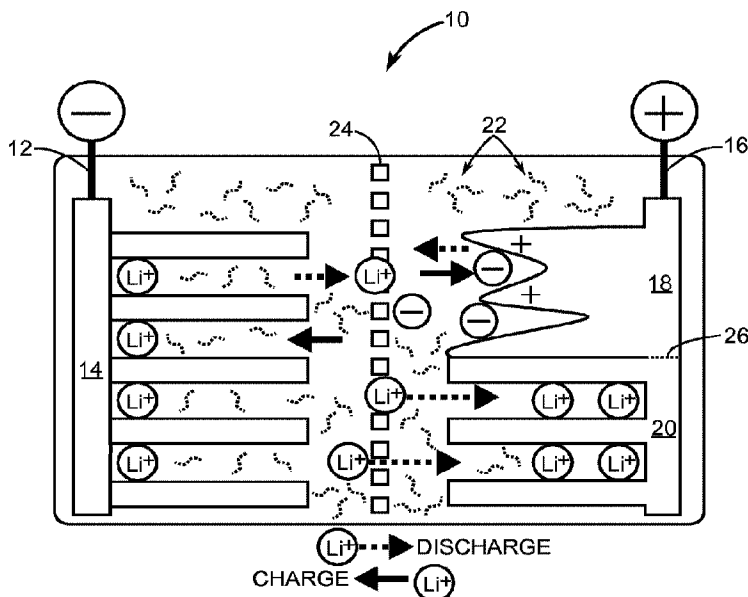




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(72) **Inventeurs/Inventors:**
EL-KADY, MAHER F., US;
KANER, RICHARD B., US
(73) **Propriétaire/Owner:**
THE REGENTS OF THE UNIVERSITY OF CALIFORNIA,
US
(74) **Agent:** AIRD & MCBURNEY LP

(54) **Titre : BATTERIE ELECTROCHIMIQUE HYBRIDE**
(54) **Title: HYBRID ELECTROCHEMICAL CELL**



(57) **Abrégé/Abstract:**

Disclosed is a hybrid electrochemical cell with a first conductor having at least one portion that is both a first capacitor electrode and a first battery electrode. The hybrid electrochemical cell further includes a second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode. An electrolyte is in contact with both the first conductor and the second conductor. In some embodiments, the hybrid electrochemical cell further includes a separator between the first conductor and the second conductor to prevent physical contact between the first conductor and the second conductor, while facilitating ion transport between the first conductor and the second conductor.



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(71) Applicant: THE REGENTS OF THE UNIVERSITY
OF CALIFORNIA [US/US]; 1111 Franklin Street,
Twelfth Floor, Oakland, California 94607 (US).

(72) Inventors: EL-KADY, Maher, F.; 741 Gayley Ave, Apt
#421, Los Angeles, California 90024 (US). KANER,
Richard, B.; 481 Almar Avenue, Pacific Palisades, Cali-
fornia 90272 (US).

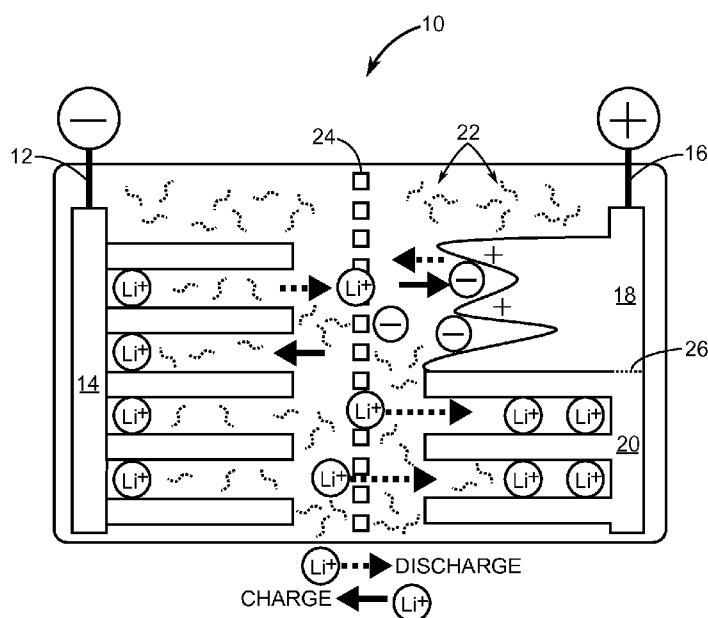
(74) Agent: FRINK, Bentley, D.; Withrow & Terranova,
P.L.L.C., 2530 Meridian Parkway, Suite 300, Durham,
North Carolina 27713 (US).

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(54) Title: HYBRID ELECTROCHEMICAL CELL



(57) Abstract: Disclosed is a hybrid electrochemic-
al cell with a first conductor having at least one por-
tion that is both a first capacitor electrode and a first
battery electrode. The hybrid electrochemical cell
further includes a second conductor having at least
one portion that is a second capacitor electrode and
at least one other portion that is a second battery
electrode. An electrolyte is in contact with both the
first conductor and the second conductor. In some
embodiments, the hybrid electrochemical cell fur-
ther includes a separator between the first conductor
and the second conductor to prevent physical con-
tact between the first conductor and the second con-
ductor, while facilitating ion transport between the
first conductor and the second conductor.

FIG. 1

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HYBRID ELECTROCHEMICAL CELL

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5 Education of Egypt through a graduate research fellowship—the Missions
Program.

Priority

[0002] This application claims the benefit of U.S. provisional patent
10 application number 62/012,835, filed June 16, 2014.

Field of the Disclosure

[0003] The disclosure relates to electrochemical cells and in particular to a
hybrid electrochemical cell having an energy density typical of a battery and a
15 power density typical of a supercapacitor.

Background

[0004] Batteries are used to power portable electronics such as smartphones,
tablets, and laptop computers. Batteries have affected various aspects of
20 modern living. There are numerous applications for batteries. Moreover,
batteries are integral for renewable energy production from sun and wind as well
as the development of electric and hybrid electric vehicles. Batteries store a large
amount of charge through electrochemical reactions and typically take hours to
recharge. What is needed is a hybrid electro-chemical cell that is quickly
25 rechargeable like a supercapacitor and that stores a large amount of charge like
a battery.

