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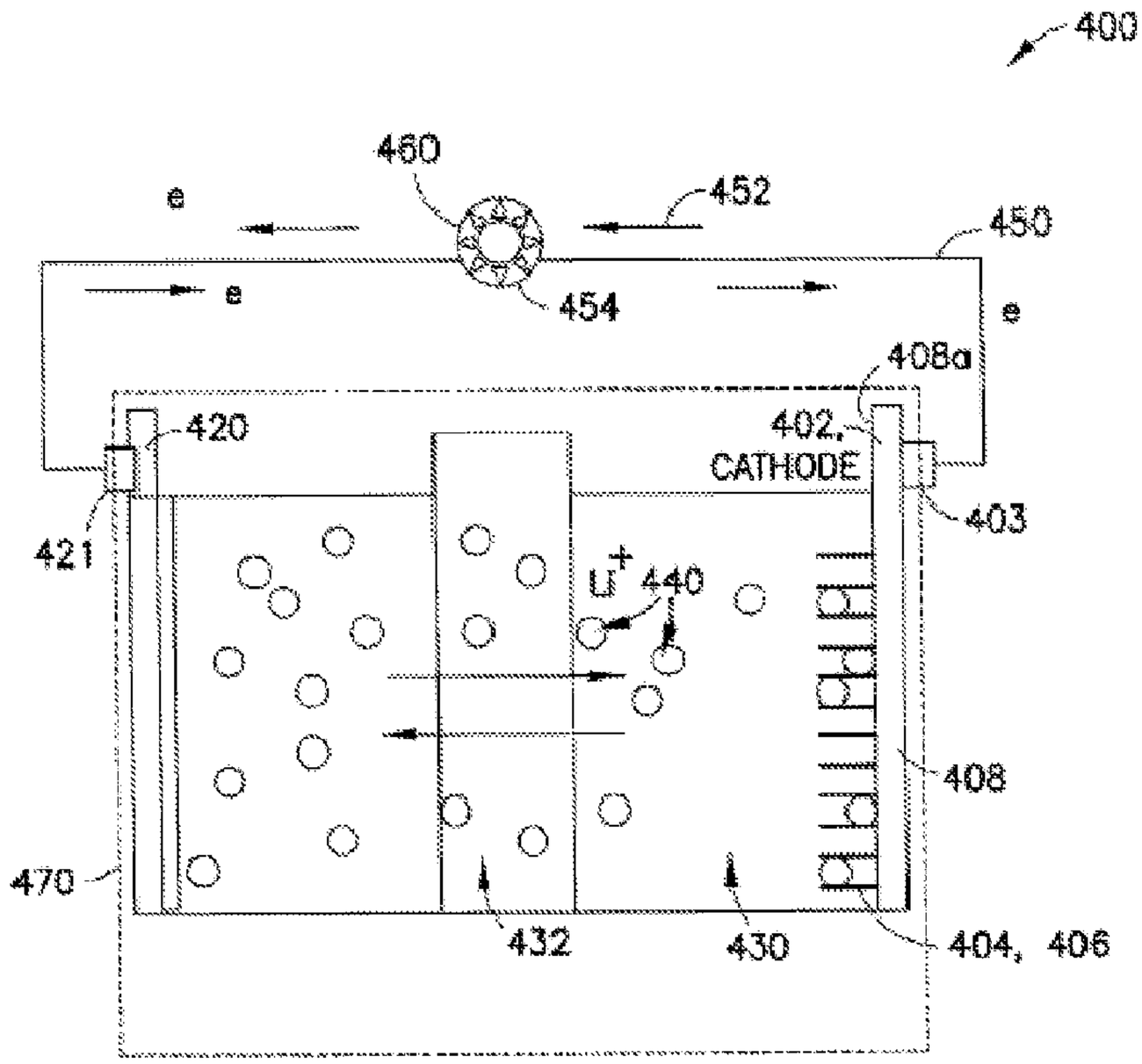
(54) Titre : BATTERIE LITHIUM-SOUFRE NANOSTRUCTUREE ET SON PROCEDE DE FABRICATION
(54) Title: NANO-STRUCTURED LITHIUM-SULFUR BATTERY AND METHOD OF MAKING SAME



(57) Abrégé/Abstract:
An apparatus (400) comprises a first conductive substrate (408) (e.g., a metal foil) having a first surface; a plurality of conductive stalks (404) (e.g., carbon nano-tubes) extending from the first surface; an electrically insulating coating (406) (e.g., sulfur) about the carbon stalks; a second conductive substrate (420) (e.g., a lithium oxide foil); and an electrolyte (430) (e.g., a polymer electrolyte) disposed between the first surface of the first conductive substrate (408) and the second conductive substrate (420). In various embodiments: the sulfur is disposed at a thickness of about 3 nanometers +1 - 1 nanometer; the stalks (404) are at a density such that a gap between them is between 2 and 200 diameters of an ion transported through the electrolyte (430); and there is a separator layer (432) within the electrolyte (430) having a porosity amenable to passage by such ions. Also detailed is a method for making the foil with the coated carbon nano-tubes.

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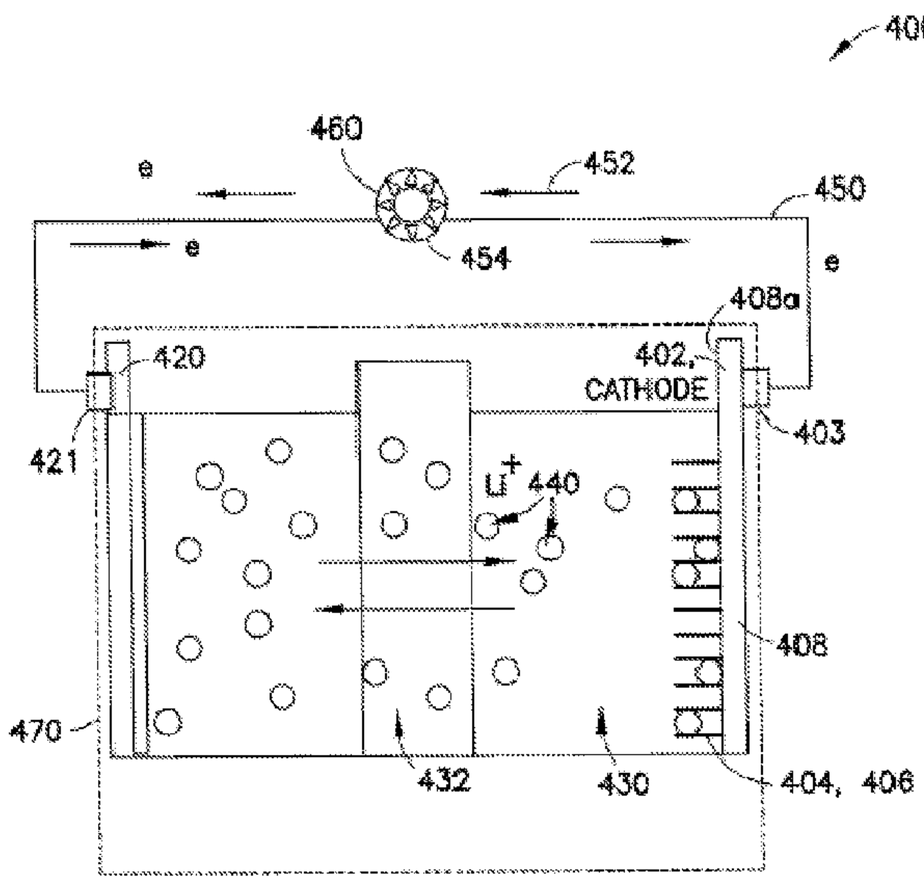

FIG.4

(57) **Abstract**: An apparatus (400) comprises a first conductive substrate (408) (e.g., a metal foil) having a first surface; a plurality of conductive stalks (404) (e.g., carbon nano-tubes) extending from the first surface; an electrically insulating coating (406) (e.g., sulfur) about the carbon stalks; a second conductive substrate (420) (e.g., a lithium oxide foil); and an electrolyte (430) (e.g., a polymer electrolyte) disposed between the first surface of the first conductive substrate (408) and the second conductive substrate (420). In various embodiments: the sulfur is disposed at a thickness of about 3 nanometers +1 - 1 nanometer; the stalks (404) are at a density such that a gap between them is between 2 and 200 diameters of an ion transported through the electrolyte (430); and there is a separator layer (432) within the electrolyte (430) having a porosity amenable to passage by such ions. Also detailed is a method for making the foil with the coated carbon nano-tubes.

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NANO-STRUCTURED LITHIUM-SULFUR BATTERY AND METHOD OF MAKING SAME

TECHNICAL FIELD:

[0001/2] The exemplary and non-limiting embodiments of this invention relate generally to electrical energy storage devices and methods for making such devices, and more specifically relate to lithium-sulfur batteries and components thereof.

