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(54) Title: EDIBLE SUPERCAPACITORS

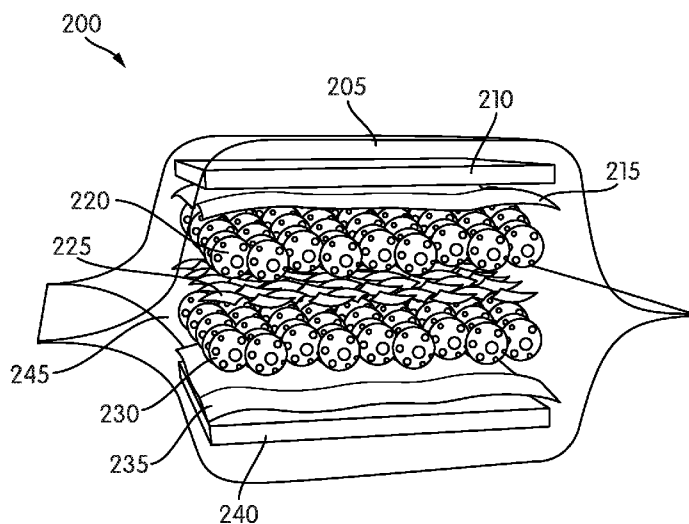


FIG. 2

(57) Abstract: Systems and methods are described for an edible capacitive power source such as a supercapacitor device. The capacitive power source includes an anode electrode, an anode current collector, a cathode electrode, and a cathode current collector, arranged in layers with a separator layer positioned between the anode electrode and the cathode electrode forming a symmetrical electrical double-layer capacitor. The anode electrode, the anode current collector, the cathode electrode, the cathode current collector, and the separator layer are all constructed of non-toxic, edible materials. The packaging material, the conductive anode tab, and the conductive cathode tab are all also constructed of non-toxic, edible materials forming a completely edible capacitive power source package.



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EDIBLE SUPERCAPACITORS

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Nos. 62/209,695, filed August 25, 2015, and 62/292,625, filed February 8, 2016, the entire contents of both of which are incorporated herein by reference.

BACKGROUND

[0002] The present invention relates to supercapacitors and methods for manufacturing supercapacitors for use in medical device applications. According to a report from EvaluatePharma, the global medical device market will reach \$440 billion by 2018. Many of these devices, such as deep brain neurostimulators, cardiac defibrillators, pacemakers and insulin pumps, require an embedded energy source.

SUMMARY

[0003] Batteries, especially Li-ion batteries, are widely used as medical device power sources. However, batteries generally contain toxic metals (e.g., lithium, lead, or cadmium) as well as many other toxic organic components in the electrolyte. Also, because of limitations relating to their internal electrochemical properties, batteries are generally not suitable for some special cases such as outputting high frequency impulses or high instantaneous power.

[0004] In various embodiments, this invention provides a very clean, non-toxic mechanism for manufacturing supercapacitors, specifically electric double-layer capacitors, that are able to accept and deliver charge much faster than batteries and tolerate a greater number of charge and discharge cycles. Various examples are provided in this disclosure for the fabrication of a novel symmetrical edible electric double-layer capacitor made entirely out of food.

[0005] In one embodiment, the invention provides a capacitive power source that includes an anode electrode, an anode current collector, a cathode electrode, and a cathode current collector, arranged in layers with a separator layer positioned between the anode electrode and the cathode electrode forming a symmetrical electrical double-layer capacitor. The anode electrode, the anode current collector, the cathode electrode, the cathode current collector, and the separator

layer are all constructed of non-toxic, edible materials. In some such embodiments, the layered arrangement is enclosed in a packaging material with a conductive anode tab and a conductive cathode tab extending from the packaging material. The conductive anode tab is coupled to the anode current collector and the conductive cathode tab is coupled to the cathode current collector. The packaging material, the conductive anode tab, and the conductive cathode tab are all also constructed of non-toxic, edible materials forming a completely edible capacitive power source package.

[0006] In some embodiments, the invention provides a supercapacitor that includes activated charcoal (e.g., from dietary supplement capsules) as the electrode material. Slurries are prepared by mixing the activated charcoal with egg white. A 23kt edible gold leaf material is used as a current collector and unbleached cellulose paper is attached at the back of the thin gold leaf for supporting purposes. Egg white is also used as a binder between the gold leaf and the cellulose paper. Roasted seaweed – for example, the type generally used for sushi, is used as a separator and gelatin sheet is used as a package material. An electrolyte drink, such as Gatorade, which contains 0.02 mol/L sodium ion and 0.003 mol/L potassium ion, is used as an electrolyte.

[0007] In some examples, the edible, food-based supercapacitors exhibit antibacterial activity capable of killing bacteria *in vitro* and are sufficiently powerful to drive a commercial snake camera with wireless charging capabilities. By storing electric charges in food, these systems demonstrate that properly assembled food materials can function as biomedical devices.

[0008] Other aspects of the invention will become apparent by consideration of the detailed description and accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Fig. 1A is an exploded view of a supercapacitor according to one embodiment.

[0010] Fig. 1B is a table listing potential non-toxic, edible materials that could be used to construct the various components of the supercapacitor of Fig. 1A.

[0011] Fig. 2 is a cross-sectional view of a specific example of a supercapacitor according to Fig. 1A.

[0012] Fig. 3A is a SEM image of the relative particle size and porous structure of the activated charcoal material in the supercapacitor of Fig. 2.

[0013] Fig. 3B is a TEM image of the relative particle size of the activated charcoal material in the supercapacitor of Fig. 2.

[0014] Fig. 4 is a graph demonstrating the output of a Brunauer-Emmett-Teller (BET) test demonstrating the surface area of the activated charcoal material of Figs. 3A and 3B.

[0015] Fig. 5 is a series of overhead images of the gelatin packaging material of the supercapacitor of Fig. 2 in a simulated gastric fluid over time during a dissolution test.

[0016] Fig. 6 is a graph of the time evolutions of strains of the supercapacitor of Fig. 2.

[0017] Fig. 7 is a graph of the CV curves for the supercapacitor of Fig. 2 at scan rates from 5mV/s to 100 mV/s.

[0018] Fig. 8 is a graph of voltage as a function of time during galvanostatic charge-discharge cycles for the supercapacitor of Fig. 2.

[0019] Fig. 9 is a graph of the specific capacitance of the supercapacitor of Fig. 2 for each cycle during the Galvanostatic charge-discharge cycles of Fig. 9.

[0020] Fig. 10 is a graph of the electrochemical impedance spectroscopy (EIS) analysis for the supercapacitor of Fig. 2 before the first discharge cycle and after 1,000 charge-discharge cycles.

[0021] Fig. 11 is a graph of energy and power densities of the supercapacitor of Fig. 2 calculated from the constant current density charge-discharge curves measured with 250 mA/g, 500 mA/g, 1 A/g, 2 A/g, and 4 A/g.

[0022] Fig. 12 is a graph of specific capacitance for six different supercapacitor material combinations for 1,000 charge-discharge cycles at a constant current density of 1 A/g.

[0023] Fig. 13 is an elevation view of an experimental set-up with a series of three edible supercapacitors powering a light emitting diode (LED) while partially immersed in a simulated gastric fluid.

[0024] Fig. 14A is an overhead view of a wireless charging system for an edible supercapacitor including a transmitter chamber and a receiver lid.

[0025] Fig. 14B is a perspective view of the transmitter chamber of Fig. 14A.

[0026] Fig. 14C is a perspective view of the receiver lid of Fig. 14B.

[0027] Fig. 15 is a graph of the current and voltage profiles during the wireless charging using the wireless charging system of Figs 14A-14C

[0028] Fig. 16 is an elevation view of an edible supercapacitor packaged in a standard 000 size capsule.

[0029] Fig. 17 is an elevation view of an experimental set-up for demonstrating the antimicrobial effect of the supercapacitor of Fig. 16 in a 3 mL *E. coli*-PBS suspension.

[0030] Fig. 18-21 are graphs of the mean colony-forming units (CFU) and standard error of the mean (SEM) for four different experiments where exponential-phase *E. coli* is exposed to alternating on-off supercapacitor mediated electrical current for 60-minutes using the experimental set-up of Fig. 17.

[0031] Fig. 22 is an overhead view of a patterned edible supercapacitor constructed using inkjet printing.

DETAILED DESCRIPTION

[0032] Before any embodiments of the invention are explained in detail, it is to be understood that the invention is not limited in its application to the details of construction and the arrangement of components set forth in the following description or illustrated in the following drawings. The invention is capable of other embodiments and of being practiced or of being carried out in various ways.

[0033] Novel and innovative medical technologies and devices have emerged to treat various diseases, such as deep brain stimulators for Parkinson's diseases, vagal nerve stimulators for epilepsy, electronic aspirin for head or facial pains, and insulin pumps for diabetes, among others. Although implantable electronic devices have revolutionized the care of patients, they harbor shortcomings such as the need for operations and perioperative complications associated with an operation, battery changes, and revisions from time to time. Biodegradable electronics and bioresolvable devices, such as individual transistors, primary battery and biosensors, and organic field effect transistors, might provide an alternative option to implantable electronics. Although biodegradable electronics might resolve the issue of repeat surgery, they may introduce other inherent shortcomings, such as limitations with structural materials and properties.

[0034] In addition to implantation of permanent and biodegradable devices, the digestive system may serve as another route for administration of electronics that can modulate cellular and organ function without the need for implantation. With the use of capsule endoscopy, electronic devices could pass through the digestive tract and modulate its function.

[0035] The systems and methods described in this disclosure bridge the food industry, material sciences, device fabrication, and biomedical engineering by demonstrating fully functional and edible supercapacitors, a type of energy source that can be used in electronics. In some implementations, all of the materials involved in generating the supercapacitor package are explicitly originated from edible and nontoxic food products, including, for example, activated charcoal, seaweed, polyelectrolyte drink, rice paper, egg, gold leaf, cooking sauces, collagen-based candy, and cheese. In some implementations, these edible supercapacitors also exhibit in vitro antibacterial activity and are capable of powering an endoscopic “snake” camera with wireless charging capability.

[0036] Fig. 1A illustrates an exploded view of a layered supercapacitor device 100. The supercapacitor 100 includes a packaging material 105 at the top and bottom of the device 100. In some implementations, as discussed in further detail below, the packing material 105 at the top and bottom of the device 100 are sealed together to enclose the other layers of the device 100 and to provide a sealed supercapacitor package. An anode conductive tab 110 is sandwiched between the packaging material layer 105 and an anode current collector layer 115 or, in some

implementations, the anode conductive tab 105 is provided as part of the anode current collector layer 115. Similarly, a cathode conductive tab 140 is sandwiched between the packaging material layer 105 and a cathode current collector layer 135 or, in some implementations, the cathode conductive tab 140 is provided as part of the cathode current collector layer 135. A first electrode layer 120 and a second electrode layer 130 are positioned between the anode current collector layer 115 and the cathode current collector layer 135 and are separated by a separator layer 125.

