a balance between the amount of cathode surface covered by the close spacing of strips, and the membrane sag towards the cathode with the wider spacing of the strips.

It may be seen from the above description and the accompanying drawings that the present invention provides a novel and useful electrical cell for use in electrical reductive coupling and similar organic syntheses, and a method for using the cell. In the preferred construction, the cell assembly is formed from separate leaves which are clamped together to form cells divided by cation-permeable membranes. As particular features of the invention, the membrane is spaced from the cathode by a plurality of membrane spacer strips, mounted parallel to the direction of catholyte flow. Another feature provides for greater pressure on the anode side of the membrane than on the cathode side, which both urges the membrane against the membrane spacer strips, and tends to prevent oxidizable catholyte components from entering the anode chamber. The plenum chambers and series of restricted orifices uniformly distribute the catholyte across the cathode surface, while the catholyte velocity is correlated with the catholyte passage dimensions so as to provide a Reynolds number as above defined of at least 2000. This latter feature insures sufficient uniform turbulence at the cathode surface to permit efficient mass transport of the reactants, suppressing undesired side reactions. The reinforcement 72 attached to the membrane frame both reinforces the frame against distortion due to fluid pressure, and prevents accidental contact between the anode surface, which might occur in the event of pressure fluctuations. As a further aspect, the membrane peripheral frame sealingly engages the anode and cathode blocks adjacent the periphery of the anode and cathode electrodes, thus avoiding compressing and distorting the anode and cathode electrodes.

Although the invention has been disclosed with specific reference to electrolytic reductive coupling reactions, various features can be used for carrying out other reactions. Thus, when performing an oxidation reaction at the anode, spacer strips 94 may be placed on the anode in addition to or in place of the spacer strips on the cathode. Avoiding pressure sealing against the electrodes prevents electrode distortion from this cause, and would be of general utility. Similarly, prevention of electrode surface polarization by sufficiently rapid movement of electrolyte through a smooth-sided passage including the surface (thus providing substantially uniform turbulence all along the electrode), is of utility in other electrolytic processes. Various other features of the invention are of broad utility.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method and in

the constructions set forth without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A method for electrolyzing acrylonitrile using a divided cell wherein a cation-permeable membrane is mounted parallel to and between anode and cathode surfaces to divide said cell into anode and cathode chambers, said cell including a plurality of parallel elongated membrane spacer members mounted between said cathode surface and said membrane and defining therewith a plurality of separate passageways, said method comprising the steps of:

- (a) pumping an aqueous electrolyte salt solution containing acrylonitrile between said cathode surface and said membrane, and in a direction parallel to said spacer members, said pumping being at a rate to provide a Reynolds number of at least 2000,
- (b) providing aqueous acid in said anode chamber at a pressure higher than the pressure of said salt solution in said cathode chamber, and
- (c) passing electric current through said cell at a current density of at least 15 amperes per square decimeter of cathode surface.

2. The method defined in claim 1, wherein said salt solution is pumped into a plenum chamber, spaced points in said plenum chamber being connected to said plurality of said passageways by a plurality of restricted apertures, said apertures and said passageways being so proportioned that at least as much pressure drop occur across said aperture as across said passageways.

3. A method for operating a divided cell wherein a cation-permeable membrane is mounted parallel to and between cathode and anode surfaces to divide said cell into anode and cathode chambers, said cell including a plurality of parallel elongated insulating membrane spacer members mounted between said cathode surface and said membrane and defining with said cathode surface and said membrane a plurality of separate parallel elongated catholyte passageways, said method comprising:

- (a) pumping a catholyte comprising acrylonitrile at substantially the same uniform high velocity through each of said passageways, said velocity being sufficiently high to provide a Reynolds number of at least 2000,
- (b) pumping an anolyte through said anode chamber, and
- (c) passing a direct current of at least 15 amperes per square decimeter of said cathode surface through said cell.

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F. C. EDMUNDSON, Primary Examiner

U.S. Cl. X.R.

204—263, 237