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(54) NANOPOROUS ELECTRODES AND RELATED DEVICES AND METHODS

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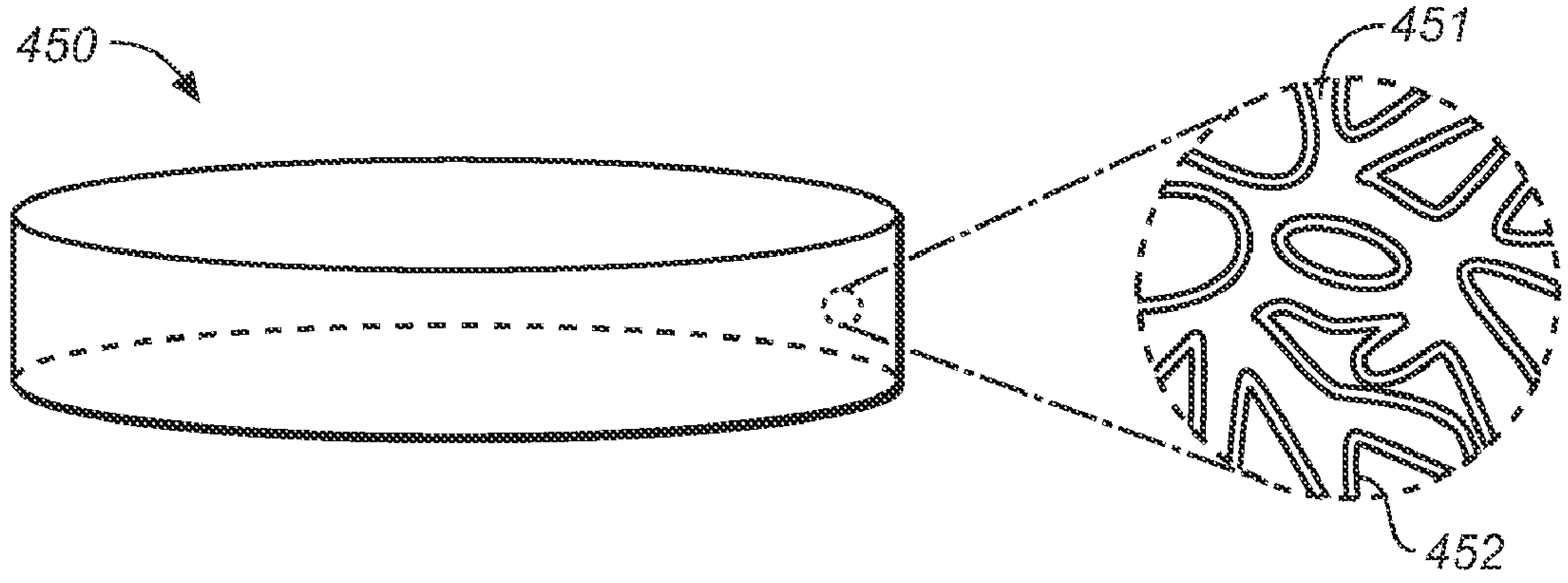
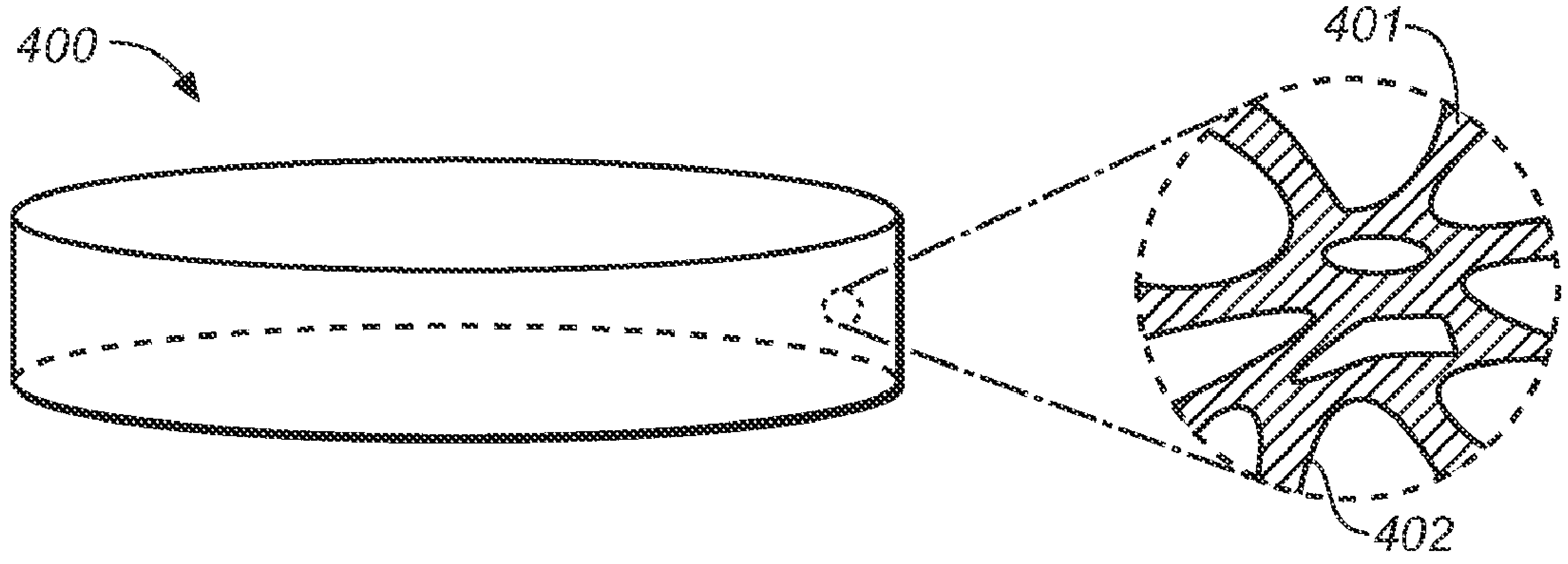
(57) ABSTRACT

High surface area electrodes formed using sol-gel derived monoliths as electrode substrates or electrode templates, and methods for making high surface area electrodes are described. The high surface area electrodes may have tunable pore sizes and well-controlled pore size distributions. The high surface area electrodes may be used as electrodes in a variety of energy storage devices and systems such as capacitors, electric double layer capacitors, batteries, and fuel cells.





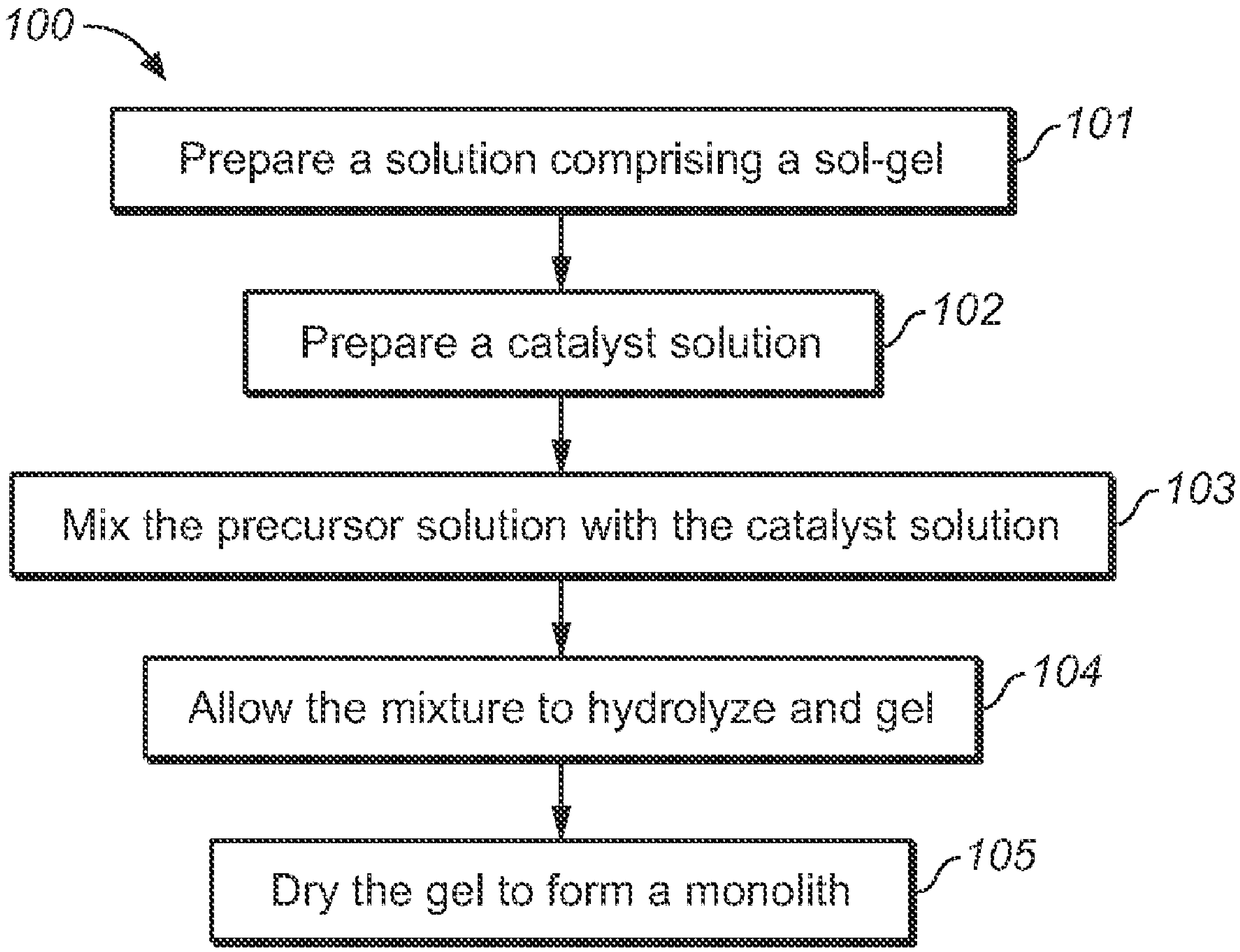
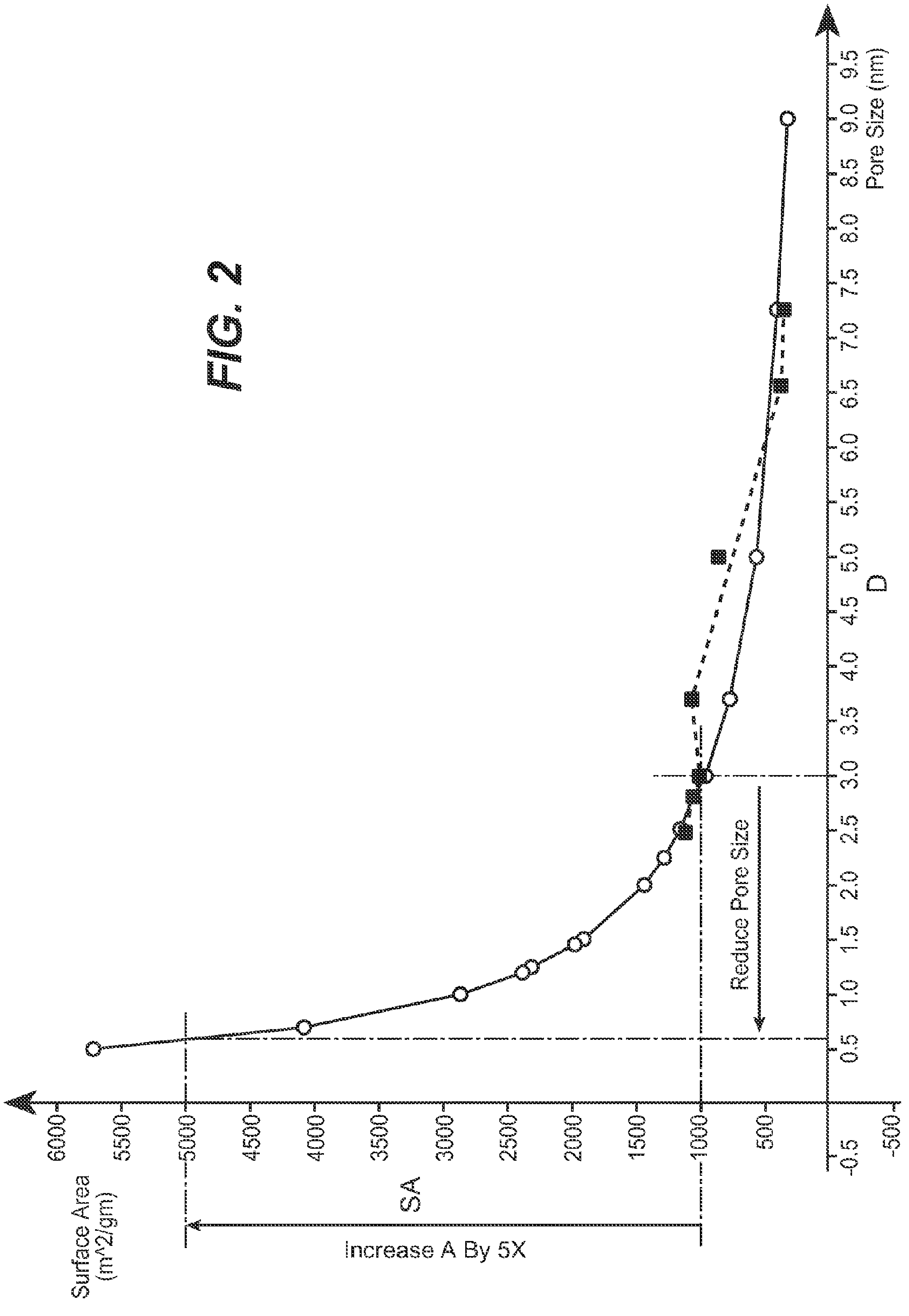

100
Prepare a solution comprising a sol-gel
101
Prepare a catalyst solution
102
Mix the precursor solution with the catalyst solution
103
Allow the mixture to hydrolyze and gel
104
Dry the gel to form a monolith
105

FIG. 1

FIG. 2


Surface Area (m^2/gm)
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
-500
SA
Increase A By 5X
-0.5
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
Pore Size (nm)
D
Reduce Pore Size