BACKGROUND:

[0003] Some requirements for modern batteries include high energy density (product of capacity and voltage) to reduce weight and/or space, the capacity for numerous charge/discharge cycles to enable longer life, and little or no memory effects so that later cycles provide similar electrical potential as earlier cycles when the battery is new.

[0004] Lithium-sulfur batteries have one electrode made of lithium and another made of sulphur. But sulphur is an insulating material (sulphur along being $5*10^{-30}$ S cm^{-1} at 25°C), so to improve conductivity in some battery implementations the sulphur electrode is compounded with carbon to act as the battery cathode. As with the conventional lithium ion batteries, charging and discharging the battery involves the movement in an electrolyte of lithium ions between the two electrodes.

[0005] The theoretical capacity of lithium-sulfur batteries is much higher than that of lithium-ion batteries because of the way the ions are assimilated at the electrodes. For example, at the sulfur electrode, each sulfur atom can host two lithium ions, while in lithium-ion batteries every host atom can accommodate only 0.5 to 0.7 lithium ions.

[0006] Making materials that take advantage of the higher theoretical capacity of lithium-sulfur (Li-S) battery has been a challenge. The fact that sulfur is an insulating material makes it difficult for electrons and ions to move in and out of capture at the sulfur electrode. So while each sulfur atom may in theory be able to host two lithium ions, in fact often only those atoms of sulfur near the surface of the material accept lithium ions. Another problem is that as the sulfur binds to lithium ions and eventually forms dilithium sulfide, it also forms a number of intermediate products called polysulfides. These dissolve in the battery's liquid electrolyte and eventually can settle in other areas of the battery, where they can block charging and discharging. Because of this, prior art lithium sulfur batteries can stop working altogether after only a few dozen cycles.

[0007] In traditional lithium ion batteries, the charge storage capability is inherently limited to about 300 mA-h/g, and to the inventor’s knowledge the maximum capacities observed are about 180 mA-h/g with high power characteristics. A lithium sulfur battery cell operates quite differently from a lithium ion battery cell. Specifically, the redox couple, which in general is the tendency of a chemical species to reduce by acquiring electrons and which specifically for lithium sulfur batteries is described by the discharge reaction $S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_3 \rightarrow Li_2S_2 \rightarrow Li_2S$. Polysulfides are reduced on the anode surface in sequence while the cell is discharging:

$$S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_3$$

Across a porous diffusion separator, the polymers of sulfur are formed at the nominal cathode as the cell charges:

$$Li_2S \rightarrow Li_2S_2 \rightarrow Li_2S_3 \rightarrow Li_2S_4 \rightarrow Li_2S_6 \rightarrow Li_2S_8 \rightarrow S_8$$

This redox couple lies near 2.2 V with respect to Li+/Li, a potential which is only

about 2/3 of that exhibited by conventional positive electrodes. However, this is offset by the very high theoretical capacity afforded by the non-topotactic `assimilation' process of 1675mAh/g.

[0008] Specifically, the chemical processes in the Li-S battery cell include lithium dissolution from the anode surface (and incorporation into polysulfides) during discharge, and lithium plating back on to the nominal anode while charging. This contrasts with conventional lithium-ion cells in which the lithium ions are intercalated in the anode and cathodes, and this distinction allows the Li-S arrangement to exhibit, in theory, a much higher lithium storage density. Compared with intercalation batteries such as lithium-ion types, Li-S cells have the opportunity to provide a significantly higher energy density. Values can approach 2,500Wh/kg or 2,800Wh/l on a weight or volume basis respectively, assuming complete reaction to Li_2S.

[0009] In practice, the various problems noted above hinders the complete reaction to form Li_2S. However, the performance of current commercial Li-S batteries is still higher than conventional lithium ion batteries as shown in Figure 1, at least in the mass energy density category which is plotted along the vertical axis. Improvements to Li-S technology is expected to follow the dashed line in which Li-S would also outperform litium ion batteries also in the volume energy density category shown along the horizontal axis of Figure 1.

[0010] To date, various carbon-sulfur composites have been used to improve the Li-S battery performance, but they have limitations owing to the scale of the contact area. Typical reported capacities are between 300 and 550 mA-h/g at moderate rates, such as are described at P. T. Cunningham, S. A. Johnson, and E. J. Cairns, J. ELECTROCHEM. SOC., 119 (1972) 1448. In response to many considerable challenges, novel advances in materials design such as new electrolytes [see for example J. H. Shin and E. J. Cairns, J. ELECTROCHEM. SOC., 155 (2008) A368] and protective films for the lithium anode [see for example K. I. Chung, W. S. Kim, and Y. K. Choi, J. ELECTROANAL. CHEM., 566 (2004) 263] have been developed. Combinations of electrolyte modification, additives and anode

protection have resulted in some promising results according to J.R. Akridge, Y. V. Mikhaylik, and N. White, SOLID STATE ION, 175 (2004) 243. Much of the difficulty still remains at the cathode, where the lack of breakthroughs has led to some cell configurations in which all the sulphides are solubilised. More recently, it has been demonstrated that cathodes based on sulphur/mesoporous carbon materials can overcome these challenges to a large degree, and exhibit stable, high, reversible capacities (up to 1,320mAh/g) with good rate properties and cycling efficiency [see for example X. Ji, K. T. Lee, and L. F. Nazar, NATURE MATERIALS, 8 (2009) 500].

[0011] Lithium-sulfur batteries, which can potentially store several times more energy than lithium ion batteries, have historically been too costly, unsafe and unreliable to make commercially. As will be shown in the exemplary embodiments below, improvements to the design of these batteries by nanotechnology can overcome such problems and bring the much more enhanced energy density Li-S batteries to the portable electronics as well as high-energy requested applications such as electric vehicles.

SUMMARY:

[0012] The foregoing and other problems are overcome, and other advantages are realized, by the use of the exemplary embodiments of this invention.

[0013] In a first aspect thereof, the exemplary embodiments of this invention provide a lithium sulphur battery comprising: a first conductive substrate comprising a first surface; a plurality of conductive stalks extending from the first surface of the first conductive substrate, the conductive stalks being aligned relative to adjacent conductive stalks; an electrically insulating coating about the conductive stalks; a second conductive substrate; an electrolyte disposed between the first surface of the first conductive substrate and the second conductive substrate; and a separator layer between the first conductive substrate and the second conductive substrate and on which the electrolyte is

disposed along opposed surfaces thereof, wherein the conductive stalks are made of carbon and the electrically insulating coating is a sulphur coating, and wherein the conductive stalks are perpendicular to the first conductive substrate and to the separator layer.

[0014] In a second aspect thereof, the exemplary embodiments of this invention provide a method of making a lithium-sulfur battery comprising: coating a catalyst on a surface of a conductive substrate; growing a layer of carbon nano-tubes on the catalyst coated surface, the nano-tubes extending from the catalyst coated surface; and applying an electrically insulating coating onto the grown carbon nano-tubes, wherein the electrically insulating coating is a sulphur coating.

[0015/16] These and other aspects of the invention are set forth with particularity below.

BRIEF DESCRIPTION OF THE DRAWINGS:

[0017] Figure 1 is a graph comparing volumetric and gravimetric energy density of a lithium-sulfur (Li-S) battery with other battery technologies, and showing "Future Li-S performance" in which embodiments of this invention fall .

[0018] Figure 2 is an expanded schematic sectional view of a portion of a Li-S battery cathode comprising aligned carbon nano-tubes coated with sulfur according to an exemplary embodiment of the invention.

[0019] Figures 3a-b are SEM images of sparsely grown carbon nano-tubes at Figure 3a and carbon nano-tubes coated with sulfur according to an embodiment of these teachings at Figure 3b.

[0020] Figure 4 is a schematic sectional view of a lithium-sulfur battery according

to an exemplary embodiment of the invention, showing also a load/charge potential and bridge circuit for completeness.

[0021] Figure 5 is a schematic perspective exploded view of a flexible lithium–sulfur battery according to these teachings using a polymer electrolyte.

[0022] Figure 6 is a logic flow diagram that illustrates the operation of a method, and a result of execution of computer program instructions embodied on a computer readable memory, in accordance with the exemplary embodiments of this invention.

DETAILED DESCRIPTION:

[0023] The embodiments detailed herein describe an exemplary nenotechnology solution to the above detailed problems with Li-S batteries. Carbon nano-structures according to the exemplary embodiments described herein increase the cathode active area significantly and function as a sulfur container.