Summary

[0005] A hybrid electrochemical cell having a first conductor with at least one
30 portion that is both a first capacitor electrode and a first battery electrode is

disclosed. The hybrid electrochemical cell further includes a second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode. An electrolyte is in contact with both the first conductor and the second conductor.

5 [0006] In some embodiments, the hybrid electrochemical cell further includes a separator between the first conductor and the second conductor to prevent physical contact between the first conductor and the second conductor, while facilitating ion transport between the first conductor and the second conductor. Moreover, at least one exemplary embodiment of the hybrid electrochemical cell
10 relies on lithium-ion (Li-Ion) chemistry. Other exemplary embodiments of the hybrid electrochemical cell are based upon nickel-cadmium (Ni-Cd) and nickel-metal hydride (Ni-MH) chemistries. Further still, some embodiments of the hybrid electrochemical cell are sized to power electric vehicles for transportation, while other embodiments are sized small enough to power implantable medical
15 devices.

[0007] Generally described herein, in certain embodiments, is an energy storage technology comprising a supercapacitor designed to store charge on the surface of large surface area materials. In some applications, the disclosed supercapacitor captures and releases energy in seconds and can do so through
20 millions of cycles. Further described herein is an improvement that provides greater charge storage capacity using, for example, power systems that combine supercapacitors and batteries that provide for a high charge storage capacity of batteries and the quick recharge of supercapacitors. Indeed, the inventors have identified, and have described methods, devices, and systems that solve several
25 long-felt and unmet needs for devices that include electrochemical energy storage having relatively fast energy recharge times in contrast to batteries with relatively slow recharge times that limit mobility of a user.

[0008] In certain aspects, described herein are power systems, methods, and devices based upon combinations of supercapacitors and batteries for various
30 applications, including by way of non-limiting examples electric and hybrid electric vehicles. For example, electric vehicles are often powered by one of the

following energy storage systems: fuel cells, batteries, or supercapacitors. However, installing only one type of conventional energy storage is often insufficient.

5 [0009] In addition, the running cost of the normally available supercapacitor and battery-based power systems is expensive and they are relatively bulky in size. As a result, such power systems are not usable in a practical manner with portable electronics, such as smartphones, tablets, and implantable medical devices.

10 [0010] Advantages of the subject matter described herein are robust and numerous. For example, one advantage of the subject matter described herein is a hybrid electrochemical cell that provides the high energy density of a battery with the high power density of a supercapacitor. In some embodiments, the hybrid electrochemical cells provided herein do not require an electronic converter and/or bulky packaging. As another example, the subject matter
15 described herein provides a hybrid electrochemical cell that combines a supercapacitor and battery that does not necessarily require wiring a battery to a supercapacitor in parallel, nor does it necessarily require expensive electronic converters that are required to control power flow between the battery and supercapacitor.

20 [0011] In one aspect, described herein are methods, devices, and systems that provide for a hybrid electrochemical cell with a first conductor having a single portion that is both a first capacitor electrode and a first battery electrode. For example, the hybrid electrochemical cell further includes a second conductor having at least one portion that is a second capacitor electrode and at least one
25 other portion that is a second battery electrode. In certain applications, an electrolyte is in contact with both the first conductor and the second conductor.

[0012] In some embodiments, the hybrid electrochemical cell further includes a separator between the first conductor and the second conductor to prevent physical contact between the first conductor and the second conductor, while still
30 facilitating ion transport between the first conductor and the second conductor. Moreover, at least one exemplary embodiment of the hybrid electrochemical cell

relies on lithium-ion (Li-Ion) chemistry. Other exemplary embodiments of the hybrid electrochemical cell are based upon nickel-cadmium (Ni-Cd) and/or nickel-metal hydride (Ni-MH) chemistries. Further still, some embodiments of the hybrid electrochemical cell are sized to power electric vehicles for transportation, while
5 other embodiments are sized small enough to power implantable medical devices.

[0013] In one aspect, provided herein are methods, devices, and systems comprising a hybrid electrochemical cell comprising: (a) a first conductor having at least a one portion that is both a first capacitor electrode and a first battery
10 electrode; (b) a second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode; and (c) an electrolyte in contact with both the first conductor and the second conductor. In some embodiments, provided herein is a method, device, and system that comprises a hybrid electrochemical cell that contains a
15 separator between the first conductor and the second conductor that is configured in a manner to prevent or reduce physical contact between the first conductor and the second conductor and that facilitates ion transport between the first conductor and the second conductor. In some embodiments, the hybrid electrochemical cell comprises lithium-ion (Li-Ion) chemistry. In further or
20 additional embodiments, the first conductor of the hybrid electrochemical cell is negative and is doped with lithium ions. In certain embodiments, the hybrid electrochemical cell comprises a first conductor that comprises a graphite negative electrode. In some embodiments, a first negative battery electrode comprises: hard carbon, silicon alloy, and/or composite alloy. In certain
25 embodiments, the second battery electrode comprises a layered metal oxide positive electrode, and the second capacitor electrode comprises an activated carbon positive electrode. In some embodiments, provided is a hybrid electrochemical cell wherein the second positive battery electrode comprises: lithium cobalt oxide, lithium manganese oxide, lithium nickel oxide, lithium nickel
30 manganese cobalt oxide, lithium nickel cobalt aluminum oxide, lithium titanium oxide, or lithium iron phosphate. In certain applications, the second capacitor

electrode and the second battery electrode are delineated. In some embodiments, the second capacitor electrode and the second battery electrode are connected internally in parallel on one cell, and wherein the capacitor electrode acts as a buffer to prevent or reduce high rate charge and discharge of the battery. In some embodiments, the ratio between the portion of the second capacitor electrode and the second battery electrode is about 1:1. In some applications, the ratio between the portion of the second capacitor electrode and the second battery electrode is within the range of from about 1:10 to about 10:1. In still further or additional embodiments, a desirable power density of the hybrid electrochemical cell is achieved with an increase of a ratio between the portion of the second capacitor electrode and the second battery electrode. In yet further or additional embodiments, an energy density of the hybrid electrochemical cell is achieved with a decrease of the ratio between the portion of the second capacitor electrode and the second battery electrode. In still further or additional embodiments, the second capacitor electrode comprises an electric double layer capacitor (EDLC) in which charge is stored in the double layers. In some of these additional embodiments, the second capacitor electrode comprises activated carbon.

