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(54) **Title:** OPTIMIZED MICROPOROUS STRUCTURE OF ELECTROCHEMICAL CELLS
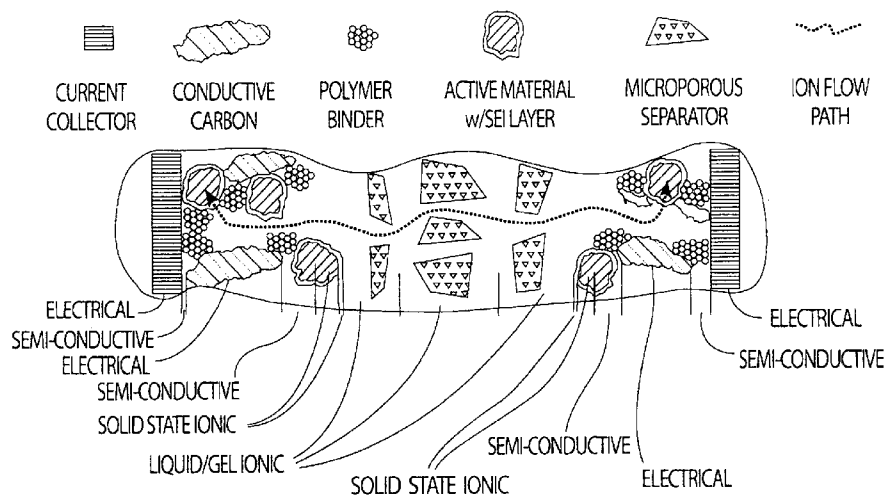
(57) **Abstract:** An optimized electrochemical cell comprised of a housing divided into two chambers, a first chamber containing a protogenous, ion-conducting liquid and a positive high density electrode including a first active material and a porous binder, surrounded by a surface in which the porosity level increases towards the surface, a second chamber containing an aprotic, ion conducting liquid and a negative high density electrode including a second active material and a porous binder, surrounded by a surface in which the porosity level increases towards the surface. A symmetric, strong, highly porous, microporous polymer membrane divides the housing into the first and second chamber. The porosity level of the polymer membrane is 25% greater than the porosity level at the surface of the positive and negative high density electrodes.

TITLE: Optimized Microporous Structure of

Electrochemical Cells

INVENTOR: Kirby Beard

UTILITY PATENT APPLICATION

CROSS REFERENCES AND RELATED SUBJECT MATTER

This application is a continuation of provisional patent application serial no. 60/814,001, filed in the United States Patent Office on June 16, 2006.

BACKGROUND OF THE INVENTION

Field of Invention

The invention relates to breakthrough technology based on an entirely new concept in electrochemical (EC) cell construction, more particularly to EC cell construction

5   utilizing novel binder matrices as an alternate means to
     providing performance benefits.

     A key requirement in EC cells is the ability of the
     binder material/formulation and associated processing
10   technique to retain adequate porosity in the components,
     while providing for maximum densification of the electrodes
     to improve cell capacity. While standard polymer binders
     and processing methods most commonly used to fabricate
     electrodes are not likely to be directly transferable into
15   the new proposed cell designs, the use of most any of a
     variety of known specialized techniques are adaptable for
     producing cell components for the proposed improved cell
     designs. A new patented high porosity polymer composition
     and process method that has proven successful in forming
20   battery separator films with >80% void content with sub-
     micron pore sizes and excellent mechanical strength is
     particularly useful to produce cell components with
     controlled pore sizes/void contents. When combined with a
     centrifugal casting manufacturing process, not heretofore
25   employed in battery electrode production, a high capacity
     electrode with high ionic conductivity necessary for fast
     charge and discharge is the result.

     Conventional lithium cells do not optimize the trade-
30   off between porosity and energy in a safe, reliable cell
     design. The typical lithium cell uses electrode binder

                                    2

5   systems that are mostly optimized for production ease.

        Most lithium battery separator technology is derived from

        off-the-shelf microporous polymer films originally

        developed for other applications and therefore not optimal

        for addressing the unique requirements of maximizing ion

10   conductivity in lithium ion batteries. Ions do not easily

        become bottlenecked within the electrodes where they are

        generated. Instead ions will readily flow until they meet a

        restriction to the flow path such as at occluded surface

        pores on either electrodes or separator or at interfaces

15   between cell components where porosity drops by a large

        amount in going across the interface. Most conventional

        cells are built with a separator that is <45% porous and

        rarely more than 55-60% porous. These separators are then

        rarely combined with electrodes that are much lower in

20   porosity usually running around 40-50% voids. The result

        is an electrochemical cell that has about the same

        void levels in the separator and the electrodes at best,

        but with electrode porosity usually being higher than the

        separator's.

25

        The more efficient electrochemical cell is one wherein

        the separator's porosity is higher than that of the

        electrode to eliminate bottlenecks to ion flow. An

        electrode can vary in density to yield from 60% voids or

30   varying percentages of 40%, 30% or 20% voids when highly

        consolidated by pressing or rolling. Therefore to obtain an

5   efficient electrochemical cell, electrode porosity level

     must be <50% or preferably <40% or even <30% but with

     separator voids at least 25% or preferably 50% to 100%

     greater than the electrode porosity levels. The most

     efficient electrochemical cell contains an electrode at 20%

10   electrode porosity level with separator void levels at >40%

     therefore containing a 100% higher porosity level in the

     separator than the electrode. Alternate efficient

     electrochemical cell configurations can include electrode

     voids at 40% and separator at 80% (100% greater) or 60%

15   (50% higher) or even only 50% (25% higher than the

     electrode). In the case where 80% high porosity separator

     is used, the electrodes could still be as high as 64% voids

     and meet these specifications of being at least 25% higher.

20   Typical electrode constructions use an impervious

     polymer binder to adhere particles of active materials and

     conductive additives to each other and to a current

     collector in a low-density coating. Since active material

     content is typically less than 50% by volume, manufacturers

25   often attempt to reduce the voids in the electrodes by

     calendaring, but these efforts often cause the polymer to

     compact between the solid particles, resulting in

     unacceptable restrictions to the flow of ions through the

     components with little real improvement in electrode

30   density. Active materials include traditional powders such

     as $LiCoO_2$ and MCMB carbon, as well as newer ones such as

5   LiFePO$_4$ and lithium titanate compounds. Purer, less

    reactive electrolyte solutions, typically using inorganic

    lithium salts in organic solvents, have evolved over the

    years to replace less stable, more costly solutions.

    Separators, typically constructed from polyolefins, are

10 produced in sheet films with various, but sub-optimal,

    porosity and thickness. The electrodes are interleaved with

    separators and mechanically compressed to ensure complete,

    intimate contact of components. The cells are then

    packaged and sealed in a flexible pouch or metal can before

15 injecting with electrolyte solutions.

    Past battery design efforts often concentrated on

    enhancements of active materials and various individual

    components, using a lamination/extraction technology

20 intended to optimize the overall construction of the

    lithium cell. Despite the lack of commercial success of

    the gel polymer system compared to liquid electrolytes and

    conventional electrode and separator components,

    improvements in the lithium cell's microstructure still

25 represents a viable approach to realizing the full

    electrochemical performance of these cells. Specifically,

    improved performance requires a cell design based on matrix

    materials having a small, uniform pore structure, optimized

    for each cell component and lacking discontinuities at the

30 component interfaces.

5   The present invention is applicable to many

electrochemical systems and is intended to overcome various

problems of current systems.

10   U.S. Patent Application 20070100012 to Beard discloses

a method of producing a symmetric, strong, highly porous,

microporous polymer film by (a) forming a layer of a

polymer solution on a substrate, the solution comprising

two miscible liquids and a polymer material dissolved

therein, and wherein the first liquid has a surface tension

15   lower than the surface energy of the polymer and the second

liquid has a surface tension greater than the surface

energy of the polymer; (b) producing a film of gelled

polymer from the layer of polymer solution; and (c) rapidly

removing the liquid from the film of gelled polymer by

20   unidirectional mass transfer without dissolving the gelled

polymer

U.S. Patent Application 20040043224 to Sternberg

discloses dimethylsulfoxide (DMSO) or dimethylacetamide

25   (DMAc) as the solvent for polyvinylidene fluoride when

casting a membrane onto a support structure, immediately

followed by immersion in a non-solvent bath, typically

methanol.

30   U.S. Patent No. 4,203,847 to Grandine discloses flat

sheet membranes formed by casting a nearly saturated PVDF

5   solution in hot acetone solvent onto a heated moving belt

which then passes (within 10 seconds) into a forming bath

containing a mixture of 80% acetone solvent and 20% water

non-solvent, followed by water washing. This produces a

thin-skinned membrane.

10

U.S. Patent No. 4,203,848 to Grandine describes the

belt and machine used in the '847 process.

U.S. Patent No. 4,384,047 to Benzinger, et al.

15   discloses the preparation of asymmetrical vinylidene

fluoride polymer ultrafiltration membranes by casting a

sheet of the polymer dissolved in a mixture of a

triethylphosphate solvent and a glycerol non-solvent, on a

smooth substrate, evaporating a portion of the solvent from

20   the sheet, immersing said sheet in a gelation liquid (ice

water), and optionally, stabilizing the gelled sheet by

heat treatment thereof.

U.S. Patent No. 4,399,035 to Nohmi, et al. discloses a

25   polyvinylidene fluoride membrane prepared by casting a dope

comprising polyvinylidene fluoride, an active solvent such

as DMAc, N-methylpyrrolidone or tetramethylurea and a minor

amount of a surfactant or mixture of surfactants into a

non-solvent bath, typically water or an alcohol.

30   Polyethylene glycol and polypropylene glycol are used as

5   surfactants and glycerin fatty acid esters are mentioned in

the description as being suitable.