[0024] As a brief overview, sulfur is coated around a plurality or 'forest' of aligned carbon nano-tubes which are grown on a flexible metal substrate. In this manner, a high percentage of the sulfur atoms sit close to the conductive carbon, making them accessible to both electrons and lithium ions. The carbon nano-tubes also aid in dealing with polysulfides, which can cause a Li-S cell to fail prematurely by preventing a high number of recharges. The carbon tubes effectively trap the polysulfides in place until they are fully converted to dilithium sulfide, which is dealt with normally in the charge/recharge cycle and so the polysulfides do not accumulate to a point where they cause the Li-S battery to fail after a few cycles. Coating the carbon with a polymer that has an affinity for polysulfides also helps keep them in place. Specifically, thiol-terminated conducting polymers/conjugated molecules (e.g. orthomercaptoaniline) can be used to keep the polysulfides in place without sacrificing the conductance. See for example: Jui-Ming Yeh, Kuan-Yeh Huang, Su-Yin Lin, Yu-Yao Wu, Chao-

Chen Huang, and Shir-Joe Liou, JOURNAL OF NANOTECHNOLOGY, 2009(2009)217469. These embodiments offer the possibility of high gravimetric capacities and theoretical energy densities ranging up to a factor of five beyond conventional Li-ion systems.

[0025] Exemplary embodiments of these teachings include highly ordered interwoven composites or layers, which show the feasibility of approaching such high gravimetric capacities. The aligned carbon nano-tube forest, which is conductive, precisely constrains sulfur nano-filler growth, which is insulative, within its spaces and generates essential electrical contact through the insulating sulfur. The structure provides access to Lithium-Carbon ingress/egress for reactivity with the sulfur, and the kinetic inhibition is diffuse within the framework of the coated carbon nano-tubes so the sorption properties of the carbon aid in trapping the polysulfides formed during redox. In a variation, there is a polymer modification of the carbon surface which further provides a chemical gradient that retards diffusion of these large anions out of the electrode, thus facilitating more complete reaction.

[0026] Now are described exemplary but non-limiting embodiments of the invention with more particularity. Consider Figure 2, which shows an expanded view of a section of the Li-S battery cathode 202 which comprises aligned carbon nano-tubes 204 coated with sulfur 206. The carbon nano-tubes extend from a first surface 208a of a first conductive substrate 208 such as for example aluminum Al, copper Cu or gold Au. In an embodiment this first conductive substrate is flexible, as is a layer of common aluminum foil. With proper cleaning for the manufacture of a battery according to these teachings, common aluminum foil can itself serve as the first conductive substrate. It is not necessary that the carbon be tubular per se, they may equally be solid protrusions from the first conductive substrate 208, but grown carbon nano-tubes are one currently available structure for implementing this portion of the invention. In general, term these as conductive stalks, which may be solid rods or hollow tubes of carbon or other conductive materials. The examples below refer to carbon stalks for ease of explanation. There is a plurality of such carbon

stalks 204 extending from the first surface 208a in a generally aligned manner, as trees in a forest or fibers which make up the pile of a carpet. The carbon stalks 204 extend generally perpendicular from the surface 208a. The term 'generally perpendicular' as used herein means perpendicular as averaged across a large multitude of closely spaced stalks, such as is shown at the micrographs of Figures 3a-b in which individual stalks may vary somewhat from true perpendicular. The forest of aligned carbon stalks 204 can be made by known mass-production techniques, as well as the sulfur coating 206 to form the overall electrodes.

[0027] In an embodiment, the thickness of the sulfur 206 about the carbon stalks, which thickness extends along the entire length 204a of the stalks and which is shown as reference number 206a, is about 3 nanometers, +/- about 1 nanometer. Even if the thickness of this sulfur layer 206 is not uniform, there is a layer of sulfur that coats substantially the entire length 204a of each stalk extending from the surface 208a. A maximum thickness of 3 nm +/- 1 nm assures that the insulative properties of the sulfur overlayer 206 do not negate the conductive properties of the underlying carbon stalks 204, enabling the ions to bind to the coated stalks when the battery is in operation (charging or discharging) despite sulfur's insulative properties. As will be evident from the process detailed below for applying this sulfur coating 206, generally the thickness 206c of the sulfur over the first surface 208a of the first conductive substrate 208 will be similar to the thickness 206a along the length 204a of the carbon stalks 204, and the thickness 206b by which the sulfur coating extends a length 204a of the carbon stalks 204 will also be similar. It is clear that the more important sulfur thickness is along the length 204a of the carbon stalk 204, since the relative surface areas along the length 204a of the stalks 204 far exceeds that which is available through the sulfur thickness 206c along the substrate 208 itself or along the tips of the carbon stalks shown as 206b. The carbon stalks 204 are spaced from one another such that, after the sulfur coating 206 is applied to the desired thickness 206a, there is a gap 210 between them which, on average across all the stalks, is at least the diameter of two lithium ions (or

whatever ion carries the electrical charge between anode and cathode in the overall battery) and is preferably not more than two orders of magnitude higher than that. This assures that an ion which is bound to a portion of the coated stalk 204 furthest from the substrate 208 does not block mobility of other ions from binding to the lower reaches of that same stalk and adjacent ones.

[0028] Preferably for the case that the stalks are embodied as nano-tubes, an average diameter (of an outermost wall if the subject nano-tube is multi-walled) is in the range from 10 to 100 nanometers, and a pitch between adjacent multi-walled carbon nano-tubes is in the range from 20 to 500 nanometers (somewhat less for single wall nano-tubes). In the carbon nano-tube array, the lithium ions are able to intercalate not only inside the multi-walled carbon nanotubes, but also in the interstices between adjacent multi-walled or single walled carbon nano-tubes. Thus a density of intercalation of the multi-walled carbon nano-tube array is significantly higher than that of graphite. The coating of sulfur around the carbon nano-tubes can be adjusted by thickness, but the minimum thickness should be around 2-3nm (larger than the diameter of the lithium ion). The atomic radius of the lithium atom is 152 pm and the diameter for a dissolved lithium ion should be less than 1 nm. The gap between coated stalks should be at least the larger than the diameter of the lithium ion, i.e. 1 nm.

[0029] Figures 3a and 3b are scanning electron microscope SEM images. Figure 3a is a higher resolution image of sparsely grown carbon nano-tubes which extend from the underlying substrate. Figure 3b is a slightly lower resolution image of similar such carbon nano-tubes with a sulfur coating over them, similar to those shown schematically at Figure 2. This perspective view of the coated stalks with reference to the scale at the bottom left of that image shows that the coated stalks are spaced sufficiently far that lithium ions, whose diameter is about 1.48 angstroms and which attach near the tip of individual coated stalks, would not impede movement of other lithium cations toward inner reaches of those same or adjacent coated stalks. Figure 3b illustrates an average gap 210 of about 30 nm, or one order of magnitude greater than the

diameter of two lithium ions.

[0030] The aligned forest of conductive stalks precisely constrains sulfur nano-filler growth within its spaces and generates essential electrical contact to the insulating sulfur. The sulfur coating 206 is such that individual stalks 204 are still apparent (given sufficient resolution as in Figure 3b), though of course in a practical embodiment some pairs or bunches of carbon stalks 204 may not be individually separable after coating due to practical limits of manufacturing precision. The imprecision in stalk alignment and spacing shown at the high resolution images of Figures 3a-b illustrate that it is *average* spacing and thickness which are the practical values for designing to a certain battery performance. Once a designer selects a desired sulfur thickness 206a along the length of the carbon stalks 204, then spacing constraints for the gap 210 between coated stalks gives the manufacturer the required density of the carbon stalks 204 which are grown on the substrate 208. If the coating 206 were too thick or the carbon stalks 204 were too densely packed, much or all of the length of the carbon stalks 204 would be unavailable for ion attachment due to the insulative properties of the sulfur.

[0031] Figure 4 illustrates in schematic form a lithium-sulfur battery 400 according to an embodiment of the invention. The carbon stalk/sulfur cathode 402 is similar to that shown at Figure 2, in which the first conductive substrate 408 is a charge collector into which current flows while in the battery charging mode, and is a charge storage medium from which current flows while the battery is in the discharge mode. In the Figure 4 embodiment the first conductive substrate is a flexible metal foil. Shown also are the carbon stalks 404 with a sulfur coating 406, extending from the first surface 408a of the first conductive substrate 408.

[0032] The anode is a second conductive substrate 420 which in the Figure 4 embodiment is a flexible lithium foil. Disposed between them is an electrolyte 430 which provides mobility for the lithium ions 440. As illustrated at Figure 4 there is a separator layer 432 having pores through which the lithium ions 440

may pass, and conventional electrolyte 430 on either side of that separator layer 432.

[0033] For completeness, Figure 4 also shows a bridge circuit 450 which couples a first terminal 403 of the cathode 402 to a second terminal 421 of the anode 420 through a load 460 (in the case of discharge 452) or potential 460 (in the case of charge 454). The cathode 402, anode 420, electrolyte 430 and separator layer 432 are all disposed within a housing 470 such as plastic or fiber or other non-conductive material, and the terminals 403, 421 penetrate the housing 470 to electrically contact the respective cathode 402 and anode 420. The battery is then disposed within a host deice which has the actual bridge circuit coupling in the load and/or charge potential 460 to the battery via the terminals 403, 421.