[0014] In another aspect, described herein are methods, devices, and systems that provide for a hybrid electrochemical cell comprising: (a) a first conductor having at least a one portion that is both a first capacitor electrode and a first battery electrode; (b) a second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode; and (c) an electrolyte in contact with both the first conductor and the second conductor, provided that at least one second capacitor electrode comprises an electric double layer capacitor (EDLC) in which charge is stored in the double layers. In some of these additional embodiments, the second capacitor electrode comprises an interconnected corrugated carbon-based network (ICCN). In certain embodiments, the interconnected corrugated carbon-based network (ICCN) electrode comprises a plurality of expanded and interconnected carbon layers that include a corrugated carbon layer. In some

embodiments, each expanded and/or interconnected carbon layer comprises at least one corrugated carbon sheet that is about one atom thick. In some embodiments, each expanded and interconnected carbon layer comprises a plurality of corrugated carbon sheets. In further or additional embodiments, the thickness of the ICCN, as measured from cross-sectional scanning electron microscopy (SEM) and profilometry, is around about 7 or about 8 μm . In some embodiments, a range of thicknesses of the plurality of expanded and interconnected carbon layers making up the ICCN is from around about 5 μm to 100 μm . In further or additional embodiments, the second capacitor electrode is redox active to store charge via intercalation pseudo-capacitance. In some of these embodiments, the second capacitor electrode comprises niobium pentoxide (Nb_2O_5).

[0015] In another aspect, described herein are methods, devices, and systems comprising a hybrid electrochemical cell comprising: (a) a first conductor having at least a one portion that is both a first capacitor electrode and a first battery electrode; (b) a second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode; and (c) an electrolyte in contact with both the first conductor and the second conductor, provided that the hybrid electrochemical cell is integrated on a micro-scale. In certain applications, the micro-hybrid electrochemical cell is flexible in size and shape. In some embodiments, the micro-hybrid electrochemical cell is integrated into an implantable medical device, a smart card, a radio frequency identification (RFID) tag, a wireless sensor, or a wearable electronic. In further or additional embodiments, the micro-hybrid electrochemical cell is incorporated into a self-powered system. In some applications, the micro-hybrid electrochemical cell is fabricated on the backside of a solar cell of a device. In some embodiments, the second capacitor electrode and the second battery electrode each has an electrode digit with a length L , a width W , and an interspace I . In certain embodiments, a length L is about 4000 μm to about 5000 μm , a width is about 300 μm to around about 1800 μm , and a interspace I is about 100 μm to about 200 μm . In further or additional

embodiments, a miniaturization of the width W of the electrode digits and the interspace I between the electrode digits in the micro-hybrid electrochemical cell reduces ionic diffusion pathways.

[0016] In yet another aspect, provided herein are methods, devices, and systems comprising a hybrid electrochemical cell comprising: (a) a first conductor having at least a one portion that is both a first capacitor electrode and a first battery electrode; (b) a second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode; and (c) an electrolyte in contact with both the first conductor and the second conductor, provided that the hybrid electrochemical cell relies on or comprises nickel-cadmium (Ni-Cd) and/or nickel-metal hydride (Ni-MH) chemistries. In certain embodiments, the first conductor is positive and includes nickel oxyhydroxide (NiOOH) that reduces to nickel hydroxide (Ni(OH)₂) during discharge. In further or additional embodiments, the second capacitor electrode and the second battery electrode are positive electrodes. In some embodiments, the second capacitor electrode and the second battery electrode are delineated. In still further or additional embodiments, the ratio between the portion of the second capacitor electrode and the second battery electrode is about 1:1. In some embodiments, the ratio between the portion of the second capacitor electrode and the second battery electrode is from about 1:10 to about 10:1. In some embodiments, a power density of the hybrid electrochemical cell is achieved with an increase of a ratio between the portion of the second capacitor electrode and the second battery electrode. In certain applications, an energy density of the hybrid electrochemical cell is achieved with a decrease of the ratio between the portion of the second capacitor electrode and the second battery electrode. In some applications, the hybrid electrochemical cell is flexible in size and shape. In some embodiments, the second capacitor electrode and the second battery electrode each has an electrode digit with a length L , a width W , and an interspace I . In certain embodiments, the length L is around about 4000 μm to about 5000 μm , the width W ranges from around about 300 μm to about 1800 μm , and the interspace I ranges from about 100 μm to about 200 μm . In

some embodiments, a miniaturization of the width W of the electrode digits and the interspace I between the electrode digits in the micro-hybrid electrochemical cell reduces ionic diffusion pathways.

[0017] In another aspect, provided is a method of manufacturing a hybrid electrochemical cell, the method comprising providing a first conductor, a second conductor and an electrolyte, wherein: (a) the first conductor has a single portion that is both a first capacitor electrode and a first battery electrode; (b) the second conductor has at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode; and (c) the electrolyte is in contact with both the first conductor and the second conductor.

[0018] In another aspect, provided is a method of manufacturing a micro-hybrid electrochemical cell comprising lithium-ion (Li-Ion) material, the method comprising growing porous positive and negative electrode materials on ICCN interdigitated patterns, wherein the ICCN pattern is created using a consumer-grade optical disc burner drive, comprising a series of steps of: (a) a first step, wherein a graphite oxide (GO) dispersion in water is dropcast onto an optical disc and dried in air to form a graphite film; (b) a second step, wherein a micro-pattern made with imaging or drafting software is directly printed onto the GO-coated optical disc, and wherein the GO film absorbs the energy from a laser and is converted into an ICCN pattern; (c) a third step, wherein anode and cathode materials are sequentially electrodeposited on the ICCN scaffold, and voltage-controlled and current-controlled electrodeposition is used to ensure conformal coating of the active materials throughout the three-dimensional (3D) structure of the ICCN; (d) a fourth step, wherein a nickel-tin alloy, silicon, or graphite micro-particles are electrodeposited onto ICCN corresponding to the anode; and (e) a fifth step, wherein a drop of electrolyte is added to provide ions that allow continuous electron flow when the micro-hybrid electrochemical cell is under load.