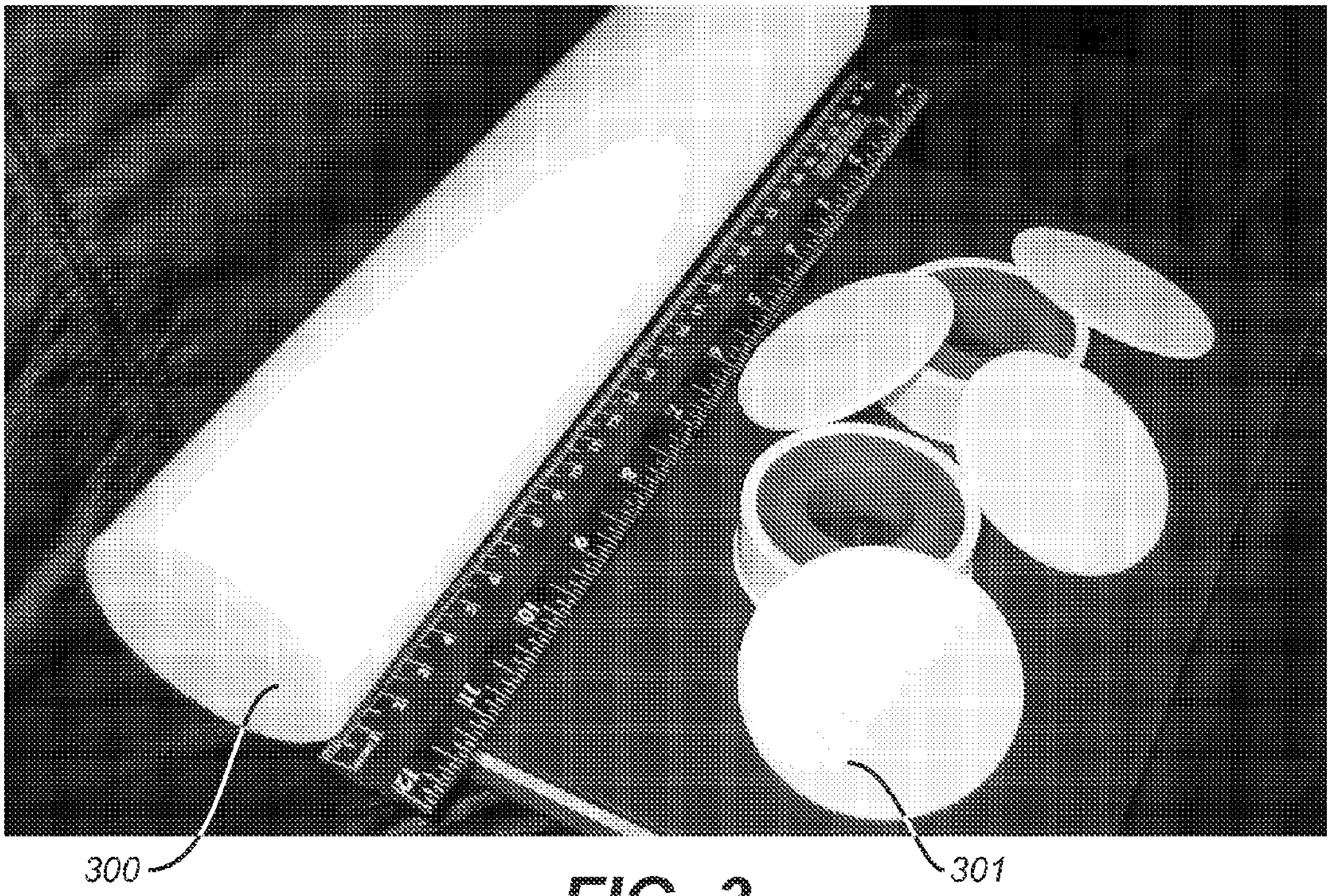


FIG. 3

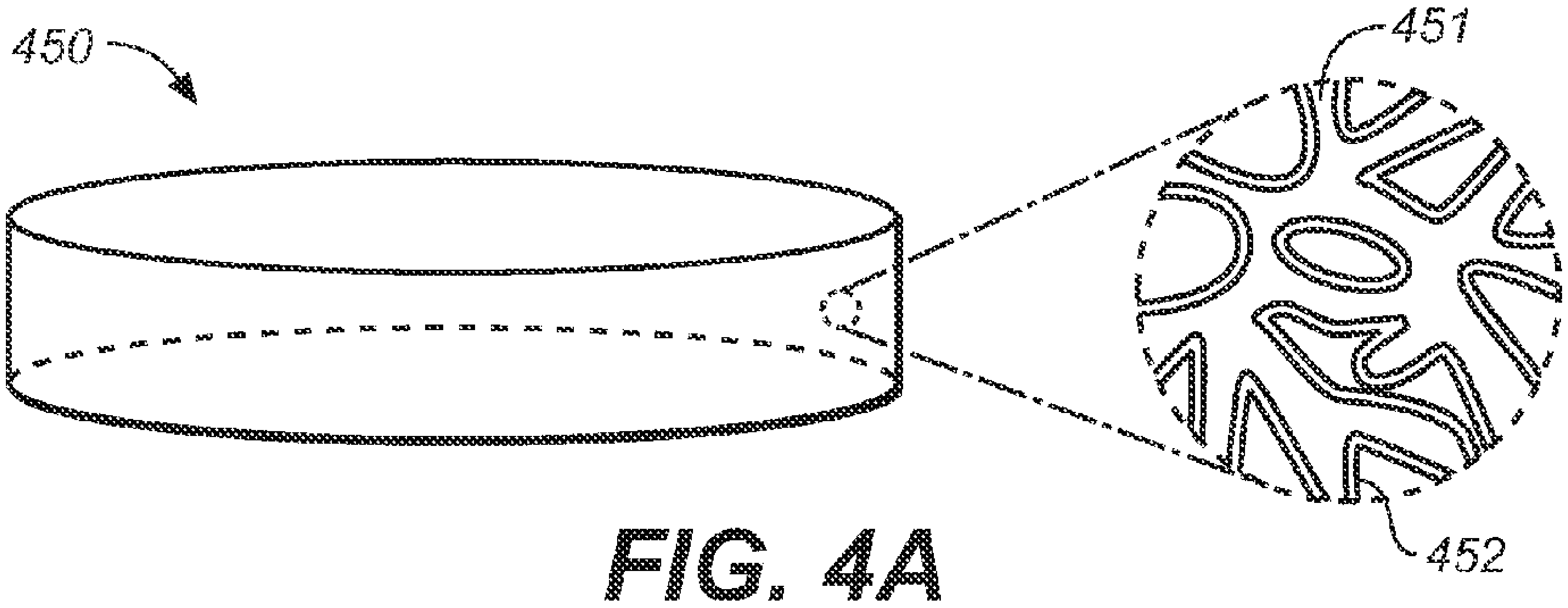


FIG. 4A

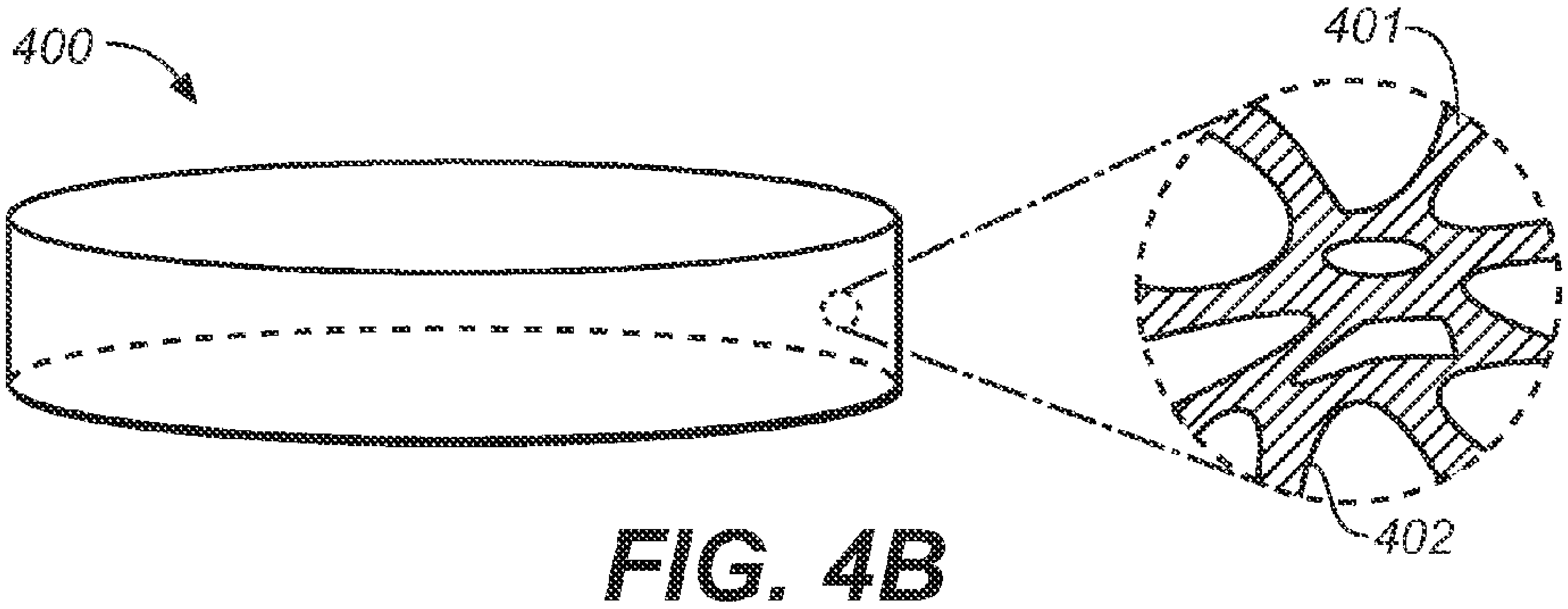


FIG. 4B

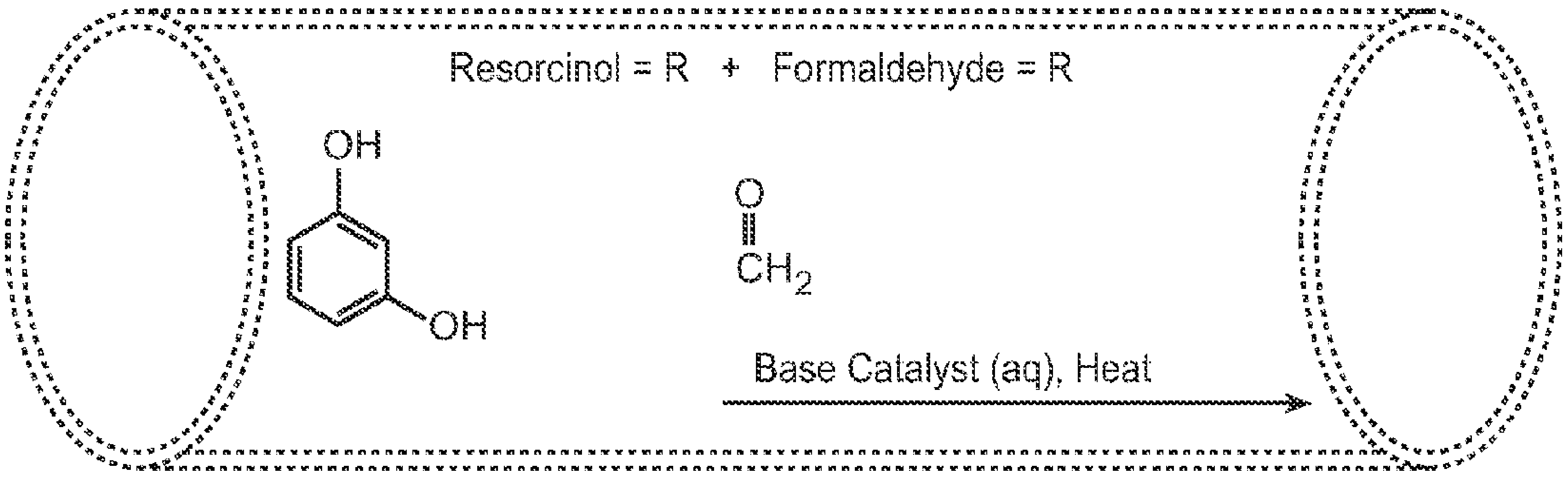


FIG. 5A

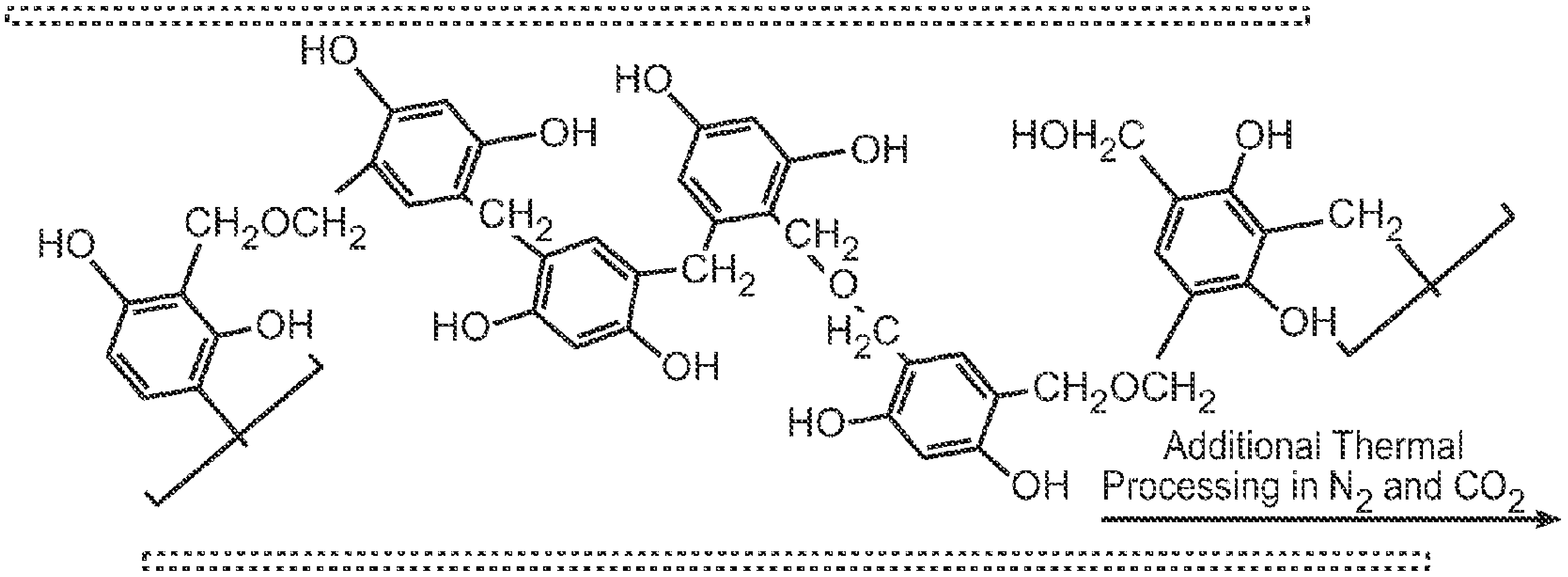


FIG. 5B

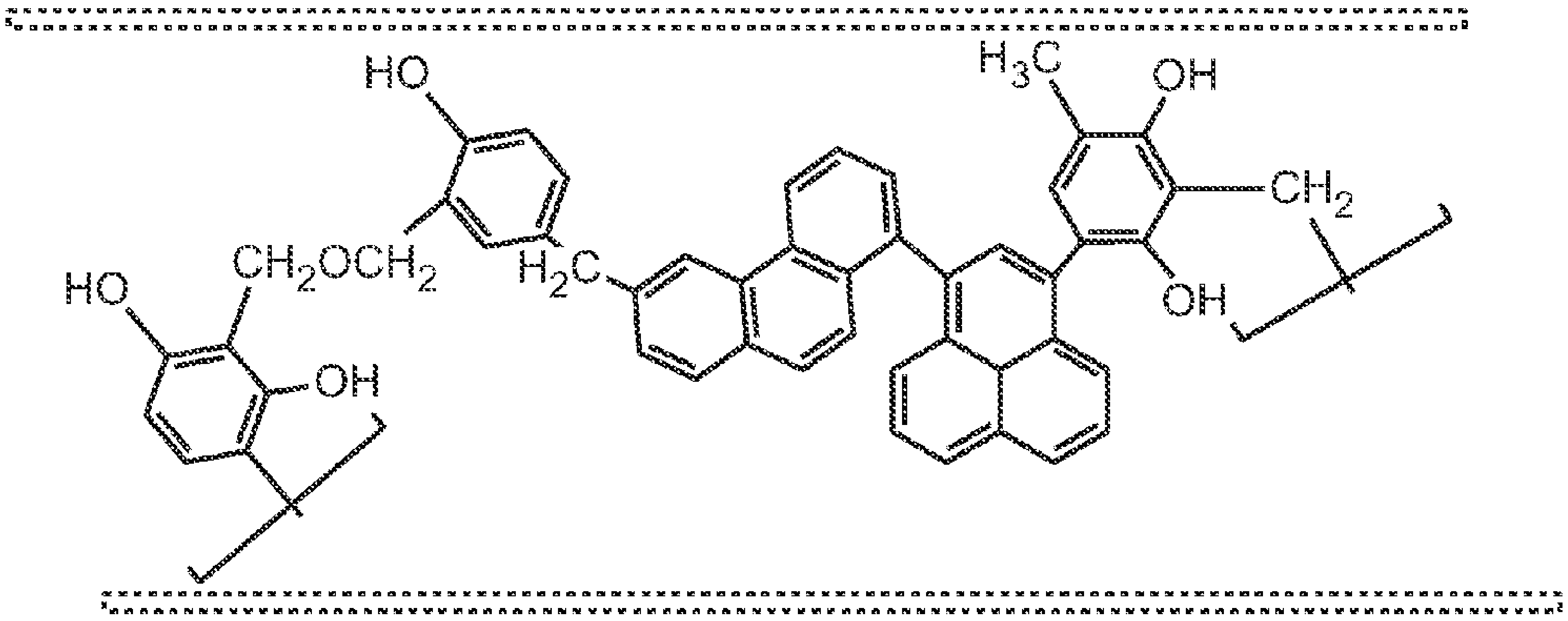


FIG. 5C

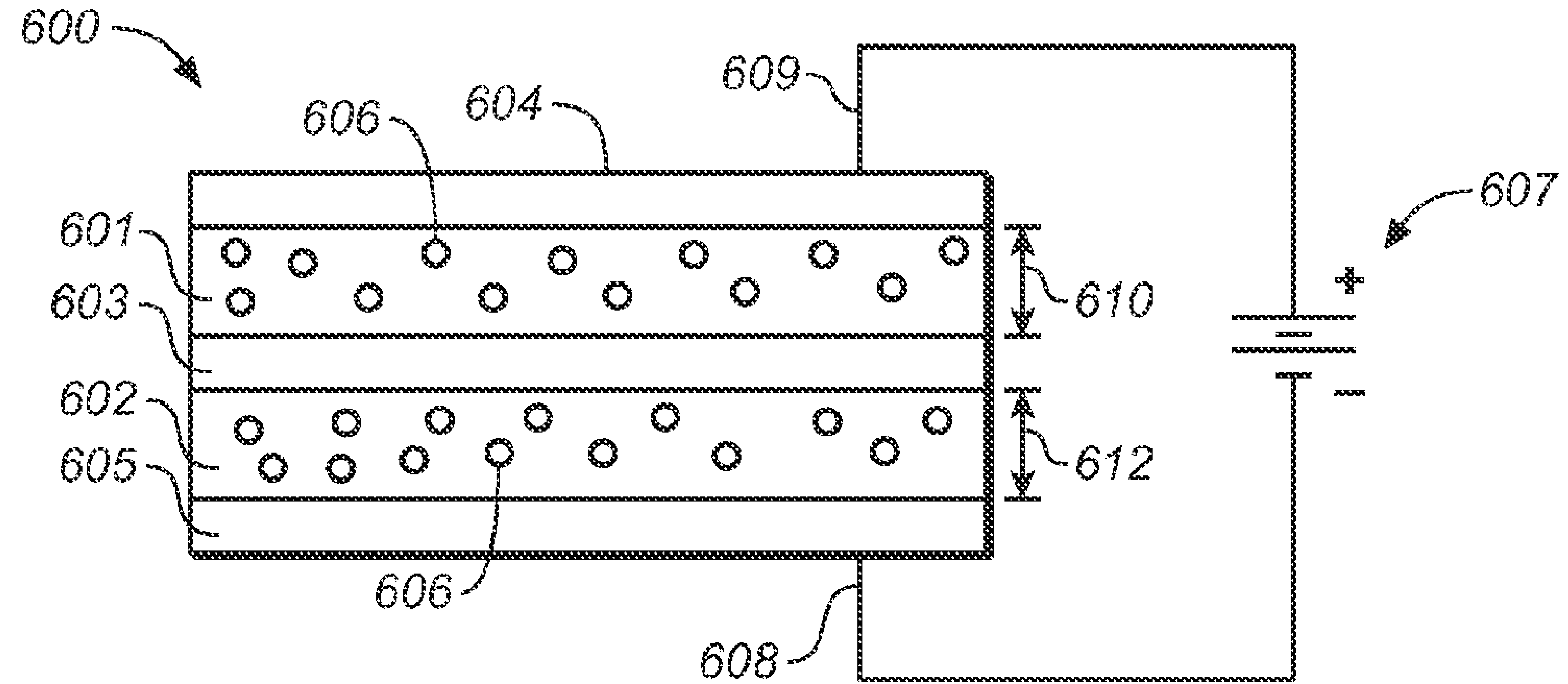


FIG. 6A

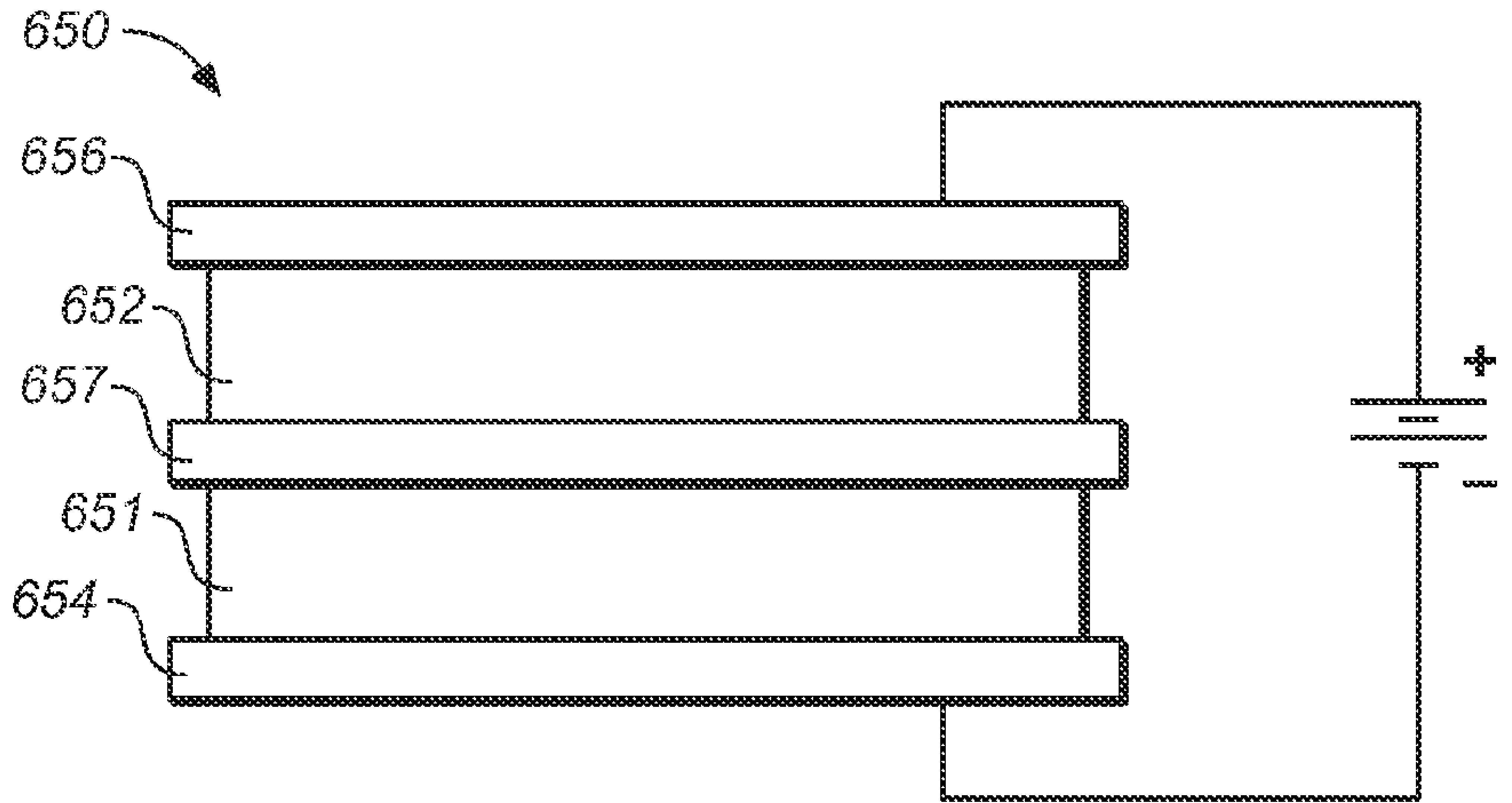


FIG. 6B

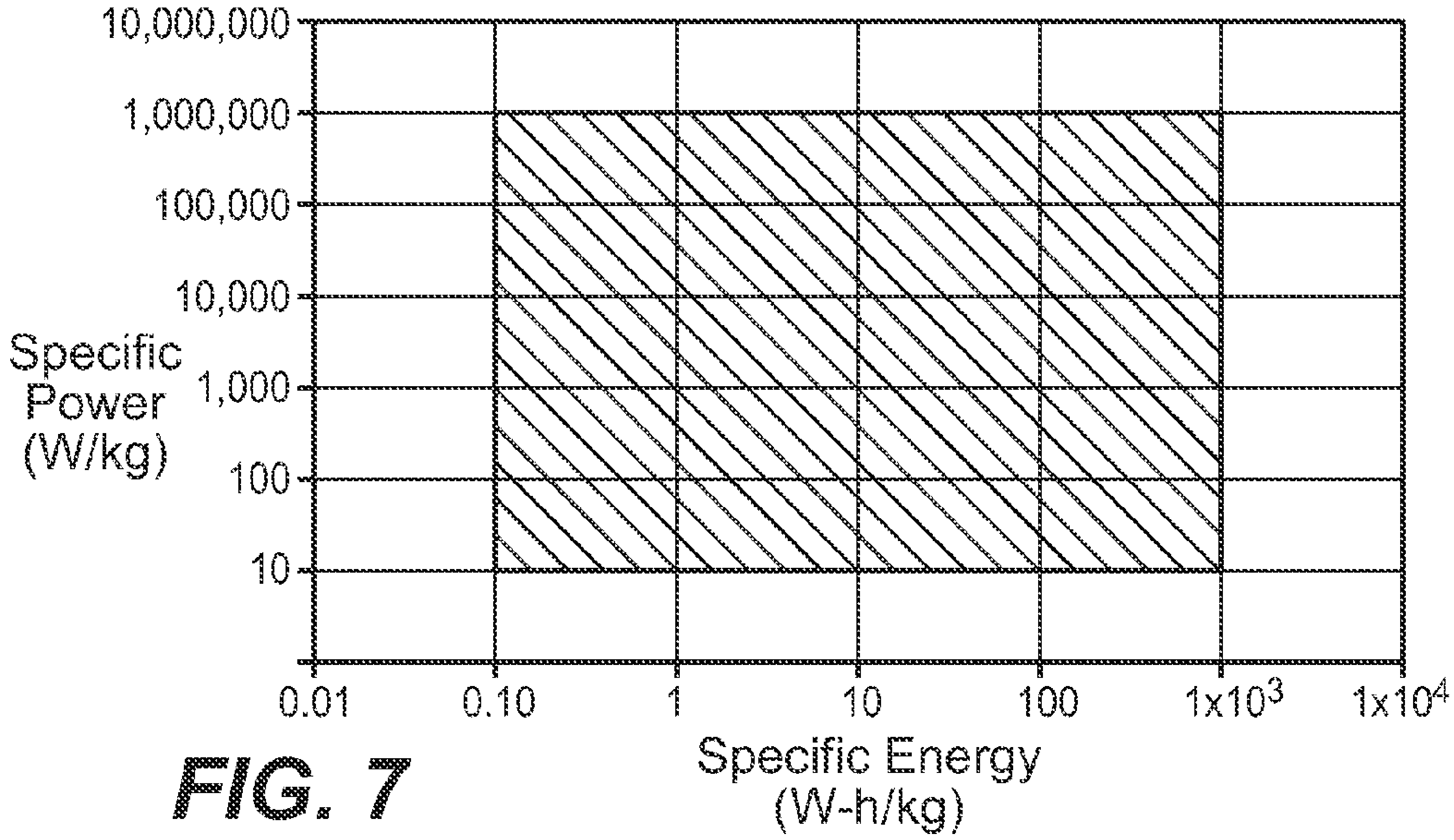


FIG. 7

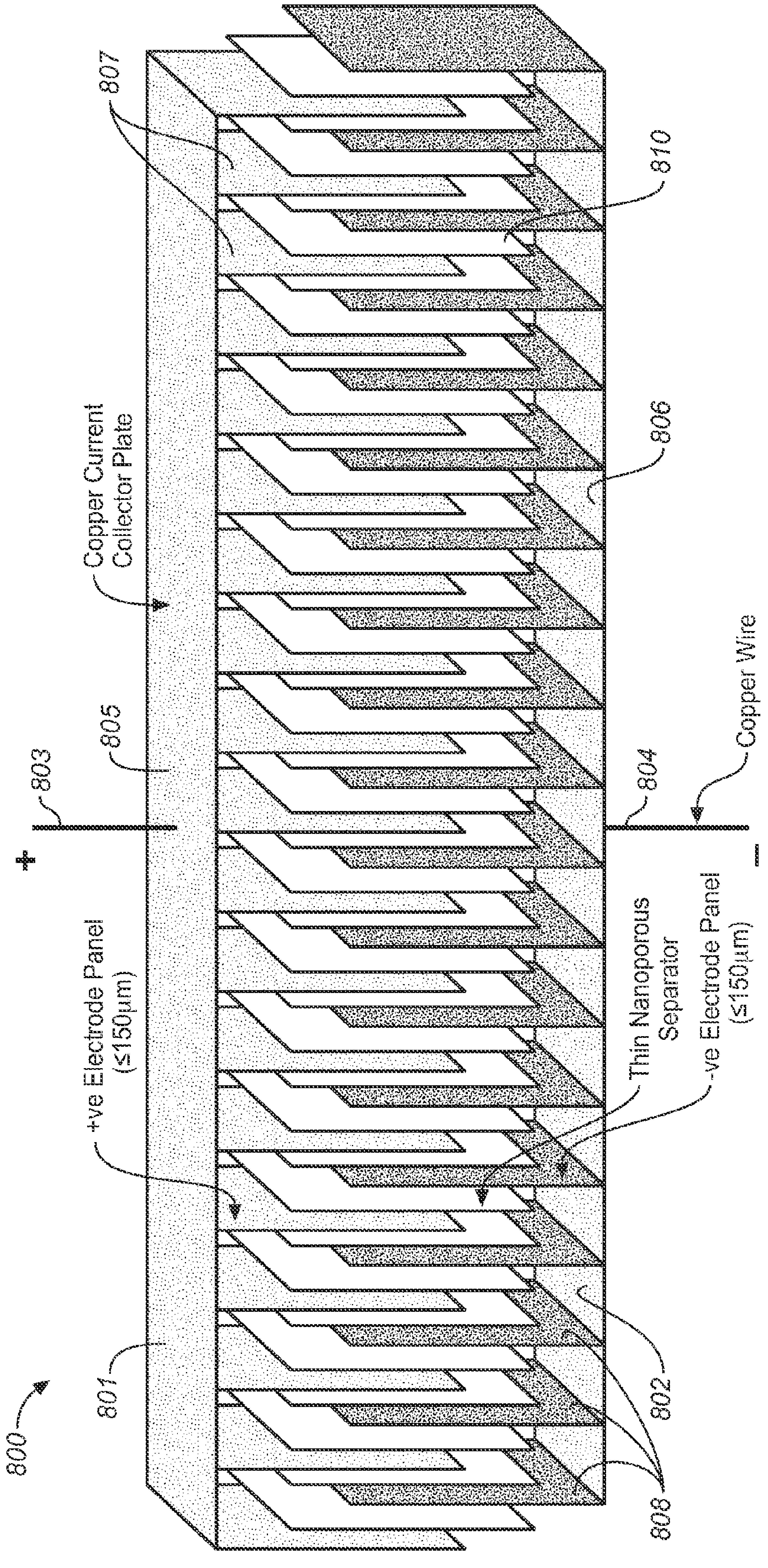

800
801
807
803
805
+
Copper Current Collector Plate
+ve Electrode Panel (≤150μm)
810
806
804
Copper Wire
−
Thin Nanoporous Separator
-ve Electrode Panel (≤150μm)
802
808