[0037] The electrode layers 120, 130 may be constructed of a conductive and porous material such as activated charcoal, copper, magnesium, and gold or silver powder paste. In some implementations, the electrode layers 120, 130 are provided by combining an electrode material (e.g., activated charcoal) with a binder such as egg white to create a slurry. The anode current collector layer 115 and cathode current collector layer 135 must be conductive and can include, for example, gold or silver leaf/foil. The separator layer 125 includes a porous insulator material and can be constructed, for example, of seaweed, air-dried meat, rice paper, pork casing, sugar sheet, vegetable paper, wafer paper (made from potato starch), or Tapioca paper. The packaging material layer 105 is generally insulating and can be provided as gelatin, potato starch, soy lecithin paper, edible waxed paper/film, or another edible film. Gummy drops, gum, or dough may also be used as a packaging material, but may require further processing. One or more of these layers may be coupled together using a sticky binding material such as, for example, egg, egg powder, sugar, GellanGun, starch, honey, extract juice from sticky food (e.g., okra or chineseavam), or carboxymethyl cellulose (CMC) (i.e., cellulose gum). In some implementations, as discussed further below, an electrolyte material may also be included within the semiconductor device 100 package. The electrolyte material contains ions and can be provided, for example, as phosphate buffered saline (PBS), an electrolytic drink such as Gatorade, lemonade, coconut water, vegetable juice (e.g., V8), gel electrolytes (e.g., barbeque sauce), Jell-O, or cheese. Fig. 1B illustrates a table of various possible food-based materials that can be used to provide layers/components of the supercapacitor device 100 illustrated in Fig. 1a.

[0038] Fig. 2 illustrates a specific example of a supercapacitor 200 constructed according to the example of Fig. 1A. All components of the supercapacitor 200 of Fig. 2 originate from food. A first segregation layer of cheese 210 and a second segregation layer of cheese 240 are provided

to separate the active supercapacitor materials from a gelatin package 205. A first current collector layer 215 and a second current collector layer 235 are gold leaf, a first electrode 220 and a second electrode 230 comprise activated charcoal, a separator 225 is seaweed, and the electrolyte 245 is Gatorade. The gelatin package 205 is sealed to encase the active supercapacitor materials and to provide a sealed, edible supercapacitor device 200. Electrical power is drawn from the supercapacitor 200 by coupling an electronic device (e.g., a swallowable, capsule-based medical device) to the anode conductive tab and the cathode conductive tab (not shown in Fig. 2) protruding from the gelatin package 205.

[0039] In order to bind discrete activated charcoal particles into a continuum film as electrodes, edible binders are employed. In particular, egg whites were used as binders in the electrodes 220, 230 of the example of Fig. 2. The presence of hydrogen bonds and ionic interactions with proteins allows the formation of films with high adhesive strength, which allows egg whites to be used as binders in food processing industries. The electrodes 220, 230 of the supercapacitor 200 was prepared by mixing activated charcoal (Nature's Way Products, Inc; Green Bay, WI) with a quantity of egg white in a mass ratio of 1:2. Egg whites primarily contain biotin and proteins such as albumin, mucoproteins, and globulins that are able to form a biomacromolecule solution with water through hydrogen bonding between the proteins and water. Deionized water was then added into the mixture with a ratio of 1:3 (activated charcoal to water). The mixture was magnetic stirred for 2 hours followed by an ultrasonication for 30 minutes in water bath. The electrodes 220, 230 in this particular example are 2 cm × 2 cm and are approximately 120 μm thick. However, other sizes and thicknesses are possible based on the design and power-requirements of the medical device to be powered by the supercapacitor 200.

[0040] Fig. 3A shows the activated charcoal used for the electrode 220, 230 under scanning electron microscope (SEM) and Fig. 3B shows the electrode 220,230 under transmission electrode microscope (TEM). These figures demonstrate that the carbon cluster is highly porous and the size of individual carbon particles is about 100nm. Therefore, this form of carbon provides a high electrode surface area for the supercapacitor 200. Fig. 4 illustrates a graph demonstrating the output of a Brunauer-Emmett-Teller (BET) test demonstrating the surface area of the activated charcoal 500 used in the electrodes 220 and 230 of Figs. 3A and 3B. The surface

area of the activated charcoal is approximately $1,400 \text{ m}^2/\text{g}$, which is comparable to activated carbon materials used in other, non-edible supercapacitor devices.

[0041] Edible metals, such as very thin gold and silver leaf that are used in artisan baking and many Eastern cuisines, may be used as current collector layers 215 and 235 in the supercapacitor 200. The sheet resistance of gold leaf with a thickness of $3\text{-}5 \text{ }\mu\text{m}$ was measured to be $0.48 \text{ }\Omega/\text{sq}$ by four-point probe. The gold leaf material used in the supercapacitor 200 has a thickness of $120 \text{ }\mu\text{m}$ and other thicknesses may be used in other implementations. In the specific example of Fig. 2, the first and second current collectors 215 and 235 were prepared by applying egg white uniformly on a chlorine-free wood fiber paper (Mondi; Graz-Seiersberg, Austria) to form an adhesive layer, then attaching an approximately $3 \text{ }\mu\text{m}$ thick 23 kt edible gold leaf (Alma Gourment Ltd; Long Island City, NY) on the paper. The gold-coated paper was then dried in ambient environment for 2 hours before being patterned into the first and second current collectors 215 and 235 with desired areas. The mixture was coated on the first and second current collectors 215 and 235 by doctor's blading followed by overnight drying in an ambient environment and 6 hours drying in a room temperature, low pressure (10 Pa) chamber to avoid thermal stress as well as remove the water in the electrode.

[0042] The materials of the separator 225 is permeable to ions while also displaying high electrical resistance to avoid electrical contact between the electrodes 220, 230 of the supercapacitor 200. Roasted seaweed (Nagai NoRi Co., Ltd; Torrance, CA) – a popular snack and also heavily used in sushi, with multilayer hydrophilic structures – is used as the separator 225 in the example of Fig. 2. Seaweed consists of multilayer hydrophilic structures with high electrical resistivity and high ion permeability. In other implementations, rice paper might be used as the separator 225 with similar results. The seaweed and rice paper were studied for their permittivity using deionized water as the passing fluid. Two-inch diameter sections of seaweed and rice paper were cut out using a circular stamp. The testing material (i.e., seaweed and rice paper) was placed at the end of a 5-inch steel chamber using a rubber gasket. Water was poured into the chamber, and the sequential pressure test was performed using regulated nitrogen from a cylinder. The fluid passing out from the chamber was collected in a beaker and placed on a weighing balance, which was connected to a computer. The data from the fluid pass was used to

calculate mass flux and permittivity. The permittivity of the roasted seaweed was measured to be 52 g/m²s.

[0043] Gelatin sheets (Modernist Pantry, LLC; York, ME) – such as used in food processes and medical capsules – are employed as the packaging layer 205 in the example of Fig. 2. Fig. 5 illustrates a cross-sectional view of an *in-situ* observation of a digestion process when a gelatin sheet 705 is immersed in a simulated gastric fluid 710 and constrained in the horizontal direction. It is observed that the gelatin sheet 705 with an initial cross-sectional area of 160 μm by 1,090 μm first swells due to the diffusion of the gastric fluid 710 into the polymeric gelatin network, and then shrinks due to the digestion of the gelatin sheet 705 and eventually becomes undetectable microscopically (using a Nikon Eclipse lv100 with a 5X objective in the example of Fig. 5) after 2.5 hours. During this process, because of the constraint in the horizontal direction, the maximum strain in the horizontal direction ($\epsilon_{\text{horizontal}}$) is only 17% while its counterpart in the thickness direction ($\epsilon_{\text{thickness}}$) is 261%. This quasi-one-dimensional constrained digestion process can be understood by a theoretical model that considers the coupling of mass diffusion, chemical reaction, and extremely large mechanical deformation. As shown in Fig. 6, the time evolutions of the strains ($\epsilon_{\text{horizontal}}$ and $\epsilon_{\text{thickness}}$) obtained from experiments and simulations agree very well.

[0044] A polyelectrolytic drink, such as Gatorade, with high concentrations of sodium, potassium, citrate, and other stabilizing agents and high ionic conductivity ($> 2 \text{ mS/cm}$) was used as the electrolyte 245 in the example of Fig. 2. Cheese slices (Lucerne Foods, Inc.; Pleasanton, CA) are positioned as a segregation layer 210, 240 between the highly hydrophilic gelatin sheet (package layer 205) and the gold leaf current collectors 215 and 235 to avoid direct contact between the gelatin sheet package layer 205 and the electrolyte 245 – and, thereby, preventing absorption of the electrolyte by the gelatin package 205. Finally, the package 205 is sealed thermally by an impulse sealer with controlled heat. Thus, an entirely edible supercapacitor is assembled using only food items.

[0045] Fig. 7 illustrates the cyclic voltammetry (CV) curves of the edible supercapacitor 200 of Fig. 2 at scanning rates from 5 mV/s to 100 mV/s. The CV curves are of clearly rectangular shape at lower scanning rates and become approximately rectangular shape at increased scanning

rates, which are ideal for capacitive properties and reversibility of a supercapacitor 200. The galvanostatic charge/discharge testing results are illustrated in Fig. 8 and show some internal resistance with a constant current density of 1 A/g.

[0046] As illustrated in Fig. 9, after 1,000 charge/discharge cycles, the specific capacitance retains 92.3% dropping from 78.8 F/g to 72.7 F/g under 1 A/g current density, which is consistent with activated carbon-based supercapacitors. The specific capacitance (C_{sp}) was calculated from the slope of the discharge capacitance $C_{sp}=2I/(m(\Delta V/\Delta t))$, where I is the applied current and m is the average mass of the two electrodes. The degradation mainly results from the electrolyte being absorbed by the gelatin sheet. To confirm, aluminized polyethylene (PE) (standard packing materials for supercapacitors) and gelatin without cheese segregation were tested for comparison. The specific capacitance using aluminized PE retains 96.9% by dropping from 76.4 F/g to 74.0 F/g after 1,000 charge/discharge cycles and thus demonstrates excellent electrochemical stability of the electrode-separator-electrolyte system. However, the specific capacitance with gelatin drops more than 50% from 73.2 F/g to less than 34.9 F/g in 100 cycles and to 4.4 F/g in 1,000 cycles. This comparison shows that cheese slices can significantly prevent electrolyte loss and improve the cycling stability.

[0047] Fig. 10 presents the electrochemical impedance spectroscopy (EIS) results after one cycle and 1,000 cycles using gelatin sheet with cheese as the packing materials. Only slight resistance increase was observed. Fig. 11 shows the energy and power densities curve calculated from the constant current density charge–discharge curves measured with 250 mA/g, 500 mA/g, 1 A/g, 2 A/g, and 4 A/g current densities.

[0048] The material possibilities of edible supercapacitors are immense due to the vast number of available food products. Other possible materials include monosodium glutamate (MSG, a flavor enhancer) as an electrolyte additive to increase the electrolyte ions density, carboxymethyl cellulose (CMC, a food additive) as a binder, silver leaf as a current collector, V8 vegetable drink and Monster Energy drink as liquid electrolytes, BBQ sauce, jello, and cheese as gel electrolytes, and gummy candy as a package material.

[0049] Fig. 12 illustrates the specific capacitance over 1000 charge/discharge cycles for supercapacitors constructed of various different combinations of food-based materials. For

1,000 charge-discharge cycles at the current density of 1 A/g, the specific capacitance increases from 78.8 F/g to 129 F/g after the addition of MSG in Gatorade due to the increase of ion densities. The specific capacitances of other liquid electrolytes (V8 vegetable and Monster Energy drinks) show different values due to different ions components and concentrations. Due to high internal resistance, the specific capacitances with gel electrolytes (BBQ sauce, jello, and cheese) are lower than those with liquid electrolytes.

[0050] As discussed above, the edible nature of the food-based supercapacitors provides a swallowable power source for various types of medical devices. Fig. 13 illustrates three supercapacitors 1500 connected in series (each of the supercapacitor 200 having an electrode area of 2 cm by 2 cm) and powering a light-emitting diode (LED) 1505 while partially immersed in a simulated gastric fluid 1510. The LED 1505 remained lit for three minutes, followed by gradual dimming and lack of emission after four minutes. After one hour, the supercapacitors 1500 were already partially dissolved in the simulated gastric fluid 1510.