[0019] Another aspect of the subject matter described herein provides for a method of manufacturing a micro-hybrid electrochemical cell relying on Ni-Cd and/or Ni-MH chemistries, the method comprising growing porous positive and

negative electrode materials on ICCN interdigitated patterns, wherein the ICCN pattern is created using an optical disc burner drive, comprising a series of steps of: (a) a first step, wherein a graphite oxide (GO) dispersion in water is dropcast onto an optical disc and dried in air to form a graphite film; (b) a second step, wherein a micro-pattern made with imaging or drafting software is directly printed onto the GO-coated optical disc, and wherein the GO film absorbs the energy from a laser and is converted into an ICCN pattern; (c) a third step, wherein voltage-controlled and current-controlled electrodeposition is used to ensure conformal coating of the active materials throughout the 3D structure of ICCN, and a metal such as lanthanum nickel (LaNi_5) or palladium (Pd) is electrodeposited on ICCN microelectrodes making up the second battery electrode that forms a portion of an anode; (d) a fourth step, wherein cadmium hydroxide ($\text{Cd}(\text{OH})_2$) is added to the ICCN corresponding to the anode; and (e) a fifth step, wherein a drop of electrolyte is added to provide ions that allow continuous electron flow when the micro-hybrid electrochemical cell is under load.

[0019a] In another aspect, the second capacitor electrode and the second battery electrode having electrode digits with a length L , a width W , and an interspace I . In another aspect, the length L is around about 0.5 cm to about 1.5 cm, the width W ranges from around about 0.05 cm to about 0.2 cm, and the interspace I is about 0.01 cm to about 0.05 cm.

[0019b] In another aspect, there is a hybrid electrochemical cell comprising:

- (a) a negative first conductor having at least a one portion that is both a first capacitor electrode and a first battery electrode;
- (b) a positive second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode, wherein the second capacitor electrode comprises an interconnected corrugated carbon-based network (ICCN) having a three-dimensional (3D) structure, wherein a metal oxide is deposited throughout the 3D structure of the ICCN; and

- (c) an electrolyte in contact with both the first conductor and the second conductor.

[0019c] In another aspect, there is a method of producing a hybrid electrochemical cell comprising:

- 5 • fabricating a negative first conductor having a single portion that is both a first capacitor electrode and a first battery electrode;
- fabricating a positive second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode, wherein the second capacitor electrode
- 10 comprises an interconnected corrugated carbon-based network (ICCN) having a three-dimensional (3D) structure, wherein a metal oxide is deposited throughout the 3D structure of the ICCN; and
- adding an electrolyte to both the first conductor and the second conductor,
- wherein a power density of the hybrid electrochemical cell is up to about
- 15 10^4 watt/kilogram (W/kg).

[0019d] In another aspect, there is a method of manufacturing a micro-hybrid electrochemical cell comprising lithium-ion (Li-Ion) material, the method comprising growing porous positive and negative electrode materials on ICCN interdigitated patterns, wherein an ICCN pattern is created using a consumer-

20 grade optical disc burner drive, comprising a series of steps of:

- (a) a first step, wherein a graphite oxide (GO) dispersion in water is dropcast onto an optical disc and dried in air to form a graphite oxide film;
- (b) a second step, wherein a micro-pattern made with imaging or drafting software is directly printed onto the GO-coated optical disc, and wherein
- 25 the GO film absorbs energy from a laser and is converted into the ICCN pattern;
- (c) a third step, wherein anode and cathode materials are sequentially electrodeposited on the ICCN pattern, and voltage-controlled and current-controlled electrodeposition is used to ensure conformal coating of active
- 30 materials throughout the three-dimensional (3D) structure of the ICCN;

(d) a fourth step, wherein a nickel-tin alloy, silicon, or graphite micro-particles are electrodeposited onto the ICCN pattern corresponding to an anode; and

(e) a fifth step, wherein a drop of electrolyte is added to provide ions that
5 allow continuous electron flow when the micro-hybrid electrochemical cell is under load,

wherein the positive electrode comprises an interconnected corrugated carbon-based network (ICCN) having a three-dimensional (3D) structure, wherein a metal oxide is deposited throughout the 3D structure of the ICCN.

10 **[0019e]** In yet another aspect, there is a method of manufacturing a micro-hybrid electrochemical cell relying on nickel-cadmium (Ni-Cd) and/or nickel-metal hydride (Ni-MH) chemistries, the method comprising growing porous positive and negative electrode materials on ICCN interdigitated patterns, wherein an ICCN pattern is created using an optical disc burner drive, comprising a series of steps
15 of:

(a) a first step, wherein a graphite oxide (GO) dispersion in water is dropcast onto an optical disc and dried in air to form a graphite oxide film;

(b) a second step, wherein a micro-pattern made with imaging or drafting software is directly printed onto the GO-coated optical disc, and wherein
20 the GO film absorbs energy from a laser and is converted into the ICCN pattern;

(c) a third step, wherein voltage-controlled and current-controlled electrodeposition is used to ensure conformal coating of active materials throughout the 3D structure of the ICCN, and a metal such as lanthanum
25 nickel (LaNi_5) or palladium (Pd) is electrodeposited on ICCN microelectrodes making up a second battery electrode that forms a portion of an anode;

(d) a fourth step, wherein cadmium hydroxide ($\text{Cd}(\text{OH})_2$) is added to the ICCN corresponding to the anode; and

(e) a fifth step, wherein a drop of electrolyte is added to provide ions that allow continuous electron flow when the micro-hybrid electrochemical cell is under load,

wherein the positive electrode comprises an interconnected corrugated carbon based network (ICCN) having a three-dimensional (3D) structure, wherein a metal oxide is deposited throughout the 3D structure of the ICCN.