FIG. 8

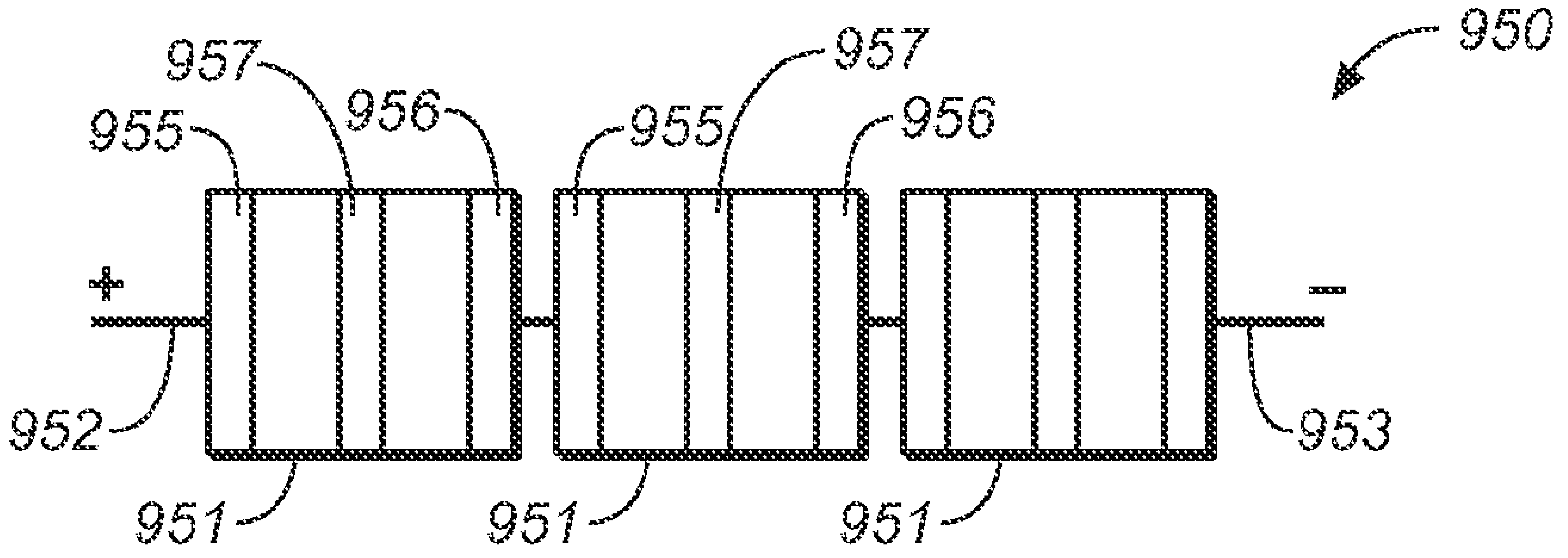

950
957
955
956
957
955
956
+
−
952
953
951
951
951

FIG. 9A

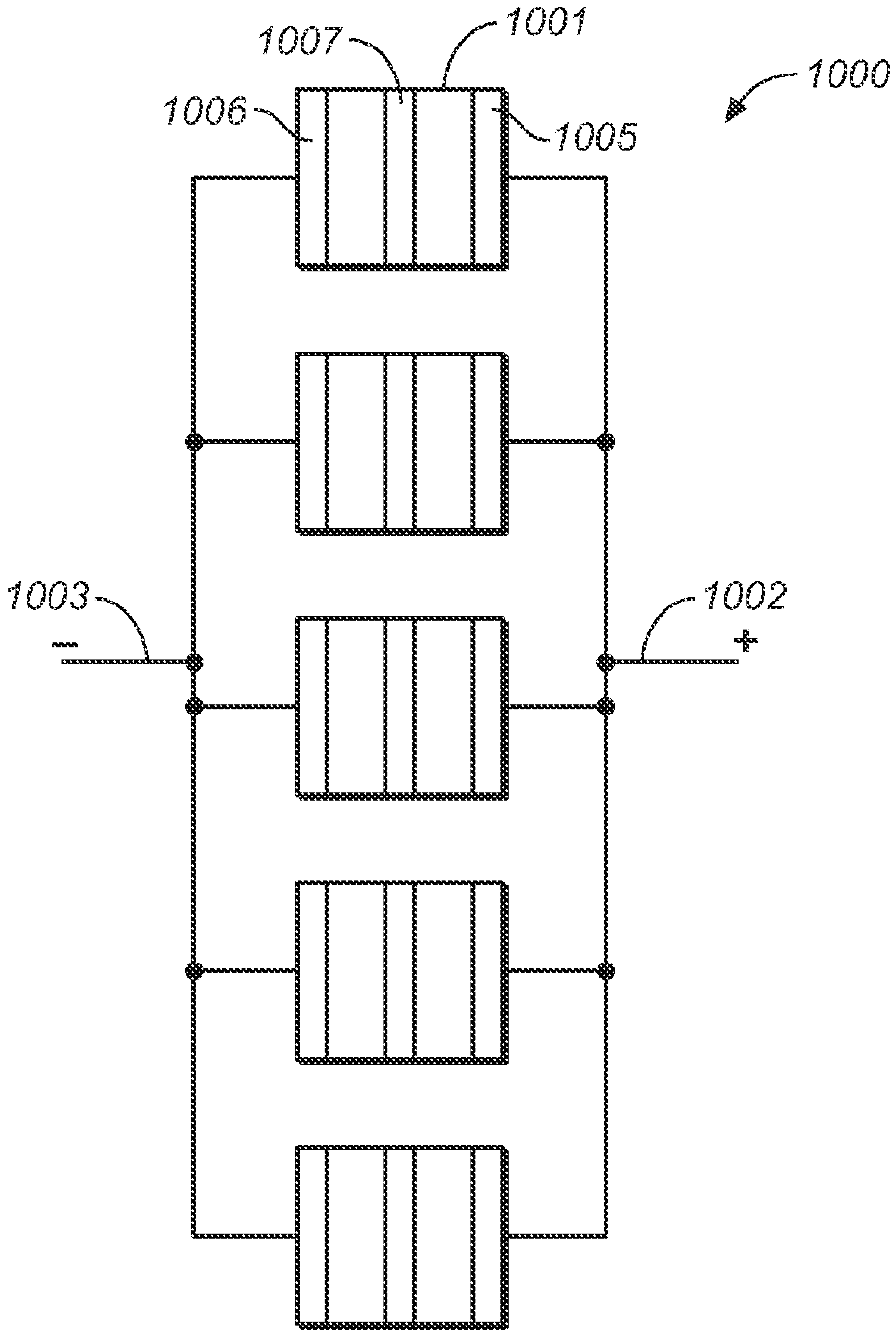
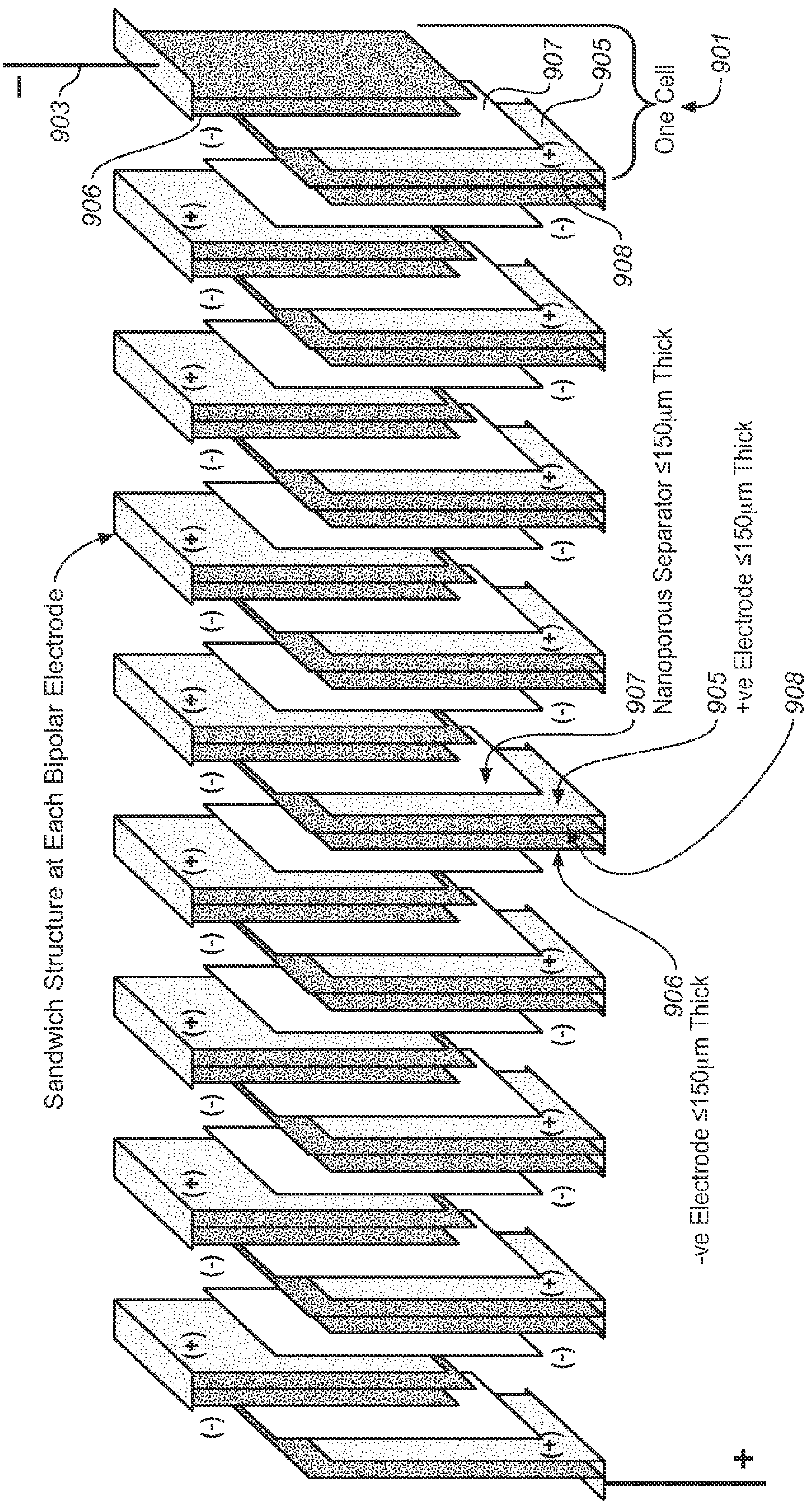

1007
1001
1000
1006
1005
1003
−
1002
+

FIG. 10



Each Bipolar Electrode is Sandwiched Between Non-porous Layers of Aluminum Foil (≤50μm Thick) Designed to Separate the Electrolyte Between Adjacent Cells

FIG. 9B

NANOPOROUS ELECTRODES AND RELATED DEVICES AND METHODS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the priority benefit of U.S. provisional patent application Ser. Nos. 61/060,451, filed Jun. 10, 2008, and 61/060,449, filed Jun. 10, 2008, which are incorporated in their entirety by reference.

FIELD OF THE INVENTION

[0002] Described herein are high surface area substrates that can be used to make high surface area electrodes for use in electrical energy storage devices, e.g., as electrodes in capacitors such as electric double-layer capacitors, or in fuel cells, or for battery electrodes.

BACKGROUND

[0003] A capacitor consists of two spaced apart electrodes with a potential applied between the electrodes. Capacitance (C) is a measure of charge (Q) stored on those electrodes at a given applied potential (V): C=Q/V. A dielectric may be inserted in between the two electrodes. The energy (E) stored by a capacitor is given by $(\frac{1}{2})\cdot CV^2$, which can be approximated by $E=\epsilon_0\epsilon_1 A/d$, where ϵ_1 is a permittivity of a medium between the electrodes, A is an effective cross-sectional area of the electrodes, and d is an effective spacing between the electrodes. Thus, to increase energy storage by a capacitor, a cross-sectional area of one or more electrodes can be increased, and/or a distance between electrodes can be decreased. Frequency-dependent equivalent series resistance (ESR) in a capacitor leads to internal heat losses. Thus, if ESR in a capacitor is reduced, power losses due to internal heat generation may be correspondingly reduced, leading to improved usable power (P) in that capacitor for a given applied voltage (V): $P=V^2/(4\cdot ESR)$.

[0004] Ultracapacitors, also known as supercapacitors or electric double layer capacitors (EDLC) comprise a cell that, in turn, comprises two electrodes immersed in an electrolyte with a separator or membrane that is permeable to ions in the electrode placed between the electrodes in the electrolyte to divide the cell into two sections. An insulating separator or membrane that is permeable to electrolyte ions may be placed in a liquid electrolyte between the electrodes to prevent the cell from shorting. As a potential is applied between the electrodes, electrolyte ions can diffuse to the surface of the electrode. No electron transfer takes place at either electrode surface; instead electrostatic interactions between the charged electrode surface and the electrolyte ions in solution build up an electric double layer at each electrode. Electrical energy is stored in the electric double layers from charge separation between the electrolyte ions and the charged electrodes. Each electrode in an EDLC is a capacitor distinguishing EDLCs from typical capacitors as described above. The very small distance between these separated charges can lead to storage of very high charge densities when high surface area electrodes are used.

[0005] Batteries rely on electrochemical reactions at electrodes. Here again, energy storage in a battery, e.g., a lithium ion battery, may in some cases be increased by increasing a surface area of an active material at an electrode surface.

[0006] Thus, a need exists for improved high surface area electrodes for energy storage devices, energy storage devices utilizing such improved high surface area electrodes, and energy storage devices exhibiting reduced equivalent series resistance.

SUMMARY

[0007] The invention provides nanoporous electrode materials, which are formed using sol-gel derived monoliths as electrode material substrates or electrode material templates. High surface area nanoporous electrodes formed using sol-gel derived monoliths as electrode substrates or electrode templates are also provided here. Any sol-gel derived monoliths may be used, but in some of the electrodes and related devices, methods and systems, the sol-gel derived monoliths may have tunable pore sizes, and well-controlled, narrow distributions of pore size distributions are possible. Thus, high surface area, nanoporous electrodes with tunable pore sizes and well-controlled pore size distributions may be formed by using the monoliths as substrates or templates for a conducting material. The high surface area nanoporous electrodes may be used as electrodes in a variety of energy storage devices such as capacitors, Electric Double Layer Capacitors (EDLC) (also referred to as ultracapacitors and supercapacitors), batteries, and fuel cells.

[0008] Some variations of the nanoporous electrode materials comprise sol-gel derived monolith which comprises an open network of pores, and a conductive material disposed on a surface of the open network of pores or partially filling the open network of pores to form a conductive network. Some variations of the nanoporous electrode materials comprise a conductive network which is obtainable or formed by a) coating a surface of an open network of pores in a sol-gel derived monolith, and b) selectively removing the material of the monolith to provide a conductive network. Some variations of the nanoporous electrode materials comprise a conductive powder which is obtainable or formed by a) coating a surface of an open network of pores in a sol-gel derived monolith with a conductive material, b) selectively removing the material of the monolith, and c) making the resulting material in step b) into a powder. Some variations of the nanoporous electrode materials comprise a conductive network which is obtainable or formed by a) at least partially filling an open network of pores in a sol-gel derived monolith with a conductive material, and b) selectively removing at least part of the material of the monolith. Some variations of the nanoporous electrode materials comprise a conductive powder which is obtainable or formed by a) at least partially filling an open network of pores in a sol-gel derived monolith with a conductive material, b) removing at least part of the material of the monolith, and c) making the resulting material in step b) into a powder.

[0009] Some variations of the nanoporous electrodes comprise a sol-gel derived monolith that, in turn, comprises an open network of pores, and a conductive material disposed on a surface of the open network of pores or partially filling the open network of pores to form a conductive network. Some variations of the nanoporous electrodes comprise a conductive network which is obtainable or formed by a) coating a surface of an open network of pores in a sol-gel derived monolith with a conductive material and b) selectively removing the material of the monolith. Some variations of the nanoporous electrodes comprise a conductive network which is obtainable or formed by a) at least partially filling an open network of pores in a sol-gel derived monolith with a conductive material, and b) selectively removing the material of the monolith. Some variations of the nanoporous electrodes are made using a conductive powder described herein.

[0010] The monolith used to form the electrode materials and the electrodes may be derived from any suitable sol-gel, e.g., a silica sol-gel. The conductive material may be derived from a non-conductive material, such as by converting one or more precursors to a conductive polymer. The conductive material may comprise any suitable material, e.g., graphite, graphite-like conductive carbon (carbide), graphene, a graphene-like material, carbon, activated carbon, conductive carbons derived from the polymerization and carbonization of carbon precursor materials like, furfural, furfuryl alcohol (2-furylmethanol), polyfurfuryl alcohol, resorcinol formaldehyde, sucrose, glucose, a metal (such as platinum, nickel, gold, palladium, molybdenum), a metal oxide (such as tin oxide, indium tin oxide, zinc oxide, molybdenum oxide, ruthenium oxide, tungsten oxide, manganese dioxide, silver oxide, nickel oxyhydroxide, aluminum doped zinc oxide, titanium oxide, vanadium pentoxide), sulfides (such as molybdenum sulfide, tungsten sulfide, iron sulfide), nitrides (such as tungsten nitride, molybdenum nitride), or combinations thereof, or conductive polymers (such as poly(3-methylthiophene)). As stated above, the electrodes may be used in an energy storage device such as a capacitor, an ultracapacitor, a fuel cell, or a battery.

[0011] The monoliths used in forming the electrode materials and the electrodes may be selected to have a preselected average pore size and/or a pore size distribution. For example, for electrodes that are to be used in an energy storage device utilizing an electrolyte, an average pore size or pore size distribution in the monolith may be selected to accommodate an ionic species contained in the electrolyte. In some applications, the sol-gel monolith may be selected to have an average pore size in a range from about 0.3 nm to about 300 nm, from about 0.3 nm to about 100 nm, from about 0.3 nm to about 30 nm, or from 0.3 nm to about 10 nm. In some variations of the electrodes, the monolith may comprise a pore size distribution where at least about 50% of the pores are within about 30% of an average pore size, within about 20% of an average pore size, or within about 10% of an average pore size.

[0012] The conductive surface area of the electrodes may be selected based on the intended application of the electrodes. For example, some electrodes may have a conductive surface area of at least about 50 m^2/g, at least about 100 m^2/g, at least about 500 m^2/g, at least about 700 m^2/g at least about 1000 m^2/g, or even higher, e.g., at least about 2000 m^2/g, at least about 2200 m^2/g, at least about 2500 m^2/g, at least about 3000 m^2/g, at least about 4000 m^2/g, or at least about 5000 m^2/g.

[0013] Energy storage devices are also provided herein. The energy storage devices may be capacitors, ultracapacitors, batteries, or fuel cells. In general, the energy storage devices comprise first and second electrodes, with an electrolyte disposed between the first and second electrodes. A separator is also disposed in the electrolyte between the first and second electrodes. If the energy storage device is a battery, capacitor, or ultracapacitor, the separator may be permeable to one or more ionic species of the electrolyte, but the separator may function to prevent electrical conduction between the electrodes. If the energy storage device is a fuel cell, the separator may comprise a proton exchange membrane. In the energy storage devices, any of the electrodes described herein may be used as the first electrode and/or the second electrode.

[0014] In some variations of the energy storage devices, the first electrode comprises a first conductive network formed from a sol-gel derived monolith by coating an open pore network of the monolith with a conductive material. In some variations, the second electrode may also comprise a second conductive network formed from a sol-gel derived monolith by coating an open pore network of the monolith with a conductive coating. The monoliths used in these electrodes may be derived from any suitable sol-gel, e.g., a silica sol-gel.

[0015] In some variations of the energy storage devices, the first electrode comprises a first conductive network formed from a sol-gel derived monolith by partially filling an open pore network of the monolith with a conductive material. In some variations, the second electrode may also comprise a second conductive network formed from a sol-gel derived monolith by partially filling an open pore network of the monolith with a conductive material. The monoliths used in these electrodes may be derived from any suitable sol-gel, e.g., a silica sol-gel.

[0016] In some variations of the devices, the sol-gel derived monolith used to form the conductive network may remain as part of the electrode to support the first conductive network. In other variations, the first conductive network and/or the second conductive network may be formed by using the sol-gel derived monolith as a template and subsequently removing completely or at least part of the material of the monolith so that the first conductive network is a stand-alone conductive network or a substantially stand-alone conductive network.

[0017] In some variations of the devices, the first electrode and/or the second electrode comprise a conductive network formed with a conductive powder which is obtainable or produced by a) coating a surface of an open network of pores or at least partially filling an open network of pores in a sol-gel derived monolith with a conductive material, b) selectively removing the material of the monolith, and c) making the resulting material in step b) into a powder.

[0018] As with the electrodes described above, the first conductive network (and the second conductive network, if present) in the energy storage devices may comprise graphite, graphite-like conductive carbon (carbide), graphene, a graphene-like material, carbon, activated carbon, conductive carbons derived from the polymerization and carbonization of carbon precursor materials like, furfural, furfuryl alcohol (2-furylmethanol), polyfurfuryl alcohol, resorcinol formaldehyde, sucrose or glucose, a metal or metal oxide such as platinum, nickel, gold, palladium, molybdenum, a metal oxide such as tin oxide, indium tin oxide, zinc oxide, molybdenum oxide, ruthenium oxide, tungsten oxide, manganese dioxide, silver oxide, nickel oxyhydroxide, aluminum doped zinc oxide, titanium oxide (e.g., titanium dioxide), vanadium pentoxide, sulfides such as molybdenum sulfide, tungsten sulfide, iron sulfide, nitrides such as tungsten nitride, molybdenum nitride, or combinations thereof, or conductive polymers such as poly(3-methylthiophene).