[0034] When there is a load 460 in the circuit 450, current in the form of electrons flows from the cathode 402 to the anode 420 along the discharge direction 452 as shown. The accumulating electrons at the anode 420 attract lithium ions 440 which are attached to the coated stalks 404/406 of the cathode 402. These lithium ions 440 mobilize through the electrolyte 430 and pass through the separator layer 432 and are attracted to the greater concentration of electrons at the anode 420 while at the same time there is a diminishing concentration of electrons holding those ions 440 at the cathode 402 due to movement of electrons from cathode 402 to anode 420 across the bridge circuit 450 in the discharge direction 452.

[0035] A reverse of the discharge process occurs in the charge process when there is a potential applied at 460 in the circuit 450. In this case, current flows from the anode 420 to the cathode 402 along the charge direction 454 as shown. The accumulating electrons at the cathode 402 attract lithium ions 440. These lithium ions 440 originated from the anode 420 and passed through the electrolyte 430 and through the separator layer 432. Electron movement is from anode 420 to cathode 402 along the bridge circuit 450 in the charge direction 454. The greater concentration of electrons at the cathode 402 with

simultaneous diminishing concentration of electrons holding those ions 440 at the anode 420 drive the cations 440 through the electrolyte 430. Once those cations 440 arrive at the cathode 402, they become attached to the coated stalks 404/406 of the cathode 402 which provide a substantially larger surface area for attachment than the first surface 408a of the first conductive substrate 402 alone would provide.

[0036] Various embodiments of the Li-S battery shown schematically at Figure 4 include any combination of the following. The first conductive substrate may be a flexible metal foil, such as for example aluminum, iron, stainless steel, copper or gold, or conductive compounds made or allowed with any one or more of those. The conductive stalks may be solid rods or hollow tubes, and may be carbon or some other conductive material. The electrically insulating coating 406 about the conductive/carbon stalks may be sulfur or compounds made therefrom, or other insulating materials which can be disposed at a requisite thickness such that, at the cation diameter level of precision, the stalks generally remain separate from one another with a gap between adjacent stalks (manufacturing imprecisions excepted). The electrolyte 430 may be any substance containing free ions that behaves as an electrically conductive medium, and for example the electrolyte may be a composite of a lithium salt and one of the following polymers: ethylene carbonate (EC), diethylene carbonate (DC) and propylene carbonate (PC). Alternatively, the electrolyte may be a room temperature ionic liquid electrolyte. The room temperature ionic liquid electrolyte may comprise 1-butyl, 3-methylimidazolium chloride ([BMIM][Cl]), 1-25% of cellulose and a lithium salt. The separator layer 432 may be, for example, a microperforated plastic film made of polyethylene (PE), polypropylene (PP), a combination of them both, or paper. The electrolyte 430 may be disposed on surfaces of the separator layer 432/plastic film. The second conductive substrate may be, for example, lithium metal oxide such as for example lithium cobalt oxide ($LiCoO_2$), lithium manganese oxide ($LiMnO_4$), lithium nickel oxide ($LiNiO_2$) and lithium iron phosphate ($LiFePO_4$).

[0037] Note that the specific embodiments for the anode and cathode in the description of Figures 2 and 4 are exemplary; other arrangements which incorporate these teachings may have the coated carbon tubes extending from the first substrate in the position of the anode and the lithium oxide substrate in the position of the cathode.

[0038] Figure 5 illustrates a particular embodiment of a Li-S battery according to these teachings made with flexible substrates, which are then rolled and hermetically sealed with leads from the anode and cathode for connecting with a bridge circuit 450 of Figure 4 in which the load or charge potential is applied. In this particular embodiment there is a nanocarbon-sulfur electrode layer 502 which is similar in structure to the cathode 402 described for Figure 4. Adjacent to the nanocarbon-sulfur electrode layer 502 is a polymer electrolyte layer 530/532 which by example may be similar to the separator layer 432 of Figure 4 with electrolyte material 430 disposed on either side. Next is a lithium foil anode layer 520 which is similar in structure to the anode 420 at Figure 4. A current collector layer 545 lies adjacent to the lithium foil anode layer 520 and is a more conductive layer than layer 520 to collect charge. There is another layer of insulator 546 and a packaging layer 547 (also insulating), which when the assembled layers are wrapped as shown at Figure 5 form the respective outermost and innermost layers of the battery 500.

[0039] Whether implemented as a rolled multi-layer apparatus 500 such as shown at Figure 5 or otherwise, embodiments of this invention with the polymer electrolyte provide a sulfur-lithium battery with enhanced energy storage as compared to the prior art. Such a Li-S battery may be deployed in portable devices such as mobile telephones or other personal electronic devices (e.g., personal digital assistants (PDAs), portable computers/laptops/palmtops, image capture devices such as digital cameras, gaming devices, music storage and playback appliances and Internet appliances), as well as vehicles such as automobiles, aircraft, watercraft and the like. These are examples and not limiting to the uses for which various embodiments of a Li-S galvanic battery

according to these teachings may be deployed.

[0040] Now is described with reference to Figure 6 an exemplary method of making a Li-S battery according to the teachings above, particularly making the first substrate with the extending conductive stalks with the sulfur coating thereon. This exemplary method employs growing carbon nano-tubes as the conductive stalks on a conductive substrate such as for example a flexible metal foil. Figure 6 is a logic flow diagram that illustrates the operation of a method, and a result of execution of computer program instructions, in accordance with the exemplary embodiments of this invention.

[0041] The exemplary method can be divided into three main steps: coating a catalyst on a surface of a conductive substrate at block 610; growing a layer of carbon nano-tubes on the catalyst coated surface at block 620, and applying an electrically insulating coating onto the grown carbon nano-tubes (e.g., sulfur) at block 630. Other portions of Figure 6 are specific implementation details for an exemplary embodiment. The various blocks shown in Figure 6 may be viewed as method steps, and/or as operations that result from operation of computer program code which controls physical manufacturing machinery which executes the method, and/or as a plurality of coupled logic circuit elements constructed to control such physical manufacturing machinery to carry out the associated function(s).

[0042] In an embodiment, the conductive substrate is a flexible metal foil such as aluminum, gold or copper as seen at block 622. For example, commercially available, 10 μm thick aluminum foil is cut and cleaned using consecutive acetone and isopropanol sonications for 5 minutes which is followed by a rinse with deionized water and drying under a nitrogen flow (e.g., with a nitrogen gun). In an embodiment the catalyst comprises iron disposed over the surface of the cleaned foil as a thin film at a thickness of a few nanometers thick. Note that the thickness of the iron film is less than 1/100 of the thickness of the 10 μm thick metal foil substrate on which the catalyst is coated, as seen at block 612. Sputtering can be used to dispose the iron film on cleaned foils, such as for

example using a DC sputtering system at a power level of 50 W and at a base pressure of $2*10^{-6}$ mbars.

[0043] In an embodiment, the layer of multi-walled carbon nano-tubes are grown on the catalyst coated surface using plasma-enhanced chemical vapor deposition (PE-CVD, for example using a system available through Aixtron AG, of Herzogenrath, Germany). In a practical embodiment, growth of the carbon nano-tubes was done in a quartz vacuum chamber on a resistively heated graphite stage. Growth temperature was controlled by a thermocouple attached to the surface of the graphite stage. Growth can be considered as comprising two stages as shown at block 624: seed formation of catalytic nano-particles, and tube growth from the seeds. For the first stage of seed formation, following deposition of the iron film catalyst, samples were placed on the graphite stage in the quartz chamber, which was then evacuated to 0.2 mbar. The samples were then heated up to 480 ^{o}C with ammonia gas (NH_3, at a 200 standard cubic centimeters per minute sccm flow rate), and annealed at this temperature for 2 minutes. Catalytic nano-particles were found on the foil after this annealing, which is important for low temperature growth of the ultimate carbon nano-tubes. This completed the seed formation stage.

[0044] For the tube growth stage, after annealing in the seed formations stage the graphite stage temperature was ramped to 530 ^{o}C. Flow of the ammonia gas was discontinued and acetylene (C_2H_2) was supplied (at a 200 sccm flow rate) as the carbon feedstock for the carbon nano-tube growth. The chamber pressure then was maintained at 10 mbar. After a growth period of 15 minutes, C2H2 and heating was turned off and samples were cooled to room temperature with nitrogen gas (200 sccm flow rate). Fifteen minutes of growth yielded multi-walled carbon nano-tubes of length 70 μm as measured from the foil substrate surface, which were aligned and closely packed. Of course, different lengths of carbon nano-tubes can be obtained, (e.g., from ranges of a few hundred nanometers to 100 μm or so) by using the above process and varying the growth time in the second stage.