[0019f] In another aspect, there is a hybrid electrochemical cell comprising: (a) a first conductor having at least a one portion that is both a first capacitor electrode and a first battery electrode; (b) a second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode, wherein the second capacitor electrode comprises an interconnected corrugated carbon-based network (ICCN) having a three-dimensional (3D) structure, wherein a metal oxide is deposited throughout the 3D structure of the ICCN; and (c) an electrolyte in contact with both the first conductor and the second conductor.

[0019g] In yet another aspect, there is a method of producing a hybrid electrochemical cell comprising: fabricating a first conductor having a single portion that is both a first capacitor electrode and a first battery electrode; fabricating a second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode, wherein the second capacitor electrode comprises an interconnected corrugated carbon-based network (ICCN) having a three-dimensional (3D) structure, wherein a metal oxide is deposited throughout the 3D structure of the ICCN; and adding an electrolyte to both the first conductor and the second conductor, wherein a power density of the hybrid electrochemical cell is from about 10^3 watt/kilogram to about 10^4 watt/kilogram (W/kg).

[0020] Those skilled in the art will appreciate the scope of the disclosure and realize additional aspects thereof after reading the following detailed description in association with the accompanying drawings.

5 **Brief Description of the Drawings**

[0021] The accompanying drawings incorporated in and forming a part of this specification illustrate several aspects of the disclosure, and together with the description, serve to explain the principles of the disclosure.

10 **[0022]** Figure 1 is a diagram of a non-limiting, illustrative depiction of a lithium ion (Li-Ion) based hybrid electrochemical cell in accordance with the present disclosure.

15 **[0023]** Figure 2 is a non-limiting, illustrative depiction of a line drawing of a sample of an interconnected corrugated carbon-based network (ICCN) that is usable to make up capacitor electrodes for hybrid electrochemical cells.

[0024] Figure 3 is a non-limiting, illustrative depiction of a diagram depicting a Li-Ion based micro-hybrid electrochemical cell.

[0025] Figure 4 is a non-limiting, illustrative depiction of a process flow diagram depicting fabrication of the micro-sized Li-Ion based hybrid electrochemical cell of Figure 3.

[0026] Figure 5 is a non-limiting, illustrative depiction of an embodiment suitable for realizing hybrid electrochemical cells of either nickel-cadmium (Ni-Cd) and/or nickel-metal hydride (Ni-MH) chemistries.

[0027] Figure 6 is a non-limiting, illustrative depiction of a micro-sized hybrid electrochemical cell based on either Ni-Cd or Ni-MH chemistries.

[0028] Figure 7 is a non-limiting, illustrative depiction of a process flow diagram illustrating fabrication of the micro-sized hybrid electrochemical cell of Figure 6.

[0029] Figure 8A is a charge-discharge graph of voltage versus time for a prior art Li-Ion capacitor.

[0030] Figure 8B is a charge-discharge graph of voltage versus time for a prior art Li-Ion battery.

[0031] Figure 8C is a non-limiting, illustrative depiction of a charge-discharge graph of an embodiment of a voltage versus time for a hybrid electrochemical cell of the present disclosure.

[0032] Figure 9 is a non-limiting, illustrative depiction of a charge-discharge graph of voltage versus time for a hybrid electrochemical cell of the present disclosure that comprises redox active niobium pentoxide (Nb_2O_5).

[0033] Figure 10A is a graph depicting a charge-discharge curve for a prior art nickel-carbon supercapacitor.

[0034] Figure 10B is a graph depicting a charge-discharge curve for both a prior art Ni-Cd battery and a prior art Ni-MH battery.

[0035] Figure 10C is a non-limiting, illustrative depiction of a charge-discharge graph of voltage versus time for embodiments of either of the Ni-Cd and the Ni-MH chemistries comprising hybrid electrochemical cells of the present disclosure.

[0036] Figure 11 is a non-limiting, illustrative depiction of a Ragone plot comparing power density versus energy density for capacitors, supercapacitors, Li-Ion capacitors, batteries, and the hybrid electrochemical cells of the present disclosure.

5 **[0037]** Figure 12A is a non-limiting, illustrative depiction of an implantable medical device having a hybrid electrochemical cell of the present disclosure integrated within.

[0038] Figure 12B is a non-limiting, illustrative depiction of a smart card having a hybrid electrochemical cell of the present disclosure integrated within.

10 **[0039]** Figure 12C is a non-limiting, illustrative depiction of a radio frequency identification (RFID) tag having a hybrid electrochemical cell of the present disclosure integrated within.

[0040] Figure 12D is a non-limiting, illustrative depiction of a wireless sensor having a hybrid electrochemical cell of the present disclosure integrated within.

15 **[0041]** Figure 12E is a non-limiting, illustrative depiction of a wearable device having a hybrid electrochemical cell of the present disclosure integrated within.

[0042] Figure 12F is a non-limiting, illustrative depiction of a solar cell having a hybrid electrochemical cell of the present disclosure integrated with the solar cell to realize an energy harvesting system.

20

Detailed Description

[0043] Upon reading the following description in light of the accompanying drawings, those skilled in the art will understand the concepts of the disclosure and will recognize applications of these concepts not particularly addressed
25 herein. It should be understood that these concepts and applications are non-limiting and fall within the scope of the disclosure and the accompanying claims.

[0044] A feature of the subject matter described herein is a hybrid electrochemical cell. In certain embodiments, the hybrid electrochemical cells described herein comprise nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH)
30 and/or lithium-ion (Li-Ion) batteries. Figure 1, for example, depicts a non-limiting structure of a Li-Ion based hybrid electrochemical cell 10 in accordance with the