U.S. Patent No. 4,464,238 to Caldwell, et al. defines

"MacMullin Number," N_{MAC}, as the ratio of the electrical

10   resistance of an electrolyte-saturated porous medium, R, to

the resistance of an equivalent thickness and area of

electrolyte, R_0. MacMullin Number is a relative measure of

resistance to movement of ions through a porous membrane.

15   U.S. Patent No. 4,629,563 to Wrasidlo discloses

ultraporous and microporous asymmetric membranes of

numerous polymers. The membranes have an entirely

reticulated structure free of large finger voids. The

reticulated support structure has a gradually increasing

20   pore size that reaches a maximum of from about 10 to about

20,000 times the diameter of the skin pores at the opposite

face. Solvents which may be used include:

dimethylformamide, dimethylacetamide, dioxane, N-Methyl

pyrrolidone, dimethylsulfoxide, chloroform, tetramethyl-

25   urea, and tetrachloroethane. The non-solvents include:

methanol, heptane, ethanol, octane, isopropanol, acetone,

amyl alcohol, methylethylketone, hexanol, methylisobutyl

ketone, heptanol, nitropropane, octanol, butyl ether,

propane, ethyl acetate, hexane, and amyl acetate. A

30   mixture of 8 parts by weight polyvinylidene fluoride, 9.3

parts by weight glycerin, and 82.7 parts by weight

5   dimethylformamide was stirred at ambient temperature for

    two hours. After degassing, the mixture had a turbidity of

    0.8 optical density at 420 nanometers and was cast into

    water to form a membrane.

10   U.S. Patent No. 4,666,607 to Josefiak describes a

    thermal gelation process. It discloses the use of a quench

    tube in the form of a U-tube, or a tank with the fiber

    moving as if in a U-tube, which can be used to produce

    polyvinylidene fluoride films or hollow fibers by extrusion

15 of a solution comprising the polymer, solvent(s) and a non-

    solvent above the temperature at which the solution will

    separate into two phases, advantageously through an air gap

    into a cooling liquid in the quench tube or tank. In the

    case of hollow fibers, a lumen forming fluid (which is not

20 a solvent for the polymer) is employed.

        U.S. Patent No. 4,810,384 to Fabre describes a process

    wherein polyvinylidene difluoride and a hydrophilic polymer

    compatible therewith are dissolved in a mixture of lithium

25 chloride, water and dimethylformamide, then cast onto a web

    and coagulated by passing the film through a water bath. A

    hydrophilic membrane that is a blend of the two polymers is

    produced.

30   U.S. Patent No. 4,933,081 to Sasaki, et al. describes

    preparation of an asymmetric micro-porous membrane having a

5   layer of minimum pores inside. The membrane is produced by

a kind of dry-wet method in which a gas is brought into

contact with the surface of the spread solution before it

is immersed in a solidifying bath to form a coacervation

phase only in the surface layer of the spread solution. A

10   homogeneous raw solution for forming a membrane was

prepared by dissolving 20 parts of polyvinylidene fluoride,

60 parts of dimethyl-acetamide as a good solvent, and a

non-solvent consisting of 10 parts of polyethylene glycol

200, 10 parts of poly(vinylpyrrolidone) and 0.7 parts of

15   water. The solution was spread evenly over a glass plate

using a doctor blade to have a spread solution thickness of

150 microns. Warm air at 60°C (relative humidity 30%) was

blown to the surface of the spread solution samples at a

rate of 0.8 m/sec for up to 30 seconds. Then the samples

20   were immediately immersed in warm water at 60°C for 2

minutes and further in cool water at 20°C. The minimum pore

layer was formed inside the membrane when warm air was

blown for 2 to less than 30 seconds. The patent also uses

water as a solvent for a film combining polysulfone and PVP

25   (the PVP dissolves readily in water). The asymmetric

membranes had pore ratios (center size to skin size)

ranging from 10 to 100.

U.S. Patent No. 4,965,291 to Kitoh, et al. discloses a

30   method of manufacturing a porous membrane by dissolving

vinylidene fluoride polymer in a good solvent such as

5   acetone and then causing solidification of the resultant

    solution in a non-solvent. The dissolution of the

    vinylidene fluoride polymer in the solvent is done in a

    predetermined pressure condition, preferably in a range of

    0.5 to 5.0 kg/cm^2.   A mixture of vinylidene fluoride and

10 vinylidene fluoride/propylene hexafluoride copolymer in a

    weight ratio of 80:20 was added to acetone as a good

    solvent such that the polymer concentration was 19.0 % by

    weight.   The resultant solution was heated to 62°C while

    pressurizing it to 1.0 kg/cm^2 with agitation to obtain a

15 uniform polymer solution. This solution was cast on a film

    which was then immersed in 1,1,2-trichloro-1,2,2-

    trifluoroethane and then dried to room temperature.

        U.S. Patent No. 5,013,339 to Mahoney describes

20 preparing a polyvinylidene fluoride polymer membrane

    containing (1) a polyvinylidene fluoride polymer, (2)

    glycerol mono-acetate, glycerol diacetate, glycerol

    triacetate, or mixtures thereof, and (3) optionally

    glycerol, wherein the polyvinylidene fluoride polymer

25 membrane so prepared is useful for a membrane liquid

    separation process such as microfiltration, ultra-

    filtration, dialysis, or membrane stripping.   Preferably

    the polyvinylidene fluoride polymer membrane is made by

    forming a mixture of the composition, heating the mixture

30 to a temperature at which the mixture becomes a homogeneous

5   fluid, and extruding, molding, or casting the homogeneous

       fluid into water to form a porous membrane.

       U.S. Patent No. 5,387,378 to Pintauro describes

       fabricating an asymmetric fluoropolymer membrane having a

10   first surface comprised of a dense layer of the

       fluoropolymer material, and an opposite second surface

       comprised of a porous layer of the fluoropolymer material,

       by (a) dissolving a fluoropolymer material in a solvent

       mixture of a low boiling point (40-60°C) solvent and a high

15   boiling point (140-200°C) solvent to form a solution; (b)

       depositing the solution on a casting surface; and (c)

       removing the solvent from the solution, to precipitate the

       membrane. The solvent removing step requires two steps:

       (i) evaporating the solvent by air drying the solution for

20   a sufficient period of time until the surface of the

       solution at the air interface has gelled, and then (ii)

       immersing the solution in a precipitation bath prepared

       from a major amount of a non-solvent and a minor amount of

       a solvent.

25

       U.S. Patent No. 5,489,406 to Beck discloses a method

       of making a porous polymeric material by heating a mixture

       containing polyvinylidene fluoride and a solvent system of

       (i) a latent solvent (a glycerol ester such as glycerol

30   triacetate, glycerol tripropionate, glycerol tributyrate

       and partially-esterified glycerol) and (ii) a non-solvent

5   (e.g. a higher alcohol, glycol or polyol), at elevated

     temperatures. The patent specifically excludes active

     solvents such as acetone. The solution is extruded as a

     fiber and then rapidly cooled so that non-equilibrium

     liquid-liquid phase separation takes place to form a

10   continu-ous polymer rich phase and a continuous polymer

     lean phase with the two phases being intermingled in the

     form of bicontinuous matrix of large interfacial area.

     Cooling is continued until the polymer rich phase

     solidifies. The polymer lean phase is then removed from

15   the solid polymeric material by a lumenal gas wash

     procedure at a pressure of about 600 kPa (87 psi).

     U.S. Patent Nos. 5,834,107, 6,110,309, and 6,146,747

     all to Wang describe preparing a polyvinylidene difluoride

20   membrane by adding a water-soluble polymer along with the

     PVDF, and then using humid air followed by hot water as the

     quench and extractant. More particularly, they provide a

     casting dope of about 12-20% by weight of PVDF and between

     up to 30% by weight of a hydrophilic polymer such as

25   polyvinylpyrrolidone, dissolved in a solvent; casting the

     dope to form a thin film; exposing the thin film to a humid

     gaseous environment; coagulating the film in a water bath;

     and then recovering a formed assymetric microporous PVDF

     membrane.

30

5   U.S. Patent No. 5,922,493 to Humphrey describes an

electrochemical cell having a positive electrode, an

absorber-separator and a negative electrode wherein at

least one of the electrodes or absorber-separator comprises

a porous poly-vinylidene fluoride. The porous

10   polyvinylidene fluoride electrodes have an electrode

material combined therewith, and the porous polyvinylidene

fluoride absorber-separator has an electrolyte material

combined therewith.

15   U.S. Patent No. 6,013,688 to Pacheco describes methods

for making microporous polyvinylidene fluoride (PVDF)

membranes from vinylidene fluoride polymers and the

products produced. The process includes dissolving the

polymer at a temperature of 20 to 50°C. in a liquid that

20   includes a solvent and a co-solvent for the polymer. The

solvent: co-solvent mixture requires at least one solvent

selected from N-methyl-2-pyrrolidone, tetrahydrofuran,

methyl ethyl ketone, dimethylacetamide, tetramethyl urea,

dimethyl sulfoxide and trimethyl phosphate. The co-solvent

25   is preferably selected from formamide, methyl isobutyl

ketone, cyclohexone, diacetone alcohol, isobutyl ketone,

ethyl acetoacetate, triethyl phosphate, propylene

carbonate, glycol ethers, glycol ether esters, and n-

butylacetate. The solution is then heated or maintained at

30   a desired temperature for a particular pore size. Then the

solution is spread onto a solid surface to form a film and

5   the solvent:co-solvent mixture is dis-placed from the film

       with a bath of a co-solvent:non-solvent liquid mixture.