[0051] Fig. 14A-14C illustrate another usage of the edible supercapacitor 200. In this example, a wireless charging system 1600 is provided to charge the supercapacitor 200 of Fig. 2. As shown in Fig. 14A., the wireless charging system 1600 includes a transmitter chamber 1605 and a receiver lid 1610. Fig. 14B is a close-up view of the transmitter chamber 1605 which includes a transmitter coil 1606 and a DC-AC converting circuit 1607 (GHH, Amazon). Fig. 14C is a close-up view of the receiver lid 1610 which includes a receiver coil 1611 and AC-DC converting circuit 1612 (GHH, Amazon). The supercapacitor 200 is integrated with the receiver coil 1611 and the AC-DC converting circuit 1612 and placed in a charging chamber that can then be charged wirelessly in an alternating electromagnetic field (with a frequency of 60 Hz) created by the transmitter coil 1606 and the DC-AC converting circuit 1607 outside the transmitter chamber 1605. Using a wireless charging system such as this, the supercapacitor 200 inside a human body can be charged in an alternating electromagnetic field that surrounds the human body. Fig. 15 illustrates a graph of the current and voltage profiles during the wireless charging using the wireless charging system of Figs 14A-14C. With 5.144 V constant voltage output from the receiver, the voltage of the supercapacitor set increases from 0.470 to 4.994 V, and the current decreases from 60 (measured at 10s) to 14.41 mA in 3 minutes. After five minutes, the voltage increases to 5.002 V while the current drops to 12 mA.

[0052] Edible supercapacitors, such as illustrated in Fig. 2, can also be used to exploit the antibacterial activity of electric current. This antibacterial activity has previously been demonstrated against planktonic *Escherichia coli*, *Klebsiella pneumoniae*, and *Proteus* species in various liquids including synthetic urine, water, and salt solutions. Moreover, low-intensity electric current reduced the numbers of viable bacteria in staphylococcal and *Pseudomonas* biofilms after prolonged exposure (1 to 7 days). However, thus far, no real device has been implemented that can be taken into human body and used to kill bacteria via low-intensity electric current.

[0053] To further assess potential biomedical applications of the edible supercapacitor, the effect of edible supercapacitor-discharged electric current on bacterial viability was investigated using *E. coli* ATCC 25922 in broth antimicrobial susceptibility experiments. Fig. 16 shows the edible supercapacitor 200 packaged in a standard 000 size gelatin capsule 1701 with electrode contacts 1703, 1705 extending from the capsule 1701. Fig. 17 shows an experimental environment including two brass rods 1801 and 1802 with a stopper 1803 inserted into a 3 mL *E. coli*-PBS suspension 1804. The electric current loop was formed by connecting the outside ends of the rods to the electrode contacts 1703, 1705 of the supercapacitor 200. Exponential-phase *E. coli* cells (~10⁷ CFU/mL) were re-suspended in phosphate-buffered saline (PBS) and exposed to alternating on (2 min) and off (2 min) cycles of electrical current for 60 min. Compared to no electrical current (growth control), a significant reduction ($P < 0.01$) was detected in the number of viable cells present after exposure to supercapacitor-mediated electrical current for 60 min as illustrated in the graph of Fig. 18. A time-dependent reduction in bacterial viability was observed, with generally lower viable cell counts detected when electrical current was applied for longer periods of time. The edible supercapacitor 200 causes significant bactericidal activity reduction (99.93% average reduction) after 60 min of alternating on-off current exposures as illustrated in the graph of Fig. 18. When the replicate experiments were separated based on amperage readings, a higher amperage correlated with a greater reduction in bacterial viability at all time-points as illustrated in the graphics of Figs. 18-21, suggesting that proper design of edible supercapacitors better controls the efficiency of antibacterial activity.

[0054] In addition to the specific methods and constructions described above, other mechanisms for manufacturing an edible supercapacitor are possible including, for example,

using inkjet printing technology. As a direct-write technology, inkjet printing transfers a pattern directly onto a substrate providing fine/specific pattern generation, non-contact injection, solution saving effects, high repeatability and scalability, and processes easily applicable to large or small areas.

[0055] In one implementation utilizing inkjet printing technology, 0.2 g of active charcoal is added to 50 mL of distilled water. 0.04 g of CMC is then added as a binder. The active charcoal/CMC mixture is subjected to centrifugation (at 6000 rpm for 20 minutes) to remove large-sized particles and agglomerates, resulting in a suitable viscosity for the inkjet printing process. A silver (Ag) nanowire suspension is then prepared in water with sucrose ester as a dispersing agent. The silver nanowire suspension is then subjected to a sonication-driven scission process to avoid clogging of the inkjet printing hardware.

[0056] An inkjet-printed resistor can then be fabricated directly on paper (e.g., A4 paper) using a commercial desktop inkjet printer (e.g., an HP Deskjet F4810) with the active charcoal/CMC mixture as the “ink.” To control the resistance of the resulting printed resistor, the same electrode pattern (e.g., a 2 cm wide rectangular shape) is printed/overwritten in the same position multiple times.

[0057] Similarly, to fabricate a supercapacitor electrode, the silver nanowire mixture is used as the “ink” to print a pattern on the paper. Fig. 22 illustrates one example of a patterned electrode printed by the inkjet printer to form the supercapacitor. This is followed by inkjet printing of the same pattern in the same position using the active charcoal/CMC mixture as the “ink.” In order to form highly interwelded silver nanowire networks, the inkjet-printed supercapacitor electrodes are subjected to UV irradiation to allow for photonic sintering of the silver nanowires. The printed electrode is then coated with an electrolyte (such as, for example, Gatorade) and the inkjet-printed electrode/electrolyte assembly is then sealed with gelatin sheets as a supercapacitor package. The silver nanowire printed layer serves as a current collector, the active charcoal as the active material of the electrode, the CMC as the binder, the Gatorade as the electrolyte, and the gelatin sheets as the packaging.

[0058] The capacity of a supercapacitor manufactured using this “printing” technique can be adjusted and varied based on the number of times that the pattern is overwritten with the same

“ink.” In one implementation, where the mass load of the active charcoal is 0.2 mg and the actual capacity of the active charcoal is 100 F/g, the capacity of one electrode will be 0.02 F (i.e., 0.2 mg x 100 F/g). Therefore, the whole capacity of the supercapacitor will be half of the electrode – that is 0.01 F. The capacity of the supercapacitor can be increased by increasing the number of times that electrode pattern is overwritten using the active charcoal/CMC mixture, thereby increasing the mass load of the active charcoal in the resulting printed electrode.

[0059] Thus, the invention provides, among other things, an edible supercapacitor that is truly edible and digestable as all components are originated from food products. The edible supercapacitors can be utilized in numerous biomedical applications including, for example, an electrical “antibacterial” for killing bacteria (e.g., *E. coli*) in vitro and a power source for a medical device such as, for example, a commercial USB camera. In addition to its antibacterial properties, the edible, food-based supercapacitors may be used as an oncological adjuvant for alimentary and other malignancies. By merging modern food engineering, materials science, device fabrications, and biomedical applications, this work has the potential to broadly and deeply impact the field of edible electronics as the horizon of search candidate materials for edible electronics has been unprecedentedly expanded. Various features and advantages of the invention are set forth in the following claims.

CLAIMS

What is claimed is:

1. A capacitive power source comprising:

an anode current collector;

an anode electrode;

a cathode electrode;

a cathode current collector; and

a separator positioned between the anode electrode and the cathode electrode,

wherein the anode current collector, the anode electrode, the separator, the cathode electrode, and the cathode current collector are arranged in layers to form a symmetrical electric double-layer capacitor, and

wherein the anode current collector, the anode electrode, the separator, the cathode electrode, and the cathode current collector are all formed of edible materials.

2. The capacitive power source of claim 1, further comprising a packaging material enclosing the anode current collector, the anode electrode, the separator, the cathode electrode, and the cathode current collector, wherein the packaging material is formed of an edible packaging material.

3. The capacitive power source of claim 2, wherein the packaging material includes at least one edible packaging material selected from a group consisting of gelatin, potato starch, soy lecithin paper, edible waxed paper, and edible waxed film.

4. The capacitive power source of claim 2, further comprising:

a first conductive tab electrically coupled to the anode current collector and protruding from the packaging material; and

a second conductive tab electrically coupled to the cathode current collector and protruding from the packaging material.

5. The capacitive power source of claim 2, further comprising a first segregation layer positioned between the packaging material and the anode current collector, the first segregation layer formed at least one edible material .

6. The capacitive power source of claim 5, wherein the at least one edible material of the first segregation layer includes cheese.

7. The capacitive power source of claim 2, further comprising an edible electrolyte, wherein the first segregation layer is positioned to prevent the edible electrolyte from contacting the packaging material.

8. The capacitive power source of claim 1, wherein the edible material of the anode current collector includes a metal foil.

9. The capacitive power source of claim 8, wherein the metal foil includes gold or silver foil.

10. The capacitive power source of claim 1, wherein two or more layers selected from a group consisting of the anode current collector, the anode electrode, the separator, the cathode electrode, and the cathode current collector are coupled together using an edible, non-toxic binder.

11. The capacitive power source of claim 10, wherein the edible, non-toxic binder includes at least one selected from a group consisting of egg, egg powder, sugar, GellanGun, honey, extract juice from sticky food, and carboxymethyl cellulose.

12. The capacitive power source of claim 1, wherein the separator includes a porous insulator material.

13. The capacitive power source of claim 12, wherein the porous insulator material of the separator includes at least one selected from a group consisting of seaweed, air-dried meat, rice paper, pork casing, sugar sheet, vegetable paper, wafer paper, and tapioca paper.

14. The capacitive power source of claim 1, wherein the edible material of the anode electrode includes a porous conductive material.

15. The capacitive power source of claim 14, wherein the porous conductive material of the anode electrode includes at least one selected from a group consisting of activated charcoal, copper, magnesium, gold powder paste, and silver powder paste.

16. The capacitive power source of claim 1, wherein each material included in the capacitive power source is a food supplement, food additive, or are an explicit food.

17. A method of operating the capacitive power source of claim 1, the method comprising:

coupling the capacitive power source to a medical device;

positioning the capacitive power source and the medical device in a digestive tract of a patient by swallowing;

powering the medical device with electrical power stored in the capacitive power source; and

allowing the capacitive power source to dissolve in the digestive tract by digestion.

18. The method of claim 17, further comprising reducing bacteria in the digestive tract by applying a current from the capacitive power source to a fluid medium within the digestive tract.

19. An edible supercapacitor comprising:

a first segregation layer formed of cheese;

a first current collector layer formed of edible gold leaf positioned adjacent to the first segregation layer;

a first electrode layer formed of activated charcoal positioned adjacent to the first current collector layer opposite the first segregation layer;

a separator layer formed of seaweed positioned adjacent to the first electrode layer opposite the first current collector layer;

a second electrode layer formed of activated charcoal positioned adjacent to the separator layer opposite the first electrode layer;

a second current collector layer formed of edible gold leaf positioned adjacent to the second electrode layer opposite the separator layer;

a second segregation layer formed of cheese positioned adjacent to the second current collector layer opposite the second electrode layer;

a packaging formed of gelatin enclosing the first segregation layer, the first current collector layer, the first electrode layer, the separator layer, the second electrode layer, the second current collector layer, and the second segregation layer; and

an edible electrolyte material enclosed within the packaging such that the first segregation layer and the second segregation layer prevent the edible electrolyte material from contacting the packaging.