present disclosure. The hybrid electrochemical cell 10 includes a first conductor 12 having a single portion 14 that is both a first capacitor electrode and a first battery electrode. In the Li-Ion based chemistry of the hybrid electrochemical cell 10, the first conductor 12 is negative and is doped with lithium ions. The hybrid electrochemical cell 10 includes a second conductor 16 having at least one portion that is a second capacitor electrode 18 and at least one other portion that is a second battery electrode 20. An electrolyte 22 is in contact with both the first conductor 12 and the second conductor 16. A separator 24 between the first conductor 12 and the second conductor 16 prevents physical contact between the first conductor 12 and the second conductor 16, while facilitating ion transport between the first conductor 12 and the second conductor 16. The second capacitor electrode 18 and the second battery electrode 20 are delineated by a horizontal dashed line 26 in Figure 1. As shown, a ratio between the portion of the second capacitor electrode 18 and the second battery electrode 20 is about 1:1. However, it is to be understood that the ratio between the portion of the second capacitor electrode 18 and the second battery electrode 20 can range from 1:10 to 10:1 (inclusive of all ratios in between those endpoints, including but not limited to, 2:9, 3:8, 4:7, 5:6, 6:5, 7:4, 8:3, and 9:2). As the portion of the second capacitor electrode 18 increases relative to the second battery electrode 20, the power density of the hybrid electrochemical cell 10 increases and the energy density decreases. Likewise, as the portion of the second battery electrode 20 increases relative to the second capacitor electrode 18, the energy density of the hybrid electrochemical cell 10 increases and the power density decreases. The ratio of the second capacitor electrode 18 relative to the second battery electrode 20 is predetermined for a given application. For example, a larger ratio of the second capacitor electrode 18 relative to the second battery electrode 20 is desirable to capture energy quickly in a regenerative braking system, while a smaller ratio of the second capacitor electrode 18 relative to the second battery electrode 20 might be desirable for energizing a power tool such as a portable electric drill.

[0045] In understanding the hybrid electrochemical cell 10, it is helpful to note that a typical lithium ion battery comprises a graphite negative electrode and a layered metal oxide positive electrode. In contrast, a lithium ion capacitor is made of a graphite negative electrode and an activated carbon positive electrode. Since the negative electrode in both designs is graphite, these two devices can be integrated into one cell by connecting internally the battery and capacitor positive electrodes in parallel. The capacitor electrode would act as a buffer to prevent high rate charge and discharge of the battery. This can potentially extend the lifetime of the battery portion of the hybrid cell by a factor of ten, leading to energy storage systems that may never need to be replaced for the lifetime of a product being powered by the hybrid electrochemical cell 10. In addition, given that the positive electrodes of the battery and the capacitor have the same operating voltage and current collector, it is possible to blend them together in one positive electrode as shown in Figure 1. As a result, the hybrid electrochemical cell 10, in certain embodiments, has only two electrodes instead of the four electrodes used in traditional power systems having battery and supercapacitor combinations. The simplified structure and design of the present disclosure's hybrid electrochemical cell 10 reduces the manufacturing cost and make powering hybrid automobiles energy efficient. Moreover, the hybrid electrochemical cell 10 combines battery technology and supercapacitor technology into a single cell using one type of electrolyte, thereby eliminating extra current collectors, electrolyte, and packaging. This means that the hybrid electrochemical cell 10 provides a higher energy density than traditional power systems that combine batteries and supercapacitors with interfacing electronics for power flow control between the batteries and supercapacitors. The hybrid electrochemical cell 10 is fabricated using commercial electrode materials, collectors, separators, binders, and electrolytes, which allows for fabrication processes that are readily scalable to industrial levels.

[0046] In some embodiments, the first battery electrode material used comprises graphite. Other materials are also suitable. For example, in some

embodiments, the first battery electrode comprises hard carbon, silicon, composite alloys Sn(M)-based and Sn(O)-based, and combinations thereof.

[0047] In certain embodiments, the second battery electrode material comprises: lithium cobalt oxide, lithium manganese oxide, lithium nickel oxide

5 **[0048]** , lithium nickel manganese cobalt oxide, lithium nickel cobalt aluminum oxide, lithium titanium oxide, and/or lithium iron phosphate, and combinations thereof.

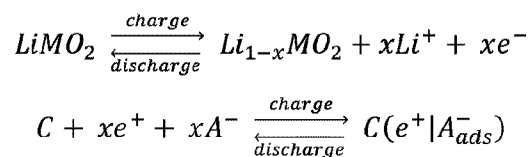
[0049] In some embodiments, the second capacitor electrode 18 is made of a material that comprises an electric double layer capacitor (EDLC) in which
10 charge is stored in double layers. In some embodiments, the second capacitor electrode 18 comprises interconnected corrugated carbon-based network (ICCN) 28 or activated carbon. In yet other embodiments, the second capacitor electrode 18 is redox active to store charge via intercalation pseudo-capacitance. In at least one embodiment, the second capacitor electrode 18 comprises
15 niobium pentoxide (Nb_2O_5).

[0050] In further or additional embodiments, provided is a lithium ion battery that comprises or consists of two electrodes and electrolyte solution providing a conductive medium for lithium ions to move between the electrodes. In certain applications, both electrodes allow lithium ions to move in and out of their
20 interiors. In the charge reactions, in certain embodiments of the subject matter described herein, lithium ions are deintercalated from the positive material and intercalated into the negative material. Similarly, in some embodiments, the reverse happens on discharge. The intercalation and deintercalation of lithium ions, in certain applications, causes the flow of electrons in an external circuit
25 (not shown).

[0051] Another advantage of the subject matter described herein are methods, devices, and systems that provide for the increased movement of ions, including for example, lithium ions, into and out of the electrodes. A problem with pure lithium ion batteries is the slow movement of lithium ions in and out of the
30 battery electrodes. As described herein, in some applications, the insertion of a supercapacitor electrode in the lithium ion-based hybrid electrochemical cell 10

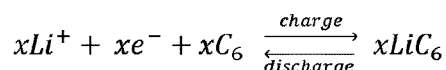
speeds up the charge-discharge process by storing charge via adsorption of ions on the surface of a carbon electrode or through fast redox reactions near the surface of an oxide electrode instead of the bulk of a layered battery material. For example, in a carbon supercapacitor electrode, the charge is stored in an electric double at the interface between the carbon and electrolyte. Here, and in these applications of the methods, devices, and systems described herein, an interface between the electrodes and electrolyte is thought of as an electrical double layer composed of the electrical charge at the surface of the carbon electrode itself and the charge of the ions disbursed in the solution at a small distance from the electrode surface. This electrical double layer is formed when a potential is applied to the electrode and causes a charging current (non-faradaic current) to pass through the hybrid electrochemical cell 10. These reactions are described below.