       U.S. Patent No. 6,432,586 to Zhang describes a

       separator for a high-energy recharge-able lithium battery

10   and the corresponding battery in which the separator

       includes a ceramic composite layer and a polymeric

       microporous layer. The ceramic layer is a mixture of

       inorganic particles in a matrix material. The ceramic layer

       is adapted, at least, to block dendrite growth and to

15   prevent electronic shorting. The polymeric layer is

       adapted, at least, to block ionic flow between the anode

       and the cathode in the event of thermal runaway.

       U.S. Patent No. 6,444,356 to Ma describes a secondary

20   lithium battery separator of a fibrous core coated with a

       polymer having improved electrode adhesion properties in a

       unitary laminated construction. The separator is made of a

       pre-formed porous non-woven mat of a first homopolymer of

       polypropylene, polyethylene, or polyvinylalcohol, coated

25   with a second homopolymer. Poros-ity of the homopolymeric

       coating, which may preferably be polyvinylidene difluoride,

       is obtained by first mixing the homopolymer with a low

       boiling solvent, e.g. acetone, and a non-aromatic aliphatic

       diester plasticizer, followed by forming a layer of the

30   polymer-diester-acetone mixture on a fiber sheet,

       incorporating the sheet into a battery and then subjecting

5   the entire structure to a vacuum to remove residual

       plasticizers.

       U.S. Patent No. 6,537,703 to DuPasquier describes

       adding an alcohol to the polymer solution as a non-solvent.

10   The alcohol, which has a low surface tension, is selected

       to evaporate at a temperature higher than the primary

       solvent (acetone), and the transition from liquid to solid

       involves selective evaporation of the acetone prior to that

       of the alcohol. This causes gelation of the polymer to

15   occur. The process results in significant shrinkage of the

       film in its thickness direction (from 250 micron wet film

       to 50 micron dry film). Moreover it requires the use of

       fumed silica (7 parts silica per 10 PFDF polymer) to

       reinforce the film strength to make thin films.

20

       U.S. Patent No. 6,586,138 to Pekala describes a

       freestanding battery separator that includes a microporous

       polymer web with passageways that provide overall fluid

       permeability which contains (i) ultra high molecular weight

25   polyethylene (UHMWPE) and (ii) a gel-forming polymer

       material. In one embodiment, the gel-forming polymer

       material is a coating on the UHMWPE web surface. In a

       second embodiment, the gel-forming polymer material is

       incorporated into the UHMWPE web while retaining overall

30   fluid permeability. Both embodiments produce hybrid gel

5   electrolyte systems in which gel and liquid electrolyte co-
exist.

U.S. Patent No. 6,994,811 to Kools describes a process
for making macrovoid-free microporous membranes from a
10 polymer solution and the membranes there-from by means of a
thermal assist, such as heating of the polymer solution
subsequent to forming a film, tube or hollow fiber of the
solution under conditions that do not cause phase
separation. The formed solution is briefly heated to
15 generate a temperature gradient through the body of the
formed solution. The polymer in solution then is
precipitated by immersion into a liquid bath of such as
methanol to form a microporous structure by. The formation
of a wide variety of symmetric and asymmetric structures
20 can be obtained using this process. Higher temperatures
and/or longer heating times effected during the heating
step result in larger pore sizes and different pore
gradients in the final membrane product.

25   U.S. Patent No. 6,998,193 to Sun describes a battery
having at least one positive electrode, at least one
negative electrode, an electrolyte, and a homogeneous
microporous membrane that contains (a) a hot-melt adhesive,
(b) an engineering plastics, (c) optionally a tackifier,
30 and (d) a filler having an average particle size of less
than about 50 microns. The microporous membrane is bound

5   permanently onto the surface of a positive electrode or a

       negative electrode. The hot-melt adhesive, engineering

       plastic and filler are distributed in the microporous

       membrane.

10   U.S. Patent Application 2004/0241550-A1 to Wensley

       describes a battery separator for a lithium battery in the

       form of a microporous membrane (generally UHMWPE) and

       coated on both sides. The coatings are made from a mixture

       of a gel forming polymer, a first solvent such as

15   tetrahydrofuran, methylethylketone, acetone, low molecular

       weight glymes, and combinations thereof, and a second

       solvent or non-solvent such as propanol, isopropanol,

       butanol, and mixtures thereof. The first solvent is more

       volatile than the second solvent. The second solvent or

20   non-solvent acts as a pore former for the gel-forming

       polymer. A small amount of water may also be added along

       with the second solvent or non-solvent. The first solvent

       is allowed to evaporate, preferably without the use of

       heat. Thereafter, the second solvent or non-solvent is

25   removed in an oven with the application of heat. The

       process also requires a controlled high humidity for

       gelation when coated onto a Celgard film. By controlling

       the relative humidity (% RH) during the coating process,

       the uniformity of resistance (measured by the MacMullin

30   Number) may be controlled. It has been determined that

       when the % RH is below 45%, the MacMullin Number (as

5   defined in US Pat. No. 4,464,238, incorporated therein by

     reference) may be controlled to be within the range of 5-

     12, preferably 5-6 with a coating density of about 0.25

     mg/cm^2.

10   Japanese Pat. No. 51-8268 uses cyclohexanone as a

     solvent for polyvinylidene difluoride. The solution is

     heated and then cooled during which time the solution

     passes through a region of maximum viscosity. The membrane

     is cast when the viscosity of the solution is decreasing.

15

           European Patent No. 223,709 discloses a mixture of

     acetone and dimethyl formamide (DMF) as a preferred solvent

     although all the usual standard or active solvents such as

     ketones, ethers such as tetrahydrofuran and 1,4 dioxane,

20   and amides such as DMF, DMAC and DMSO are described. To

     form the membrane, the polymer solution is coated onto a

     substrate and then the coating is immediately immersed into

     a bath of a poor solvent.

25   While these units may be suitable for the particular

     purpose employed, or for general use, they would not be as

     suitable for the purposes of the present invention as

     disclosed hereafter.

5   SUMMARY OF THE INVENTION

        It is an object of the invention to produce a unique

ion battery which increases battery capacity and

performance by overcoming low porosity in the separator

10   while achieving high density electrodes thereby increasing

ion flow within the battery components.

        It is an object of the invention to produce a means

for eliminating restrictions to ion flow as well as

15   detrimental interfacial discontinuities between components

in electrochemical cells.

        It is another object of the invention to provide a

means for overcoming low porosity in the polymer membrane

20   while increasing density in the electrodes thereby

increasing battery capacity over extended cycling.

        It is another object of the invention to provide a

convenient means for improving communication of electrolyte

25   solutions with cell components and to provide free

unrestricted ionic transport throughout the cell during

operation.

        It is another object of the invention to provide a

30   means for including an unprecedented level of porosity

(>80% within the polymer phase) that can be used to produce

5   both highly densified electrodes and highly porous

     separators in a durable matrix.

     It is a further object of the invention to provide

     pores in these components that can be tailored to different

10   size requirements, tortuousness, and void distributions.

     It is another object of the invention to provide a

     low-cost formulation and manufacturing process adaptable to

     various battery constructions, including laminated

15   electrodes, without creating major interfacial resistances.

     It is a further object of the invention to eliminate

     design defects and achieve the capabilities inherent in the

     active materials and electrolytes thereby obtaining cell

20   performance which can reach 50% of capabilities, a 50%

     improvement over the current state of the art.

     The present invention combines the highly densified

     electrode with a symmetric, strong, highly porous,

25   microporous polymer film that functions as a separator

     between the positive and negative electrodes within the

     electrochemical cell. The high strength and uniform

     porosity of the polymer film allow for more efficient

     travel of ions, resulting in maximum current flow within

30   the electrochemical cell. The invention combines improved

     ion availability resulting from the highly densified

21

5   electrodes with unimpeded flow of ions through the

symmetric, strong, highly porous, microporous polymer film

to create an electrochemical cell of improved capacity and

efficiency.

10   To the accomplishment of the above and related objects

the invention may be embodied in the form illustrated in

the accompanying drawings. Attention is called to the

fact, however, that the drawings are illustrative only.

Variations are contemplated as being part of the invention,

15 limited only by the scope of the claims.

5   BRIEF DESCRIPTION OF THE DRAWINGS

    In the drawings, like elements are depicted by like

reference numerals. The drawings are briefly described as

follows.

10

    FIG 1 is a sectional view across a typical lithium

cell electrode pair for modeling hypothetical electrical

and ionic resistances with electrolyte solution/gel filling

pore spaces, and including a comparison of ideal cell stack

15 construction versus conventional technology.

    FIG 2 is a sectional view showing two extremes of cell

pore structure.

20   FIG 3 is a schematic illustration of an embodiment

showing a cross section of an electrode with porous or

conductive binder with a separator applied to the

electrode.

25   FIG 4 is a schematic illustration of an embodiment

showing a cross section of an electrode with porous or

conductive binder with a separator made from the porous

binder material.

5   FIG 5 is a schematic illustration of an embodiment

showing a cross section of an electrode with a solid

binder.

5   DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention is an improved technology in

electrochemical cell construction. Novel processes are

employed to produce components with characteristics that

10   enhance performance over existing electrochemical cells.

Specifically, a component for an electrochemical cell is

formed using centrifugal forces to densify an electrode or

electrode material. In some embodiments, a binding agent

may be used to mechanically bind active material for

15   processing and normal operation. The binding agent may be

a dispersed solid material as well as a pore forming

material. Thus densified, the electrode has enhanced

efficiency and power capability as more active material is

available per unit volume to react with the surrounding

20   electrolyte. Furthermore, the centrifugation process

results in a high density active material that becomes

increasingly porous near its surface, allowing the

electrolyte to contact and react with a larger surface area

of active material. In some embodiments, multiple layers of

25   a device may be constructed using single or plural

centrifugal processing steps.