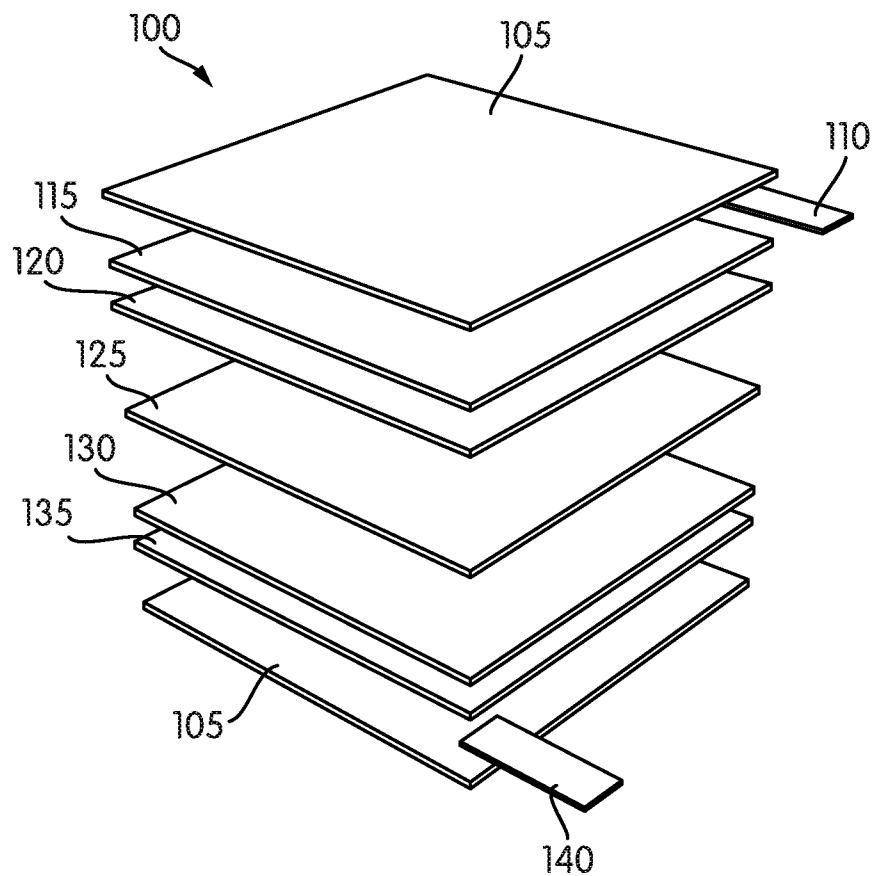


FIG. 1A

BINDER	CURRENT COLLECTOR	ELECTROLYTE	SEPARATOR	SEGREGATION LAYER	PACKAGE
Egg	Au	Gatorade+MSG	Seaweed	Cheese	Gelatin
Egg	Au	Monster drink	Rice Paper	Cheese	Gelatin
CMC	Au	V8 drink	Seaweed	Cheese	Gummy Candy
Egg	Ag	BBQ Sauce	Seaweed	---	Gelatin
CMC	Au	Jello	---	---	Gummy Candy
CMC	Ag	Cheese	---	---	Gummy Candy