[0052] The following equations describe the charge storage mechanism of certain embodiments of the hybrid electrochemical cell 10, for example, when using graphite as the first battery electrode and lithiated metal oxide as the second battery electrodes and carbon as the second capacitor electrode. At the positive electrode charge storage occurs through a combination of double layer adsorption capacitance and lithium ion insertion.



In this scheme, $LiMO_2$ represents a metal oxide positive material, such as $LiCoO_2$, x is a fraction $0 < x < 1$. C is a high surface area form of carbon, e^+ is a hole, and A^- is an electrolyte anion, and $(e^+|A_{ads}^-)$ refers to an electric double layer (EDL) formed at the interface between the carbon electrode and electrolyte.

At the negative electrode, lithium ion insertion into and out of graphite is described by the following equation.



[0053] Figure 2 is a non-limiting illustration of a line drawing of a sample of an interconnected corrugated carbon-based network (ICCN) 28, which is made up of a plurality of expanded and interconnected carbon layers that include corrugated carbon layers such as a single corrugated carbon sheet 30. In one embodiment, each of the expanded and interconnected carbon layers comprises at least one corrugated carbon sheet that is one atom thick. In another embodiment, each of the expanded and interconnected carbon layers comprises a plurality of corrugated carbon sheets 30. In this specific example, the thickness of the ICCN 28, as measured from cross-sectional scanning electron microscopy (SEM) and profilometry, was found to be around about 7.6 μm. In one embodiment, a range of thicknesses of the plurality of expanded and interconnected carbon layers making up the ICCN 28 is from around about 1 μm to about 100 μm. In some embodiments, the thickness of the plurality of expanded and interconnected carbon layers making up the ICCN 28 is from around about 2 μm to about 90 μm, from about 3 μm to about 80 μm, from about 4 μm to about 70 μm, from 5 μm to about 60 μm, from about 5 μm to about 50 μm, 5 μm to about 40 μm, 5 μm to about 30 μm, 5 μm to about 20 μm, 5 μm to about 10 μm, from about 5 μm to about 9 μm, or from about 6 μm to about 8 μm.

[0054] In some embodiments, hybrid electrochemical cells in accordance with the present disclosure are also made on a micro-scale which will enable a relatively large number of applications for a new generation of electronics. For example, a micro-hybrid electrochemical cell, in some embodiments, are integrated into implantable medical devices, smart cards, radio frequency identification (RFID) tags, wireless sensors, and even wearable electronics. Integrated micro-hybrid electrochemical cells, in some applications, also serve as a way to better extract energy from solar, mechanical, and thermal sources and thus make more efficient self-powered systems. Micro-hybrid electrochemical cells, in certain embodiments, are also fabricated on the backside of solar cells in both portable devices and rooftop installations to store power generated during the day for use after sundown, helping to provide electricity around the clock

when connection to the grid is not possible. Each of these applications is made possible by the subject matter described herein based in part on the flexibility in size and shape of the micro-hybrid electrochemical cells described herein.

Moreover, in further or additional embodiments, provided is a thin form factor for the battery that allows for thinner portable electronics.

5 [0055] Figure 3 is a non-limiting diagram illustrating a lithium ion-based micro-hybrid electrochemical cell 32. The micro-hybrid electrochemical cell 32 includes a first conductor 34 having a single portion 36 that is both a first capacitor electrode and a first battery electrode. In the lithium ion-based chemistry of the micro-hybrid electrochemical cell 32, the first conductor 34 is negative and is doped with lithium ions. The micro-hybrid electrochemical cell 32 includes a second conductor 38 having at least one portion that is a second capacitor electrode 40 and at least one other portion that is a second battery electrode 42. An electrolyte 44 is in contact with both the first conductor 34 and the second conductor 38. The second capacitor electrode 40 and the second battery electrode 42 each have electrode digits with a length L, a width W, and an interspace I. In an exemplary millimeter scale embodiment, the length L is around about 4800 μm , the width W ranges from around about 330 μm to around about 1770 μm , and the interspace I is typically around about 150 μm . While these dimensions are exemplary, it is to be understood that a further miniaturization of the width W of the electrode digits and the interspace I between the electrode digits in the micro-hybrid electrochemical cell 32 would reduce ionic diffusion pathways, thus leading to the micro-hybrid electrochemical cell 32 having even higher power density. In an exemplary centimeter scale embodiment, the length L is around about 1.2 cm, the width W ranges from around about 0.05 cm to around about 0.2 cm, and the interspace I is typically around about 0.05 cm.

25 [0056] In some embodiments, the micro-hybrid electrochemical cell 32 is integrated by growing porous positive and negative electrode materials on ICCN interdigitated patterns. In general, methods for producing the micro-hybrid electrochemical cell 32 having electrodes made of a patterned ICCN typically

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include an initial step of receiving a substrate having a carbon-based oxide film. Once the substrate is received, a next step involves generating a light beam having a power density sufficient to reduce portions of the carbon-based oxide film to an ICCN. Another step involves directing the light beam across the carbon-based oxide film in a predetermined pattern via a computerized control system while adjusting the power density of the light beam via the computerized control system according to predetermined power density data associated with the predetermined pattern. Exemplary light sources for generating the light beam include but are not limited to a 780 nm laser, a green laser, and a flash lamp. The light beam emission of the light sources may range from near infrared to ultraviolet wavelengths.

[0057] An exemplary process for fabricating the micro-hybrid electrochemical cell 32 is schematically illustrated in Figure 4. In some embodiments, the ICCN pattern is created using a consumer-grade digital versatile disc (DVD) burner drive. In a first step, a graphite oxide (GO) dispersion in water is dropcast onto a DVD disc and dried in air to form a graphite oxide film 46 (step 100). A micro-pattern made with imaging or drafting software is directly printed onto the GO-coated DVD disc 48 (step 102). The GO film absorbs the energy from a laser and is converted into an ICCN pattern. With the precision of the laser, the DVD burner drive renders the computer-designed pattern onto the GO film to produce the desired ICCN circuits. In certain applications, the ICCN pattern is designed to have three terminals: an ICCN supercapacitor-like electrode and two battery electrodes. In some embodiments, the capacity of the supercapacitor electrode is boosted by the electrophoretic deposition of activated carbon micro-particles.