The present invention is an optimized electrochemical

cell comprised of a housing divided into two chambers, a

5   first and a second chamber. The first chamber containing a
    protogenous, ion-conducting liquid and a positive high
    density electrode including a first active material and a
    porous binder, surrounded by a surface in which the
    porosity increases towards the surface. The second chamber
10 containing an aprotic, ion conducting liquid and a negative
    high density electrode including a second active material
    and a porous binder, surrounded by a surface in which the
    porosity increases towards the surface. The optimized
    electrochemical cell also contains a symmetric, strong,
15 highly porous, microporous polymer membrane which divides
    the housing into the first and second chamber. In the
    optimized electrochemical cell, the porosity of the polymer
    membrane is at least 25% greater than the porosity at the
    surface of the positive and negative high density
20 electrodes.

    Lithium cell batteries are a plurality of
    electrochemical cells connected together. The design of
    these batteries can be modeled as an array of electrical
25 and ionic resistances as shown in FIG 1. More porous
    components improve conductivity levels throughout the cell
    and directly affect power and capacity. The performance of
    these cells is greatly impacted by the structure of the
    components, including path length and cross-sectional area
30 for ion flow within the pores of the various cell
    components.

5

To improve overall cell conductivity and performance, modification of the pathways for ion conduction through the electrodes and separators is needed as shown in FIG 2. The dashed line shows a typical cell using calendared, low

10 density electrodes and a commercial separator. The double line 210 indicates the cell design goal of higher density electrodes with increasing porosity towards the surface, along with a more highly open separator layer.

15 *1. Method for producing a high density electrode*

FIG 3 is a schematic illustration of an electrode. The electrode 302 has a current conductor 304 with active material 306 held in a matrix of porous or conductive

20 binder 308. A separator 310 is applied to the electrode 302. The electrode 300 illustrates an active material 306 that may be densified or compacted using a centrifuge. The matrix of a binder 308 may hold the active material 306 in place for stability during manufacturing and enhanced

25 durability in a finished device. The binder 308 may be a porous binder with pores sized smaller than the smallest nominal size of the active material 306.

In alternate electrode embodiments, the smallest

30 active material particle size may be ten times or more larger than the nominal pore size of the binder. In some

5   cases, a solid conductive binder 308 may be used. Such a

binder may also serve as a solid electrolyte. When a solid

conductive binder is used, it may be desirable to have very

few voids between the conductive binder and the active

material. Similarly, a porous binder may also be applied

10   in a manner that few voids are present, other than the

pores within the porous binder. The separator 310 in the

electrode 300 may be a separately applied film that is

attached by heat, pressure, or another process or

combination of processes. The separator 310 may be applied

15   by spraying, extruding, casting, or other processes whereby

the separator 310 may be applied with a transport media.

The transport media may be evaporated, drawn off, or

otherwise removed from the separator 310.

20   A further method for making the positive high density

electrode is by adding a binder to the first active

material to form an unprocessed electrode material, mixing

said first active material with the binder using a

transport medium. The first active material, which has a

25   specific gravity that is at least 10 percent higher than

the specific gravity of the transport medium, is processed

in a centrifuge to produce a processed electrode material

and is then processed into an electrochemical device.

30   In a typical version of the electrode 302, the

composition may be between 40% and 70% by volume active

5   material, with 2% to 30% by volume porous binder having 50-
       90% micropores. The remaining volume may be voids.

       The separator 310 and/or the current collector 304 may
       be used to provide mechanical stability and durability to
10   the assembly during manufacturing and use. The active
       material 306 is illustrated in many different particle
       sizes, including particles that may be 10 times as large as
       the size of a smaller particle. In other embodiments of
       the separator, the pore size may be the same nominal size
15   or even larger than the smallest size of active material
       particles. In some embodiments of the separator, a mixture
       of large and small particles may result in denser
       electrodes during the centrifugal process step than uniform
       sized particles. In some embodiments of the separator, the
20   pore size may be larger than the size of the smallest size
       of the active material particles. By using a centrifugal
       compaction process, the active materials may be
       mechanically interlocked so that small particles of active
       material may not migrate and cause shorts or other
25   problems. Additionally, a porous binder may aid in holding
       the compacted and mechanically interlocked particles
       together.

       In FIG 4 the electrode 401 has a current collector
30   402, active material 404, and a porous or conductive binder
       406. The electrode 401 has an electrode portion 408 and a

5   separator 410. The separator portion 410 may be made from

       the porous binder material 406. Embodiment 400 is similar

       to embodiment 300 with the exception that excess porous or

       conductive binder 406 forms the separator 410. During a

       centrifugal process step, centrifugal forces may force the

10   active material 404 to consolidate against the current

       collector 402 and excess porous or conductive binder 406

       may rise to the surface to form the separator 410. Such a

       process is possible when the specific density of the active

       material is higher than the specific gravity of the porous

15   or conductive binder 406. When the porous or conductive

       binder 406 has a higher specific gravity than the active

       material 404, such a structure may be formed in a

       centrifuge, but the separator side would be toward the

       outer radius of the centrifuge. The difference between the

20   specific gravities of the active material 404 and the

       porous or conductive binder 406 may affect the centrifugal

       process step. When the difference is great, the active

       material 404 may separate with less time or force in the

       centrifuge. When the difference is small, the centrifugal

25   processing time and/or force may be substantially higher to

       force the separation of the two materials. In many

       embodiments, the active material 404 may be mixed with the

       binder material 406 in a liquid, paste, gel, slurry, or

       other form that uses a transport media. The transport

30   media may function as a solvent for either or both of the

       active material 404 or porous or conductive material 406.

5   In some embodiments, the transport media or a portion of

the transport media may serve as a pore forming material

for the binder.

In FIG 5 the electrode 502 has a current collector

10   504, active material 506, and a solid binder 508. The

solid binder is dispersed around the active material 506 so

that the active material 506 may be mechanically held but

with some gaps to allow electrolyte to contact the active

material 506. Embodiment 500 may be formed using a

15   centrifugal process step to consolidate the active material

506. In some embodiments of the , the solid binder 508 may

be processed with the active material 506 in a centrifuge,

while in other embodiments the binder 508 may be applied

after centrifugal processing. A solid binder 508 may be

20   applied using a transport media that contains the binder

508 in suspension or solution. During a centrifugal

processing step, the solid binder 508 may be deposited or

precipitated and bound with the active material 506. In a

typical version of embodiment 500, the composition may be

25   between 40% and 70% by volume active material, with 5% to

30% by volume solid binder. The remaining volume may be

voids. Various samples of separators with varied porosity

(40 to >80%) along with a commercially available separator

were tested for cycling capability at high rates. The

30   increased porosity across these samples would be expected

5   to correlate with increased high rate performance, which

     indeed is the general case.

     2. Method for producing a highly porous polymer membrane

10   A method of producing a symmetric, strong highly

     porous, microporous, polymer membrane is by (a) forming a

     layer of a polymer solution on a substrate, where the

     polymer solution comprises two miscible liquids and a

     polymer material is dissolved, and where the two miscible

15   liquids are composed of, (i) a principal liquid that has a

     surface tension at least 5% lower than the surface energy

     of the polymer and (ii) a second liquid that has a surface

     tension at least 5% greater than the surface energy of the

     polymer, (b) producing a film of gelled polymer from the

20   layer of polymer solution under conditions sufficient to

     provide a non- wetting, high surface tension solution

     within the layer of polymer solution, and (c) rapidly

     removing the liquid from the film of gelled polymer by

     unidirectional mass transfer without dissolving the gelled

25   polymer to produce the strong, highly porous, microporous

     polymer film.

     In another embodiment of the polymer membrane the

     method for producing a symmetric, strong, highly porous,

30   microporous polymer membrane is by (a) preparing a solution

     of one or more polymers in a mixture of a principal liquid

5 which is a solvent for the polymer and a second liquid
   which is miscible with the principal liquid, where (i) the
   principal liquid has a surface tension at least 5% lower
   than the surface energy of the polymer, (ii) the second
   liquid has a surface tension at least 5% higher than the
10 surface energy of the polymer, (iii) the normal boiling point
   of the principal liquid is less than 125°C and the normal
   boiling point of the second liquid is less than about
   160°C, (iv) the polymer has a lower solubility in the second
   liquid than in the principal liquid, and (v) the solution
15 is prepared at a temperature less than about 20°C above the
   normal boiling point of the principal liquid and while
   precluding any substantial evaporation of the principal
   liquid. Next, (b) reducing the temperature of the solution
   by at least 5°C to between the normal boiling point of the
20 principal liquid and the temperature of the substrate upon
   the solution is to be cast. Finally, (c) casting the polymer
   solution onto a high surface energy substrate to form a
   liquid coating thereon, said substrate having a surface
   energy greater than the surface energy of the polymer,
25 and (d) removing the principal liquid and the second liquid
   from the coating by unidirectional mass transfer without
   use of an extraction bath, (ii) without re-dissolving the
   polymer, and (iii) at a maximum air temperature of less
   than about 100°C in a period of about 5 minutes, to form the
30 strong, highly porous, thin, symmetric polymer membrane.

5   In a third embodiment of the polymer membrane the

method for producing a symmetric, strong, highly porous,

microporous polymer membrane is by (a) dissolving about 3

to 20% by weight of a polymer in a heated multiple liquid

system comprising (a) a principal liquid which is a solvent

10   for the polymer and (b) a second liquid to form a polymer

solution, wherein (i) the principal liquid has a surface

tension at least 5% lower than the surface energy of the

polymer, (ii) the second liquid has a surface tension at

least 5% greater than the surface energy of the polymer;

15   and (iii) the polymer has a lower solubility in the second

liquid than it has in the principal solvent liquid.