[0019] In some variations of the energy storage devices, at least one of an average pore size and a pore size distribution in the sol-gel derived monolith may be selected based on a dimension of an ionic species in the electrolyte. An average pore size in a monolith may be selected in a range from about 0.3 nm to about 300 nm, about 0.3 nm to about 100 nm, about 0.3 nm to about 30 nm, or about 0.3 nm to about 10 nm. In certain variations, at least about 50% of pores in the monolith may be within about 30%, or within about 20% of an average pore size. The first electrode in the devices may for example have a conductive surface area that is at least about 50 m^2/g, at least about 100 m^2/g, at least about 150 m^2/g, at least about 200 m^2/g, at least about 500 m^2/g, at least about 700 m^2/g, at least about 1000 m^2/g, or even higher, e.g., at least about 2000 m^2/g, at least about 3000 m^2/g, at least about 4000 m^2/g, or at least about 5000 m^2/g.

[0020] Some of the energy storage devices described here may be ultracapacitors that have a specific energy of about 0.1 W-h/kg to about 1000 W-h/kg, e.g., at least about 0.1 W-h/kg, at least about 1 W-h/kg, at least about 10 W-h/kg, at least about 30 W-h/kg, at least about 50 W-h/kg, at least about 100 W-h/kg, at least about 120 W-h/kg, at least about 150 W-h/kg, at least about 170 W-h/kg, at least about 190 W-h/kg, at least about 200 W-h/kg, at least about 300 W-h/kg, at least about 400 W-h/kg, at least about 500 W-h/kg, or as high as about 1000 W-h/kg. Ultracapacitors described here may have a specific power of about 10 W/kg or higher, e.g., about 10 W/kg, about 50 W/kg, about 100 W/kg, about 500 W/kg, about 1 kW/kg, about 5 kW/kg, about 10 kW/kg, about 50 kW/kg, about 100 kW/kg, or even higher.

[0021] Asymmetric ultracapacitors are disclosed herein. In general, the asymmetric ultracapacitors comprise a first electrode configured to store charge electrostatically, a second electrode configured to store charge via a reversible faradaic process, an electrolyte disposed between the first and second electrodes, and a separator that is permeable to the electrolyte also disposed between the first and second electrodes. In an asymmetric capacitor, the first electrode may be derived from a sol-gel monolith comprising an open pore network coated or at least partially filled with a conductive material suitable for electrostatic charge storage and discharge, and/or the second electrode may be derived from a sol-gel monolith comprising an open pore network coated or at least partially filled with a conductive material suitable for faradaic charging and discharging. Any other electrodes described herein may also be used for the first electrode and/or the second electrode.

[0022] The energy storage devices described herein may be used in a variety of applications, e.g., to provide back up power in electronic devices such as computers or to function as rechargeable power sources in handheld devices. Ultracapacitors as disclosed here may be used in hybrid electric engines such as those used in hybrid electric vehicles. For example, ultracapacitors may be used for load-leveling to extend the life of a battery, to supply power to augment peak power delivery of the battery during startup or acceleration, or to power auxiliary functions such as power steering, power windows, or lighting.

[0023] Methods for making nanoporous electrode materials and electrodes are described here. In general, these methods comprise providing a sol-gel derived monolith that, in turn, comprises an open network of pores, and coating a surface of the open network of pores or at least partially filling the network of pores with a conductive material to form a conductive network. The methods may further comprise a step of removing completely or partially the material of the monolith to create a stand-alone conductive network or substantially stand-alone conductive network. Methods of making electrodes using conductive nanoporous powder are also described. In some variations, the methods comprise a) coating a surface of the open network of pores in a sol-gel derived monolith or at least partially filling the network of pores in a sol-gel derived monolith with a conductive material to form a conductive network; b) removing completely or partially the material of the monolith to create a stand-alone conductive network or substantially stand-alone conductive network; c) making the resulting material in step b) into a conductive powder; and d) using the powder to make an electrode. For example, the electrode may be made by mixing the conductive powder with a binder, and drying the mixture on a surface to form a film. The methods may be used to make an electrode for a capacitor, an ultracapacitor, a battery, or a fuel cell. The monoliths used in the methods may be derived from any suitable sol-gel, but in some variations, the monoliths are derived from silica sol-gels.

[0024] Some of these methods for making electrodes may comprise selecting the sol-gel derived monolith to have a predetermined average pore size and/or pore size distribution, e.g., an average pore size and/or pore size distribution selected to accommodate an ionic species of the electrolyte. For example, the methods may comprise selecting monoliths having an average pore size in a range from about 0.3 nm to about 300 nm, about 0.3 nm to about 100 nm, about 0.3 nm to about 30 nm, or about 0.3 nm to about 10 nm. Further, monoliths may be selected to have a pore size distribution such that at least about 50% of pores are within about 30%, or within about 20% of an average pore size.

[0025] The methods for making an electrode may comprise slicing a sol-gel wafer from a sol-gel derived monolith, and coating a surface of the open network of pores or at least partially filling the open network of pores in the wafer to make a conductive network. These methods may comprise slicing a sol-gel wafer having a thickness of about 1 mm or less, e.g., about 800 microns, about 500 microns, about 250 microns, about 200 microns, about 150 microns, or about 100 microns. The wafers may also be made by methods comprising casting the gel formulation into a mold or container comprising multiple slots, wherein each slot comprising opposing parallel sidewalls and hydrophobic inner surfaces, and shrinking the gel in the slots to form a sol-gel derived monolith.

[0026] Some methods for making electrodes may comprise forming a sol-gel derived monolith having a preselected average pore size and/or a pore size distribution by reacting a sol-gel precursor with water in the presence of a catalyst, and controlling a rate of gelation with the catalyst. The catalyst may comprise hydrofluoric acid and, in some cases, the catalyst may comprise a second acid in addition to the hydrofluoric acid. A molar ratio of hydrofluoric acid to the precursor may be increased to increase an average pore size. If present, the second acid may be any suitable acid, but in some variations may be selected from the group consisting of HCl, HNO_3, H_2SO_4, organic acids, and combinations thereof. In some cases, the second acid may be a weak acid having a first pK_a that is about 2 or greater, e.g., about 2 to about 5, or about 2 to about 4.

[0027] In the methods, coating the surface of the open pore network may comprise synthesizing a layer of graphite or a layer of a graphite-like material (e.g., conductive carbon) on the surface, e.g., by polymerizing a polymer material made from the precursors resorcinol and formaldehyde, furfural, furfuryl alcohol (2-furylmethanol), polyfurfuryl alcohol, sucrose or glucose on the surface of the open pore network. In certain variations, coating the surface may comprise depositing a conductive species, e.g., a metal and/or a metal oxide, on the surface using chemical vapor deposition and/or atomic layer deposition. In some circumstances, the open pore network may be impregnated with a colloidal solution of a metal, the monolith may be dried to remove liquid from the colloidal solution, and the metal particles may be coalesced together, e.g., by melting or using rapid thermal processing, to form the conductive network in the open pore network.

[0028] The methods may comprise coating the surface of the open pore network to provide a conductive surface area of at least about 50 m^2/g, at least about 100 m^2/g, at least about 150 m^2/g, at least about 200 m^2/g, at least about 250 m^2/g, at least about 300 m^2/g, at least about 400 m^2/g, at least about 500 m^2/g, at least about 800 m^2/g, at least about 1000 m^2/g, or even higher, e.g., at least about 1200 m^2/g, at least about 1500 m^2/g, at least about 1800 m^2/g, at least about 2000 m^2/g, or even higher, e.g., at least about 3000 m^2/g, at least about 4000 m^2/g, or at least about 5000 m^2/g.

[0029] Additional methods of making electrodes are provided here. In general, these methods comprise providing a sol-gel derived monolith comprising an open pore network, coating or at least partially filling the open pore network with a conductive material, and selectively removing the sol-gel derived monolith to provide a conductive electrode. In some variations, at least partially filling comprises impregnating a material into the open pore network, and subsequently converting the material into a conductive material. These methods may be used to make an electrode for a capacitor, an ultracapacitor, a battery, or a fuel cell.

[0030] The sol-gel derived monoliths used in these methods may be selected to have an average pore size in a range from about 0.3 nm to about 300 nm, about 0.3 nm to about 100 nm, about 0.3 nm to about 30 nm, or about 0.3 nm to about 10 nm. Further, for any average pore size, the sol-gel derived monoliths may be selected to have a pore size distribution such that at least about 50% of pores in the monolith have a pore size that is within about 30% of the average pore size, within about 20% of the average pore size, or within about 10% of the average pore size.

[0031] In these methods, at least partially filling the open pore network may comprise impregnating the open pore network with a colloidal solution comprising conductive particles, e.g., metal and/or metal oxide particles. In other variations, at least partially filling the open pore network may comprise impregnating the open pore network with one or more precursors to a conductive polymer, and polymerizing the one or more precursors in situ to form a conductive electrode comprising the conductive polymer.

[0032] In the methods, impregnating the open pore network may comprise synthesizing graphite or a graphite-like material (e.g., conductive carbon) within the pore structure, e.g., by polymerizing a polymer material made from the precursors resorcinol and formaldehyde, furfural, furfuryl alcohol (2-furylmethanol), polyfurfuryl alcohol, sucrose or glucose within the open pore network. In some circumstances, the open pore network may be impregnated partially or fully with a colloidal solution of a metal, the monolith may be dried to remove liquid from the colloidal solution, and the metal particles may be coalesced together, e.g., by melting or using rapid thermal processing, to form the conductive network in the open pore network.

[0033] Certain variations of these methods may be used to form electrodes having a conductive surface area of at least about 50 m^2/g, at least about 100 m^2/g, at least about 150 m^2/g, at least about 200 m^2/g, at least about 250 m^2/g, at least about 300 m^2/g, at least about 350 m^2/g, at least about 400 m^2/g, at least about 450 m^2/g, at least about 500 m^2/g, at least about 700 m^2/g, at least about 800 m^2/g, at least about 1000 m^2/g, at least about 1200 m^2/g, at least about 1500 m^2/g, at least about 1800 m^2/g, at least about 2000 m^2/g, or even higher, e.g., at least about 3000 m^2/g, at least about 4000 m^2/g, or at least about 5000 m^2/g.

[0034] The invention also provides electrodes made or obtainable by any of the methods described herein, and electrodes equivalent to any the electrodes made by any of the methods described herein. In some variations, the electrodes comprise a continuous skeletal framework formed of a conductive material. In some variations, the electrodes comprise a continuous skeletal framework formed of a conductive material that is formed using a sol-gel derived monolith as a template. Some variations of the nanoporous electrodes comprise a monolithic conductive material which comprises an open network of pores, wherein the monolithic conductive material is substantially an inverse of a sol-gel derived monolith described herein.

[0035] Methods for storing energy are provided here. These methods comprise applying a potential between first and second conductive electrodes to build up stored charge therebetween, wherein at least one of first and second conductive electrodes is an electrode described herein, for example, has been derived from a sol-gel derived monolith comprising an open network of pores coated or at least partially filled with a conductive material.

[0036] Energy storage systems are also provided here. These systems comprise multiple interconnected energy storage cells, wherein each energy storage cell comprises two electrodes configured to be oppositely charged and an electrolyte disposed between the two electrodes. At least one of the two electrodes is an electrode described herein, such as in at least one of the cells comprises an electrode derived from a sol-gel monolith comprising an open network of pores coated or at least partially filled with a conductive material. In these energy storage systems, the monolith used may be derived from any suitable sol gel, but in some cases, it is derived from a silica sol gel. In the systems, at least some of the multiple cells may be connected in series, or at least some of the multiple cells may be connected in parallel.

BRIEF DESCRIPTION OF THE FIGURES

[0037] FIG. **1** illustrates an example of a method for making a sol-gel derived monolith (such as a silica sol-gel derived monolith) that can be used in the electrodes described herein.

[0038] FIG. **2** illustrates a relationship between a pore size and a surface area of an open pore network in a sol-gel derived monolith (such as a silica sol-gel derived monolith).

[0039] FIG. **3** illustrates an example of a silica sol-gel derived monolith sliced into wafers that can be used in the electrodes described herein.

[0040] FIGS. **4A-4B** illustrate examples of conductive coatings as applied to open pore networks of sol-gel derived monoliths to form conductive networks threading through the open pore networks.

[0041] FIGS. **5A-5C** illustrate schematically an example of a process that may be used to synthesize a graphite-like layer in situ to form a conductive coating on a surface of an open pore network. FIGS. **5A-5C** provides a schematic diagram of a route to a "graphite like" structure resulting from the polymerization of R and F and subsequent thermal processing. FIG. **5A** shows the pores immersed in an aqueous solution of monomer and catalyst. FIG. **5B** shows a polymer fragment resulting from the polymerization. FIG. **5C** shows a conception of a "graphite like" material that results from thermal processing in N_2 and CO_2 as the polymer density approaches that of graphite.

[0042] FIG. **6**A illustrates a variation of an ultracapacitor; FIG. **6**B illustrates a variation of an asymmetric ultracapacitor.

[0043] FIG. **7** graphically illustrates combinations of specific power and specific energy that may be achieved with ultracapacitors described herein.

[0044] FIG. **8** illustrates an example of an electrode assembly that may be used in an ultracapacitor.

[0045] FIGS. **9**A-**9**B illustrate examples of energy storage systems comprising series-connected cells.

[0046] FIG. **10** illustrates an example of an energy storage system comprising cells connected in parallel.

DETAILED DESCRIPTION

[0047] High surface area electrodes formed using nanoporous sol-gel derived monoliths as electrode substrates or electrode templates are provided here. Any sol-gel derived monoliths may be used to form the electrodes, but in some of the electrodes and related devices, methods and systems, nanoporous sol-gel derived monoliths having tunable pore sizes, and well-controlled, narrow distributions of pore size distributions may be used. Thus, nanoporous, high surface area electrodes with tunable pore sizes and well-controlled pore size distributions may be formed by using such sol-gel derived monoliths as substrates or templates for a conducting network formed within the continuous open pore network. The high surface area electrodes may be used as electrodes in a variety of energy storage devices such as capacitors, ultracapacitors, batteries, and fuel cells.

[0048] As used herein, the terms "nanoporous materials" and "nanoporous electrodes" are meant to encompass structures having pores ("nanopores") having a dimension, e.g., a cross-sectional diameter, in a range from about 0.1 nm to about 100 nm. "Nanoparticles" as used herein is meant to encompass materials having a cross-sectional dimension, e.g., a diameter, in a range from about 0.1 nm to about 100 nm. Ranges as used herein are meant to be inclusive of any end points to the ranges indicated, as well as numerical values in between the end points.

[0049] It should also be noted that as used herein and in the claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly indicates otherwise.

[0050] It is understood that aspect and variations of the invention described herein include "consisting" and/or "consisting essentially of" aspects and variations.

[0051] In some variations, reference to "about" a value or parameter refers to variation in the numerical quantity that can occur, for example, through typical measuring and handling procedures used; through inadvertent error in these procedures; and through differences in the manufacture, source, or purity of the compounds employed to make the compositions or carry out the methods. Reference to "about" a value or parameter herein includes (and describes) embodiments that are directed to that value or parameter per se. For example, description referring to "about X" includes description of "X".

[0052] As used herein "average pore size" is meant to encompass any suitable representative measure of a dimension of a population of pores, e.g., a mean, median, and/or mode cross-sectional dimension such as a radius or diameter of that population of pores. The mean pore size, median pore size, and mode pore size of a pore size distribution in a monolith may in some cases be essentially equivalent, e.g., by virtue of a very narrow and/or symmetrical pore size distribution. For convenience only, the following description includes three headings: electrodes, energy storage devices, and systems. However, it should be understood that these organizational headings are not meant to be limiting in any way. For example, any of the electrodes described herein may be used in connection with any of the energy storage devices or systems described herein, and any of the energy storage devices described herein may be used in connection with any of the systems described herein.

I. Electrodes

[0053] High surface area electrodes are described herein. In general, the electrodes comprise a sol-gel derived monolith comprising an open network of pores, where the open pore network has been made to be conductive. The high surface area of the open network of pores can thus be used as a substrate or a template for the conductive coating or filling that makes up the conductive backbone of the electrode. In other variations, the high surface area of the open pore network can be used as a substrate or template for a conductive coating or filling to allow for faradaic charge storage. In other variations, the open network of pores in the monolith may be at least partially filled (including substantially or completely filled) with a conductive material. The electrodes may comprise a current-spreading conductive plate in electrical contact with the conductive network formed in the open pore network. The sol-gel derived monolith material may either be left more or less intact in the electrodes, e.g., to support the conductive network, or the monolith material may be removed, e.g., dissolved, to leave behind the conductive framework that has been formed in the open pore network.

[0054] The monolith used to form the electrodes may be derived from any suitable sol-gel, e.g., a silica sol-gel derived monolith. The monolith may be selected to have any desired characteristic or combination of characteristics, e.g., composition, average pore size, pore size distribution, surface area, or any combination thereof. By preselecting an average pore size, pore size distribution, or surface area, these properties may be at least partially mapped onto the conductive coating disposed on the open pore network or conductive framework formed in the open pore network, thus affecting a resulting conductive surface area of the electrode. In some variations in which the electrodes are to be used in combination with an electrolyte, e.g., in a capacitor, ultracapacitor, battery or fuel cell, an average pore size may be selected to accommodate an ionic species in the electrolyte.

[0055] Generally, a sol-gel process starts with forming a colloidal solution (a "sol" phase), and hydrolyzing and polymerizing the sol phase to form a solid but wet and porous "gel" phase. The gel phase can be dried in a controlled manner, but generally not under supercritical conditions, so that fluid is removed to leave behind a dry monolithic matrix having an open network of pores (a xerogel). The term "xerogel" as used herein is meant to refer to a gel monolith that has been dried under nonsupercritical temperature and pressure conditions. The dry gel monolith can then be calcined to form a solid glass-phase monolith with connected open pores. The dry gel monolith can be further densified, e.g., sintered, at elevated temperatures to convert the monolith into a glass or ceramic.

[0056] In general, the microstructure of sol-gel derived monoliths that may be used in the electrodes described herein may be characterized in terms of a total pore volume, referring to a total volume of pores per unit mass, a surface area, referring to a surface area within the open network of pores per unit mass, a porosity, referring to fraction of the total volume of a monolith occupied by open pores, an average pore size, referring to an average (e.g., mean, median or mode) cross-sectional dimension (e.g., diameter or radius) of pores in a monolith, and a pore size distribution. The bulk surface area of a monolith may be measured in m^2/g, and may be measured for example by using B.E.T. (Brunauer, Emmett and Teller) surface analysis techniques. In general, multiple point B.E.T. analysis may be performed to determine the bulk surface area. An average pore size, a pore size distribution, and a total pore volume may be measured by an analyzer capable of resolving pore sizes to 0.3 nm or smaller, e.g., Quantachrome Quadrasorb™ SI-Krypton/Micropore Surface Area and Pore Size Analyzer, available from Quantachrome Instruments, Quantachrome Corporation (http://www.quantachrome.com, last visited May 11, 2008). The total pore volume may be measured in cm^3/g, and is the inverse of the bulk density of a monolith.

[0057] A population of pores can be modeled as a set of spheres each having a diameter (d) equal to an average pore size for that population, which may be measured with a pore size analyzer as described above, an individual pore surface area ($A=\pi\cdot d$ **2**), and an individual pore volume ($V=(1/6)\cdot\pi\cdot d^3$). A calculated bulk surface area (SA) may be determined using the density ρ of a material making up the sol-gel matrix (e.g., for silica sol-gel, the density of silica forming the matrix is 2.1-2.2 g/cm^3) and the following relationship in Equation 1:

$$SA=(1/\rho)[A/V]. \quad \text{(Eq. 1).}$$

[0058] A calculated bulk density (ρ_B) of the monolith may be determined from the total pore volume (TPV) and the density ρ of a material making up the sol-gel matrix using the following relationship in Equation 2:

$$\rho_B=1/[(1/\rho)+TPV] \quad \text{(Eq. 2).}$$

Thus, the fraction of pores (porosity), or % pores (by volume) in a monolith may be given by TPV/[(1/ρ)+TPV].

[0059] In general, the monoliths described herein can be formed by hydrolyzing a precursor. The microstructure of the sol-gel derived monoliths described here may be affected, and therefore controlled by, rates of hydrolysis and polymerization. The precursor can be any suitable precursor, e.g., a metal- or metalloid-containing compound having ligands or side groups that can be hydrolyzed to form a sol, and then polymerized (gelled) to form a sol-gel. As is discussed in more detail herein, the hydrolysis and polymerization process can be catalyzed using a catalyst in solution.

[0060] FIG. **1** provides a flow diagram of an example of a method for forming a sol-gel derived monolith (such as a silica sol-gel derived monolith). There, method **100** comprises preparing a precursor solution as shown in step **101**, and preparing a catalyst solution as shown in step **102**. The precursor solution and the catalyst solution may be mixed together to form a reaction (step **103**). The solution used in the reaction mixture in step **103** may be aqueous, or may comprise one or water-miscible organic solvents in combination with water. For example, an alcohol such as methanol, ethanol, or any alcohol having the general formula $C_nH_{2n+1}OH$, where n may be for example 0 to 12. Alternatively or in addition, formamide may be used in reaction mixture. The hydrolysis and polymerization reaction process may be allowed to proceed (step **104**). After the wet gel is formed, the gel may be dried to form a monolith (step **105**). It should be noted that the steps illustrated in method **100** need not be performed in any particular order, and steps may be combined together. For example, steps **101** or **102** may be reversed, or steps **101** and **102** may be combined into a single step, or steps **101**, **102**, and **103** may be completed simultaneously. Each of the steps in the methods is described in more detail below.

[0061] In some variations, the methods of making a silica sol-gel derived monolith comprising hydrolyzing a SiO_2 precursor with water in the presence of a catalyst to form a sol; gelling the sol; and drying the gelled sol. In some variations, the catalyst is preselected to obtain a porous SiO_2-containing monolith having a pore volume of between about 0.3 cm^3/g to about 2.0 cm^3/g, and a predetermined average pore diameter in a range from about 0.3 nm to about 30 nm with at least about 60% of pores having a pore size within about 20% of the average pore size.

[0062] Non-limiting examples of hydrolyzable side group that can be used in precursors include hydroxyl, alkoxy, halo, and amino side groups. In many cases, silica (SiO_2) sol-gels may be formed, e.g., using alkylorthosilicate, fluoralkoxysilane, or chloroalkoxysilane precursors. However, in other cases, sol-gels based on germanium oxide, zirconia, titania, niobium oxide, tantalum oxide, tungsten oxide, tin oxide, hafnium oxide, alumina, or combinations thereof may be formed using appropriate precursors. For example, germanium alkoxides, e.g., tetratheylorthogermanium (TEOG), zirconium alkoxides, titanium alkoxides, vanadium alkoxides, or aluminum alkoxides may be used as precursors to form sol-gels incorporating the respective metal or metalloid elements.