[0045] The tube density depends on the ion diameter in the final battery (depending on the material of the other conductive foil) and the thickness of the insulating overlayer/sulfur (and of course the diameter of the nano-tubes themselves since the operative constraint in for ions to penetrate the gap between the coated nano-tubes). Exemplary guides to a proper nano-tube density are given above with reference to Figure 2, and a general statement of the end-goal for determining that density is shown also at block 626 of Figure 6.

[0046] The third main step is then applying an electrically insulating coating to the grown carbon nano-tubes, the coating comprising for example sulfur, which is also noted at block 622. In the practical embodiment, pure sulfur (negligible volume of contaminants excepted) was used in this step but compounds containing sulfur can also be used such as for example aromatic polysulfur tricyclic compounds. The sulfur was ground to a fine powder, sprinkled over the grown carbon nano-tubes and the entire foil assembly was heated to 160 ^{0}C, which fused the sulfur to the aligned carbon nano-tubes as a coating as shown at block 632. As will be appreciated, fusing powdered sulfur over multiple nano-tubes may leave certain portions along the length of a few nano-tubes uncoated, and so the nano-tubes are substantially coated with the sulfur coating, substantially meaning at least 95% (and more preferably 98%) of the exterior surface of all nano-tubes taken as a whole has a sulfur-based coating over it.

[0047] For completeness, at block 634 the battery is formed by disposing the surface with the coated nano-tubes opposite a second conductive substrate within a housing, and disposing an electrolyte within the housing between that surface from which the coated nano-tubes extend and the second conductive substrate, and also providing first and second conductive terminals external of the housing which electrically couple through the housing to the respective first and second conductive substrates. The formed battery is then disposed by a downline manufacturer within a host device such as for example a mobile phone, laptop computer, or a vehicle (car, boat, airplane) within which at least one of a

load and a voltage potential are coupled to the first and to the second terminals via a bridge circuit. The bridge circuit itself is part of the host device.

[0048] Exemplary embodiments of the invention detailed above provide the technical effect of a flexible nano-structured lithium-sulfur battery with enhanced energy density. Such a battery based on the teachings set forth above exhibits advantages over conventional batteries in at least a higher power density on a weight or volume basis respectively than any traditional lithium or lithium ion batteries (and in some embodiments significantly higher), and extended battery life as compared to conventional batteries which have the technical effect of extending the practical applications in which a galvanic battery can be economically used beyond multi-functional portable electronics to higher electric demand devices such as electric vehicles (automobiles, watercraft, and possibly aircraft given the higher power density per weight).

[0049] We stipulate that some of the features of the various non-limiting and exemplary embodiments of this invention may be used to advantage without the corresponding use of other described features (e.g., the coated conductive stalks may find some other practical implementation apart from a battery as described), and the various optional features detailed herein may be combined individually or in any multitude of combinations into the broader aspects of the invention detailed herein. As such, the foregoing description should be considered as merely illustrative of the principles, teachings and exemplary embodiments of this invention within the scope of the appended claims, and not in limitation thereof.

What is claimed is:

1. A lithium sulphur battery comprising:

a first conductive substrate comprising a first surface;

a plurality of conductive stalks extending from the first surface of the first conductive substrate, the conductive stalks being aligned relative to adjacent conductive stalks;

an electrically insulating coating about the conductive stalks;

a second conductive substrate;

an electrolyte disposed between the first surface of the first conductive substrate and the second conductive substrate; and

a separator layer between the first conductive substrate and the second conductive substrate and on which the electrolyte is disposed along opposed surfaces thereof,

wherein the conductive stalks are made of carbon and the electrically insulating coating is a sulphur coating, and

wherein the conductive stalks are perpendicular to the first conductive substrate and to the separator layer.

2. The battery according to claim 1, in which the conductive stalks extend perpendicular from the first surface.

3. The battery according to claim 1 or 2, in which the sulphur coating is disposed at a thickness of about 3 nanometers.

4. The battery according to claim 3, in which the plurality of conductive stalks are disposed at a density such that a gap between the conductive stalks having the conductive coating applied thereabout is between about 2 and 200 diameters of an ion which passes between the first and second conductive substrates and is attached to the coated conductive stalks by electrical attraction while the apparatus is in operation as a galvanic battery.

5. The battery according to claim 3, in which the second conductive substrate comprises an oxide of lithium.

6. The battery according to claim 5, wherein the separator layer has a porosity amenable to passage by ions moving between the first conductive substrate and the second conductive substrate.

7. The battery according to claim 6, in which the electrolyte comprises a polymer.

8. The battery according to any one of claims 2 to 7, in which the conductive stalks are carbon nano-tubes which are directly attached to the first surface of the first substrate.

9. The battery according to any one of claims 1 to 8, further comprising a bridge circuit which electrically couples a first terminal of the first conductive substrate to a second terminal of the second conductive substrate, and at least one of a load and a voltage potential for discharging or charging the battery, respectively, disposed within the bridge circuit.

10. A method of making a lithium-sulfur battery comprising:

coating a catalyst on a surface of a conductive substrate;

growing a layer of carbon nano-tubes on the catalyst coated surface, the nano-tubes extending from the catalyst coated surface; and

applying an electrically insulating coating onto the grown carbon nano-tubes,

wherein the electrically insulating coating is a sulphur coating.

11. The method according to claim 10, in which the conductive substrate is a first conductive substrate and the method further comprises, after applying the electrically insulating coating:

disposing the surface opposite a second conductive substrate within a housing;

disposing an electrolyte within the housing between the surface and the second conductive substrate; and

forming a battery by providing a first conductive terminal external of the housing which electrically couples through the housing to the first conductive substrate and a second conductive terminal external of the housing which electrically couples through the housing to the second conductive substrate.

12. The method according to claim 10 or 11, in which the conductive substrate on which the catalyst is coated is a flexible foil made of aluminum, copper or gold.

13. The method according to claim 10 or 11, in which the catalyst comprises iron and coating the catalyst comprises sputtering a film of iron under a vacuum to a final thickness no greater than about 1/100 of a thickness of the conductive substrate on which the catalyst is coated.

14. The method according to claim 10, in which the growing the layer of carbon nano-tubes on the catalyst coated surface comprises a first stage of seed formation of catalytic nano-particles, and a second stage of tube growth from the formed seeds, in which the tube growth is in a direction perpendicular to the catalyst coated surface of the conductive substrate.

15. The method according to claim 14, in which the first stage comprises using plasma-enhanced chemical vapor deposition on the catalyst coated conductive substrate disposed in a heated vacuum chamber into which ammonia gas is flowed, and thereafter annealing the catalyst coated conductive substrate to form the catalytic nano-particles on the coated surface.

16. The method according to claim 14 or 15, in which the second stage comprises flowing a carbon feedstock gas into a heated chamber into which

the catalyst coated conductive substrate with the catalytic nano-particles is disposed.

17. The method according to claim 10 or 11, in which applying the electrically insulating coating comprises disposing powder comprising sulfur over the grown carbon nano-tubes and heating to fuse the disposed powder to the carbon nano-tubes.

18. The method according to claim 11, further comprising disposing the battery within a host device and coupling at least one of a load and a voltage potential to the first and second terminals via a bridge circuit of the host device.

19. The method according to claim 11, in which the grown carbon nano-tubes are disposed on the surface at a density such that a gap between the carbon nano-tubes with the electrically insulating coating thereon is between about 2 and 200 diameters of an ion which passes between the first and second conductive substrates and is attached to the coated carbon nano-tubes by electrical attraction while the battery is in operation.

20. The method according to any one of claims 10 to 19, in which the sulfur coating is disposed at a thickness of about 3 nanometers.