FIG. 1B

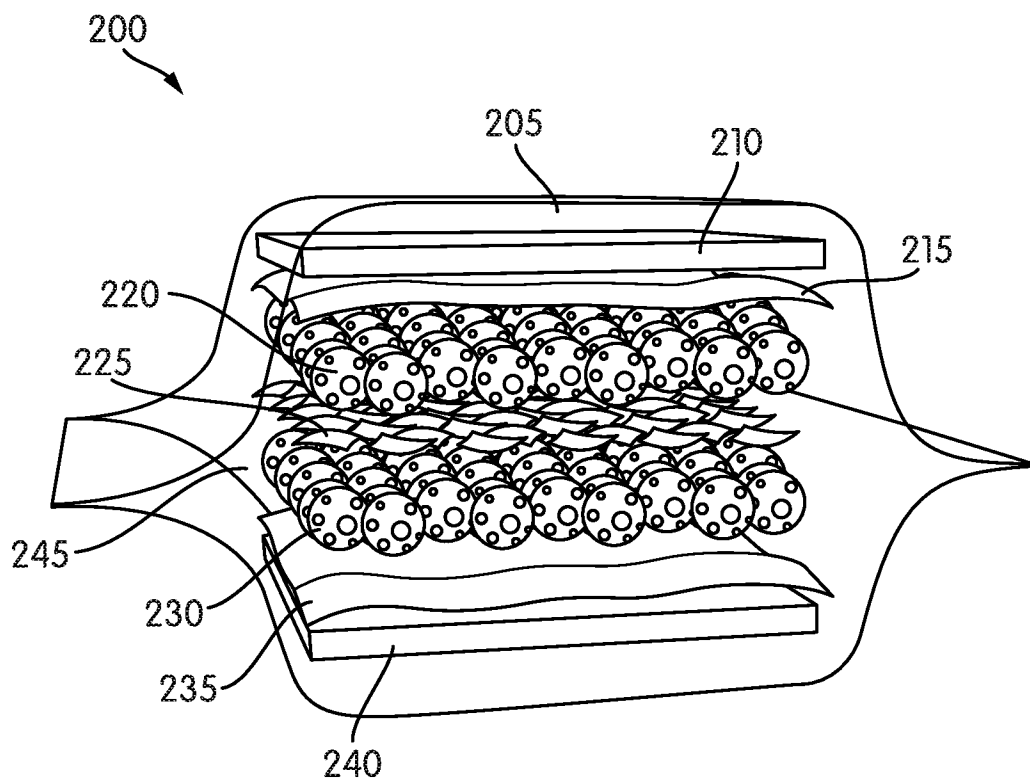


FIG. 2

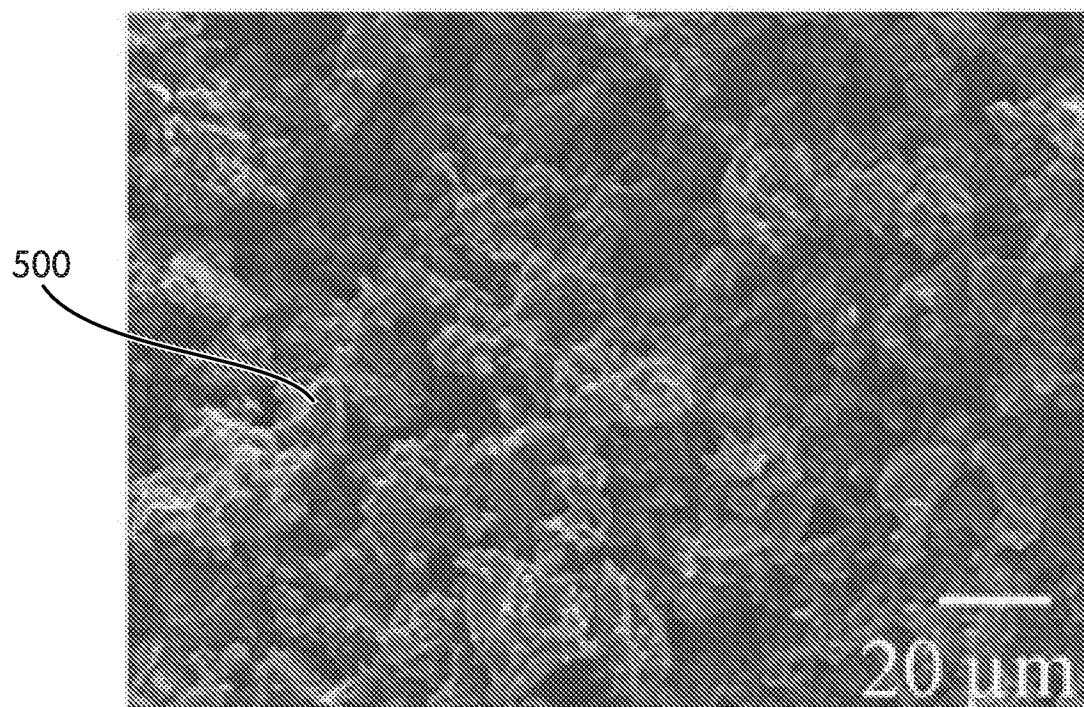


FIG. 3A

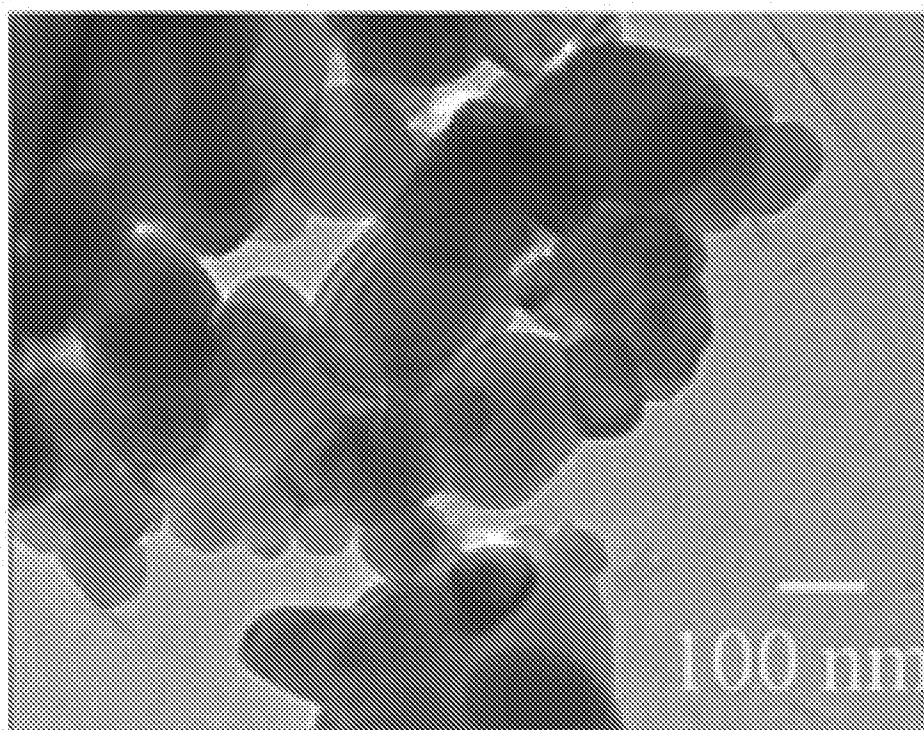


FIG. 3B

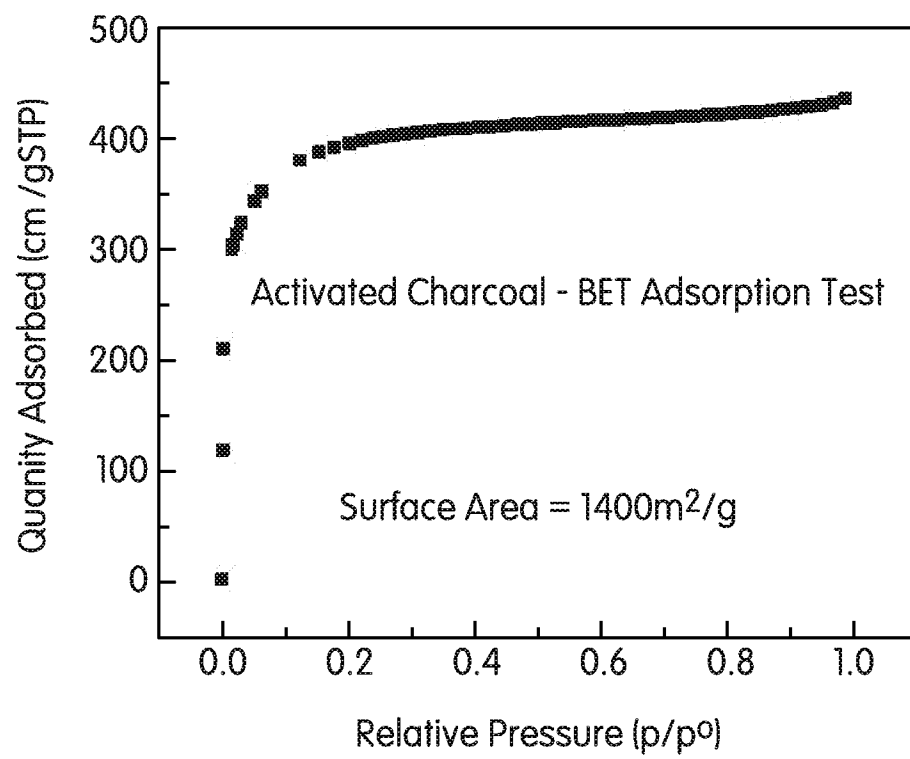


FIG. 4

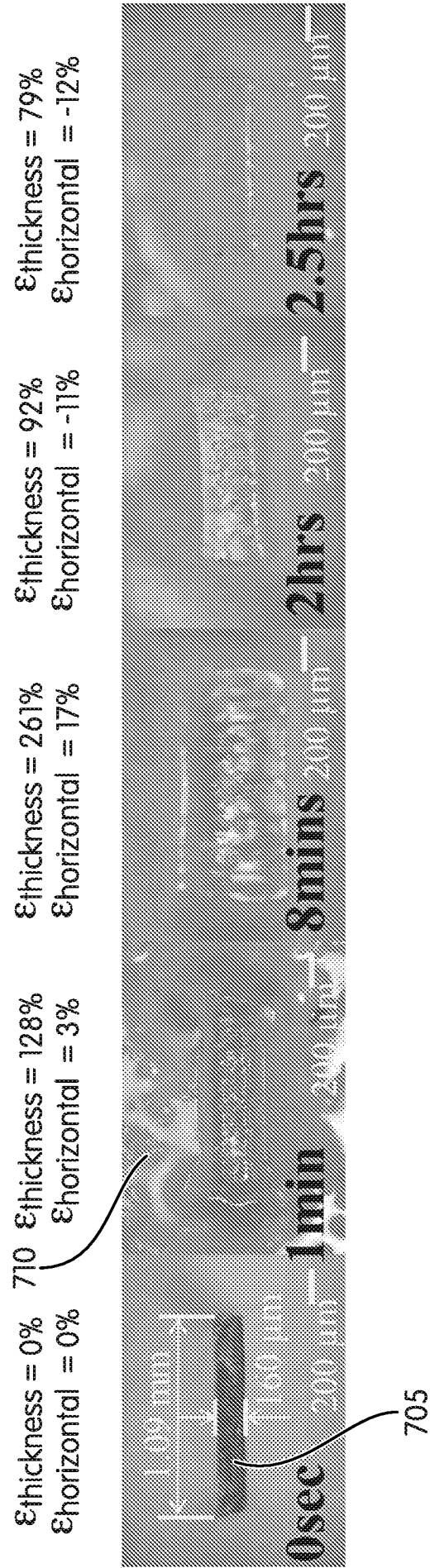


FIG. 5

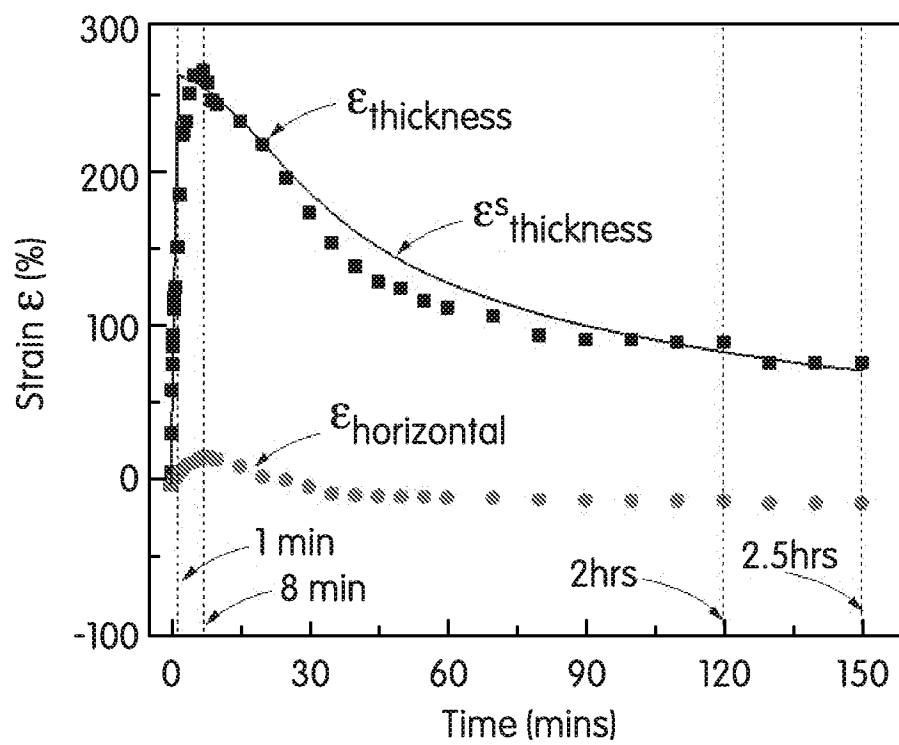


FIG. 6

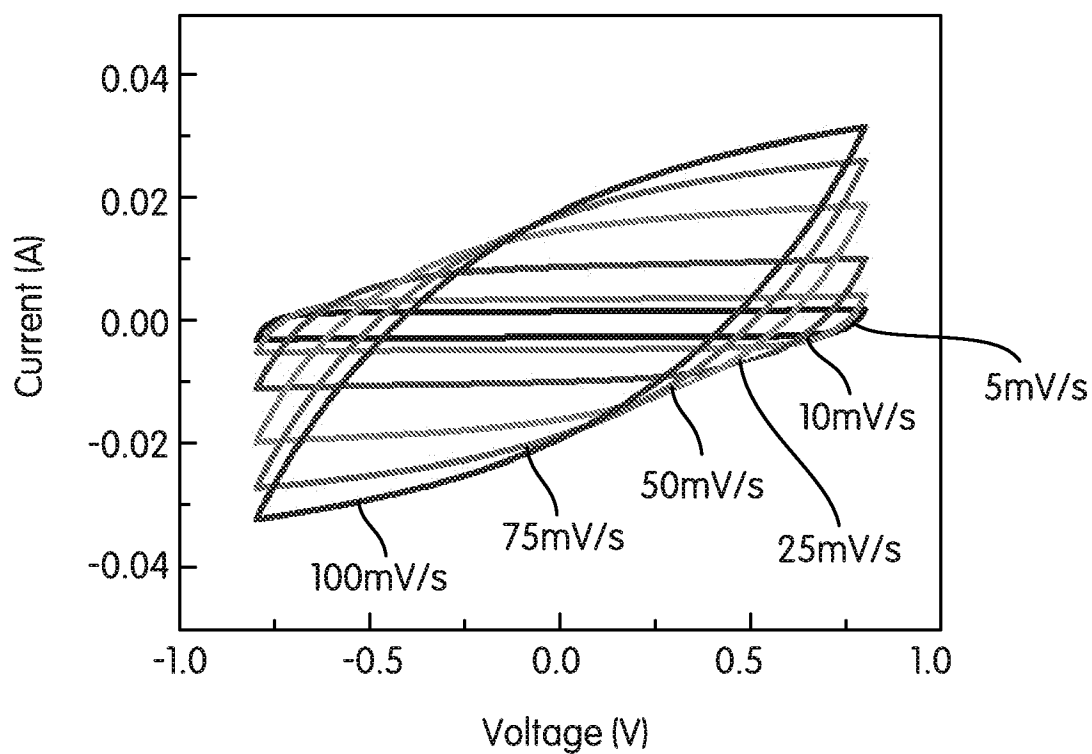


FIG. 7

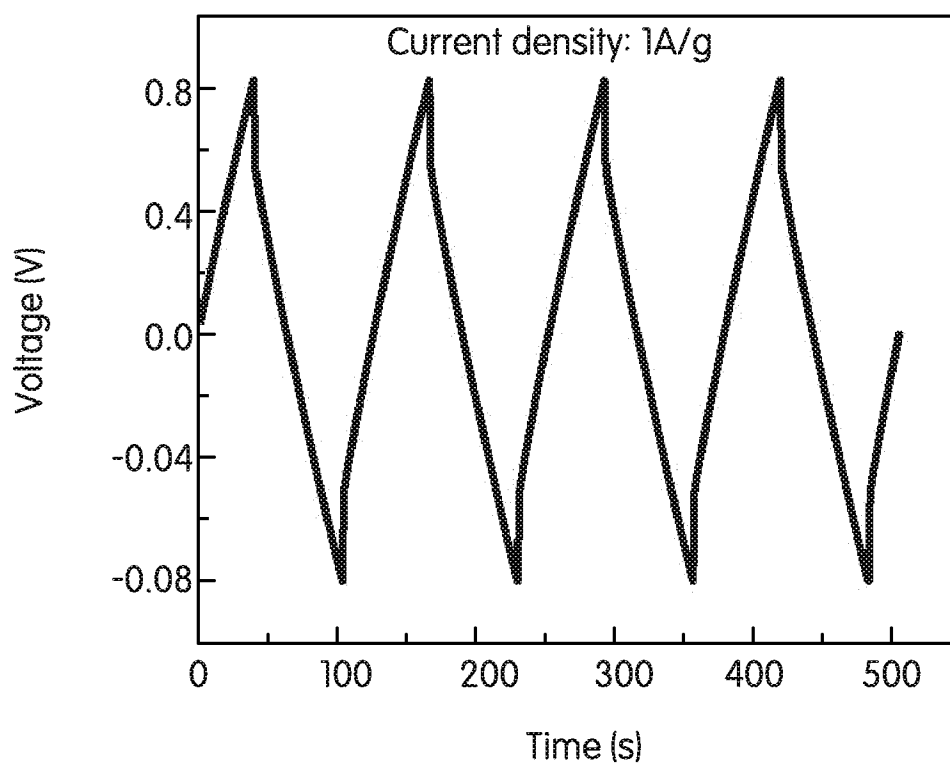


FIG. 8

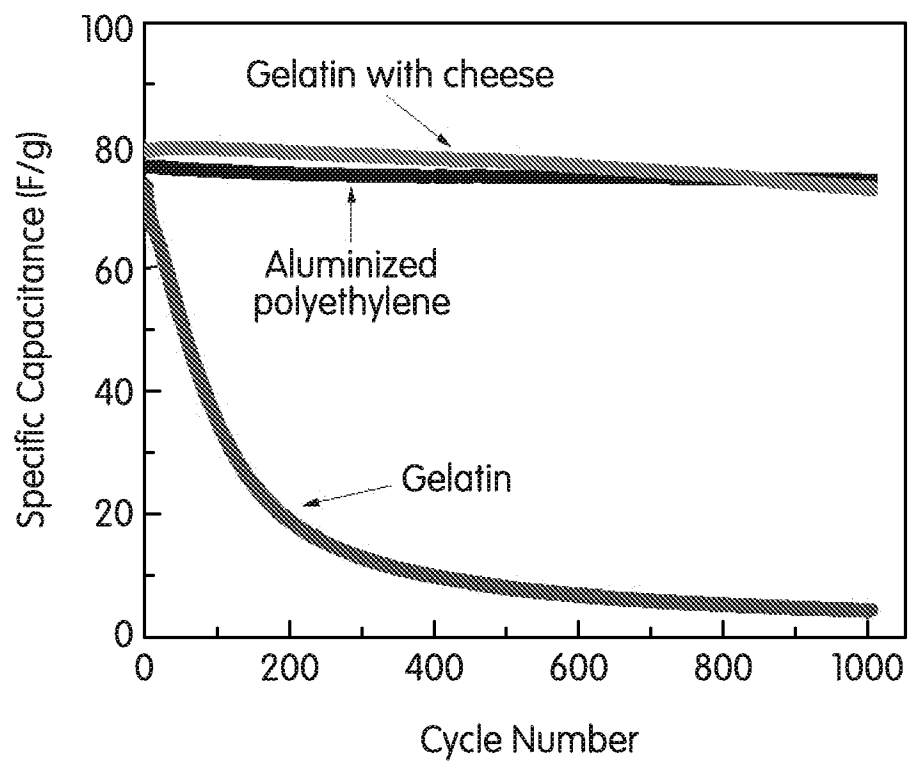


FIG. 9

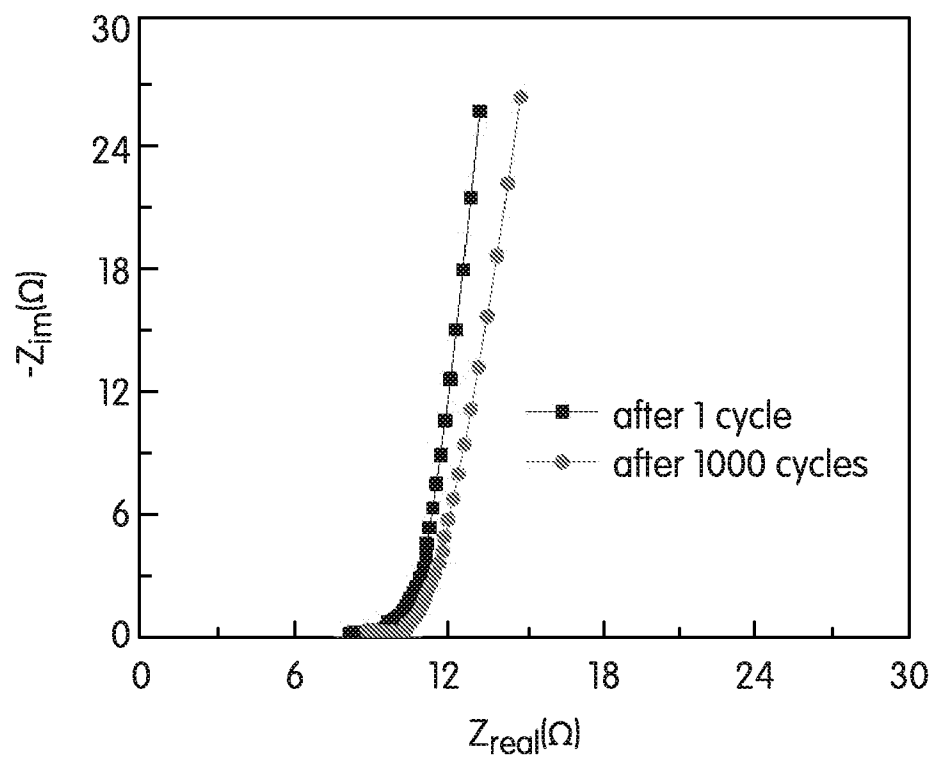


FIG. 10

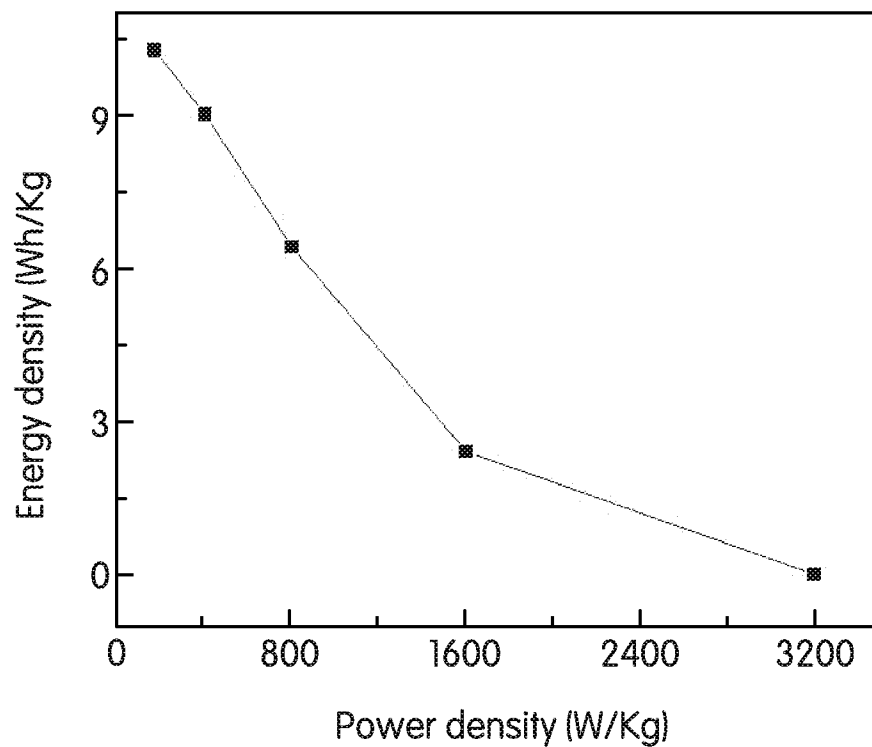


FIG. 11

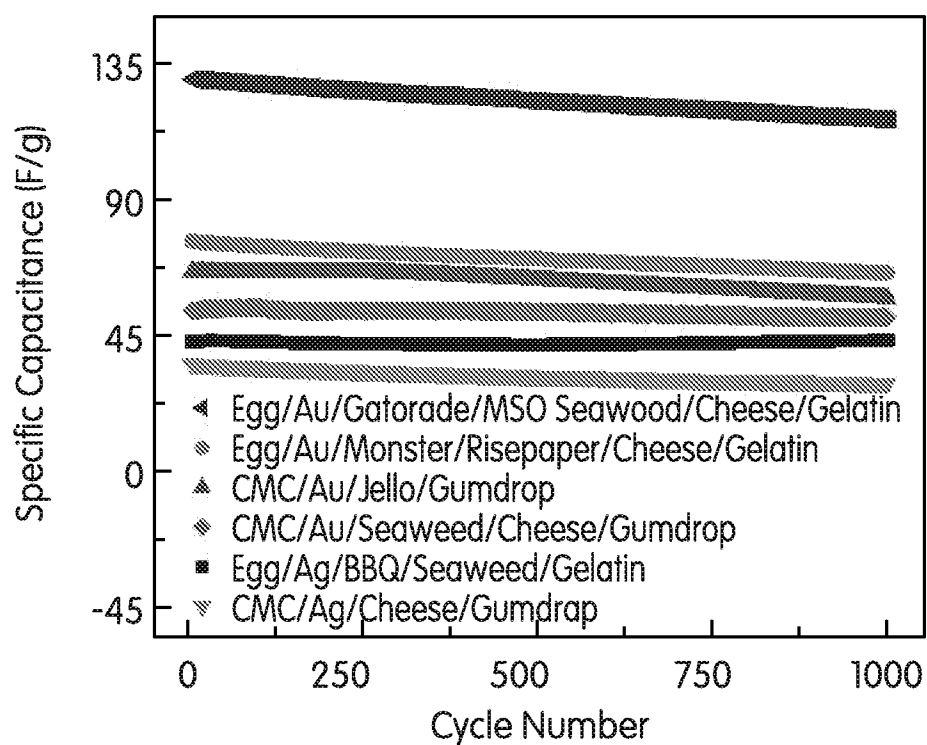


FIG. 12

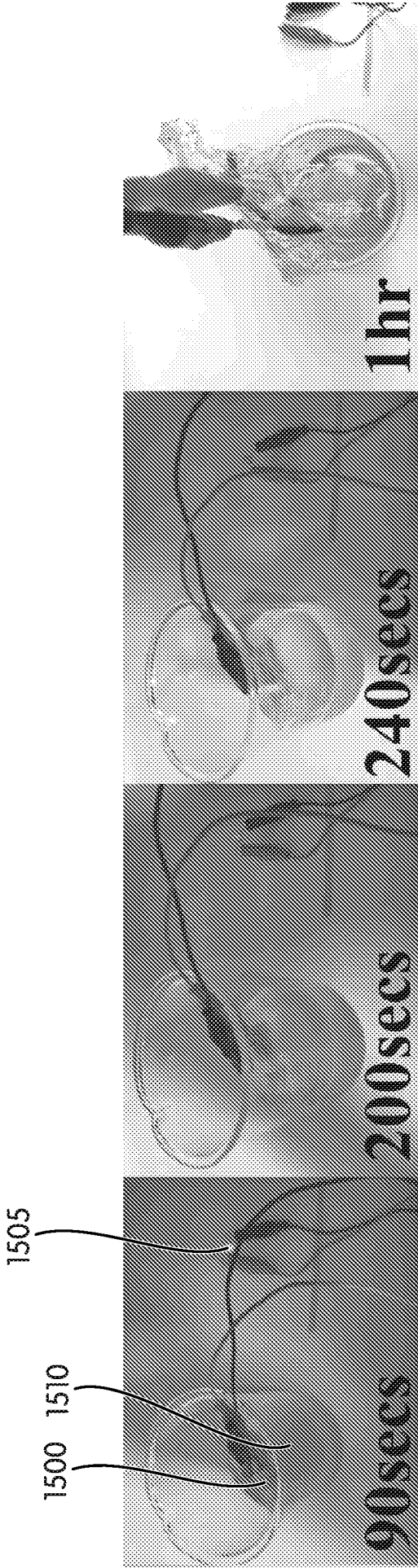


FIG. 13



FIG. 14A