Next, (b) reducing the temperature of the solution by at

least 5°C to between the normal boiling point of the

principal liquid and the temperature of the substrate upon

20   which it will be cast; (c) casting a film of the fully

dissolved solution onto a substrate which has a higher

surface energy than the surface energy of the polymer; (d)

precipitating the polymer to form a continuous gel phase

while maintaining at least 70% of the total liquid content

25   of the initial polymer solution. The precipitation caused

by a means selected from the group consisting of cooling,

extended dwell time, solvent evaporation, vibration, or

ultrasonics, and (e) removing the residual liquids without

causing dissolution of the continuous gel phase by

30   unidirectional mass transfer without any extraction bath,

at a maximum film temperature which is less than the normal

5   boiling point of the lowest boiling liquid, and within a

     period of about 5 minutes, to form a strong, highly porous,

     thin, symmetric polymer membrane.

         Each of the processes for producing the highly porous

10   polymer membrane begins with the formation of a solution of

     one or more soluble polymers in a liquid medium that

     comprises two or more dissimilar but miscible liquids. To

     form highly porous products, the total polymer

     concentration will generally be in the range of about 3 to

15   20% by weight. Lower polymer concentrations of about 3 to

     10% are preferred for the preparation of membranes having

     porosities greater than 70%, preferably greater than 75%,

     and most preferably greater than 80% by weight. Higher

     polymer concentrations of about 10 to 20% are more useful

20   to prepare slightly lower porosity membranes, i.e. about 60

     to 70%.

         A suitable temperature for forming the polymer

     solution generally ranges from about 40°C up to about 20°

25   above the normal boiling point of the principal liquid,

     preferably about 40 to 80°C, more preferably about 50°C to

     about 70°C. A suitable pressure for forming the polymer

     solution generally ranges from about 0 to about 50 psig.

     Preferably a sealed pressurized system is used.

30

         This polymer membrane requires the presence of at

     least two dissimilar but miscible liquids to form the

     polymer solution from which a polymer film is cast. The

     first "principal" liquid is a better solvent for the

35   polymer than the second liquid and has a surface tension at

5   least 5%, preferably at least 10%, lower than the surface
       energy of the polymer involved. The second liquid may be a
       solvent or a non-solvent for the polymer and has a surface
       tension at least 5%, preferably at least 10%, greater than
       the surface energy of the polymer. The invention does not
10   require and avoids the use of a special gelation medium.

           The principal liquid is at least 70%, preferably about
       80 to 95%, by weight of the total liquid medium. The
       principal liquid can dissolve the polymer at the
15   temperature and pressure at which the solution is formed.
       The dissolution will generally take place near or above the
       boiling temperature of the principal liquid, usually in a
       sealed container to prevent evaporation of the principal
       liquid. The principal liquid has a greater solvent strength
20   for the polymer than the second liquid. Also the principal
       liquid has a surface tension at least about 5%, preferably
       at least about 10%, lower than the surface energy of the
       polymer. The lower surface tension often leads to better
       polymer wetting and hence greater solubilizing power.
25

           The second liquid, which generally represents about 1
       to 10% by weight of the total liquid medium, must be
       miscible with the first liquid. It does not normally
       dissolve the polymer as well as the first liquid at the
30   selected temperature and pressure and it has a higher
       surface tension than the surface energy of the polymer.
       Preferably the second liquid does not wet the polymer at
       the gelation temperature though it may wet the polymer at
       more elevated temperatures.
35

5   This process for producing a highly porous membrane
     uses a unique liquid medium for forming the polymer
     solution. The liquid medium is rapidly removable at a
     sufficiently low temperature that the liquid removal does
     not cause the formed polymer gel to re-dissolve during the
10   liquid removal process. The liquid medium is devoid of
     plasticizers. The liquids that form the liquid medium are
     relatively low boiling point materials. Generally the
     liquids normally boil at temperatures less than about 125°C,
     preferably about 100°C and below. Somewhat higher boiling
15   point second liquids, i.e. up to about 160°C, may be used if
     at least about 60% of the total liquid medium is removable
     at a low temperature, e.g. less than about 50°C. The
     balance of the liquid medium can be removed at a higher
     temperature and/or under reduced pressure. Suitable
20   removal conditions depend upon the specific liquids,
     polymers, and concentrations utilized.

          Preferably the liquid removal is completed within a
     short period of time, e.g. less than 5 minutes, preferably
25   within about 2 minutes, and most prefer-ably within about
     1.5 minutes. Rapid low temperature liquid removal, prefer-
     ably using air flowing at a temperature of about 80°C and
     below, most prefer-ably at about 60°C and below, without
     immersion of the membrane into an-other liquid has been
30   found to produce a membrane with enhanced uniformity. The
     liquid removal is preferably done in a tunnel oven with an
     opportunity to remove and/or recover flammable, toxic or
     expensive liquids. The tunnel oven temperature is
     generally operated at a temperature less than about 90°C,
35   preferably less than about 60°C.

5

The polymer solution as formed may be supersaturated, but more commonly it will not be. When the solution is not initially supersaturated, it can become supersaturated upon cooling prior to film formation. Alternatively, it can
10 become supersaturated after film formation by means of evaporation of a portion of the principal liquid. In each of the these cases, a polymer gel is formed while there is still sufficient liquid present to generate the desired high void content in the resulting polymer film when that
15 remaining liquid is subsequently removed.

After the polymer solution has been prepared, it is then formed into a thin film. The film-forming temperature is preferably lower than the solution-forming temperature.
20 The film-forming temperature should be sufficiently low that a polymer gel will rapidly form. That gel must then be stable throughout the liquid removal procedure. A lower film-forming temperature can be accomplished, for example, by pre-cooling the substrate onto which the solution is
25 deposited, or by self-cooling of the polymer solution by controlled evaporation of a small amount of the principal liquid.

The film-forming step usually occurs at a lower
30 temperature (and often at a lower pressure) than the solution-forming step. Commonly, it occurs at or about room temperature. However, it can occur at any temperature and pressure if precipitation of the polymer is caused by means other than cooling, e.g. by slight drying, extended
35 dwell time, vibrations, or the like. Application as a thin

5   film allows the polymer to precipitate in a geometry
     defined by the interaction of the liquids of the solution.

        The thin film may be formed by any suitable means.
     Extrusion or flow through a controlled orifice or by flow
10   through a doctor blade is most common. The substrate onto
     which the solution is deposited should have a surface
     energy higher than the surface energy of the polymer.
     Examples of suitable substrate materials (with their
     surface energies) include copper (44 dynes/cm), aluminum
15   (45 dynes/cm), glass (47 dynes/cm), polyethylene
     terephthalate (44.7 dynes/cm), and nylon (46 dynes/cm).
     Preferably a metal, metallized or glass surface is used.
     More preferably the metallized surface is an aluminized
     polyalkylene such as aluminized polyethylene and aluminized
20   polypropylene.

        In view of the thinness of the films, the temperature
     throughout is thought to be relatively uniform, though the
     outer surface may be slightly cooler than the bottom layer.
25   Thermal uniformity may enable the subsequent polymer
     precipitation to occur in a more uniform manner.

        The polymer membranes should be cooled/dried in a
     manner that prevents coiling of the polymer chains. Thus
30   the cooling/drying should be conducted rapidly, i.e. within
     about 5 minutes, preferably within about 3 minutes, most
     preferably within about 2 minutes, because a rapid
     solidification of the spread polymer solution facilitates
     retention of the partially uncoiled orientation of the
35   polymer molecules when first deposited from the polymer
     solution.

5

The process of producing the polymer membranes entails producing a film of gelled polymer from the layer of polymer solution under conditions sufficient to provide a non-wetting, high surface tension solution within the layer

10   of polymer solution. Preferably gelation of the polymer into a continuous gel phase occurs while maintaining at least 70% of the total liquid content of the initial polymer solution. More particularly, the precipitation of the gelled polymer is caused by a means selected from the

15   group consisting of cooling, extended dwell time, solvent evaporation, vibration, or ultrasonics. Then, the balance of the liquids are removed by a unidirectional process, usually by evaporation, from the formed film to form a strong micro-porous membrane of geometry controlled by the

20   combination of the two liquids in the medium. The present invention of producing the highly porous separator avoids the use of a liquid bath to extract the liquids from the membrane. Rather, the liquid materials preferably evaporate at moderate temperatures, i.e. at a temperature

25   lower than that used for the polymer dissolution to prepare the polymer solution. The reduced temperature may be accomplished by the use of cool air or even the use of forced convection with cool to slightly warmed air to promote greater evaporative cooling.

30

The interaction among the two liquids (with their different surface tension characteristics) and the polymer (with a surface energy intermediate the surface tensions of the liquids) yields a membrane with high porosity and

35   relatively uniform pore size throughout its thickness. The surface tension forces act at the interface between the

5   liquids and the polymer to give uniformity to the cell
     structure during the removal step. The resulting product
     is a solid polymeric membrane with relatively high porosity
     and uniformity of pore size. The strength of the membrane
     is surprisingly high, due to the more linear orientation of
10   polymer molecules.

        The ratio of the principal liquid to the second liquid
     at the point of gelation needs to be such that the surface
     tension of the composite liquid phase is greater than the
15   surface energy of the polymer. For example, if the
     composite liquid phase (after partial evaporation of a
     portion of acetone as the principal liquid to cool the cast
     liquid and cause a supersaturated condition) contains 80 wt
     % acetone having a surface tension of 23.5 dynes/cm and 20
20   wt % of water as the second liquid having a surface tension
     of 72.5 dynes/cm yields a total surface tension of 33.3
     dynes/cm (18.8 + 14.5) based upon the weight fraction and
     53.3 based upon mol fraction.