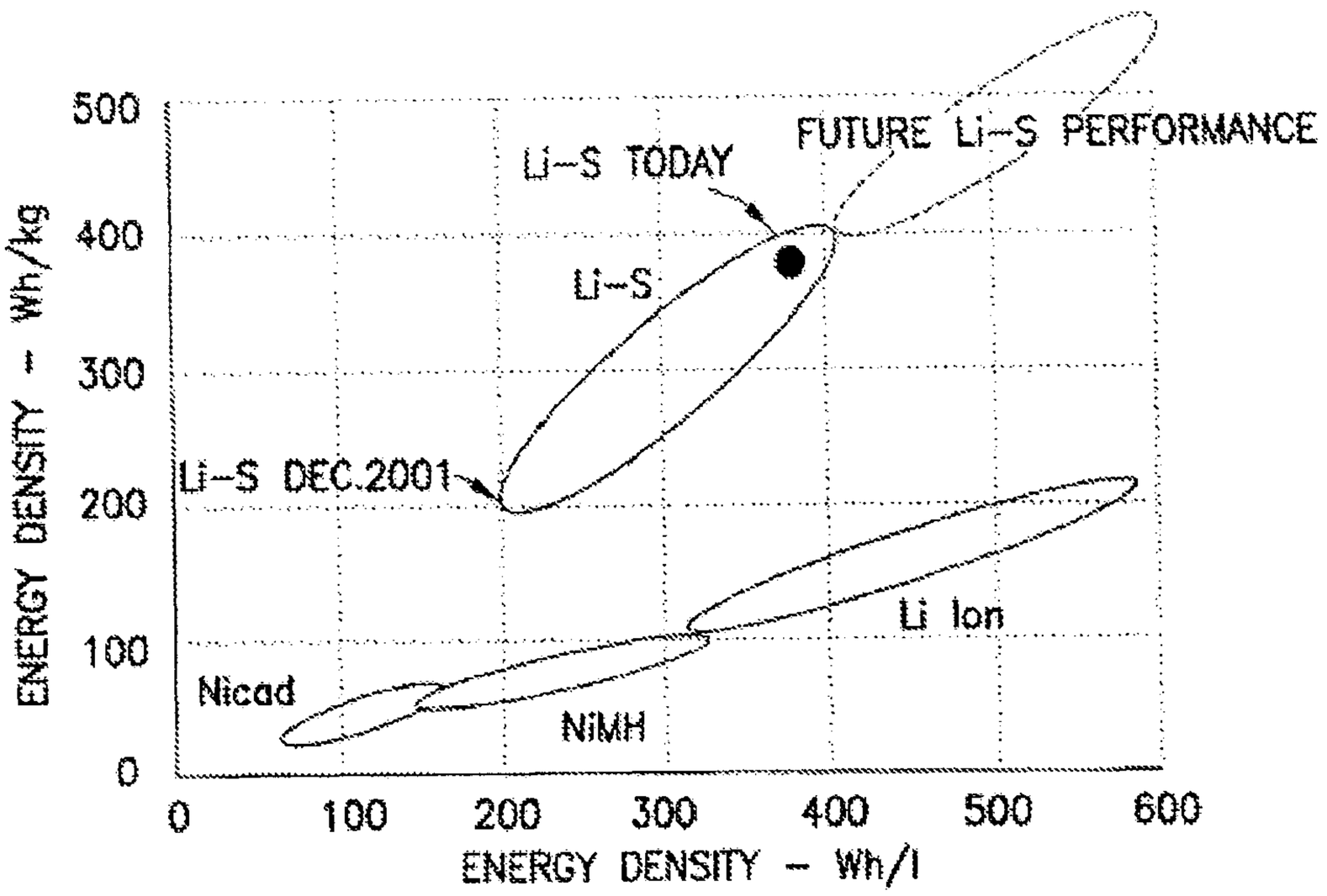

FIG.1
(PRIOR ART)