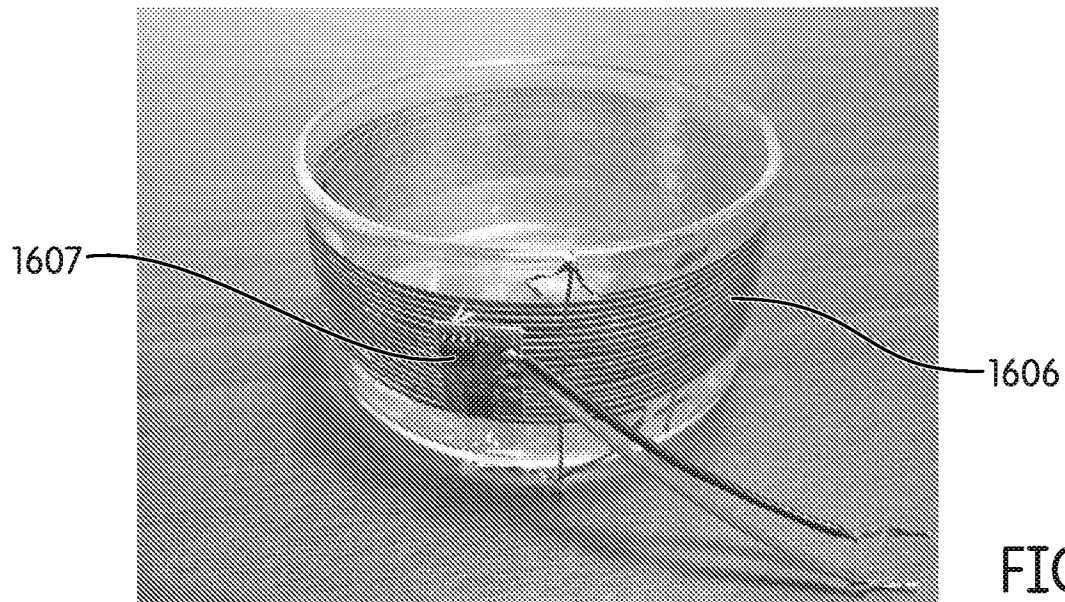


FIG. 14B

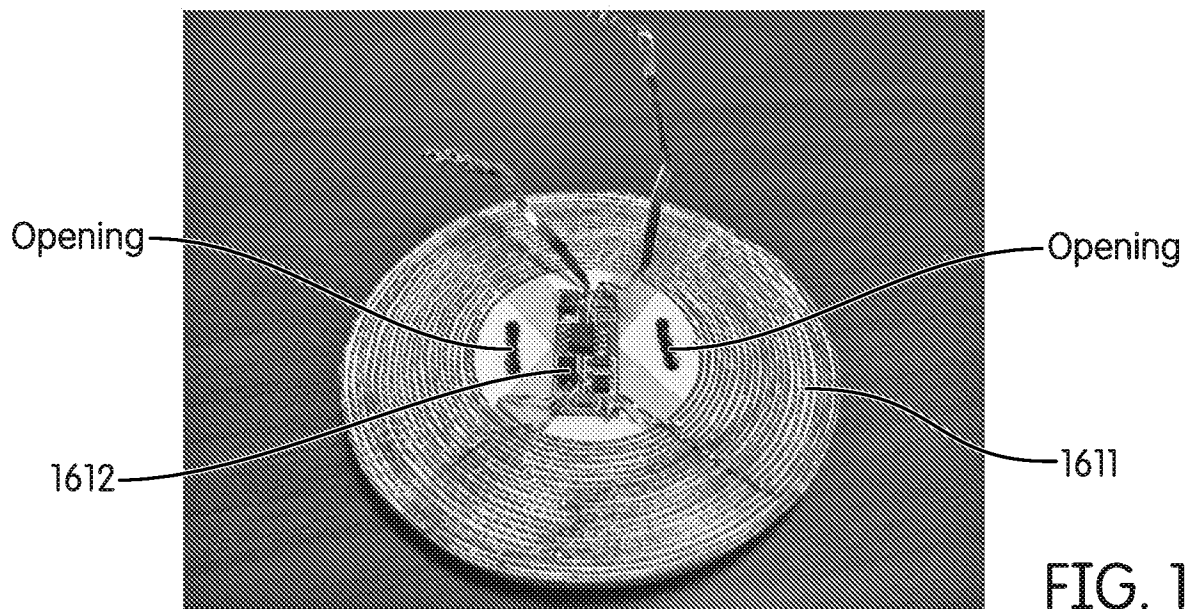


FIG. 14C

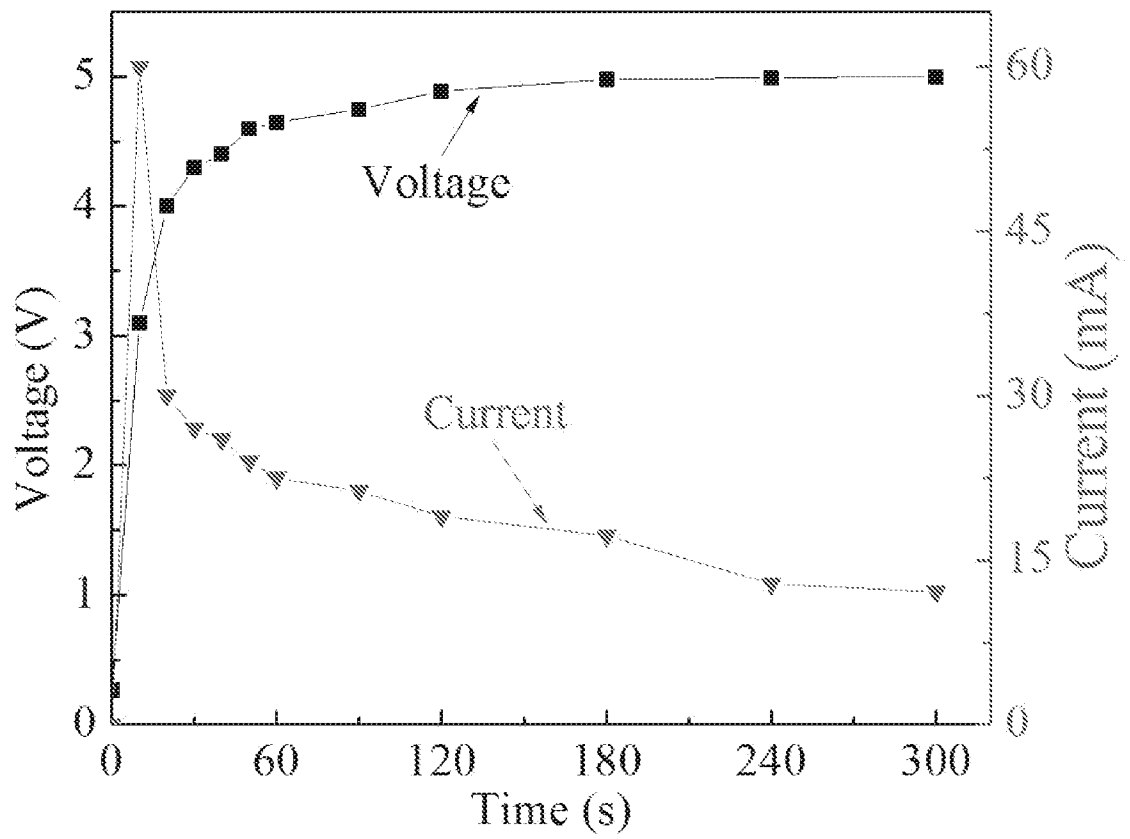


FIG. 15

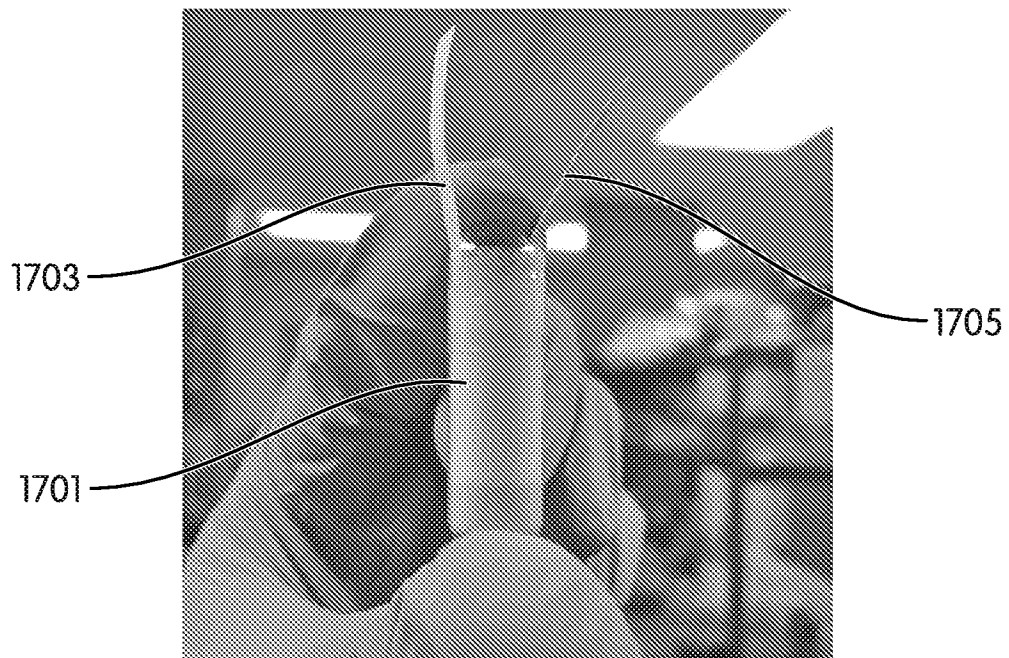


FIG. 16

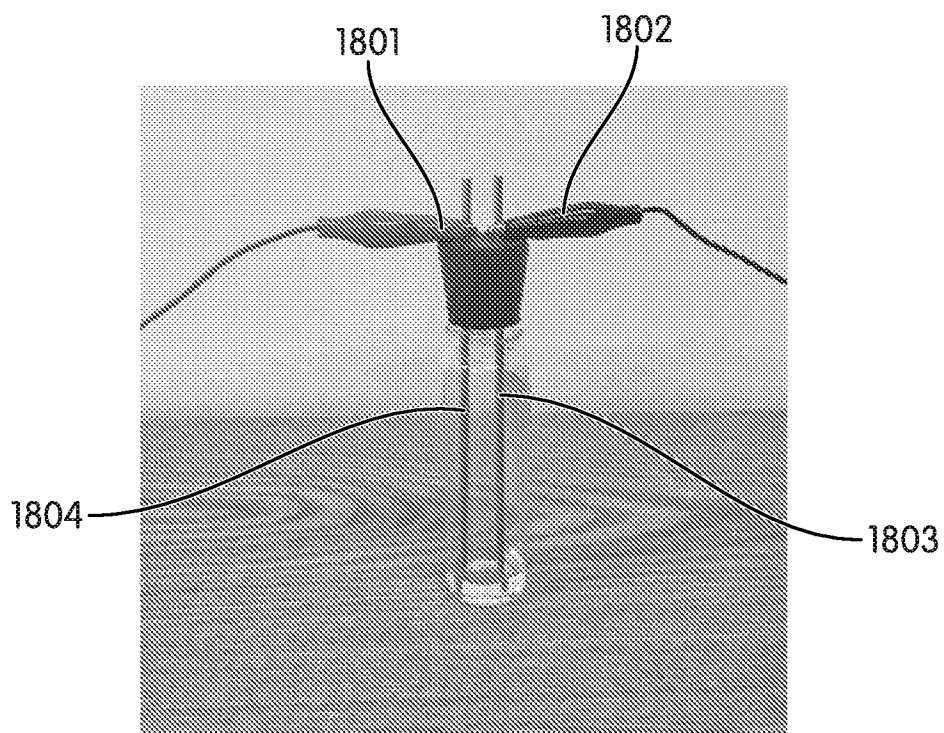


FIG. 17

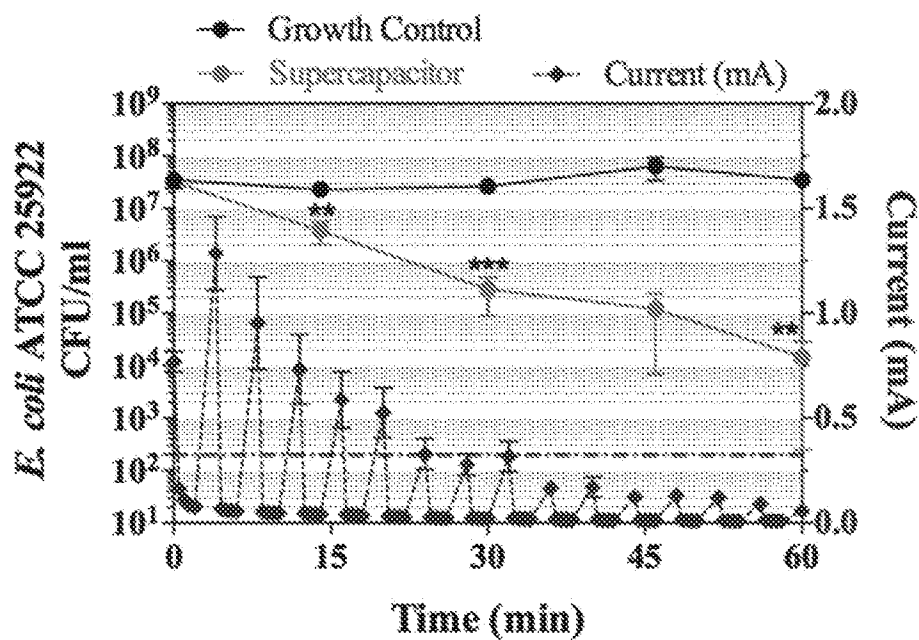


FIG. 18

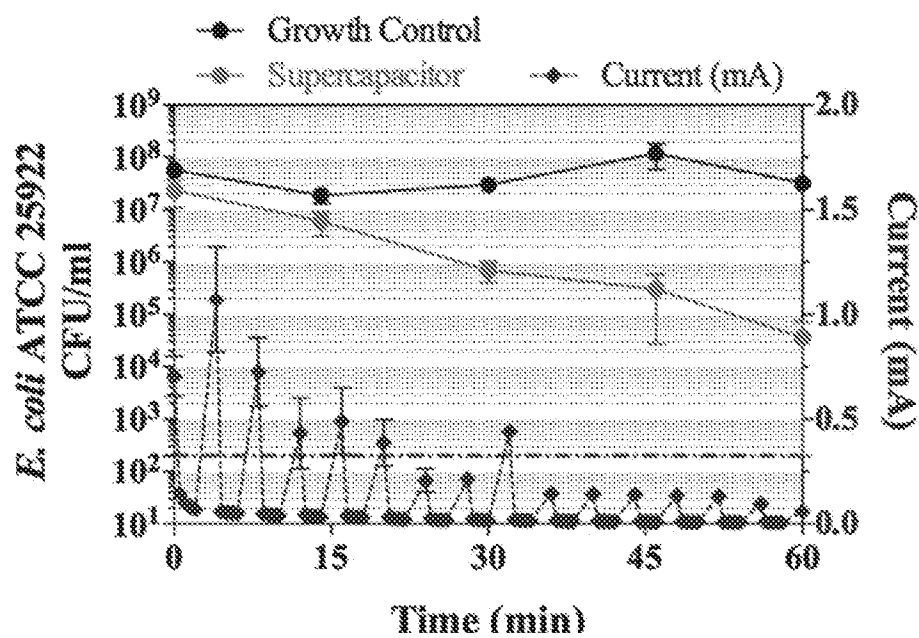


FIG. 19

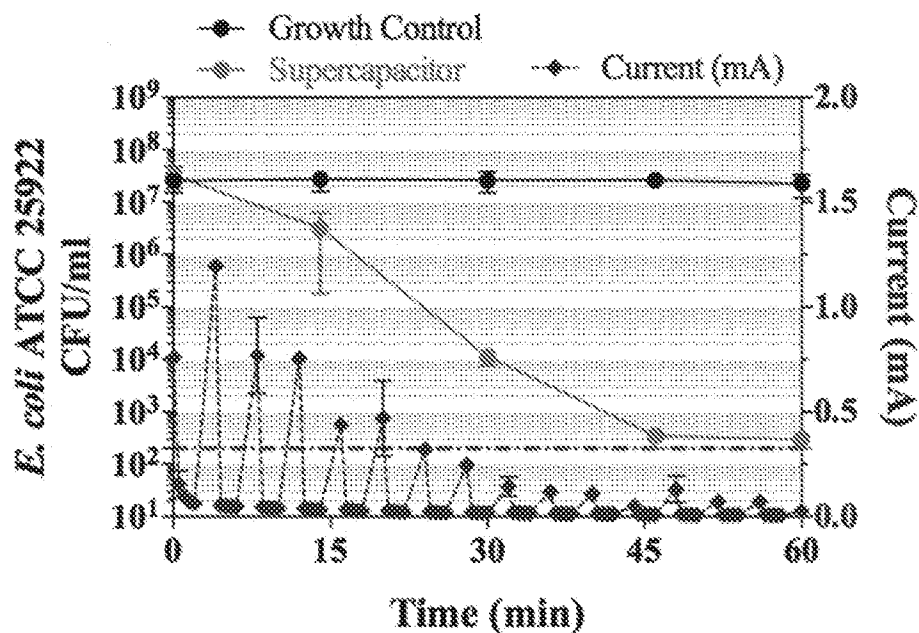


FIG. 20

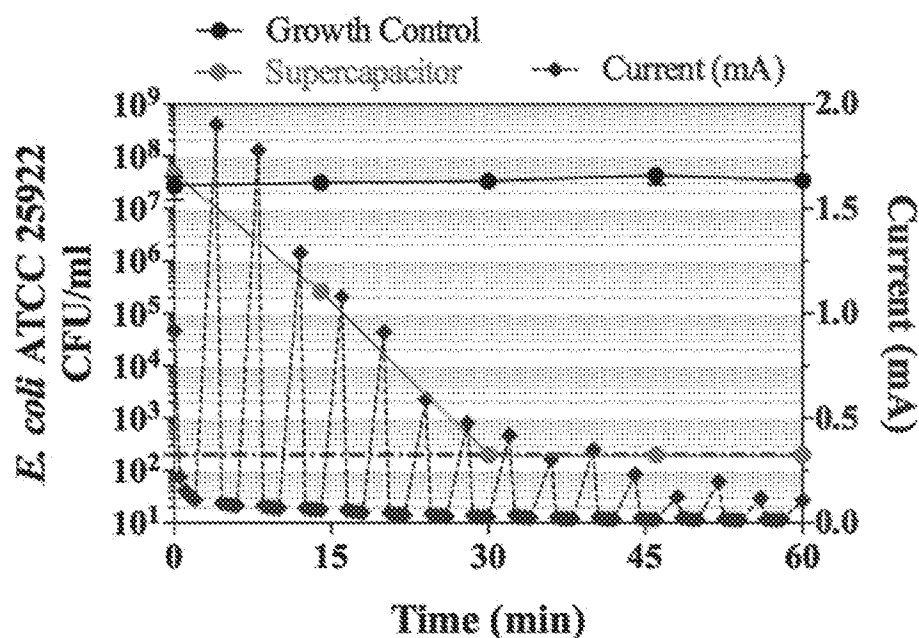


FIG. 21

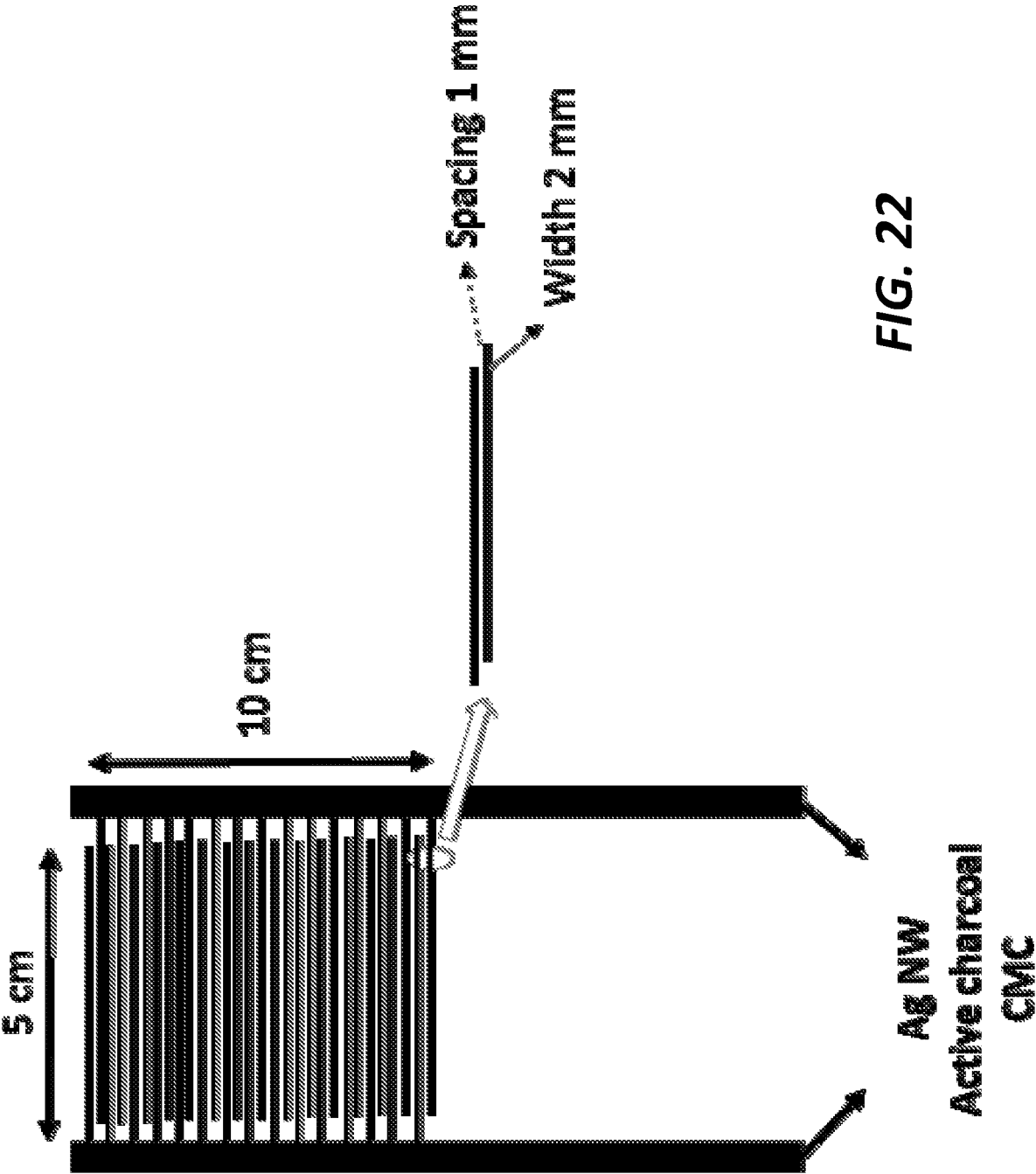


FIG. 22

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/048602**A. CLASSIFICATION OF SUBJECT MATTER****H01G 11/70(2013.01)i, H01G 11/26(2013.01)i, H01G 11/52(2013.01)i, H01G 11/76(2013.