25   Thermodynamic calculations show that adiabatic cooling
     of a solution can be significant initially and that the
     temperature gradient through such a film is very small (in
     contrast to concentration gradients of the prior art). The
     latter is thought responsible for the exceptional
30   uniformity obtained by the present invention of producing
     highly porous polymer membranes.

        Adiabatic cooling calculations based on the
     formulation of Example 1 below, show that the temperature
35   drop starts out at 3.1°C for each 1 percent of acetone that

41

5   evaporates from the film. The temperature gradient across
    a 500-micron thick wet film would then be 0.13°C for each 1%
    of acetone evaporated from the film. By the time that 4%
    of the acetone evaporates (presumed adiabatically) the
    temperature drop can be 12°C and the temperature gradient is
10 only 0.52°C. If the substrate is pre-cooled this
    temperature drop can be increased considerably while
    maintaining a low temperature gradient.

    After gelation has occurred, somewhat higher
15 temperatures can be used to facilitate removal of the
    remaining liquids therefrom, so long as the temperature is
    not so high that the gel re-dissolves. The maximum liquid
    removal temperature is preferably less than about 100°C,
    more preferably less than about 80°C, and most preferably
20 less than about 60°C.

    The polymers used to produce the microporous membranes
    of the present invention are organic polymers.
    Accordingly, the microporous polymers comprise carbon and a
25 chemical group selected from hydrogen, halogen, oxygen,
    nitrogen, sulfur and a combination thereof. Preferably,
    the composition of the microporous polymer includes a
    halogen. Preferably, the halogen is selected from the
    group consisting of chloride, fluoride, and a mixture
30 thereof.

    Suitable polymers for use herein are either semi-
    crystalline or a blend of at least one amorphous polymer
    and at least one crystalline polymer.
35

42

5   Preferred semi-crystalline are selected from the group
consisting of polyvinylidene fluoride, polyvinylidene
fluoride- hexafluoropropylene copolymer, polyvinyl
chloride, polyvinylidene chloride, chlorinated polyvinyl
chloride, polymethyl methacrylate, and mixtures of two or
10   more of these semi-crystalline polymers.

Preferably the products produced by the process of
this producing highly porous polymer membranes are used as
a battery separator. For this use, the polymer will most
15   commonly comprise a polymer selected from the group
consisting of polyvinylidene fluoride (PVDF),
polylvinylidene, fluoride-hexafluoropropylene copolymer
(PVDF-HFP), polyvinyl chloride, and mixtures thereof.
Still more preferably the polymer will comprise at least
20   about 75% polyvinylidene fluoride.

The "MacMullin" or "McMullin" Number measures
resistance to ion flow as defined in US Pat. No. 4,464,238,
the subject matter of which is incorporated herein by
25   reference. The MacMullin Number is "a measure of
resistance to movement of ions. The product of MacMullin
Number and thickness defines an equivalent path length for
ionic transport through the separator. The MacMullin Number
appears explicitly in the one-dimensional dilute solution
30   flux equations which govern the movement of ionic species
within the separator; it is of practical utility because of
the ease with which it is determined experimentally." The
lower a MacMullin Number the better for battery separators.
Products of the present invention have a low MacMullin
35   number, i.e. about 1.05 to 3, preferably about 1.1 to less
than 2, most prefer-ably about 1.2 to about 1.8.

5

Good tortuosity is an additional attribute of the
highly porous polymer membranes. A devious or tortuous
flow path with multiple interruptions and fine pores acts
as a filter against penetration of invading solids.
10   Tortuosity of the flow path can be helpful to prevent
penetration by loose particles from an electrode or to
minimize growth of dendrites through a separator that might
cause electrical shorts. This characteristic cannot be
quantified, except by long-term use, but it can be observed
15   qualitatively by viewing a cross-section of the porosity as
seen. Each orifice (many about 1 micron in diameter)
between adjacent voids represents a filter to capture loose
particles or a barrier to growth of dendrites.

20   The polymer membranes produced are generally uniform
and symmetric, i.e. the substrate side pores are
substantially similar in size to the central and the air
side pores. Pores which vary in diameter by a factor of
about 5 or less are sufficiently uniform for the membrane
25   to function in a symmetric manner. While some variation in
pore sizes is evident in the figures and it may be of merit
in an electrode separator where loose particles or
dendrites are a particular problem, generally the more
symmetric a membrane, the better performance as a battery
30   separator. Prior art asymmetric PVDF membranes have had
variations in pore sizes ranging from 10 to several
hundred.

Numerous polymer membranes have been prepared using
35   variations of the procedure of Example 1 and have provided
films with thickness ranging from about 15 to 100 microns,

5   with porosities up to 95%, with Gurley flow numbers as low
       0.1 second, and MacMullin numbers of 1.05 to 1.5.
       Permeabilities were as high as 1870 cm micron cpoise/minute
       Torr. Mercury porosimetry tests have shown the presence of
       some large pores ranging from 0.2 micron diameter up to 7

10   microns in different membranes, but with average pore sizes
       ranging from about 0.2 to 1.0 micron. Films have been
       produced with average pore diameters of 0.245 micron (85%
       porosity) and 0.398 microns (86% porosity). Prior art
       films have shown far smaller average pore diameters, e.g.

15   0.064 micron and correspondingly a far lower porosity
       (57%).

       The percentage of blind pores ranges from less than 1%
       to a maximum of 10% in some inferior films. Surface areas

20   are usually in the range of about 5 to 8 sq. meters/gm.

       Highly porous membranes have been cast directly onto
       battery electrodes and onto porous structures (e.g. non-
       woven films) thus obviating or facilitating mechanical

25   transfer. This permits higher porosity separators to be
       made without the necessity of high tensile strength and
       tensile modulus.

       Where additional strength or stiffness may be needed

30   for handling purposes, micro- or nano-particles can be
       added to the formulation with such particulates residing
       within the polymer phase. A few such additives include
       silica aerogel, talc, and clay.

35

5   The method for improving battery capacity can now best

be understood. The methods mentioned above produced the

highly dense electrode and the highly porous polymer

membrane which are utilized below.

10   3.   *Improving battery capacity using an optimized*

electrochemical cell

Battery capacity is increased by using the above

described methods in combination to produce an optimized

15   electrochemical cell. Specifically, the optimized

electrochemical cell is produced by first making a

positive, high density electrode, and a negative high

density electrode as described supra. Next, a symmetric,

strong highly porous, microporous polymer member is

20   produced using one of the preferred processes described

supra.

The natural result when discharging ions from the

second active material of the negative high density

25   electrode through the aprotic ion conducting liquid of the

second chamber is an increasing rate capability of the ion

flow. This is caused by reducing interfacial resistance to

ion flow, by increasing porosity of the polymer membrane

using the methods described supra by controlling pore size

30   and solids distribution, to levels below those at the

surface of the bulk components of the electrochemical cell.

5   Also, the interfacial resistance at an electrode and the
     separator must not exceed the value in the chambers. The
     ion conductivity of the separator must meet or exceed that
     in either or both electrodes. The ions are then accepted
     into the first active material of the positive high density
10   electrode of the first chamber through the protogenous ion
     conducting liquid. Recharging of the electrochemical cell
     is then possible by adding an energy source to the positive
     high density electrode and causing the ions to travel from
     the positive high density electrode of the first chamber
15   through the protogenous ion conducting liquid and the
     polymer membrane to the negative high density electrode of
     the second chamber. A secondary optimized electrochemical
     cell is thus created by repeating discharging of the ions
     and continuing the method.
20

       In conclusion, herein is presented an optimized
     microporous structure of electrochemical cells. The
     invention is illustrated by example in the drawing figures,
     and throughout the written description. It should be
25   understood that numerous variations are possible, while
     adhering to the inventive concept. Such variations are
     contemplated as being a part of the present invention.

5   CLAIMS

What is claimed is:

1. An optimized electrochemical cell, comprising:

10

          a housing divided into two chambers, a first and

          a second chamber, said first chamber containing

          protogenous ion-conducting liquid and a positive

          high density electrode including a first active

15   material and a porous binder, surrounded by a

          surface having a porosity level, wherein the

          porosity level increases towards the surface,

          said second chamber containing an aprotic, ion

          conducting liquid and a negative high density

20   electrode including a second active material and

          a porous binder, surrounded by a surface having a

          porosity level, wherein the porosity level

          increases towards the surface; and

25   a symmetric, strong, highly porous, microporous

          polymer membrane dividing the housing into said

          first and second chamber, and said polymer

          membrane having a porosity level.

30   2. The optimized electrochemical cell of claim 1, wherein
          the porosity level of the polymer membrane is greater

5   than the porosity level at the surface of the positive
       and negative high density electrodes.

3.   The optimized electrochemical cell of claim 2, wherein
       the polymer member has a porosity level 25% greater
10   than the porosity level at the surface of the positive
       and negative high density electrodes.

4.   A battery comprising a plurality of electrochemical
       cells as claimed in claim 3, connected thereto.

15

5.   An optimized electrochemical cell, comprising:

       a housing divided into two chambers, a first and
       a second chamber, said first chamber containing
20   protogenous ion-conducting liquid and a positive
       high density electrode including a first active
       material and a porous binder, surrounded by a
       surface having a porosity level, wherein the
       porosity level increases towards the surface,
25   said second chamber containing an aprotic, ion
       conducting liquid and a negative high density
       electrode including a second active material and
       a porous binder, surrounded by a surface having a
       porosity level, wherein the porosity level
30   increases towards the surface; and

5   a symmetric, strong, highly porous, microporous

           polymer membrane dividing the housing into said

           first and second chamber, and said polymer

           membrane having a porosity level, wherein the

           porosity level of the polymer membrane is greater

10   than the porosity level at the surface of the

           positive and negative high density electrodes and

           the porosity level of the polymer membrane is 25%

           higher than the porosity level of the high

           density electrodes.