[0063] As stated above, silica sol-gels may be formed using alkylorthosilicates as precursors, e.g., tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS). In general, the stoichiometric hydrolysis reaction to form the sol can be described as:

$$(RO)_4Si+4H_2O\rightarrow 4ROH+Si(OH)_4,$$

where R may for example be an ethyl group or a methyl group. Following this hydrolysis step, gelation can occur, in which the $Si(OH)_4$ condenses and polymerizes to form a network of SiO_2 and H_2O. The SiO_2 network so formed comprising open-necked pores, and H_2O may be present in the open pores. The reaction as described above is aqueous, and may comprise one or water-miscible organic solvent in combination with water. For example, an alcohol such as methanol, ethanol, or any alcohol having the general formula $C_nH_{2n+1}OH$, where n may be for example 0 to 12. Alternatively or in addition, formamide may be used in the hydrolysis of the precursors. Two competing mechanisms may be operative that affect the microstructure of the monolith: formation of isolated silica particles, and formation of silica chains that form a fibril-like network.

[0064] The SiO_2 precursor may be hydrolyzed under either nonstoichiometric or stoichiometric hydrolysis conditions. In some variations, the molar ratio of water to precursor is about 3:1 or less, about 2.5:1 or less, about 2.25:1 or less, or about 2:1. In some variations, hydrolysis is performed directly with water and no solvent (such as an alcohol, including methanol and ethanol) is added into the reaction.

[0065] The microstructure of a sol-gel derived monolith that can be used to form an electrode for an energy storage device may be controlled by varying any one or any combination of several reaction parameters. For example, U.S. Pat. No. 4,851,150, U.S. Pat. No. 4,849,378, U.S. Pat. No. 5,264,197, U.S. Pat. No. 6,884,822, U.S. Pat. No. 7,001,568, U.S. Pat. No. 7,125,912, PCT WO 2006/068797, U.S. provisional application Ser. No. 61/060,449 (filed Jun. 10, 2008), and U.S. patent application Ser. No. ______ entitled "Nanoporous Materials and Related Methods" (Attorney Docket No. 64334-20001.00, filed on Jun. 10, 2009), each of which is hereby incorporated by reference herein in its entirety, describe a variety of methods for making sol-gel derived monoliths wherein in one or more reaction parameters is varied to control an average pore size and/or a pore size distribution.

[0066] Catalysts can be used to adjust, e.g., increase, rates of hydrolysis and polymerization, and correspondingly adjust the rate of gel formation, which can affect the microstructure in the resulting monolith. Further, a reaction temperature or temperature profile may be used to adjust a rate of gel formation. A catalyst may be an acid or a base. In some variations, the catalyst comprises an organic acid (such as formic acid, acetic acid, citric acid, or mixtures thereof). In some variations, a catalyst may comprise a first acid and a second acid, where the second acid catalyzes the hydrolysis reaction, and the first acid is capable of etching, dissolving, and/or redepositing in the sol matrix (e.g., a SiO_2 matrix), which may have the effect of increasing size of redeposited nanoparticles in the sol-gel matrix formation, leading to correspondingly increased nanopores size. Thus, the second acid of the catalyst may be added first to the sol-gel precursors to activate hydrolysis, and the first acid may be added subsequently to tune the pore size in the sol-gel. In other variations, the first and second acids of the catalyst may be added simultaneously. Of course, the first acid and/or the second acid of the catalyst may comprise a mixture of acids. In certain instances, the first acid, e.g., a matrix (e.g., SiO_2) dissolving component, of the catalyst may comprise hydrofluoric acid (HF), or a source of HF. HF sources that may be used include suitable fluorine-containing compounds that can produce HF during hydrolysis, or during polymerization (gelation).

[0067] Fine tuning of an average pore size and/or a pore size distribution in the resulting monolith may be accomplished by varying any one or any combination of the following reaction conditions: an amount of HF relative to a precursor; an amount of H_2O relative to a precursor; an amount of a solvent relative to a precursor; varying an amount of a second acid relative to a precursor; an amount of a second acid relative to an amount of HF; and/or a reaction temperature. The relative amounts of the precursor, H_2O and solvent, if present, may be stoichiometric or nonstoichiometric.

[0068] Further, the properties of the second acid, if used, may be selected to control at least one of an average pore size and a pore size distribution, and in some cases an average pore size and a pore size distribution associated with that average pore size. For example, a strong acid, e.g., an acid having a first pK_a that is lower about −1 or lower, e.g., HCl, H_2SO_4, HNO_3, or a combination thereof, may be used as a second acid in addition to HF to catalyze the hydrolysis and/or the gelation processes. In some variations, a weak acid, e.g., an acid having a first pK_a that is about 2 or greater, e.g., a first pK_a of about 2 to about 5, or about 2 to about 4. For example, citric acid, acetic acid, formic acid, or combinations thereof, may be used as a second acid in addition to HF as a catalyst. In some variations, the second acid is an organic acid (e.g., citric acid, acetic acid, formic acid) which can be removed or burned from the gelled sol during the drying process. In certain variations, an intermediate acid, e.g., an acid having a first pK_a that is between −1 and 2, e.g., oxalic acid, mellitic acid, or ketomalonic acid, may be used in combination with HF.

[0069] In general, narrow pore size distributions with a tunable average pore size may be produced by hydrolyzing and polymerizing the precursor in the presence of a relatively low amount of HF compared to the precursor. For example, if a non-stoichiometric amount of water relative to precursor is used, e.g., by using 2 moles of water relative to one mole of a precursor such as TEOS or TMOS, the molar ratio of HF to the precursor used in the methods described herein may be about 0.01:1 or less, e.g., about 0.01:1, about 0.009:1, about 0.008:1, about 0.007:1, about 0.006:1, about 0.005:1, about 0.004:1, about 0.003:1, about 0.002:1, or about 0.001:1. In another example, if a non-stoichiometric amount of water relative to a precursor is used, e.g., 2.25 moles of water relative to one mole of a precursor such as TEOS or TMOS, the molar ratio of HF to the precursor used in the methods may be about 0.1:1, about 0.09:1, about 0.085:1, about 0.08:1, about 0.075:1, about 0.07:1, about 0.065:1, about 0.06:1, about 0.055:1, about 0.05:1, about 0.045:1, or about 0.4:1. For these non-stoichiometric situations, a molar ratio of the second acid to the starting material (e.g., the precursor) may be about 0.075:1, about 0.07:1, about 0.065:1, about 0.06:1, about 0.055:1, about 0.05:1, about 0.04:1, about 0.03:1, about 0.02:1, about 0.018:1, about 0.015:1, about 0.01:1, about 0.008:1, about 0.005:1, about 0.003:1, or about 0.001:1. The second acid in these instances may be any suitable acid, e.g., a strong acid (such as HCl, H_2SO_4, HNO_3, or a combination thereof), a weak acid (such as citric acid, acetic acid, formic acid, or a combination thereof), or an intermediate acid.

[0070] If a stoichiometric amount of water relative to a precursor is used, a molar ratio of HF to precursor that is about 0.01:1 or less may be used, e.g., about 0.01:1, about 0.009:1, about 0.008:1, about 0.007:1, about 0.006:1, about 0.005:1, about 0.004:1, about 0.003:1, about 0.002:1, about 0.001:1, about 0.0005:1, or even less, and in some cases no HF may be used. In general, an amount of HF used in a catalyst may be increased to increase an average pore size. To achieve fine control of pore size and/or pore size distribution, the amount of HF may be adjusted using fine increments, e.g., by changing the molar ratio of HF relative to the precursor in increments of about 0.005 or about 0.001. A molar ratio of a second acid may be about 0.01:1 or less, e.g., about 0.01:1, about 0.009:1, about 0.008:1, about 0.007:1, about 0.006:1, about 0.005:1, or even less, and in some cases, no second acid may be used. Here again, the second acid may be any suitable acid, e.g., a strong acid such as HCl, H_2SO_4, HNO_3, or a combination thereof, a weak acid, or an intermediate acid.

[0071] In certain variations, under either nonstoichiometric or stoichiometric hydrolysis conditions, the second acid may be a weak acid that has a first pK_a of about 2 or higher, or about 3 or higher. Some of these weak acids may be organic acids, or small molecule acids. In some cases, the first pK_a of the weak acid may be about 2 to about 5, e.g., about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, or about 5. In certain variations, the first pK_a of the weak acid may be about 2 to about 4. Non-limiting examples of weak acids that may be used include citric acid, acetic acid, formic acid, ascorbic acid, succinic acid, benzoic acid, acetoacetic acid, malic acid, pyruvic acid, vinyl acetic acid, tartaric acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid, itaconic acid, hemimellitic acid, trimellitic acid, malonic acid, dicarboxylic acids such as methyl dicarboxylic acid, ethyl dicarboxylic acid, n-propyl dicarboxylic acid, isopropyl dicarboxylic acid, dimethyl dicarboxylic acid, methylethyl dicarboxylic acid, ethyl-n-propyl dicarboxylic acid, di-n-propyl dicarboxylic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, amino acids such as alanine, aspartic acid and glutamic acid.

[0072] For any of the methods described here, a temperature or temperature profile used in the hydrolysis and polymerization process used in making the wet porous gel monoliths may be varied to tune a reaction rate, which can in turn affect monolith microstructure. Thus, different temperatures or temperature profiles may be used, and may depend on a catalyst selected. In some situations, a temperature or temperature ramp that includes temperatures below ambient may be used for gelation, e.g., as described in U.S. Pat. No. 6,884,822, which is incorporated herein by reference in its entirety. In other instances, elevated reaction temperatures may be used, which may be at least in part due to exothermic hydrolysis reaction. Reaction temperatures may range from about 0° C. to about 80° C., or from about 15° C. to about 125° C., or from about 45° C. to about 100° C. In some cases, a reaction temperature may be naturally ramped up during the hydrolysis process due to the exothermic reaction, e.g., from about 0° C. to about 100° C. over a period of about 1 to 2 hours. For example, an exothermic hydrolysis reaction solution may be mixed while the reaction temperature ramped from about 0° C. to about 70° C. over a period of about 1 to 2 hours. The mixture may then be cast into an appropriate mold and held at an appropriate temperature, e.g., from about 0° C. to about 70° C. (such as about 33° C.) for an additional 1 to 30 hours to allow further gelation. In some cases, the mixture may be held in a mold at about 20° C. for 1 to 2 hours to allow gelation, held at about 20° C. for an additional 12 to 24 hours to allow the gelled sol to begin shrinkage (e.g., about 0.5% to about 5% volume shrinkage), and then removed from the mold, or remained in the mold for further drying process.

[0073] As indicated above, the wet, porous monoliths as prepared by any of the methods provided above may be formed in a mold so that it may be dried in a desired shape and configuration. Any suitable molding method or technique, and any suitable drying method or technique as described herein, now known, or later developed, may be used to form and dry the wet gels formed herein. A mold for example may be formed of polyethylene, polystyrene, polytetrafluoroethylene (Teflon™), polymethylpentene (PMP), glass, or any combination thereof. Further, a mold surface may be treated or conditioned so as to impart a desired surface quality to the molded monolith, e.g., hydrophobically treated. For example, a mold surface may be chemically cleaned, physically cleaned, and/or have static charges removed.

[0074] Suitable examples of molding and drying techniques and methods are described in U.S. Pat. No. 6,884,822 entitled “Sol-Gel Process Utilizing Reduced Mixing Temperature,” U.S. Pat. No. 6,620,368 entitled, U.S. Pat. No. 5,264,197 entitled “Sol-Gel Process for Providing a Tailored Gel Microstructure,” U.S. Pat. No. 4,849,378 entitled “Ultraporous Gel Monoliths Having Predetermined Pore Sizes and Their Production,” U.S. Pat. No. 4,851,150 entitled “Drying Control Additives for Rapid Production of Large Sol-Gel Derived Silicon, Boron and Sodium Containing Monoliths,” U.S. Pat. No. 4,851,373 entitled “Large Sol-Gel SiO_2 Monoliths Containing Transition Metal and Their Production,” U.S. Pat. No. 5,071,674 entitled “Method for Producing Large Silica Sol-Gel Doped with Inorganic and Organic Compounds,” U.S. Pat. No. 5,196,382 entitled “Method for Production of Large Sol-Gel SiO_2 Containing Monoliths of Silica with and without Transition Metals,” U.S. Pat. No. 5,023,208 entitled “Sol-Gel Process for Glass and Ceramic Articles,” U.S. Pat. No. 5,243,769 entitled “Process for Rapidly Drying a Wet, Porous Gel Monolith,” U.S. Pat. No. 7,000,885, entitled “Apparatus and Method for Forming a Sol-Gel Monolith Utilizing Multiple Casting,” 7,001,568, entitled “Method of Removing Liquid from Pores of a Sol-Gel Monolith,” 7,026,362, entitled “Sol-Gel Process Utilizing Reduced Mixing Temperatures,” 7,125,912, entitled “Doped Sol-Gel Materials and Method of Manufacture Utilizing Reduced Mixing Temperatures”, each of which is incorporated herein by reference in its entirety.

[0075] In general, a wet, porous monolith that has been placed in a mold may be held in a storage area under generally ambient conditions for about one to three days. After this initial period, the monolith may be removed from the mold or remained in the mold. Subsequently, a monolith may be dried under controlled, but not necessarily supercritical, drying conditions. The drying conditions can remove liquid, e.g., water and/or a solvent such as an alcohol from the interior of the porous network under controlled conditions such that the monolith does not crack and the integrity of the monolith remains intact. During drying, the monolith shrinks, and capillary forces in the pores increase as liquid is drawn out. Thus, any suitable drying temperature profile and/or drying atmosphere may be used with the monoliths formed such to avoid cracking of the monoliths, e.g., by keeping capillary forces due to the liquid being extracted below the limit of the pore walls to withstand such forces. The temperature profile used for drying can be adjusted so that the evaporation rate of liquid from the pores is approximately the same as or less than the diffusion rate of the liquid through the pores. In some cases, a modulated temperature profile (temperature cycling) may be used. Temperature cycling in some instances may reduce a drying time. Drying profiles may be used that allow drying of a monolith over a time period of a few days or less, e.g., within a week, or within 5 days, or within 3 days, or within 2 days, or within 1 day. As is described in more detail below, the extent of reaction (e.g., shrinkage) and drying may be monitored by weight loss, vapor pressure and/or physical (e.g., microscopic) inspection.

[0076] For example, monoliths as described here may be dried using the methods similar to those described in U.S. Pat. No. 6,620,368 which has already been incorporated herein by reference in its entirety. That is, a portion of the liquid (e.g., water and/or alcohol) in the pores of the wet monolith may be removed while the gel remains wet at least in an outer circumferential outer region of the monolith. Thus, the gel can dry more or less from the inside out, e.g., the outer peripheral region of the monolith may dry after an inner core region of the monolith has substantially dried.

[0077] In some cases, drying methods and techniques may be used that are similar to those described in U.S. Pat. No. 7,001,568, which has already been incorporated herein by reference in its entirety. That is, the monoliths may be dried by removing a portion of liquid, e.g., water and/or an alcohol such as ethanol, from pores of a body of a gel monolith while both an inner core region and an outer peripheral region of the gel remain wet. The gel may be allowed to shrink and become denser while the inner core region and the outer peripheral region remain wet. After this initial partial drying procedure, the remainder of the liquid may be removed from the monolith by applying a modulated temperature gradient between the outer peripheral region and the inner core region.

[0078] As stated above, any suitable method, technique, instrument, or combination thereof may be used for monitoring the extent of reaction and corresponding monolith shrinkage, e.g., mass loss, vapor pressure, and/or physical inspection. It may be desired to monitor shrinkage using a relatively precise technique, as incomplete or nonuniform reaction or drying may lead to cracking, or may lead to broadened distributions of pore sizes. For example, shrinkage of the monolith may be monitored locally and microscopically over its body to gauge an extent and uniformity of shrinkage. Such microscopic monitoring may be conducted using any suitable tools or technique. Any technique that is capable of detecting and resolving micron sized or submicron sized distance changes may be suitable. For example, any type of displacement sensor that is capable of about 1 μm, about 0.5 μm, about 0.1 μm, or even finer resolution may be used. Contact or non-contact techniques may be used to monitor the drying of a monolith. Physical shrinkage measurements may be made on a continuous basis, or may be made at selected time intervals. Multiple displacement sensors may used, e.g., to measure displacement along different dimension such as a cross-sectional dimension (e.g., a width, diameter or radius) or a longitudinal dimension (e.g., a height or length). In some cases, multiple displacement sensors may be used to monitor shrinkage in different regions of a monolith. Linear, two-dimensional, or three-dimensional displacement sensing tools may be used. The monolith may be placed on a vibration-controlled support, e.g., an optical table, to improve accuracy and precision of displacement measurements.

[0079] Non-limiting examples of contact-type displacement sensors that may be used to monitor shrinkage of a monolith include dial indicators, linear variable differential transformers (LVDT), and differential variable reluctance transformers (DVRT). Non-limiting examples of non-contact displacement sensors that may be used include eddy-current (inductive) type magnetic field displacement sensors and optical displacement sensors. For example, any commercially-available laser displacement sensor that is capable of 1 μm or less resolution may be used. Laser displacement sensors may be scanning, e.g., to monitor a surface, or non-scanning varieties, e.g., to monitor a targeted position. Non-limiting examples of suitable vendors for contact and/or non-contact displacement sensors include Keyence, Inc. (www.sensorcentral.com), Acuity, Inc. (www.acuity.com), Micro-Epsilon, Inc. (www.micro-epsilon.com), MTI Instruments, Inc. (www.mtiinstruments.com), Honeywell, Inc. (www.honeywell.com/sensing), Baumer, Ltd. (www.baumerelectric.com), Banner Engineering, Inc. (www.bannerengineering.com), and Microstrain, Inc. (www.microstrain.com). It may be desired to use a displacement measurement technique that is substantially temperature-sensitive or allows for temperature compensation, e.g., an optical displacement t sensor or a DVRT. Combinations of displacement sensor technologies may be used, e.g., one type may be used to monitor a longitudinal dimension, whereas another type of sensor may be used to monitor a cross-sectional dimension.

[0080] Thus, the shrinkage of one or more dimensions and/or one or more regions of a monolith may be monitored to detect a plateau in the shrinkage process. In many cases, shrinkage may be monitored at multiple positions to detect a plateau has been reached throughout the body of the monolith, instead of only in portions of the monolith. A plateau may be reached when shrinkage is less than about 100 ppm, less than about 5 ppm, less than about 1 ppm, or even less. For example, a plateau may be reached when dimensional changes are about 1 μm or less. In some cases, a relatively imprecise measurement technique such as mass loss may be used for monitoring an initial shrinkage phase, whereas a more precise monitoring technique as described above may be used for monitoring final shrinkage. The shrinkage may be carried out at a temperature in the range of about 70° C. to about 90° C. Generally, before reaching shrinkage plateau, no gas is used to purge the vapor out of the monolith.

[0081] Thus, the shrinkage and drying of the gels can be described in terms of a two phase treatment. In a first phase, the wet gel structure has reached its final shrinkage (e.g., monitored b physical displacement as described above) with its internal open pores still filled with its own pore liquid (e.g., molecular species such as water molecules and alcohol molecules). Thereafter, in a second phase, the monolith can be heated to remove any residual liquid in the pores. The heat treatment itself can include multiple heat treatment stages. In a first heat treatment stage, temperatures greater than the boiling point of the molecular species inside the porous gel structure may be used, e.g., to overcome capillary forces within the pores. In some cases, in this stage, a temperature ramp from about 80° C. to about 200° C., from about 90° C. to about 180° C., or from about 90° C. to about 120° C. may be used to drive off molecular water, alcohol (e.g., ethanol), and catalysts remaining in the pores. During the first heat treatment stage, the heating condition is sufficient to evaporate the molecular species from inside the pores, but is insufficient cause removal of chemisorbed molecular species. Thus, a temperature ramp from about 200° C. to about 450° C., or from about 180° C. to about 400° C. may be used to burn off molecular water, alcohol (e.g., ethanol), remaining in the pores in a second heat treatment stage, as is described in more detail below. No purging gas is used before the pore liquid are totally evaporated to become vapor phase. A temperature ramp used any of the heat treatment stages may depend on the dimensions, especially a thickness, of a monolith, but for a rod-shaped or brick-shaped monolith having a thickness of several cm, this temperature ramp may occur over about 1 hour to about 2 hours. After all the pore liquid becomes vapor phase, a nitrogen atmosphere (or inert gas such as helium or argon), or air atmosphere may be used to purge or exchange vaporized pore liquid out. At this stage, the temperature is increased from 120° C. to 180° C. to get rid of all and any molecular water and alcohol inside the pore of gel.

[0082] As stated above, in a second heat treatment stage, chemisorbed species that still remain in the pores may be burned off in an air atmosphere. Thus, the temperatures used in this stage of the heat treatment may be sufficient to burn off chemisorbed alcohol or other organic species such as higher molecular weight alcohols that are still present in the pores, but insufficient to cause the pores to close. For the this stage, air or N_2/O_2 combination may be introduced at about 140° C. to about 200° C. or about 180° C. to about 200° C. and the temperature increased to a baking temperature in a range from about 400° C. to about 800° C., e.g., about 400° C., about 450° C., about 500° C., about 600° C., or about 700° C. The baking time for the second stage of the heat treatment may be varied based on a thickness of a monolith. For example, a block-shaped or rod-like monolith having a thickness of several centimeters may be baked for about 2 to about 5 hours. In some cases, the second stage of the heat treatment can form hydroxyl reaction sites, e.g., at a density of about 4 to about 6 hydroxyl groups per nm^2. Such hydroxyl reaction sites may be used for reactively coating a surface of the pores, e.g., applying conductive coating so that the monolith may be used as a substrate for a high surface area electrode, as is described in more detail below.

[0083] In some variations, the invention provides a method of drying the gels described herein, the method comprising heating the gel that has reached shrinkage plateau at a temperature that the molecular species (including alcohol, water, and catalysts) are in vapor phase (e.g., at a temperature in the range of 90° C. to 120° C.); introducing a gas (such as nitrogen) to purge or exchange the vaporized molecular species out of the pores (e.g., at a temperature in the range of about 120° C. to about 180° C.); and burning the gel to remove chemisorbed species out the pores in the presence of N_2/O_2 combination or air (e.g., at a temperature in the range of about 140° C. to about 450° C.).

[0084] In some cases, a monolith may be sliced into thin wafers, e.g., wafers having a thickness of about 1 mm, about 0.9 mm, about 0.8 mm, about 0.7 mm, about 0.6 mm, about 0.5 mm, about 0.4 mm, about 0.3 mm. about 0.2 mm, about 0.15 mm, or about 0.1 mm. Any suitable slicing or cutting technique or tool may be used to form such wafers, e.g., a saw or any other kind of cutting tool, e.g., a wire saw, a diamond saw, or a water jet cutting tool. For thin wafers, the times for the heat treatment to drive off molecular species and/or burn chemisorbed species as described above may be dramatically reduced. For example, a 200 μm thick wafers may be baked at about 400° C., about 450° C., or about 500° C. for less than an hour, e.g., about 10 minutes, to burn off chemisorbed species.