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01G 11/70; B82B 1/00; A61N 1/36; H02J 7/00; H01G 9/058; H01G 9/145; H01M 6/42; H01M 2/02; H01G 11/26; H01G 11/52; H01G 11/76

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: capacitor, anode, cathode, collector, separator, edible, food, patient

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012-0259376 A1 (GLENN GODDEN) 11 October 2012	1-4, 8-18
A	See paragraphs [0041]-[0063] and figures 1-6.	5-7, 19
Y	US 2008-0165471 A1 (KENJI KOJIMA et al.) 10 July 2008	1-4, 8-18
A	See paragraphs [0047]-[0048], [0078]-[0094], [0144]-[0145] and figures 1-2.	5-7, 19
A	JP 2007-335443 A (MITSUBISHI ELECTRIC CORP.) 27 December 2007	1-19
A	See abstract, paragraphs [0014]-[0040] and figures 1-2.	
A	US 2003-0165735 A1 (TOMOKI NOBUTA et al.) 04 September 2003	1-19
A	See abstract, paragraphs [0036]-[0058] and figures 1-3.	
A	US 2011-0228447 A1 (KISHOR PURUSHOTTAM GADKAREE et al.) 22 September 2011	1-19
A	See abstract, paragraphs [0014]-[0030] and figures 1-3.	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

21 November 2016 (21.11.2016)

Date of mailing of the international search report

21 November 2016 (21.11.2016)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea



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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/048602

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