15

     6. A battery comprising a plurality of electrochemical

        cells as claimed in claim 5, connected thereto.

     7. A method for improving battery capacity, using the

20   optimized electrochemical cell of claim 5, the steps

        comprising:

           (a) making a positive high density electrode;

25   (b) making a negative high density electrode;

           (c) producing a symmetric, strong, highly porous,

        microporous polymer membrane;

5   (d) discharging ions from second active material

           of the negative high density electrode through the

           aprotic ion conducting liquid of the second chamber;

           (e) increasing rate capability of the ion flow by

10   reducing interfacial resistance to ion flow by

           increasing porosity of the polymer membrane by

           controlling pore size and solids distribution; and

           (f) accepting ions into the first active material

15   of the positive high density electrode of the first

           chamber through the protogenous ion conducting

           liquid.

     8. The method of claim 7, further comprising the step of

20   (g) adding an energy source to the positive high

           density electrode and causing the ions to travel from

           said positive high density electrode of the first

           chamber through the protogenous ion conducting liquid

           and the polymer membrane to the negative high density

25   electrode of the second chamber.

     9. The method of claim 8, further comprising making a

           secondary optimized electrochemical cell by repeating

           steps (d) through (g).

30

5   8. The method of claim 7, the steps further comprising
          making the positive high density electrode by adding a
          binder to the first active material to form an
          unprocessed electrode material, mixing said first
          active material with said binder using a transport
10   medium, said first active material having a specific
          gravity that is at least 10 percent higher than a
          specific gravity of said transport medium, processing
          said unprocessed electrode material in a centrifuge to
          produce a processed electrode material, and
15   constructing said first processed electrode material
          into an electrochemical device.

       9. The method of claim 7, the steps further
          comprising making the negative high density electrode
20   by adding a binder to the second active material to
          form an unprocessed electrode material, mixing said
          second active material with said binder using a
          transport medium, said first active material having a
          specific gravity that is at least ten percent higher
25   than a specific gravity of said transport medium,
          processing said unprocessed electrode material in a
          centrifuge to produce a processed electrode material,
          and constructing said first processed electrode
          material into an electrochemical device.

30

5   10. The method of claim 7, the steps further comprising

the producing a symmetric, strong, highly porous,

microporous polymer film by (a)forming a layer of

a polymer solution on a substrate, wherein the

polymer solution comprises two miscible liquids and

10   a polymer material dissolved therein, and wherein the

two miscible liquids comprise(i)a principal liquid

that has a surface tension at least 5% lower than the

surface energy of the polymer and(ii)a second liquid

that has a surface tension at least 5% greater than

15   the surface energy of the polymer, (b)producing a

film of gelled polymer from the layer of polymer

solution under conditions sufficient to provide a non-

wetting, high surface tension solution within the

layer of polymer solution, and(c)rapidly removing the

20   liquid from the film of gelled polymer by

unidirectional mass transfer without dissolving the

gelled polymer to produce the strong, highly porous,

microporous polymer film.

25   11. The method of claim 7, the steps further comprising

producing a symmetric, strong, highly porous,

microporous polymer membrane by (a)preparing a

solution of one or more polymers in a mixture of a

principal liquid which is a solvent for the polymer

30   and a second liquid which is miscible with the

principal liquid, wherein (i)the principal liquid has

5   a surface tension at least 5% lower than the surface

energy of the polymer,(ii)the second liquid has a

surface tension at least 5% higher than the surface

energy of the polymer,(iii)the normal boiling point of

the principal liquid is less than 125°C and the normal

10   boiling point of the second liquid is less than about

160°C,(iv)the polymer has a lower solubility in the

second liquid than in the principal liquid, and (v)

the solution is prepared at a temperature less than

about 20°C above the normal boiling point of the

15   principal liquid and while precluding any substantial

evaporation of the principal liquid,(b) reducing the

temperature of the solution by at least 5°C to between

the normal boiling point of the principal liquid and

the temperature of the substrate upon the solution is

20   to be cast,(c)casting the polymer solution onto a high

surface energy substrate to form a liquid coating

thereon, said substrate having a surface energy

greater than the surface energy of the polymer, and

(d)removing the principal liquid and the second liquid

25   from the coating by unidirectional mass transfer

without use of an extraction bath, (ii) without re-

dissolving the polymer, and (iii) at a maximum air

temperature of less than about 100°C in a period of

about 5 minutes, to form the strong, highly porous,

30   thin, symmetric polymer membrane.

5   12. The method of claim 7, the steps further comprising

producing a symmetric, strong, highly porous,

microporous polymer membrane strong, thin, symmetric

microporous polymer membrane by (a) dissolving about 3

to 20% by weight of a polymer in a heated multi-ple

10   liquid system comprising (a) a principal liquid which

is a solvent for the polymer and (b) a second liquid

to form a polymer solution, wherein (i) the principal

liquid has a surface tension at least 5 % lower than

the surface energy of the polymer, (ii) the second

15   liquid has a surface tension at least 5% greater than

the surface energy of the polymer; and (iii) the

polymer has a lower solubility in the second liquid

than it has in the principal solvent liquid; (b)

reducing the temperature of the solution by at least

20   5°C to between the normal boiling point of the

principal liquid and the temperature of the substrate

upon which it will be cast; (c) casting a film of the

fully dissolved solution onto a substrate which has a

higher surface energy than the surface energy of the

25   polymer; (d) precipitating the polymer to form a

continuous gel phase while maintaining at least 70% of

the total liquid content of the initial polymer

solution, said precipitation caused by a means elected

from the group consisting of cooling, extended dwell

30   time, solvent evaporation, vibration, or ultrasonics;