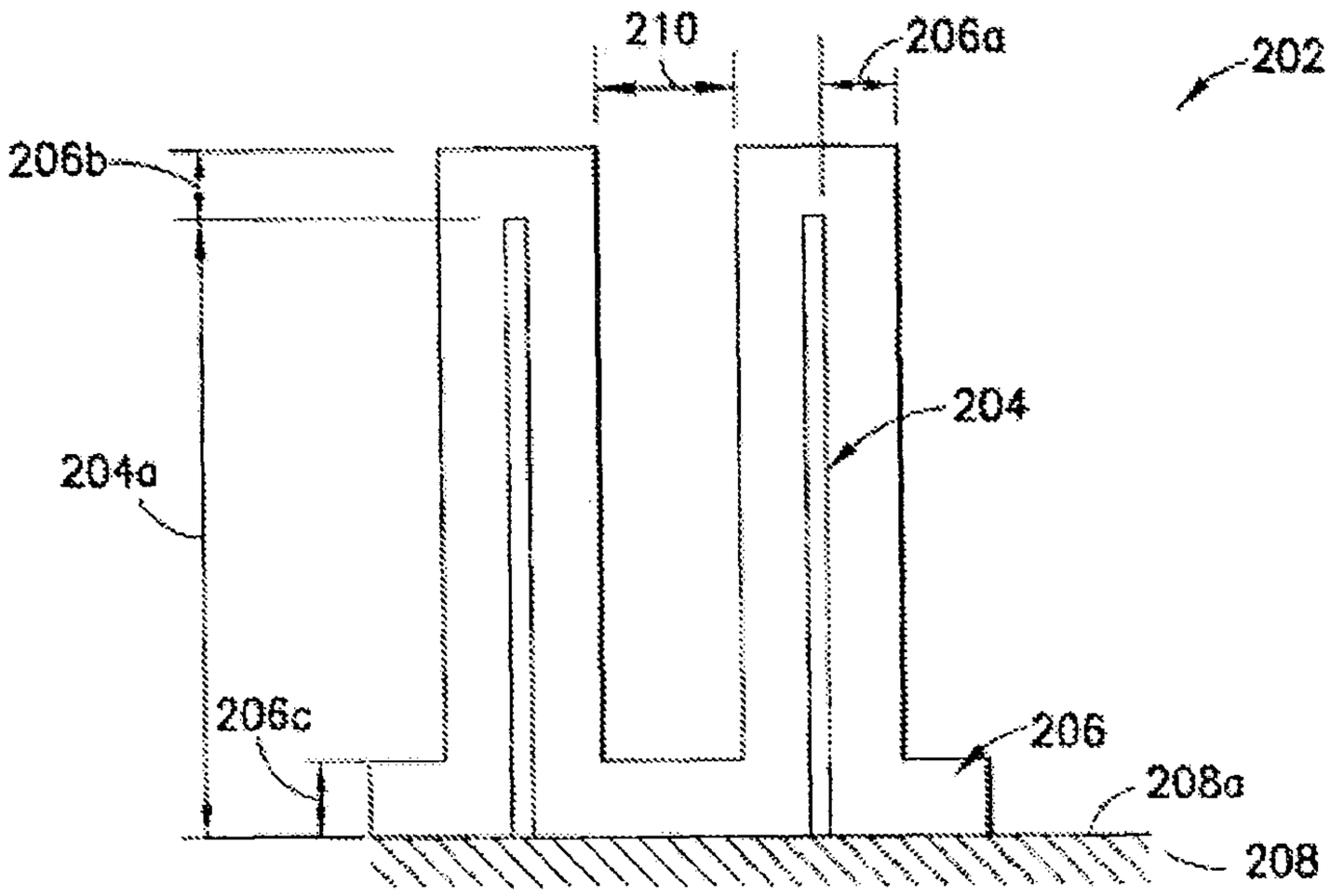

FIG.2

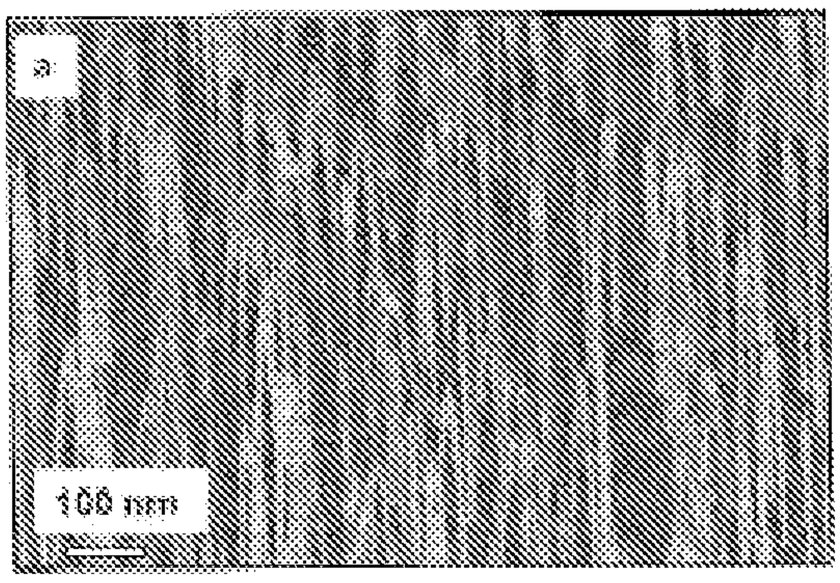

FIG.3a

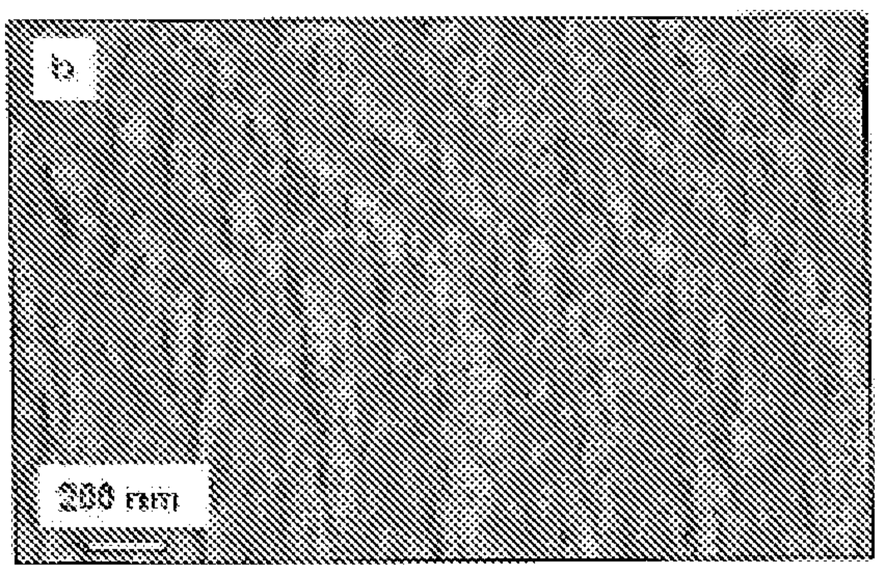

FIG.3b

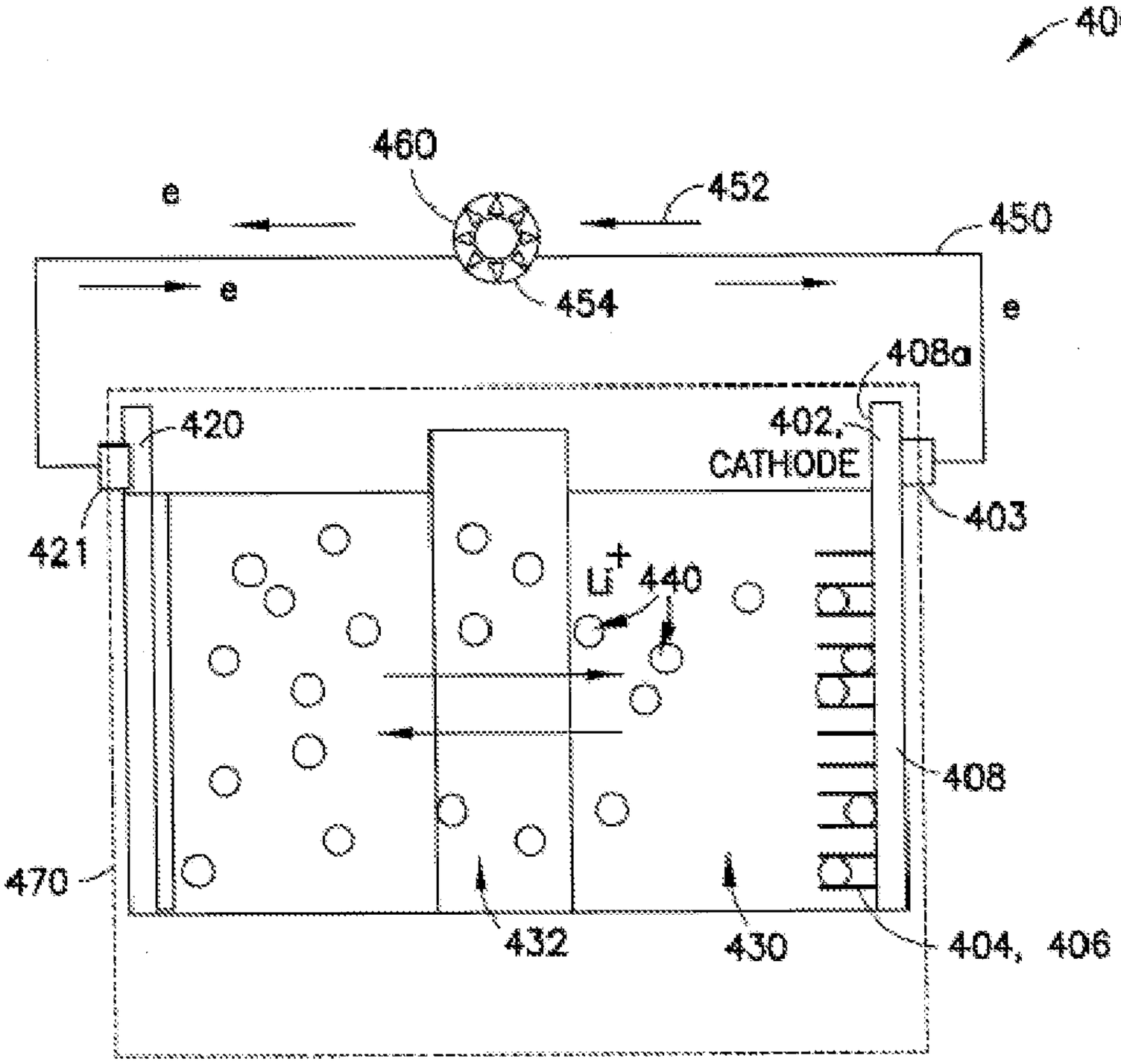

FIG.4

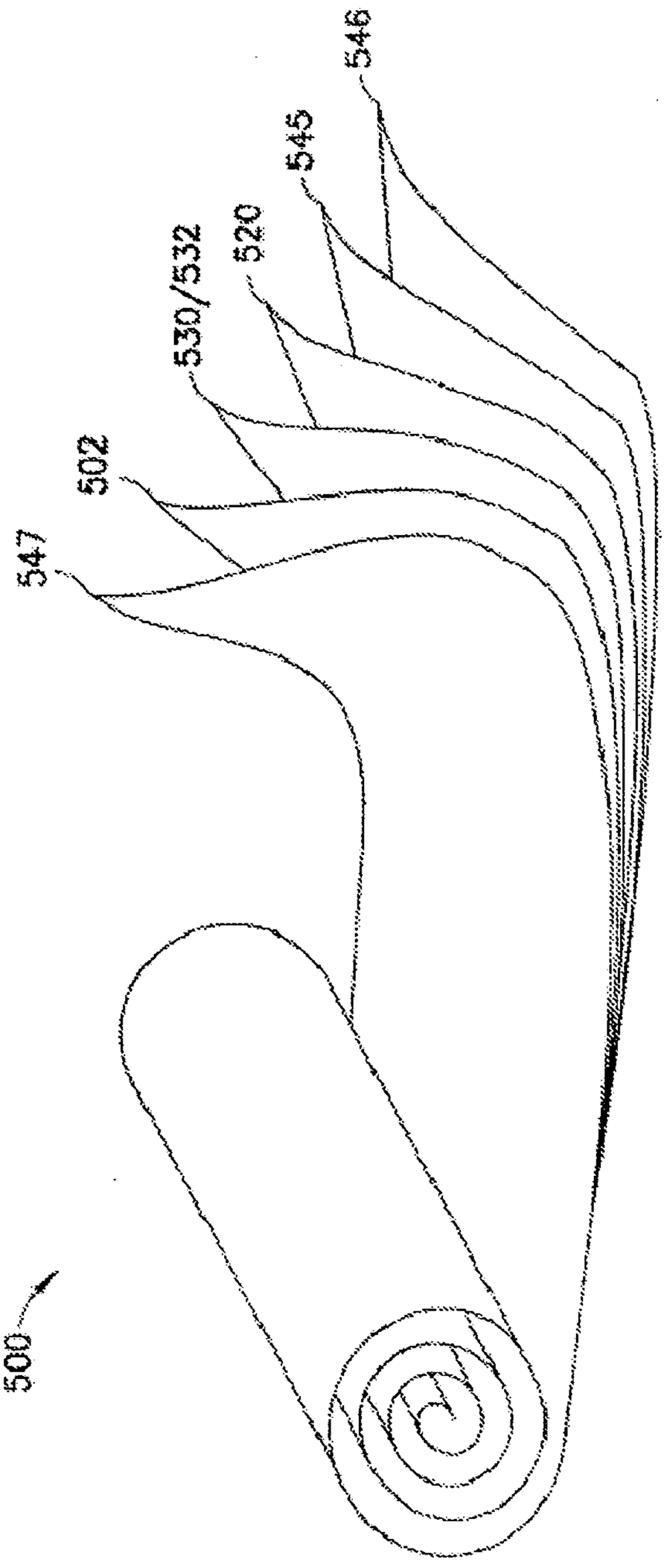

FIG.5

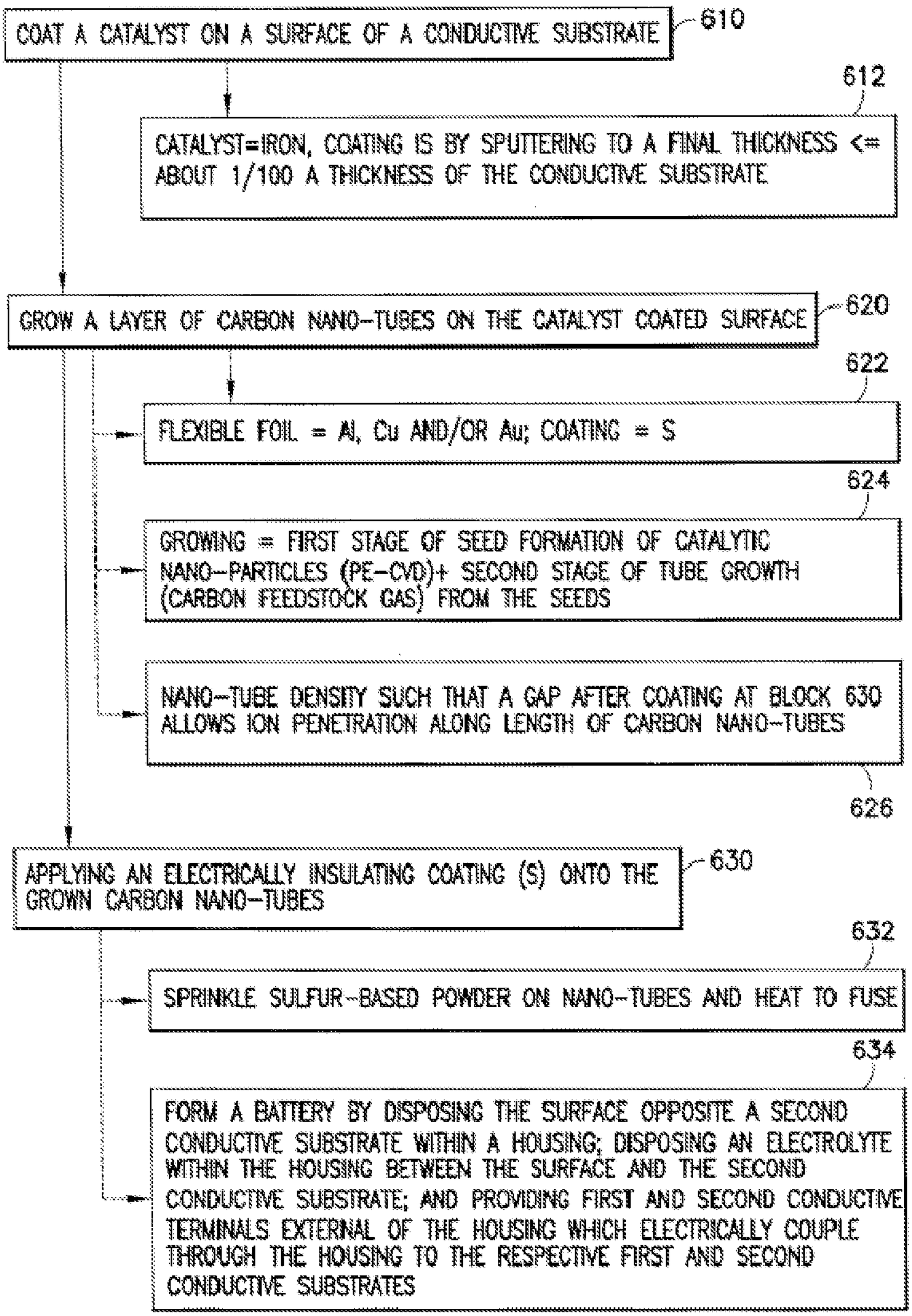
COAT A CATALYST ON A SURFACE OF A CONDUCTIVE SUBSTRATE
610
612
CATALYST=IRON, COATING IS BY SPUTTERING TO A FINAL THICKNESS <= ABOUT 1/100 A THICKNESS OF THE CONDUCTIVE SUBSTRATE
GROW A LAYER OF CARBON NANO-TUBES ON THE CATALYST COATED SURFACE
620
622
FLEXIBLE FOIL = Al, Cu AND/OR Au; COATING = S
624
GROWING = FIRST STAGE OF SEED FORMATION OF CATALYTIC NANO-PARTICLES (PE-CVD)+ SECOND STAGE OF TUBE GROWTH (CARBON FEEDSTOCK GAS) FROM THE SEEDS