[0085] In certain variations, thin wafers may be molded. For example, wafers may be formed by casting the gel formulation into a mold or container comprising multiple slots, each slot comprising opposing, closely-spaced parallel sidewalls and hydrophobic inner surfaces. The gel can then undergo shrinkage in the slots in the mold, as described above. The spacing between the parallel sidewalls in the slots can be set so that the resulting sol-gel wafer has a desired thickness, and a cross-sectional dimension of the slots can be selected so that the resulting sol-gel wafer has a desired cross-sectional area. After molding such sol-gel wafers, they can undergo further shrinkage and drying as described above. In some cases, the molded sol-gel wafers may undergo further shrinkage and drying while still in the mold, whereas in certain circumstances, the molded wafers may be removed from the mold to undergo one or more shrinkage or drying steps. As stated above, for thin wafers, the times for heat treatment for thin wafers may be shortened compared to those for block-like monoliths. Wafers may have a thickness of about 1 mm, about 0.9 mm, about 0.8 mm, about 0.7 mm, about 0.6 mm, about 0.5 mm, about 0.4 mm, about 0.3 mm. about 0.2 mm, about 0.15 mm, or about 0.1 mm.

[0086] In certain variations, one or more additional components may be added during the hydrolysis and polymerization of the gels described herein. For example, one or more drying control agents may be used, such as those described in U.S. Pat. No. 4,851,150, which has already been incorporated herein by reference in its entirety. Further, one or more porogens may be added, such as those described in International Patent Publication No. WO 2006/068797, which has already been incorporated herein by reference in its entirety.

[0087] The monoliths made according to the methods described herein may have microstructure having a desired microstructure and a desired surface area for the open network of pores. As stated above, the total pore volume of a monolith may be determined using a pore size analyzer such as a Quantachrome Quadrasorb™ SI Krypton/Micropore analyzer, and the bulk density of a monolith may then be calculated using the total pore volume and the density of the material making up the framework in the monolith. The monoliths according to the methods described here may have a total pore volume of at least about at least about 0.1 cm^3/g, at least about 0.2 cm^3/g, at least about 0.3 cm^3/g, at least about 0.4 cm^3/g, at least about 0.5 cm^3/g, at least about 0.6 cm^3/g, at least about 0.7 cm^3/g, at least about 0.8 cm^3/g, at least about 0.9 cm^3/g, at least about 1 cm^3/g, at least about 1.1 cm^3/g, at least about 1.2 cm^3/g, at least about 1.3 cm^3/g, at least about 1.4 cm^3/g, at least about 1.5 cm^3/g, at least about 1.6 cm^3/g, at least about 1.7 cm^3/g, at least about 1.8 cm^3/g, at least about 1.9 cm^3/g, at least about 2.0 cm^3/g, or even higher. Thus, some monoliths may have a total pore volume in a range from about 0.3 cm^3/g to about 2 cm^3/g, or from about 0.5 cm^3/g to about 2 cm^3/g, or from about 0.5 cm^3/to about 1 cm^3/g, or from about 1 cm^3/g to about 2 cm^3/g. A porosity of the monoliths may be about 30% to about 90% by volume, e.g., about 30% to about 80%, about 40% to about 80%, or about 45% to about 75%. In some variations, the porosity may be lower than about 30% by volume or higher than about 90% by volume, e.g., up to about 95% by volume.

[0088] An average pore size (such as average pore diameter) of the pores in the open pore network formed in the monoliths described herein may be tunable of a range from about 0.3 nm to about 300 nm, about 0.3 nm to about 100 nm, about 0.3 nm to about 50 nm, about 0.3 nm to about 30 nm, or about 0.3 nm to about 10 nm. For example average pore sizes of about 0.3 nm, about 0.5 nm, about 0.8 nm, about 1 nm, about 2 nm, about 3 nm, about 4 nm, about 5 nm, about 6 nm, about 7 nm, about 8 nm, about 9 nm, or about 10 nm may be preselected and achieved using the methods described herein. For any preselected average pore size achieved in the monoliths described herein, a relatively narrow distribution around that average may be achieved. For example, at least about 50%, at least about 60%, at least about 70%, or at least of about 75% of the pores may be within about 40%, within about 30%, within about 20%, or within about 10% of an average size. In certain variations, at least about 50% of the pores may be within about 1 nm, within about 0.5 nm, within about 0.2 nm, or within about 0.1 nm of an average pore size. As used herein "within" a designated percentage or designated amount of an average pore size is meant to encompass that percentage deviation or a lesser percentage deviation, or that amount of deviation or a lesser amount of deviation to either the higher side or a lower side of the average pore size. That is, a pore size distribution that is within about 20% of an average pore size is meant to encompass pore sizes in a range from the average pore size minus 20% of that average pore size to the average pore size plus 20% of that average pore size, inclusive.

[0089] Thus, some variations of monoliths may have an average pore size that can be selected in a range from about 0.3 nm to about 300 nm, or in a range from about 0.3 nm to about 100 nm, or in a range from about 0.3 nm to about 30 nm, or in a range from about 0.3 nm to about 10 nm, and a distribution such that at least about 50% or at least about 60% of the pores are within about 20% of the average pore size, or within about 10% of the average pore size. Certain variations may have even tighter pore size distributions, e.g., monoliths may have an average pore size selectable in a range from about 0.3 nm to about 30 nm or in a range from about 0.3 nm to about 10 nm, and have a distribution such that at least about 50% of pores are within about 10% of the average. For monoliths having relatively small average pore sizes, e.g., 5 nm or smaller, e.g., about 5 nm, about 4 nm, about 3 nm, about 2 nm, about 1 nm, about 0.5 nm, or about 0.3 nm, at least 50% of the pores may be within about 1 nm, about 0.5 nm, about 0.2 nm, or about 0.1 nm of the average.

[0090] In general, the surface area of a monolith increases for smaller particles sizes, and in particular when a pore size decreases below about 3 nm, the corresponding surface area increases rapidly, e.g., exponentially or approximately exponentially. The surface area of a monolith may be measured by using the B.E.T. surface area method, or may be calculated using an average pore size as described above (Eq. 1). In general, the surface area of a monolith increases for smaller particles sizes, and in particular when a pore size decreases below about 3 nm, the corresponding surface area increases rapidly in a nonlinear manner, e.g., exponentially or approximately exponentially. This relationship is illustrated graphically in FIG. **2**. There, a bulk surface area (SA) in m^2/g has been calculated for versus average pore diameter (D) as described above in connection with Eq. 1. Data point symbols indicate bulk surface areas measured by B.E.T. analysis. Monoliths with dramatically increased surface areas may be prepared by the methods described herein, e.g., where the average pore size may be controlled to be about 3 nm or smaller.

[0091] As shown, as a pore size decreases from about 3 nm to about 0.6 nm, the corresponding surface area increases from about 1000 m^2/g to about 5000 m^2/g, e.g., a five-fold increase. Monoliths with dramatically increased surface areas may be used for the high surface area electrodes described herein, where the average pore size may be controlled to be about 5 nm or smaller, or about 3 nm or smaller.

[0092] Thus, a surface area of the open pore network in the monoliths used in the high surface area electrodes described herein may be about 50 m^2/g to about 5000 m^2/g, or even higher, e.g., at least about 50 m^2/g, at least about 100 m^2/g, at least about 150 m^2/g, at least about 200 m^2/g, at least about 300 m^2/g, at least about 400 m^2/g, at least about 500 m^2/g, at least about 600 m^2/g, at least about 700 m^2/g, at least about 800 m^2/g, at least about 1000 m^2/g, at least about 1200 m^2/g , at least about 1400 m^2/g , at least about 1600 m^2/g , at least about 1800 m^2/g , at least about 2000 m^2/g, at least about 2200 m^2/g, at least about 2400 m^2/g, at least about 2600 m^2/g, at least about 2800 m^2/g, at least about 3000 m^2/g, at least about 3500 m^2/g, at least about 4000 m^2/g, at least about 4500 m^2/g, or at least about 5000 m^2/g.

[0093] A molded, dried monolith may be further processed to make a substrate or template for a high surface area electrode. For example, a monolithic rod or brick can be sliced into wafers, e.g., using a saw or any kind of cutting tool, e.g., a wire saw, a diamond saw, or a water jet cutting tool. Wafers so formed can have any suitable thickness, e.g., about 1 mm or less, about 0.5 mm or less, about 0.25 mm or less, about 0.2 mm or less, about 0.15 mm or less, or 0.1 mm or less. Referring now to FIG. **3**, a monolithic sol-gel silica rod **300** having a cross-sectional diameter of about 3 inches and a length of about 20 inches can be sliced into over one thousand wafers **301** each having a thickness of about 250 microns or less. In certain variations, wafers may be molded, as described above.

[0094] A conductive material or a material that can be converted into a conductive material by subsequent processing may be applied to (e.g., by coating or impregnating) any suitably formed sol-gel derived monolith, e.g., a monolith as molded and dried, or a monolith that has been molded, dried, and subsequently processed, e.g., by slicing into wafers as described above in connection with FIG. **3**. The material used for coating and/or impregnating may comprise any suitable material, e.g., graphite, graphite-like conductive carbon carbide, carbon, activated carbon, conductive carbons derived from the polymerization and carbonization of carbon precursor materials like, furfural, furfuryl alcohol (2-furylmethanol), polyfurfuryl alcohol, resorcinol formaldehyde, sucrose, and glucose, a metal such as platinum, nickel, gold, palladium, molybdenum, a metal oxide such as tin oxide, indium tin oxide, zinc oxide, molybdenum oxide, ruthenium oxide, tungsten oxide, manganese dioxide, silver oxide, nickel oxyhydroxide, aluminum doped zinc oxide, titanium oxide, vanadium pentoxide, sulfides such as molybdenum sulfide, tungsten sulfide, iron sulfide, nitrides such as tungsten nitride, molybdenum nitride or combinations thereof, conductive polymers such as poly(3-methylthiophene). As used herein, a "graphite-like" material is a carbon-based material that is similar to graphite but has a conductivity and a density approaching that of graphite. As the density of a graphite-like material is increased toward that of graphite, the conductivity of a graphite-like material correspondingly approaches that of graphite. A graphite-like material may contain more defects than graphite, or may contain impurities. As stated above, the electrodes may be used in a capacitor, an ultracapacitor, a fuel cell, or a battery and the electrodes may, based in part on choice of conductive coating material, be capable of being charged and discharged both or individually electrostatically or faradiacally.

[0095] Of course, the composition of a conductive coating formed on the open network of pores or the conductive composition filled into the open network of pores used in the electrodes can affect electrical properties of the electrodes described herein. For example, conductive material selection can affect the electrical conductivity of the electrode, as well as energy-handling capabilities, e.g., whether the electrode is suitable for relatively high voltages and/or relatively high currents. Further, conductive material selection can affect contact resistance of the electrode, which can contribute to ESR.

[0096] In general, the conductive coating on the open network of pores may be relatively uniform, e.g., to prevent high resistance regions that can lead to hot spots and subsequent failure. In some cases, the conductive coating may be uniform throughout an entire open network of pores of a sol-gel derived monolith. In other instances, an open network of pores is only partially coated with a conductive coating. However, in these cases, the partial coating may still be generally continuous over a relatively large surface area of the monolith, rather than forming isolated islands of conductive coating, so as to provide a substantial conductive surface area. In the instance where the conductive materials are filled into the pores the same considerations apply; and the conductive network within open pore network of pores may be uniform or in other instances non-uniform but still connected and conductive forming a conductive monolith network within the open network of pores.

[0097] The thickness of the coating can also affect the electrical properties of the electrodes. For example, if a relatively thin conformal conductive coating is used to coat the open pore network, the conductive surface area may be close to that of the underlying open pore network. An example of such an electrode is depicted in FIG. **4**A. There, electrode **450** comprises an open network of pores **451**. In this variation, the network **451** is lined with a relatively conformal conductive coating **452**. In other instances, e.g., for high current or voltage applications, the open pore networks may be substantially filled with the conductive coating. An example of such an electrode is illustrated in FIG. **4**B. There, electrode **400** comprises an open network of pores **401** that is substantially filled with a conductive material **402**. In this variation, the conductive surface area of the electrode **401** is less than the surface area of the open network of pores as it existed in monolith **401** before coating.

[0098] It should be noted that the conductive pathways formed by making the open pore network in sol-gel derived monoliths conductive are generally continuous conductive pathways, rather than conductive pathways that are formed from point-point contacts between discrete conductive particles. Therefore, the high internal resistance that can result from particle-particle contacts, e.g., carbon-carbon contacts, may not be present or dominant in the electrodes described here. Therefore, the electrodes may have overall lower internal resistance, lower ESR, and higher conductivity. Besides reducing power losses due to resistance between conductive particles, the increased conductivity may allow thicker electrodes to be made, which may increase surface area even more, and increase physical robustness of the electrodes.

[0099] Any suitable method or technique may be used to make the open pore network in the sol-gel derived monoliths conductive. For example, the surface of the open pore network may be coated or the open network of pores may be partially filled with graphite, a graphite-like material, or a conducting carbon derived from the polymerization and carbonization of carbon precursor materials like but not limited to, furfural, furfuryl alcohol (2-furylmethanol), polyfurfuryl alcohol, resorcinol formaldehyde, sucrose, and glucose. For example, coating may be achieved by synthesizing a layer of graphite or a layer of a graphite-like material on the surface. In other instances, a layer of carbide may be formed on the surface of the open pore network. In still other cases, metal or conductive metal oxides may be deposited in the open pore network, e.g., by chemical vapor deposition techniques such as atomic layer deposition. In some situations, a colloidal solution containing a metal and/or conductive metal oxide may be impregnated into the porous network, the liquid of the colloidal solution removed, and the metal and/or metal oxide particles allowed to coalesce, e.g., by melting or rapid thermal processing.

[0100] Any method for in situ synthesis of a conductive carbon coating, e.g., graphite, graphite-like conducting carbon and/or carbide, in an open pore network in a silica sol-gel derived monolith described herein, now known, or later developed, may be used. For example, suitable methods for forming carbon-based conductive coatings a silica surface are provided in C. Lin et al., *J. Electrochem. Soc.* 146 (1999) 3639, C. Lin and J. A. Ritter, *Carbon* 35 (1997) 1271, and C. Lin et al., *Carbon* 38 (2000) 849, each of which is incorporated by reference herein in its entirety.

[0101] An illustrative example of an in situ synthesis of a carbon-based, graphite-like conductive coating (e.g., conductive carbon) on an open pore network in a silica sol-gel derived monolith is shown in FIGS. **5**A-**5**C. A liquid phase comprising resorcinol (R) and formaldehyde (F) can be introduced into the sol-gel and then polymerized in the presence of a base catalyst (e.g., KOH, Na_2CO_3, NaOH: potassium hydroxide, sodium carbonate, and sodium hydroxide) and heat to form a polymer layer threaded through the open pore network. FIG. **5**A illustrates pores immersed in an aqueous solution comprising monomer and catalyst, and FIG. **5**B shows a polymer fragment resulting from the polymerization. Unreacted residual materials such as resorcinol and/or formaldehyde that may be adsorbed onto the nanoporous surface may be removed by washing with organic solvents like acetone, drying and evaporation, e.g., at a temperature from about 40° C. to about 120° C. Following drying, the modified sol-gel can be exposed to carbonizing conditions in an inert atmosphere (e.g., nitrogen atmosphere) and may be followed by thermal treatment with carbon dioxide from about 200° C. to about 1200° C. to form a graphite-like layer on the silica nanoporous surface. FIG. **5**C illustrates a conception of a graphite-like material resulting from the thermal processing in nitrogen and carbon dioxide as described above in connection with FIG. **5**B. In the polymeric layer comprising graphite-like sections as illustrated conceptually in FIG. **5**C, the density approaches that of graphite.

[0102] In some variations, atomic layer deposition (ALD) or chemical vapor deposition (CVD) may be used to apply metal and/or conductive metal oxide particles to the open pore network in a sol-gel derived monolith. ALD may be used to build up a conformal and relatively uniform conducting film on the open pore network. As is known, ALD can be used to deposit such conformal coatings of conductive oxides, nitrides, sulfides and metals. For example, as described in Jeffrey W. Elam et al., *J. Nanomaterials* 2006 (2006) 1-5, which is hereby incorporated by reference in its entirety, titanium tetrachloride may be reacted with H_2O at a deposition temperature of 100° C. to produce a conformal layer of titanium dioxide on nanoporous materials, diethyl zinc may be reacted with H_2O at a deposition temperature of 177° C. to produce a conformal coating of ZnO on nanoporous materials, vanadyl oxytriisopropoxide may be reacted with H_2O_2 to produce a conformal coating of V_2O_5 on nanoporous materials, and Pd hexafluoroacetylacetonate may be reacted with formaldehyde at a reaction temperature of 200° C. to produce a conformal coating of palladium on nanoporous materials.

[0103] Any form of chemical vapor deposition now known or later developed may be used to form a conductive coating on an open pore network of the monoliths used in the electrodes. For example, thermal chemical vapor deposition, electron beam chemical vapor deposition, and/or sputtering may be used to form a metal layer or conductive metal oxide layer. The conductive coating itself may comprise any suitable material, e.g., graphite, graphite-like conductive carbon carbide, carbon, a metal such as platinum, nickel, gold, palladium, molybdenum, a metal oxide such as tin oxide, indium tin oxide, zinc oxide, molybdenum oxide, ruthenium oxide, tungsten oxide, manganese dioxide, silver oxide, nickel oxyhydroxide, aluminum doped zinc oxide, titanium oxide, vanadium pentoxide, sulfides such as molybdenum sulfide, tungsten sulfide, iron sulfide, nitrides such as tungsten nitride, molybdenum nitride or combinations thereof.

[0104] In some cases, aluminum doped zinc oxide (ZnO:Al) may be used as a conductive coating. ZnO:Al also may be used in combination with zinc oxide, titatanium dioxide, indium tin oxide, tin oxide, platinum, nickel, gold, palladium or vanadium pentoxide. A conductive coating having a tunable resistivity may be produced by varying an amount of aluminum oxide doped into zinc oxide. ZnO:Al coatings may be produced by any suitable method, e.g., ALD, CVD, magnetron sputtering, electron beam evaporation, and pulsed laser deposition. Methods for making ZnO:Al conductive coatings are provided in S.-H. K. Park et al., *Japanese Journal of Applied Physics* 44 (2005), L242-L245, which is hereby incorporated by reference herein in its entirety. For example, if ALD is used to build up the films, diethyl zinc (DEZ) (zinc precursor) and H_2O (oxygen precursor) can be alternately injected into a reactor in which a substrate is held at 180° C., using nitrogen as a carrier gas with a flow rate of 100 sccm, and using pulsing times of 1.65 seconds for DEZ and H_2O, and a nitrogen purge time of 4.4 seconds. Aluminum can be doped into the films by introducing an aluminum precursor such as trimethylaluminum into the reaction chamber with certain DEZ deposition cycles, e.g., about one injection of trimethylaluminum per 19 injections of DEZ. The injections of DEZ, H_2O, and trimethylaluminum can be repeated any number of cycles to build up a desired layer thickness. In some variations, a layer of Al_2O_3 may be built up on top of the ZnO:Al layer. Methods for making ZnO:Al films using magnetron sputtering are described in K. Elmer et al, *Thin Solid Films,* 247 (1994), 15-23, and using pulsed laser deposition are described in Z. Y. Ning et al., *Thin Solid Films,* 307 (1997), 50-53, each of which is incorporated herein by reference in its entirety. ZnO:Al films may have a resistivity in a range from about 5×10^{-4} ohm-cm to about 1×10^{-2} ohm-cm, or from about 5×10^{-4} ohm-cm to about 1×10^{-3} ohm-cm.

[0105] As stated above, metal and/or metal oxide particles in an aqueous colloidal solution may be allowed to ingress into an open pore network in the monoliths used to make the electrodes described herein. The solvent may then be drawn off, leaving metal and/or conductive metal oxide particles lining the pores. Any technique may then be used to allow the metal and/or conductive metal oxide particles to coalesce to form a continuous conductive network. For example, the monolith may be subjected to rapid high temperature excursions to melt or coalesce the particles, similar to rapid thermal processing (RTP) that is used in the semiconductor industry. If desired, this process can be repeated to build up a conductive network. Any suitable metal and/or conductive metal oxide particles may be used build up a conductive network. RTP may be used in this instance to reduce the thermal budget and/or to prevent thermal equilibrium from reducing or restricting the ability of the conductive material to diffuse during thermal processing. During RTP, conductive particles may be subject to temperatures ranging from about 200° C. to about 1200° C. with ramp rates varying from about 20° C./sec to about 250° C./sec. Typical processing times for RTP are less than about 1 minute. In general, the particles may be nanoparticles having an outer dimension smaller than that of the nanopores present in the monolith. For example, gold nanoparticles may be deposited in the open pore network as described above, and then subjected to RTP conditions to form a continuous gold network threading its way through the monolith.

[0106] In still other variations, reaction precursors to conducting polymer films may be impregnated into a nanoporous monolith. Concentrations of the reaction precursors can be adjusted so as to coat the open pore network of the monolith with the precursor. In situ polymerization reaction conditions such as the presence of catalysts, pH, temperature profile, and reaction time, can be adjusted to result in a polymer coating on the open pore network. Following formation of a continuous polymer film threading its way through the open pore network, post reaction processing, e.g., carbonization, may be used to convert the polymer film into a conducting film on the open pore network or convert the polymer to fill. For example, as described above, furfuryl alcohol may be introduced and polymerized in the open network of pores of the silica sol-gel derived monolith. The sol-gel derived monolith can be fabricated as a thin free standing wafer. A 100% solution of furfuryl alcohol is then introduced into the pore network of the water at room temperature. The wafer containing the furfuryl alcohol is then heated between 80 and 135° C. for from between 5 and 25 hours to initiate polymerization. This process can be repeated several times to maximize pore impregnation by the furfural. The wafer containing the polymerized furfuryl alcohol is then removed to a furnace to be heat to a final temperature of between 600 and 1100° C. under an inert atmosphere to complete the carbonization process and generate a conducting carbon material. The template can then be removed partially or completely. In some cases, the wafer containing the polymerized furfuryl alcohol is removed at lower temperatures from between 300 and 600° C. and the template is removed partially or completely. The free standing or partially free standing polymerized furfuryl alcohol is returned to the furnace for additional thermal treatment to complete the carbonization process and generate a conducting carbon monolith. Additionally, in the case of monomers like furfuryl alcohol which polymerize in a linear chain, cross-linking agents can be added to the reaction mixture prior to heating to increase the connectivity of the polymer. For example, lysine 5% by weight can be used. Another example, as described above, resorcinol and formaldehyde in aqueous solution may be polymerized in situ in the open pore network of a silica sol-gel derived monolith, wherein small amounts of base may be added to catalyze the polymerization. Examples of suitable reaction conditions are provided in C. Lin and J. A. Ritter, *Carbon* 35 (1997) 1271, which has already been incorporated herein by reference in its entirety. In both the above examples, post-polymerization processing in the presence of an oxidizing gas, e.g., CO_2, at elevated temperature may be used to increase the density of the film formed from the polymer film. As the density of the film increases, the film becomes more graphite-like, leading to increasing conductivity with increasing density. Post-polymerization process in the presence of an oxidizing gas may be completed using processing times up to about 10 hours, and at processing temperatures in a range from about 200° C. to about 1200° C.