and (e) removing the residual liquids without causing

5   dissolution of the continuous gel phase by

           unidirectional mass transfer without any extraction

           bath, at a maximum film temperature which is less than

           the normal boiling point of the lowest boiling liquid,

           and within a period of about 5 minutes, to form a

10   strong, highly porous, thin, symmetric polymer
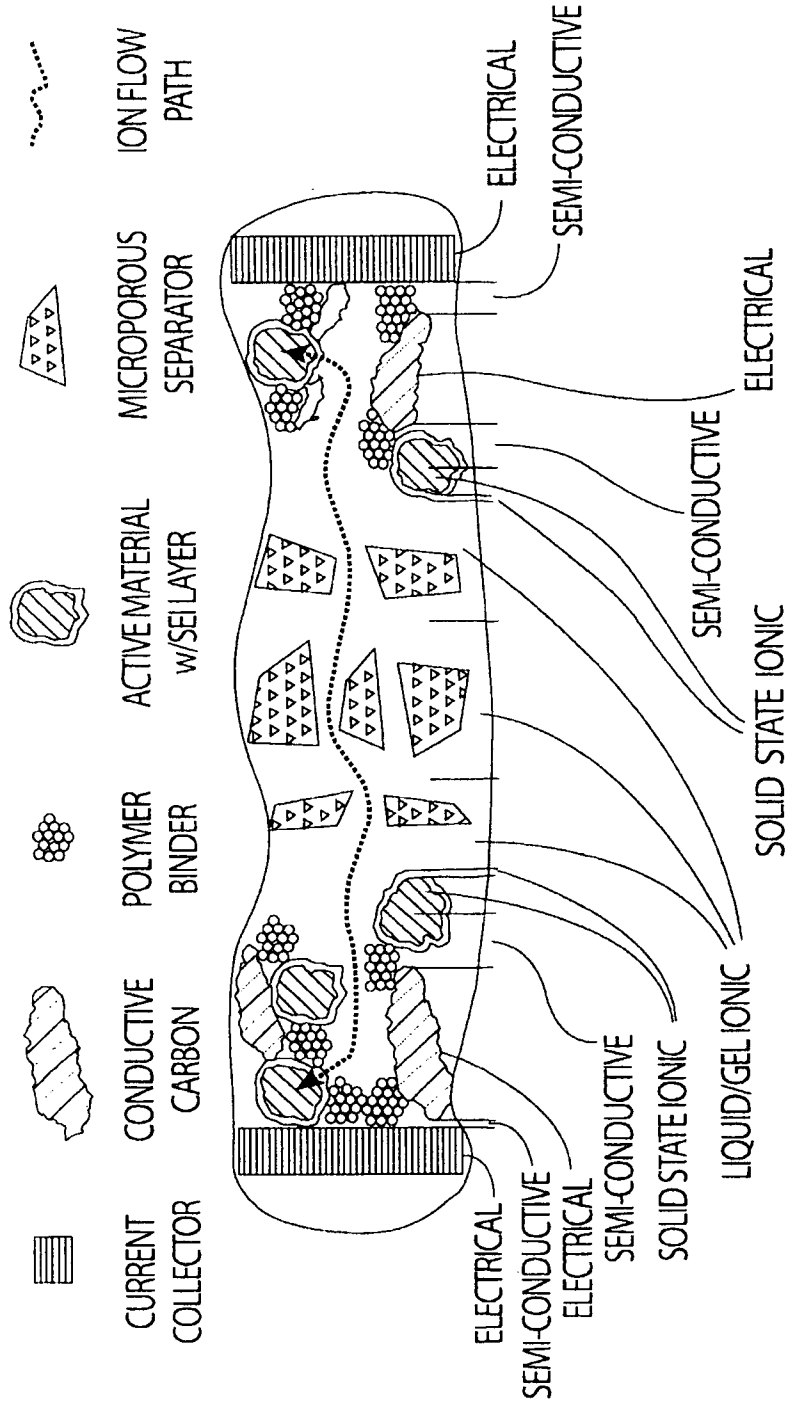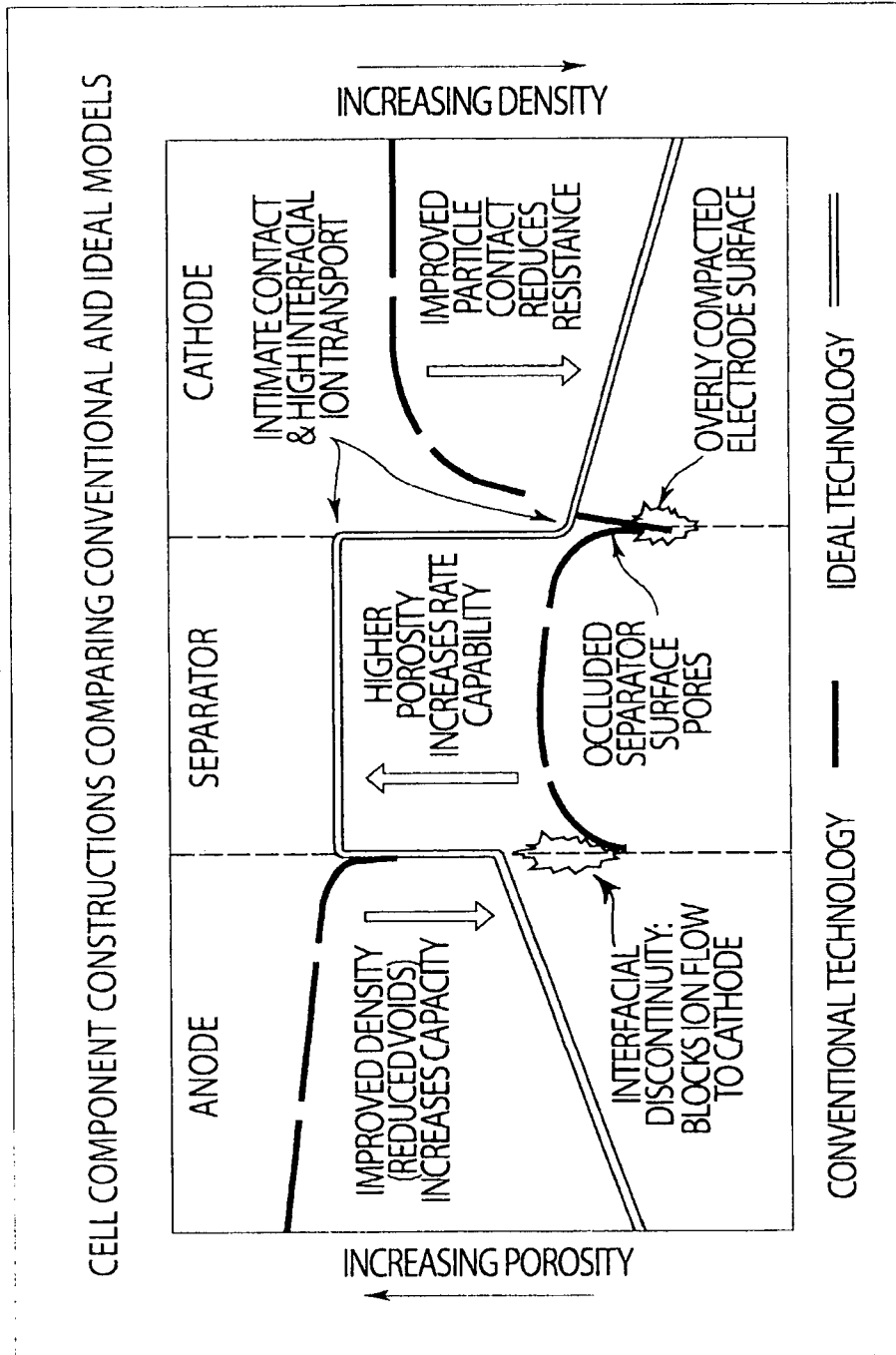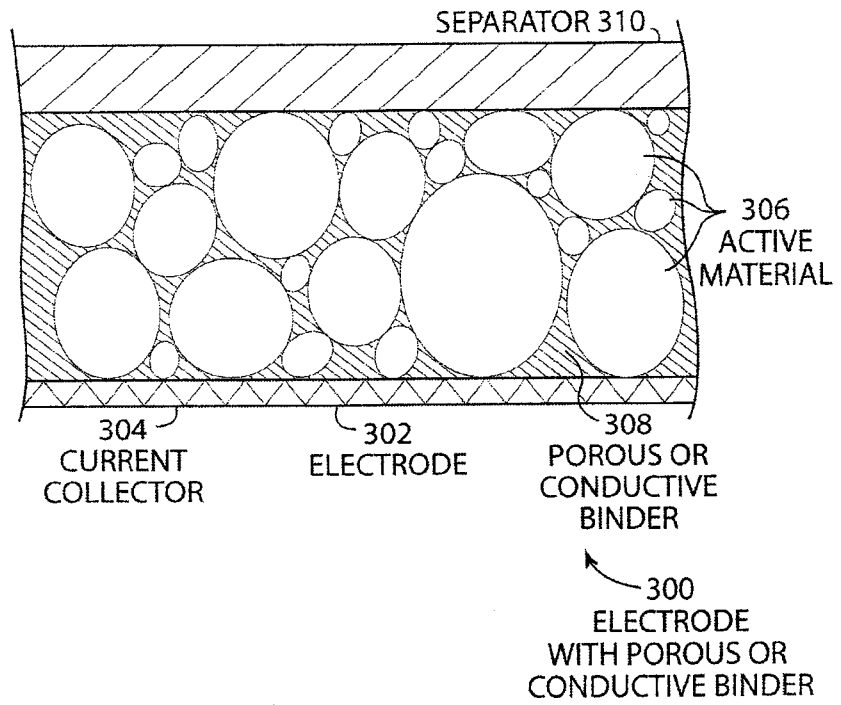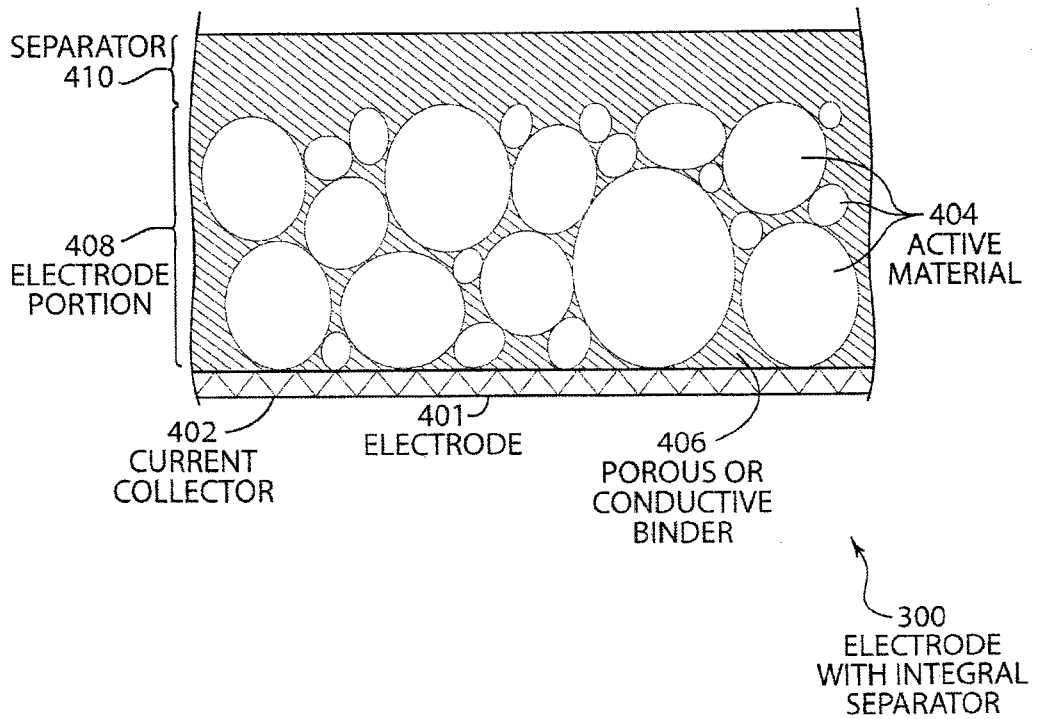
           membrane.

FIG. 1

FIG. 2

CELL COMPONENT CONSTRUCTIONS COMPARING CONVENTIONAL AND IDEAL MODELS

INCREASING DENSITY

CATHODE

INTIMATE CONTACT & HIGH INTERFACIAL ION TRANSPORT

IMPROVED PARTICLE CONTACT REDUCES RESISTANCE

OVERLY COMPACTED ELECTRODE SURFACE

SEPARATOR

HIGHER POROSITY INCREASES RATE CAPABILITY

OCCLUDED SEPARATOR SURFACE PORES

ANODE

IMPROVED DENSITY (REDUCED VOIDS) INCREASES CAPACITY

INTERFACIAL DISCONTINUITY: BLOCKS ION FLOW TO CATHODE

INCREASING POROSITY

CONVENTIONAL TECHNOLOGY _____

IDEAL TECHNOLOGY ======

SEPARATOR 310

306
ACTIVE
MATERIAL

304
CURRENT
COLLECTOR

302
ELECTRODE

308
POROUS OR
CONDUCTIVE
BINDER

300
ELECTRODE
WITH POROUS OR
CONDUCTIVE BINDER

FIG. 3

SEPARATOR
410

408
ELECTRODE
PORTION

404
ACTIVE
MATERIAL

402
CURRENT
COLLECTOR

401
ELECTRODE

406
POROUS OR
CONDUCTIVE
BINDER

300
ELECTRODE
WITH INTEGRAL
SEPARATOR

FIG. 4

FIG. 5