NANO-TUBE DENSITY SUCH THAT A GAP AFTER COATING AT BLOCK 630 ALLOWS ION PENETRATION ALONG LENGTH OF CARBON NANO-TUBES
626
APPLYING AN ELECTRICALLY INSULATING COATING (S) ONTO THE GROWN CARBON NANO-TUBES
630
632
SPRINKLE SULFUR-BASED POWDER ON NANO-TUBES AND HEAT TO FUSE
634
FORM A BATTERY BY DISPOSING THE SURFACE OPPOSITE A SECOND CONDUCTIVE SUBSTRATE WITHIN A HOUSING; DISPOSING AN ELECTROLYTE WITHIN THE HOUSING BETWEEN THE SURFACE AND THE SECOND CONDUCTIVE SUBSTRATE; AND PROVIDING FIRST AND SECOND CONDUCTIVE TERMINALS EXTERNAL OF THE HOUSING WHICH ELECTRICALLY COUPLE THROUGH THE HOUSING TO THE RESPECTIVE FIRST AND SECOND CONDUCTIVE SUBSTRATES

FIG.6

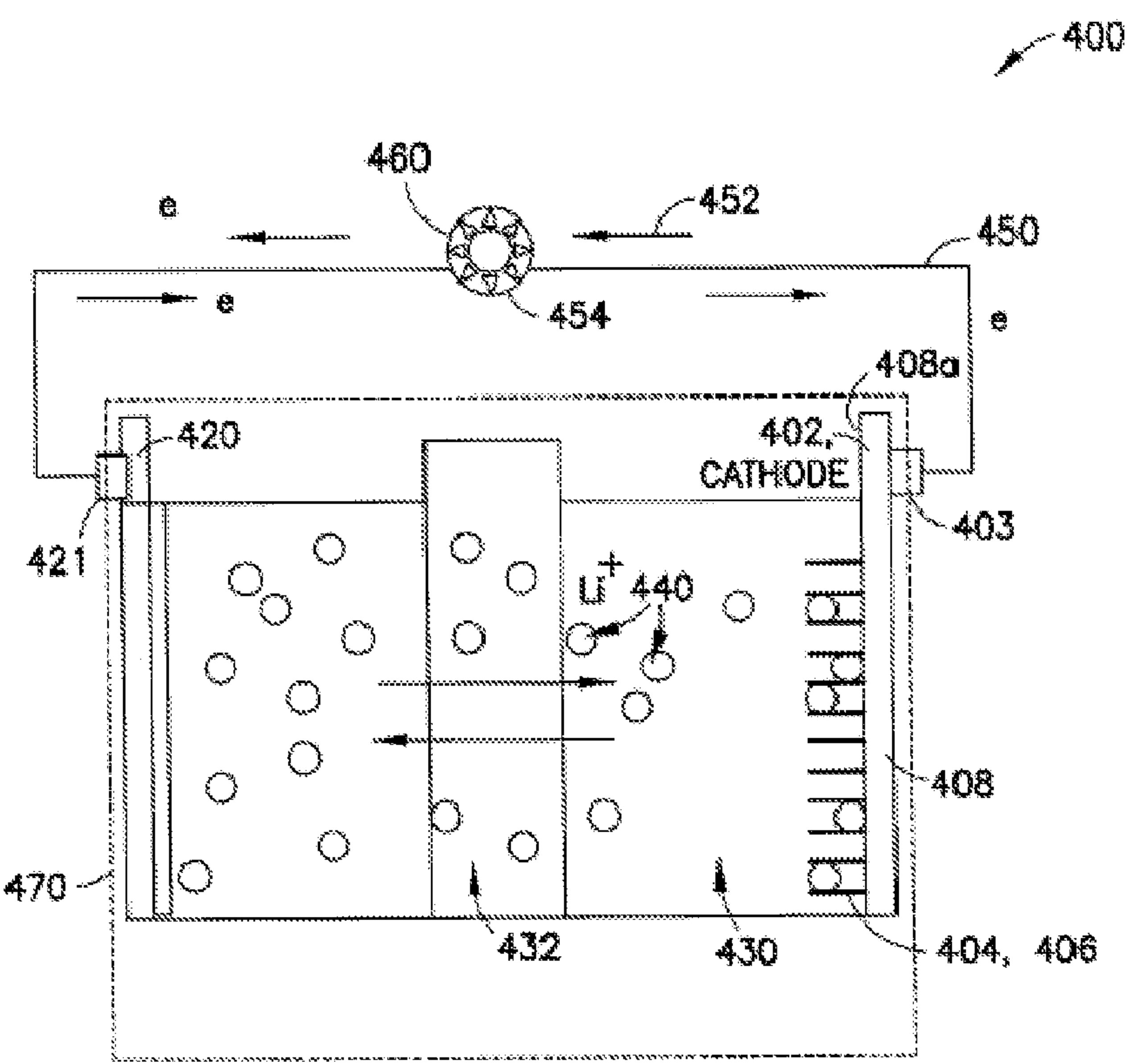
400
460
452
450
e
e
e
454
408a
420
402,
CATHODE
403
421
Li+
440
408
470
432
430
404, 406

FIG.4