[0107] An indicated above, the addition of a conductive layer to an open pore network in a sol-gel derived monolith may affect the surface area. Thus, the conductive surface area may be relatively close to that of the underlying monolith if a relatively thin conformal layer is applied, or the conductive surface area may be somewhat less, e.g., a factor of 2, or a factor of 3, or an even higher factor, than that of the underlying monolith. Any of the electrodes described herein may have a conductive surface area that is about 20 m^2/g to about

5000 m^2/g, or even higher, e.g., at least about 20 m^2/g, at least about 30 m^2/g, at least about 40 m^2/g, at least about 50 m^2/g, at least about 60 m^2/g, at least about 70 m^2/g, at least about 80 m^2/g, at least about 90 m^2/g, at least about 100 m^2/g, at least about 120 m^2/g, at least about 150 m^2/g, at least about 180 m^2/g, at least about 200 m^2/g, at least about 220 m^2/g, at least about 250 m^2/g, at least about 280 m^2/g, at least about 300 m^2/g, at least about 320 m^2/g, at least about 350 m^2/g, at least about 380 m^2/g, at least about 400 m^2/g, at least about 420 m^2/g, at least about 450 m^2/g, at least about 480 m^2/g, at least about 500 m^2/g, at least about 550 m^2/g, at least about 600 m^2/g, at least about 650 m^2/g, at least about 700 m^2/g, at least about 750 m^2/g, at least about 800 m^2/g, at least about 850 m^2/g, at least about 900 m^2/g, at least about 950 m^2/g, at least about 1000 m^2/g, at least about 1100 m^2/g, at least about 1200 m^2/g, at least about 1300 m^2/g, at least about 1400 m^2/g, at least about 1500 m^2/g, at least about 1600 m^2/g , at least about 1700 m^2/g , at least about 1800 m^2/g , at least about 1900 m^2/g, at least about 2000 m^2/g, at least about 2200 m^2/g , at least about 2400 m^2/g , at least about 2600 m^2/g, at least about 2800 m^2/g, at least about 3000 m^2/g, at least about 3500 m^2/g, at least about 4000 m^2/g, at least about 4500 m^2/g, or at least about 5000 m^2/g. These electrodes may have an average pore size in a range from about 0.3 nm to about 100 nm, from about 0.3 nm to about 30 nm, from about 0.3 nm to about 10 nm. In some variations, the electrodes have a pore size distribution wherein at least about 50% of the pores are within about 30% of an average pore size, within about 20% of an average pore size, or within about 10% of an average pore size.

[0108] Additional variations of high surface area conductive electrodes are provided herein. These electrodes comprise a continuous skeletal framework formed of a conductive material that is formed using a sol-gel derived monolith as a template. Thus, these electrodes may be formed by substantially filling an open pore network with a conductive material, as described herein, e.g., as illustrated and discussed in connection with FIG. **4**B. After a three-dimensional conductive network is formed in the monolith, the sol-gel template may be selectively removed, or at least partially removed leaving behind a free-standing or substantially free-standing conductive framework. The sol-gel template may be removed using any suitable technique, e.g., by dissolving using a suitable solvent. For example, for silica sol-gel monoliths, hydrofluoric acid (HF) may be used to dissolve the monolith and leave behind a conductive framework. The dissolution temperatures will range near room temperature and may be controlled from about 20° C. to about 60° C. The dissolution concentrations of HF used can vary from about 1% to about 48% (e.g., from about 1% to about 30%) HF by weight. In some cases, it may be desired to leave behind a residual amount of the monolith to impart structural strength to the conducting framework. Another method used for template removal is the dissolution of the template using a 0.1 M to 5 M solution of NaOH at 30° C. to 75° C. to dissolve the silica and leave a free standing or substantially free standing conductive framework in place. As with the other electrode variations described herein, these free-standing high surface area electrodes may be used as electrodes in any device requiring high surface area electrodes, e.g., energy storage devices such as capacitors, e.g., ultracapacitors, batteries, and fuel cells.

[0109] As these electrodes are made using the open pore network of a sol-gel derived monolith as a template, their conductive surface may be similar to that of the template. However, since the conductive material has been used to fill the open pore network, the conductive surface area of the resulting free-standing electrodes may be lower than that of the sol-gel template. These electrodes may have a conductive surface area that is about 50 m^2/g to about 5000 m^2/g, or even higher, e.g., at least about 50 m^2/g, at least about 60 m^2/g, at least about 70 m^2/g, at least about 80 m^2/g, at least about 90 m^2/g, at least about 100 m^2/g, at least about 120 m^2/g, at least about 150 m^2/g, at least about 180 m^2/g, at least about 200 m^2/g, at least about 220 m^2/g, at least about 250 m^2/g, at least about 280 m^2/g, at least about 300 m^2/g, at least about 320 m^2/g, at least about 350 m^2/g, at least about 380 m^2/g, at least about 400 m^2/g, at least about 420 m^2/g, at least about 450 m^2/g, at least about 480 m^2/g, at least about 500 m^2/g, at least about 550 m^2/g, at least about 600 m^2/g, at least about 650 m^2/g, at least about 700 m^2/g, at least about 750 m^2/g, at least about 800 m^2/g, at least about 850 m^2/g, at least about 900 m^2/g, at least about 950 m^2/g, at least about 1000 m^2/g, at least about 1100 m^2/g, at least about 1200 m^2/g, at least about 1300 m^2/g, at least about 1400 m^2/g, at least about 1500 m^2/g, at least about 1600 m^2/g, at least about 1700 m^2/g , at least about 1800 m^2/g, at least about 1900 m^2/g , at least about 2000 m^2/g, at least about 2200 m^2/g, at least about 2400 m^2/g, at least about 2600 m^2/g, at least about 2800 m^2/g, at least about 3000 m^2/g, at least about 3500 m^2/g, at least about 4000 m^2/g, at least about 4500 m^2/g, or at least about 5000 m^2/g. These electrodes may have an average pore size in a range from about 0.3 nm to about 300 nm, from about 0.3 nm to about 100 nm, from about 0.3 nm to about 30 nm, from about 0.3 nm to about 10 nm. In some variations, the electrodes have a pore size distribution wherein at least about 50% of the pores are within about 30% of an average pore size, within about 20% of an average pore size, or within about 10% of an average pore size.

[0110] The electrodes described herein made of carbon material may has a resistivity between about 0.001 Ω-cm to about 0.1 Ω-cm, such as from about 0.001 Ω-cm to about 0.05 Ω-cm, about 0.001 Ω-cm to about 0.01 Ω-cm, or about 0.001 Ω-cm to about 0.005 Ω-cm.

[0111] The electrode material described herein can be made into powders using methods known in the art, such as by grinding, using ball mill or jet milling techniques. The electrode can be made from the conductive powder using methods known in the art. See Bonnefoi, L. et al *J. Power Sources* 79 (1999), 37-42; and U.S. Pat. No. 6,187,061. In one variation, for example, a suspension of the conductive powder and a binder in a appropriate solvent can be cast upon or spread out on a current collector; the wet film is then allowed to dry at room temperature or dried by thermal treatment in vacuum. In another variation, a dried film can be prepared first from the conductive powder and a binder; and is then attached or plated on to the current collector. The thickness of the film is from about 50 to about 1000, about 50 to about 500, about 50 to about 200, about 75 to about 200, about 100 to about 200, about 75 to about 125, about 125 to about 175, about 90 to about 120, about 120 to about 150, about 150 to about 180, about 180 to about 210, or about 140 to about 160 microns. The conductive powder is a powder of any one or a mixture of more than one of the electrode materials described herein. The binder is a suitable polymeric material such as polytetrafluoroethylene (PTFE), carboxymethylcellulose (CMC), polyvynilidiene chloride (PVDC), and the like. The amount of the binder material used is less than or about any of 20%, 15%, 10%, 8%, 5%, 3% or 1% by weight relative to the weight of the conductive powder material. A suitable solvent (e.g. acetone, water, 1-methyl-2-pyrrolidine (NMP), tetrahydrofurane (THF)) is used for suspending the conductive powder and the binder. For example, water can be used when CMC is used as a binder, NMP can be used when PTFE is used as a binder, or THF can be used when PVDC is used as a binder.

II. Energy Storage Devices

[0112] Energy storage devices are described herein. In general, the devices comprise a cell that has first and second electrodes across which a potential may be applied. An electrolyte is provided in the cell between the first and second electrodes. A separator is provided in the electrolyte to prevent the cell from shorting. For example, if the device is a capacitor, an ultracapacitor or battery, the separator is insulating and permeable to ions of the electrolyte so that ions can diffuse to the electrodes to build up the electric double layers at the electrode surfaces, but does not allow substantial current to flow in the electrolyte between the electrodes. If the device is a fuel cell, the separator may comprise a proton exchange membrane. Any electrodes described herein may be used as the first and/or the second electrode in the energy storage device. For example, in the energy storage devices, the first electrode comprises a first conductive network formed by coating an open pore network of a sol-gel derived monolith, e.g., a silica sol-gel derived monolith, with a conductive coating. In some variations of the devices, the first conductive network may remain in the monolith in the first electrode, as described above. In other variations, the first conductive network may be a stand-alone or substantially stand-alone conductive network. These electrodes are described above, and are formed by selectively removing the monolith template after filling an open pore network of the monolith with a conductive material to form the first conductive network. In some energy storage devices, the second electrode also comprises a conductive network formed by coating an open pore network of a sol-gel derived monolith with a conductive coating.

[0113] In certain variations, at least one electrode in the energy storage devices (e.g., an ultracapacitor) may comprise a sol-gel derived monolith comprising an open network of pores, and a conductive network formed by coating a surface of the open network of pores with a material that lends itself to faradaic charge storage and discharge, e.g., a material selected from the group consisting of ruthenium oxide, molybdenum oxide, molybdenum nitride, molybdenum sulfide, tungsten oxide, tungsten nitride, tungsten sulfide, manganese dioxide, iron sulfide, silver oxide, nickel oxyhydroxide, and combinations thereof, and poly(3-methylthiophene) leading to the formation of an asymmetric capacitor.

[0114] Any of the high surface area electrodes derived from a nanoporous sol-gel derived monolith as described herein may be used in the devices. Further, the first electrode and the second electrode may be the same or different. For example, if the energy storage device is a capacitor, both electrodes may be high surface area electrodes formed from sol-gel derived monoliths as described herein. In other variations, the first and second electrodes may be different. For example, if the energy storage device is a battery, an anode may be a high surface area electrode formed from sol-gel derived nanoporous electrode that comprises a reactive species.

[0115] In the energy storage devices, an average pore size and/or a pore size distribution may be selected to accommodate an ionic species of the electrolyte. For example, in an ultracapacitor, an ion of the electrolyte must be able to access the pores of a high surface area electrode as described herein to take advantage of that surface area. If the topography of the conductive surface contains features of a scale too small to accommodate the ionic species of the electrolyte, the effective conductive surface area is reduced. For example, a substantial fraction of the pores in an electrode may have a dimension of about 1 nm to about 2 nm. Further, in some cases, the pore sizes may be adjusted to be generally smaller than a salvation shell of an ionic species in the electrolyte. This may allow the ionic species to move even closer to an electrode surface. Creating a broad distribution of pore sizes may lead to underutilized volume in the electrodes due to relatively low surface area sections and underutilized surface area in the electrodes due to pore sizes that are too small to accommodate an ionic species. Thus, an electrode may have its pore size finely tuned as described herein to increase electrolyte-electrode interactions, and to increase effective utilization of the conductive surface area of the electrodes. In some instances, the electrodes may be customized or selected for use with particular electrolytes.

[0116] In some variations, the energy storage device may be an ultracapacitor. An example of an ultracapacitor is provided in FIG. **6**A. There, ultracapacitor **600** comprises a first nanoporous electrode **601** and a second nanoporous electrode **602** separated by an insulating separator **603**. Current spreading plates **604** and **605** are placed in electrical contact with the nanoporous electrodes **601** and **602**, respectively. An electrolyte **606** is present between the first and second electrode and ionic species of the electrolyte interpenetrates the nanopores in each of the electrodes **601** and **602**. When a potential (e.g., from a battery **607**) is applied between the two electrodes **601** and **602** via electrical leads **609** and **608**, respectively, ions of the electrolyte migrate to the electrode having the opposite charge, including through the separator **603** that is permeable to ions of the electrolyte, to store charge. The ultracapacitor illustrated in FIG. **6**A may be sealed in a container (not shown). Any suitable type of container now known or later developed may be used, e.g., a barrel-shaped can, or a flat coin-shaped can.

[0117] The current spreading plates may be formed of any metal, and have any thickness selected to withstand the voltage and or current levels to which the ultracapacitor will be exposed. For example, in variations, the current spreading plates may comprise copper, nickel, or aluminum.

[0118] The electrodes may comprise any of the high surface area nanoporous electrodes described herein. Although the example shown in FIG. **6**A includes two nanoporous electrodes, variations are contemplated in which only one of the electrodes is a nanoporous electrode, and the other electrode is a standard electrode, e.g., a carbon-based electrode. As described above, the nanoporous electrodes may have an average pore size and pore size distribution selected to allow ingress of an ionic species of electrolyte into the pores, so that the ion can take advantage of the high surface area. In addition, also as described above, the size of the pores may be finely tuned so as to be sized smaller than a salvation sphere of the ionic species to allow that ion to approach even closer to the conductive electrode surface.

[0119] A thickness of an electrode (shown as dimension **610** for electrode **610** and as dimension **612** for electrode **612** in FIG. **6**A) may be any suitable thickness. Factors that may be considered in selecting an electrode thickness include an electrode porosity, a device voltage rating, a surface area of an electrode, a composition of an electrode, and a conductivity of an electrode. In some cases, an electrode thickness may be about 100 microns, about 150 microns, about 200 microns, about 250 microns, about 300 microns, about 350 microns, about 400 microns, about 450 microns, about 500 microns, about 600 microns, about 700 microns, about 800 microns, about 900 microns, or about 1 mm. Electrodes may be formed from sliced sol-gel derived monoliths, e.g., as illustrated and described in connection with FIG. **3**.

[0120] As stated above, the electrodes in an ultracapacitor may be the same or different. In some cases, the electrodes described herein may be used in asymmetric ultracapacitors, i.e., a capacitor in which one electrode comprises a capacitive material that stores charge electrostatically, and one electrode that comprises a material that stores charge via a fast, reversible faradaic process (electron transfer) at a certain electrode potential. Non-limiting examples of capacitive materials include carbonaceous materials, conducting metals and metalloids, and conducting metal oxides. Non-limiting examples of materials that lend themselves to faradaic charge storage include inorganic oxides, sulfides, or nitrides such as oxides, sulfides or nitrides of molybdenum and tungsten, ruthenium oxide, manganese dioxide, iron sulfide, silver oxide, nickel oxyhydroxide, and conducting polymers such as polythiophenes (e.g., poly(3-methylthiophene). Thus, in an asymmetric ultracapacitor, the anode may comprise a capacitive material that has a capacity for electrostatic charge storage, and the cathode may comprise a material that has high faradaic charge storage capacity.

[0121] In an asymmetric ultracapacitor, the anode and/or the cathode may be formed from a nanoporous sol-gel monolith as described herein. For example, the cathode of an asymmetric ultracapacitor may be derived from a sol-gel monolith in which the open pore network has been coated with a carbonaceous material such as graphite, or a graphite-like conducting carbon, a metal or metalloid, or a conducting metal oxide as described herein. As described above, the sol-gel monolith may remain as a support for the electrode, or may function as a template that is substantially removed to result in a high surface area conductive framework that had been formed within the open pore network. The anode of an asymmetric ultracapacitor may be derived from a sol-gel monolith in which the open pore network has been coated with a material that lends itself to faradaic charge storage as described above. Here again, the sol-gel monolith may remain as a support for the anode, or may function as a template that is substantially removed to result in a high surface area conductive framework that had been formed within the open pore network. In some variations of asymmetric ultracapacitors, a sol-gel derived cathode may be used in combination with another type of anode, and a sol-gel derived anode may be used in combination with another type of cathode. Non-limiting examples of alternative cathodes and anodes that may be used in any combination with any of the sol-gel derived electrodes are for example described in U.S. Pat. No. 7,199,997, and A. Balducci et al., *Applied Physics A* 82 (2006), 627-632, each of which is incorporated herein by reference in its entirety.

[0122] An example of an asymmetric ultracapacitor is shown in FIG. **6**B. There, asymmetric ultracapacitor **650** comprises current spreading plates **654** and **656**. The anode **651** is in electrical contact with current spreading plate **654** and the cathode **652** is in electrical contact with current spreading plate **656**. The anode **651** may comprise a material that has high faradaic charge storage capacity, and the cathode **652** may comprise a capacitive material that has high electrostatic storage capacity. An insulating separator **657** that is porous to the electrolyte (not shown) is disposed between the anode **651** and cathode **652**. The anode **651** and/or the cathode **652** may be nanoporous electrodes derived from sol-gel monoliths as disclosed herein. The asymmetric ultracapacitor illustrated in FIG. **6**B may be sealed in a container (not shown). Any suitable type of container now known or later developed may be used, e.g., a barrel-shaped can, or a flat coin-shaped can.

[0123] The electrolyte used in the ultracapacitors (symmetric or asymmetric) may be any suitable electrolyte described herein, otherwise known, or later discovered. For example, the electrolyte may be organic or inorganic. The electrolyte may be selected based on a voltage rating of the ultracapacitor. Organic electrolytes may be selected for ultracapacitors designed to have a voltage rating of about 1.5V to about 3V, or from about 2V to about 3V. Such organic electrolytes may have dielectric constant of about 40. An ionic liquid may be used for devices designed to have a higher voltage rating, e.g., about 5V to about 6V, or about 5V to about 7V. The dielectric constant of ionic liquid electrolytes may be about 30. For low voltage ratings, e.g., voltage ratings below about 2.5V or about 3V, an aqueous electrolyte may be used. Such aqueous electrolytes may have a dielectric constant of about 10.

[0124] Non-limiting examples of suitable organic electrolytes include carbonates such as propylene carbonate, ethylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, methyl ethyl carbonate, methyl butyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, butyl propyl carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, 1,2-pentene carbonate, 2,3-pentene carbonate; nitriles such as acetonitrile, acrylonitrile, propionitrile; sulfoxides such as dimethyl sulfoxide, diethyl sulfoxide, ethyl methyl sulfoxide, benzylmethyl sulfoxide; amides such as formamide, dimethyl formamide; pyrrolidones such as N-methylpyrrolidone; esters such as p-butyrolactone, γ-butyrolactone, γ-valerolactone, β-valerolactone, γ-butyrolactone, 2-methyl-γ-butyrolactone, acetyl-γ-butyrolactone, phosphate triesters; and ethers such as 1,2-dimethoxyethane, 1,2-ethoxyethane, diethoxyethane, methoxyethoxyethane, dibutoxyethane, nitromethane, dimethoxypropane, diethyoxypropane, methoxyethoxypropane, tetrahydrofuran, 2-methyl-tetrahydrofuran, alkyltetrahydrofurans, dialkyltetrahydrofurans, alkoxytetrahydrofurans, dialkoxytetrahydrofurans, 2-methyltetrahydrofuran, 1,2-dioxolane, 1,3-dioxolane, 1,4-dioxolane, 2-methyldioxolane, 4-methyl-dioxolane, alkyl-1,3-dioxolanes, sulfolane, 3-methylsulfolane, diethyl ether, diethylene glycol dialkyl ethers, diethylene glycol dialkyl ethers, triethylene glycol dialkyl ethers, tetraethylene glycol dialkyl ethers, alkylpropionates, dialkyl malonates, alkyl acetates, methyl formate, methyl acetate, methyl propionate, ethyl propionate, and maleic anhydride.

[0125] In some variations of the ultracapacitors, e.g., asymmetric ultracapacitors, solvent-free ionic liquids may be used as electrolytes, e.g., 1-butyl-3-methyl-imidazolium tetrafluoroborate, 1-butyl-3-methyl-imidazolium hexafluorophosphate, and N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)-imide.

[0126] The separator used in the ultracapacitors (symmetric or asymmetric) may be any suitable separator, and as described above, is electrically insulating and permeable to ions of the electrolyte so that the ions can migrate to the electrodes, but prevent shorting of the capacitor. Non-limiting examples of separators include thin paper films, or Celgard™ separator films. In some variations, a sol-gel derived separator may be used, where the sol-gel derived separator is designed to have an appropriate permeability for ions in the electrolyte.

[0127] FIG. **7** illustrates various combinations of specific powers (W/kg) and specific energy (W-h/kg) that may be achieved with the ultracapacitors (symmetric or asymmetric) described here. There, the cross-hatched region representing specific powers greater than about 10, and specific energies of about 0.1 W-h/kg to about 1000 W-h/kg indicates the range of specific powers and specific energies that may be delivered with the ultracapacitors described here. Thus, some of the ultracapacitors may have a specific energy of at least about 0.1 W-h/kg, at least about 1 W-h/kg, at least about 10 W-h/kg, at least about 30 W-h/kg, at least about 50 W-h/kg, at least about 100 W-h/kg, at least about 120 W-h/kg, at least about 150 W-h/kg, at least about 170 W-h/kg, at least about 190 W-h/kg, at least about 200 W-h/kg, at least about 300 W-h/kg, at least about 400 W-h/kg, at least about 500 W-h/kg, or as high as about 1000 W-h/kg. Ultracapacitors described here may have a specific power of about 10 W/kg or higher, e.g., about 10 W/kg, about 50 W/kg, about 100 W/kg, about 500 W/kg, about 1 kW/kg, about 5 kW/kg, about 10 kW/kg, about 50 kW/kg, about 100 kW/kg, or even higher.

[0128] Ultracapacitors (symmetric or asymmetric) as described herein may be capable of many charge/discharge cycles, e.g., greater than about 3×10^5 cycles. Further, the ultracapacitors may have very high charge and discharge efficiencies, e.g., about 90% or greater, about 95% or greater, about 98% or greater, about 99% or greater, about 99.5% or greater, about 99.8% or greater, about 99.9% or greater, or very close to 100%.

[0129] In an ultracapacitor described herein where the conductive material in the electrode is made of conductive carbon from any source, the capacitance of the carbon material may be in a range from about 15 F/g to about 500 F/g. In an ultracapacitor device described herein, the capacitance may be in the range of about 3 F/g to about 125 F/g for electrodes made with conductive carbon. In an asymmetric ultracapacitor device described herein, the capacitance may be in the range about 6 F/g to about 250 F/g.

[0130] Ultracapacitors (asymmetric or symmetric) having alternate electrode configurations are possible. For example, the electrodes described herein may form a portion of an interdigitated electrode assembly. Such an interdigitated electrode assembly may be used to increase an energy storage capacity or voltage rating of an ultracapacitor. Referring now to FIG. **8**, ultracapacitor **800** comprises a first electrode assembly **801**, and a second electrode assembly **802**. A potential (not shown) may be placed between the first and second electrode assemblies with electrical leads **803** and **804**, respectively. The first electrode assembly **801** comprises a first metal or metallized current spreading plate **805** with which electrical lead **803** makes electrical contact, and the second electrode assembly **804** comprises a second metal or metallized current spreading plate **806** with which electrical lead **804** makes electrical contact. Extending generally perpendicularly from first current spreading plate **805** of the first electrode assembly **801** is a series of spaced-apart electrodes **807**. Any one or any combination of the electrodes **807** may comprise a high surface area electrode as described herein. For example, any single one, any subset, or all of the electrodes **807** may comprise a high surface area silica sol-gel derived electrode having a thickness of about 150 microns. Similarly, extending perpendicularly from the second current spreading plate **806** of the second electrode assembly **802** is a series of spaced-apart electrodes **808**. Here again, any single electrode **808**, any subset of the electrodes **808**, or all of the electrodes **808** may comprise a high surface area electrode as described herein. Any one of the electrodes **808** may comprise a high surface area silica sol-gel derived electrode having a thickness of about 150 microns. The electrodes **807** and **808** may be interdigitated with each other as shown in FIG. **8**. Separating the electrodes **807** and **808** are separators **810**. An electrolyte (not shown) is dispersed in the cell in the volume **811** between the electrode assemblies **801** and **802**, filling the volume between the interdigitated electrodes **807** and **808**. The electrolyte may be any electrolyte described herein, otherwise known or later developed. The separators **810** are porous to ionic species in the electrolyte, and may be any separators described herein, otherwise known, or later developed.

[0131] Electric double layer capacitors (EDLCs) have applications in a variety of technology areas which require energy storage and energy delivery rapidly and repetitively with relatively high power. For example, EDLC may be used in the automobile sector like hybrid-electric vehicles of various types where the EDLC could be used to augment the vehicle battery, leveling the load on the battery by powering acceleration and recovering energy during braking, thereby increasing battery life and reducing battery size and weight. Another general application area would be in the motion capture of energy that would otherwise be wasted; for example, the capture of energy in the repetitious up and down movement of heavy shipping containers (Miller and Burke *The Electrochemical Society Interface* Spring 2008, 53-57). Additionally, applications could be found for bulk energy storage by electric utilities by storing off-peak electricity at night for use during the day or other grid applications like load leveling solar and wind electric generating farms. Many additional applications could be found in consumer electronics and power tools.

III. Systems

[0132] Energy storage systems are also provided here. These systems comprise multiple energy storage cells, at least some of which may be connected in series or in parallel. In these systems, each energy storage cell comprises two electrodes configured to be oppositely charged and an electrolyte disposed between the two electrodes. At least one electrode in at least one of the cells comprises an electrode that has been derived from a sol-gel monolith as described herein. For example, at least one of the electrodes in the multi-cell energy storage systems may comprise a sol-gel monolith having an open pore network that has been coated with a conductive coating, or a conductive network formed from a sol-gel monolith by coating or filling its open pore network with a conductive material, and substantially removing the sol-gel template to provide a stand-alone conductive framework. In certain systems, more than one or all electrodes may be derived from sol-gel monoliths. In these energy storage systems, the monolith used may be derived from any suitable sol gel, but in some cases, it is derived from a silica sol gel. Such multiple cell energy storage systems may be used in applications requiring increased energy storage capacity and/or increased voltage ratings.

[0133] Examples of energy storage systems are provided in FIGS. **9**A-**9**B. Referring first to FIG. **9**A, system **950** comprises multiple energy storage cells **951** connected in series. An external potential (not shown is applied across the series arrangement using electrical leads **952** and **953**. Each cell **951** comprises an ultracapacitor (symmetric or asymmetric). At least one of cells **951** may comprise an ultracapacitor as described herein, e.g., similar to that illustrated in FIG. **6**A or **6**B. Thus, each cell comprises a first electrode **955** and an opposite polarity second electrode **956**, and a separator **957** that is permeable to ionic species in an electrolyte (not shown) that is present in each cell. Each positive polarity electrode of a cell is connected to a negative polarity electrode of an adjacent cell so that the cells are arranged in electrical series. The entire system may be sealed in any suitable container, e.g., in a housing or barrel shaped can, or a lower profile relatively flat container.

[0134] Referring next to FIG. **9**B, system **900** comprises multiple energy storage cells **901** connected in series. An external potential (not shown) is applied across the entire series, using electrical leads **902** and **903**. Each cell **901** comprises an ultracapacitor (symmetric or asymmetric). At least one of the cells **901** may comprise an ultracapacitor as described herein, e.g., similar to that illustrated in FIG. **6**A or **6**B. Thus each cell **901** comprises a first electrode **905** and an opposite polarity second electrode **906**. Separating the first and second electrodes is a separator **907** that is permeable to ionic species in the electrolyte (not shown) that is present in each cell. Each positive polarity electrode of a cell is connected to a negative polarity electrode of an adjacent cell so that the cells are arranged in electrical series. In this particular variation, adjacent electrodes are configured as bipolar electrode structures, where electrodes of opposite polarity are separated by electrolyte and a solid layer **908** that is nonporous to the electrolyte. As illustrated, opposite polarity electrodes may be arranged in an interdigitated manner relative to each other. The entire system may be sealed in any suitable container, e.g., a box or barrel shaped can, or a lower profile flatter container.

[0135] For energy storage systems comprising series-connected cells, such as those illustrated in FIG. **9**A or **9**B, the electrodes used may be any electrodes described herein. At least one of the electrodes in the system **900** or system **950**, which may be either a positive electrode or a negative electrode, is derived from a sol-gel as described herein.

[0136] Another example of an energy storage system is provided in FIG. **10**. There, system **1000** comprises multiple energy storage cells **1001** connected in parallel. An external potential (not shown) is applied across the parallel arrangement using electrical leads **1002** and **1003**. Any one of or all of the cells **1001** may comprise an ultracapacitor similar to that illustrated in FIG. **6**A or **6**B. Thus, each cell **1001** comprises a first electrode **1005** and an opposite polarity second electrode **1006**. Separating the first and second electrodes is an insulating separator **1007** that is permeable to ionic species in the electrolyte (not shown) that is present in each cell. Each positive polarity electrode of a cell is connected to the positive polarity electrodes of other cells in the circuit, and each negative polarity electrode of a cell is connected to the negative polarity electrodes of other cells in the circuit so that the cells are connected in parallel. At least one of the electrodes in the in one of the cells **1001** in system **1000** is a high surface area electrode derived from a sol-gel as described herein.

[0137] The ultracapacitors described herein may be used in a variety of applications. For example, they may be used to replace batteries in certain applications, e.g., for handheld electronic applications. In other situations, they may provide backup power for electronic devices, e.g., for computers. The ultracapacitors may be used in combination, e.g., in a parallel circuit, with a battery to augment peak power delivery of that battery. The ultracapacitors may be used as energy storage devices in a hybrid-electric engine such as a hybrid-electric engine used to power vehicles.

[0138] The following Example is provided to illustrate but not limit the invention.

Example 1

Process for Preparing a Monolithic Carbon Electrode Material Using a Nanoporous Monolith as a Template

[0139] The template used to form the monolithic carbon electrode material was made from a thin sol-gel wafer. The wafer was fabricated by casting a silica sol-gel solution into a mold. The chemical composition and molar ratio of the components of the sol-gel solution were 1 TEOS (tetraethyl orthosilicate), 2.25H_2O (water), 0.075 HF (hydrofluoric acid) and 0.01 HCl (hydrochloric acid). These chemicals were then mixed, cast into a mold and left sitting at room temperature for up to 3 hours. The sample (sol-gel plus mold) was then placed in an incubator at 33° C. to age for up to 72 hours. The sample was then removed to an oven and baked at 160° C. under nitrogen for up to 24 hours (the ramp to 160° C. was done in air and the nitrogen turned on at 160° C.). After the drying step at 160° C. the sample was then sintered in a furnace at 720° C. for 2 hours in air. The resulting silica wafer had a surface area of 570 m^2/g with an average pore diameter of 5 nm; and 69.5% of the pores in the resulting silica wafer were within 20% of the average pore diameter of 5 nm. A wafer having 1 mm in thickness and 25 mm in diameter was generated.

[0140] The first step in the formation of a monolithic carbon electrode material was to take the silica sol-gel derived wafer having 1 mm in thickness and 25 mm in diameter and impregnate it with furfuryl alcohol. This was accomplished by placing the wafer in a shallow container that was filled with enough furfuryl alcohol to cover the wafer and allowing it to soak for up to five hours. The furfuryl alcohol saturated wafer was then removed from the container and excess furfuryl alcohol was cleaned from the surface of the wafer. The furfuryl alcohol saturated wafer was then heated at 123° C. in air for 16 hours to create polyfurfuryl alcohol throughout the porous silica network of the wafer. This composite material was then heated under nitrogen at 365° C. for five hours.

[0141] The sample was cooled to room temperature. The composite wafer was then soaked in concentrated HF and sonicated for one hour to remove the silica template leaving a monolith carbon wafer in its place. The carbon monolith was heated to 1000° C. for 3 hours in a 5% CO_2, 95% N_2 atmosphere. The sample was then cooled to room temperature. The resulting material was tested for surface area, resistivity, and capacitance. This material had a measured BET surface area of 700 m^2/g and average pore diameter of 9 nm; and 46.4% of the pores were within 30% of the average pore diameter of 9 nm. The resistivity of the material was 5 Ω-cm and had a measured capacitance of 50 F/g. Without wishing to be bound by theory, the relatively high resistivity may be due to defects in the linear chains formed during the furfuryl alcohol polymerization process. Resistivity may be lowered by adding cross-linking agents (such as lysine) to improve the connectivity of the carbon framework as well as by optimizing the carbonization process to maximize the graphite-like nature of the final material.

[0142] This disclosure is illustrative and not limiting. Further modifications will be apparent to one skilled in the art in light of this disclosure and such modifications are intended to fall within the scope of the appended claims. Each publication and patent application cited in the specification is incorporated herein by reference in its entirety as if each individual publication or patent application were specifically and individually put forth herein.

What is claimed is:

1. An electrode for use in an energy storage device, the electrode comprising:

a sol-gel derived monolith comprising an open network of pores; and

a conductive material deposed on a surface of the open network of pores or partially filling the open network of pores to form a conductive network.

2. The electrode of claim **1**, comprising a silica sol-gel derived monolith.

3. The electrode of claim **1**, wherein at least one of an average pore size and a pore size distribution in the open pore network is selected based on an ionic species of an electrolyte used in the energy storage device.

4. The electrode of claim **1**, wherein the conductive material comprises graphite, a graphite-like material, graphene, a graphene-like material, or carbon.

5. The electrode of claim **1**, wherein the conductive material is carbon derived from the polymerization and carbonization of one or more carbon precursor materials selected from the group consisting of furfural, furfuryl alcohol, polyfurfuryl alcohol, resorcinol formaldehyde, sucrose and glucose.

6. The electrode of claim **1**, wherein the conductive material comprises a metal, metal oxide, metal sulfide, or metal nitride selected from the group consisting of platinum, nickel, gold, palladium, molybdenum, tin oxide, indium tin oxide, zinc oxide, aluminum doped zinc oxide, vanadium pentoxide, titanium dioxide, molybdenum oxide, ruthenium oxide, molybdenum sulfide, tungsten oxide, tungsten sulfide, tungsten nitride, manganese dioxide, iron sulfide, silver oxide, nickel oxyhydroxide, molybdenum nitride and combinations thereof.

7. The electrode of claim **1**, wherein the sol-gel derived monolith has an average pore diameter between about 0.3 nm and about 30 nm.

8. The electrode of claim **1**, wherein the sol-gel derived monolith has an average pore diameter between about 0.3 nm and about 10 nm.

9. The electrode of claim **1**, wherein the sol-gel derived monolith has a pore size distribution wherein at least about 50% of pores are within about 30% of an average pore size.

10. The electrode of claim **1**, wherein the sol-gel derived monolith comprises a pore size distribution wherein at least about 50% of pores are within about 20% of an average pore size.

11. The electrode of claim **1**, comprising a conductive surface area of at least about 500 m^2/g.

12. The electrode of claim **1**, configured for use in a capacitor, an electric double layer capacitor, a battery, or a fuel cell.

13. A method for making an electrode, the method comprising:

a) providing a sol-gel derived monolith comprising an open network of pores; and

b) coating a surface of the open network of pores or partially filling the open network of pores with a conductive material to form a conductive network.

14. The method of claim **13**, wherein the sol-gel derived monolith comprises a silica sol-gel derived monolith.

15. The method of claim **13**, wherein the sol-gel derived monolith comprises a predetermined average pore size and/or pore size distribution to accommodate an ionic species of the electrolyte.

16. The method of claim **13**, wherein the sol-gel derived monolith is a wafer made from slicing a monolithic rod or casting in a mold.

17. The method of claim **13**, wherein the sol-gel derived monolith having a preselected average pore size and/or pore size distribution is made by reacting a sol-gel precursor with water in the presence of a catalyst, and controlling a rate of gelation using the catalyst.

18. The method of claim **17**, wherein the catalyst comprises hydrofluoric acid, and the molar ratio of the hydrofluoric acid relative to the sol-gel precursor is increased to increase an average pore size.

19. The method of claim **18**, wherein the catalyst comprises hydrofluoric acid and a second acid.

20. The method of claim **19**, wherein the second acid is selected from the group consisting of HCl, HNO_3 and H_2SO_4.

21. The method of claim **19**, wherein the second acid is selected from the group consisting of formic acid, acetic acid, and citric acid.

22. The method of claim **19**, wherein the second acid has a pK_a that is about 2 to about 4.

23. The method of claim **17**, wherein the sol-gel derived monolith has a preselected average pore size in a range from about 0.3 nm to about 30 nm.

24. The method of claim **17**, wherein the sol-gel derived monolith has a preselected average pore diameter in a range from about 0.3 nm to about 10 nm.

25. The method of claim **13**, wherein coating the surface of the open pore network with a conductive material comprises synthesizing a graphite layer or a graphite-like layer on the surface.

26. The method of claim **25**, wherein the graphite-like layer is formed by polymerizing resorcinol and formaldehyde in situ in the open pore network and sintering the resulting polymer to form the graphite-like layer.

27. The method of claim **13**, wherein coating the surface of the open pore network with a conductive material comprises depositing a conductive metal, metal oxide, metal sulfide or metal nitride on the surface using chemical vapor deposition.

28. The method of claim **13**, wherein coating the surface of the open pore network with a conductive material comprises building up a conductive layer comprising a metal, metal oxide, metal sulfide or metal nitride using atomic layer deposition.

29. The method of claim **13**, wherein coating the surface of the open pore network with a conductive material comprises impregnating the open pore network with a colloidal solution of a metal and/or metal oxide, drying the monolith to remove liquid from the colloidal solution, and coalescing the metal and/or metal oxide particles together to form the conductive electrode surface.

30. The method of claim **29**, wherein the metal and/or metal oxide particles are coalesced together using rapid thermal processing.

31. The method of claim **13**, wherein partially filling the open network of pores comprises impregnating the open network of pores with a carbon precursor material selected from the group consisting of furfural, furfuryl alcohol, polyfurfuryl alcohol, resorcinol formaldehyde, sucrose and glucose, and coverting the carbon precursor material into a conductive carbon material by polymerization and carbonization of the carbon precursor material in the open network of pores.

32. The method of claim **13**, wherein the electrode has a conductive surface area of at least about 500 m^2/g.

33. An electrode made by the method of claim **13**.

34. A method of making an electrode, the method comprising:

a) providing a sol-gel derived silica monolith comprising an open network of pores;

b) coating a surface of the open network of pores or at least partially filling the open network of pores with a conductive material; and

c) selectively removing the silica material in the monolith to provide a conductive network.

35. The method of claim **34**, wherein the open network of pores are substantially filled with the conductive material.

36. The method of claim **34**, wherein at least partially filling the open network of pores comprises impregnating the open network of pores with a colloidal solution of metal and/or metal oxide particles.

37. The method of claim **34**, wherein at least partially filling the open network of pores comprises impregnating the open network of pores with one or more precursor to a conducting polymer, and reacting the one or more precursors to form the conductive network.

38. The method of claim **37**, wherein at least partially filling the open network of pores comprises impregnating the open network of pores with one or more carbon precursor materials selected from the group consisting of furfural, furfuryl alcohol, polyfurfuryl alcohol, resorcinol formaldehyde, sucrose and glucose, and converting the one or more carbon precursor materials into carbon by polymerization and carbonization.

39. The method of claim **34**, adapted for making a conductive network having a conductive surface area of at least about 500 m^2/g.

40. The method of claim **34**, wherein the sol-gel derived silica monolith has an average pore diameter between about 0.3 nm and about 10 nm.

41. The method of claim **34**, wherein the sol-gel derived silica monolith has a pore size distribution wherein at least about 50% of pores are within about 20% of an average pore size.

42. An electrode made by the method of claim **34**.

43. The electrode of claim **42**, configured for use in a capacitor, an electric double layer capacitor, a battery, or a fuel cell.

44. A method of making an electrode material, the method comprising:

a) providing a silica sol-gel derived monolith comprising an open network of pores;

b) coating a surface of the open network of pores or at least partially filling the open network of pores with a conductive material to form a conductive network;

c) selectively removing the silica material in the monolith to provide a conductive network; and

d) making the resulting material from step c) into a conductive powder.

45. The method of claim **44**, wherein at least partially filling the open network of pores comprises impregnating the open network of pores with one or more carbon precursor materials selected from the group consisting of furfural, furfuryl alcohol, polyfurfuryl alcohol, resorcinol formaldehyde, sucrose and glucose, and converting the one or more carbon precursor materials into carbon by polymerization and carbonization.

46. The method of claim **44**, wherein the silica sol-gel derived monolith has an average pore diameter between about 0.3 nm and about 10 nm, and/or has a pore size distribution wherein at least about 50% of the pores are within about 20% of the average pore size.

47. The method of claim **44**, adapted for making a conductive network having a conductive surface area of at least about 500 m^2/g.

48. An electrode material made by the method of claim **44**.

49. A method of making an electrode, the method comprising:

a) mixing an electrode material made by the method of claim **44** with a binder; and

b) drying the mixture formed in step a) on a surface to form a thin film.

50. An electrode made by the method of claim **49**.

51. The electrode of claim **50**, configured for use in a capacitor, an electric double layer capacitor, a battery, or a fuel cell.

52. An energy storage device comprising:

first and second electrodes;

an electrolyte disposed between the first and second electrodes; and

a separator disposed between the first and second electrodes;

wherein the first electrode and/or the second electrode comprise a conductive network formed from a sol-gel derived monolith by coating a surface of an open pore network of the monolith or at least partially filling an open pore network of the monolith with a conductive material.

53. The energy storage device of claim **52**, wherein the sol-gel derived monolith remains as a part of the first electrode and/or the second electrode to support the conductive network.

54. The energy storage device of claim **52**, wherein the conductive network in the first electrode and/or the second electrode is formed by using the silica sol-gel derived monolith as a template and subsequently removing at least part of the material of the monolith so that the conductive network is substantially a stand-alone conductive network.

55. The energy storage device of claim **52**, wherein the energy storage device is an electric double layer capacitor that has a specific energy of at least about 10 W-h/kg.

56. The energy storage device of claim **52**, wherein the energy storage device is an electric double layer capacitor that has a specific energy of at least about 100 W-h/kg.

57. The energy storage device of claim **52**, wherein the energy storage device is an electric double layer capacitor that has a specific power of at least about 10 W/kg.

58. The energy storage device of claim **52**, wherein the energy storage device is an electric double layer capacitor that has a specific power of at least about 100 W/kg.

59. The energy storage device of claim **52**, wherein the energy storage device is an electric double layer capacitor that has a specific power of at least about 1 kW/kg.

60. The energy storage device of claim **52**, wherein the energy storage device is an electric double layer capacitor that is configured for energy storage in a hybrid-electric engine.

61. The energy storage device of claim **52**, wherein the energy storage device is an electric double layer capacitor that is configured to augment peak power of a battery in a circuit.

62. A method for storing energy, the method comprising applying a potential between first electrode and second electrode, wherein the first electrode and/or the second electrode comprise a conductive network formed from a sol-gel derived monolith by coating a surface of an open pore network of the monolith or at least partially filling an open pore network of the monolith with a conductive material.

63. An energy storage system comprising multiple interconnected cells, each cell comprising two electrodes configured to be oppositely charged and an electrolyte disposed between the two electrodes, wherein at least one of the electrodes comprises a conductive network formed from a sol-gel derived monolith by coating a surface of an open pore network of the monolith or at least partially filling an open pore network of the monolith with a conductive material.

64. The energy storage system of claim **63**, wherein the sol-gel derived monolith remains as part of the first electrode and/or the second electrode, and the conductive material forms a conductive coating or filling within the open pore network.

65. The energy storage system of claim **63**, wherein the first electrode and/or the second electrode comprise a conductive network formed by substantially removing the material of the sol-gel derived monolith following coating or filling the open pore network with the conductive material.

66. The energy storage system of claim **63**, wherein at least some of the multiple cells are connected in series.

67. The energy storage system of claim **63**, wherein at least some of the multiple cells are connected in parallel.

68. The energy storage system of claim **63**, further comprising a separator disposed between the two electrodes.

69. An asymmetric ultracapacitor comprising a first electrode configured to store charge electrostatically, and a second electrode configured to store charge via a reversible faradaic process, wherein the first electrode is derived from a sol-gel derived monolith comprising an open pore network coated or filled with a conductive material and/or the second electrode is derived from a sol-gel derived monolith comprising an open pore network coated or filled with a conductive material.

70. The asymmetric ultracapacitor of claim **69**, wherein the first electrode is derived from a sol-gel derived monolith comprising an open network of pores coated or partially filled with a conductive carbonaceous material.

71. The asymmetric ultracapacitor of claim **69**, wherein the first electrode is configured to be positively charged.

72. The asymmetric ultracapacitor of claim **69**, wherein the second electrode is derived from a sol-gel derived monolith comprising an open pore network coated or partially filled with a material selected from the group consisting of ruthenium oxide, molybdenum oxide, molybdenum nitride, molybdenum sulfide, tungsten oxide, tungsten nitride, tungsten sulfide, manganese dioxide, iron sulfide, silver oxide, nickel oxyhydroxide, and combinations thereof, and poly(3-methylthiophene).

73. The asymmetric ultracapacitor of claim **69**, wherein the second electrode is configured to be negatively charged.

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