[0058] In further or additional embodiments, anode and/or cathode materials are sequentially electrodeposited on the ICCN scaffold. Voltage-controlled and current-controlled electrodeposition is used to ensure conformal coating of the active materials throughout the three-dimensional (3D) structure of the ICCN. For example, manganese dioxide (MnO_2) is electrodeposited on the ICCN microelectrodes making up the second battery electrode 42 (Figure 3) that forms

a portion of a cathode and is followed by a lithiation of MnO_2 in molten lithium nitrate (LiNO_3) and lithium hydroxide (LiOH) (step 104). In some embodiments, polyaniline is used as an alternative to the cathode material. Next, a nickel-tin alloy, silicon, or even graphite micro-particles are electrodeposited onto ICCN
5 corresponding to the anode (step 106). To complete the micro-hybrid electrochemical cell 32, a drop of electrolyte 52 is added to provide ions that allow continuous electron flow when the micro-hybrid electrochemical cell 32 is under load (step 108).

[0059] In some embodiments, the micro-hybrid electrochemical cell 32 is
10 realized using nickel-cadmium (Ni-Cd) and nickel-metal hydride (Ni-MH) chemistries in a similar manner to that of the lithium ion-based hybrid electrochemical cell 10 (see Figure 1) except that the chemistry of Ni-Cd or Ni-MH batteries is combined with a Ni-carbon asymmetric supercapacitor.

[0060] Figure 5 depicts a non-limiting structure for a hybrid electrochemical
15 cell 54 for Ni-Cd and Ni-MH chemistries in accordance with the present disclosure. In some embodiments, the hybrid electrochemical battery cell 54 includes a first conductor 56 having a single portion 58 that is both a first capacitor electrode and a first battery electrode. In some embodiments, in either of the Ni-Cd and/or Ni-MH based chemistries of the hybrid electrochemical cell
20 54, the first conductor 56 is positive and includes nickel oxyhydroxide (NiOOH) that reduces to nickel hydroxide (Ni(OH)_2) during discharge. In some embodiments, the hybrid electrochemical cell 54 includes a second conductor 60 having at least one portion that is a second capacitor electrode 62 and at least one other portion that is a second battery electrode 64. In some embodiments,
25 the ions that collect on the second battery electrode 64 comprise a metal hydride represented by X in the metal hydride case or Cd(OH)_2 represented by Y in the Ni-Cd case. In certain applications, an electrolyte 66 is in contact with both the first conductor 56 and the second conductor 60, whereby a separator 68 between the first conductor 56 and the second conductor 60 prevents physical contact
30 between the first conductor 56 and the second conductor 60, while facilitating ion transport between the first conductor 56 and the second conductor 60. In some

embodiments, the second capacitor electrode 62 and the second battery electrode 64 are delineated by a horizontal dashed line 69 in Figure 5. As shown, a ratio between the portion of the second capacitor electrode 62 and the second battery electrode 64 is 1:1. However, it is to be understood that the ratio between the portion of the second capacitor electrode 62 and the second battery electrode 64 can range from 1:10 to 10:1 (inclusive of all ratios in between those endpoints, including but not limited to, 2:9, 3:8, 4:7, 5:6, 6:5, 7:4, 8:3, and 9:2).

[0061] In some embodiments, as the portion of the second capacitor electrode 62 increases relative to the second battery electrode 64, the power density of the hybrid electrochemical cell 54 increases and the energy density decreases. Likewise, in further or additional embodiments, as the portion of the second battery electrode 64 increases relative to the second capacitor electrode 62, the energy density of the hybrid electrochemical cell 54 increases and the power density decreases. In certain applications, the ratio of the second capacitor electrode 62 relative to the second battery electrode 64 is predetermined for a given application. For example, a larger ratio of the second capacitor electrode 62 relative to the second battery electrode 64 is desirable to capture energy quickly in a regenerative braking system, while a smaller ratio of the second capacitor electrode 62 relative to the second battery electrode 64 might be desirable for energizing a power tool such as a portable electric drill.

[0062] In certain applications this design uses a negative electrode made of activated carbon in which the charge is stored in the electric double layer, while the positive electrode is pseudocapacitive (typically NiOOH) where the charge is stored through redox reactions in the bulk of the material. An aqueous alkaline solution is used as an electrolyte in the same way as in Ni-Cd and Ni-MH batteries. Because the positive electrode in Ni-Cd and Ni-MH batteries is NiOOH, the same as in traditional Ni-Cd asymmetric supercapacitors, in certain embodiments, provided is an integration of both devices into one cell by connecting the battery and capacitor negative electrodes in parallel. In further or additional embodiments, also provided is a blend of the battery and capacitor negative electrodes into one electrode.

[0063] Figure 6 is a non-limiting diagram depicting a micro-hybrid electrochemical cell 70 based on either Ni-Cd or Ni-MH chemistries. In some embodiments, the micro-hybrid electrochemical battery cell 70 includes a first conductor 72 having a single portion 74 that is both a first capacitor electrode and a first battery electrode. In further or additional embodiments, during fabrication of the micro-hybrid electrochemical cell 70, the first conductor 56 is positive and is doped with NiOOH for use with either Ni-Cd or Ni-MH chemistries. In some embodiments, the micro-hybrid electrochemical cell 70 includes a second conductor 76 having at least one portion that is a second capacitor electrode 78 and at least one other portion that is a second battery electrode 80. In some embodiments, an electrolyte 82 is in contact with both the first conductor 72 and the second conductor 76. For example, the second capacitor electrode 78 and the second battery electrode 80 each have electrode digits with a length L, a width W, and an interspace I. In an exemplary embodiment the length L is around about 4800 μm , the width W ranges from around about 330 μm to around about 1770 μm , and the interspace I is typically around about 150 μm . While these dimensions are exemplary, it is to be understood that a further miniaturization of the width W of the electrode digits and the interspace I between the electrode digits in the micro-hybrid electrochemical cell 70 would reduce ionic diffusion pathways, thus leading to the micro-hybrid electrochemical cell 70 having even higher power density.

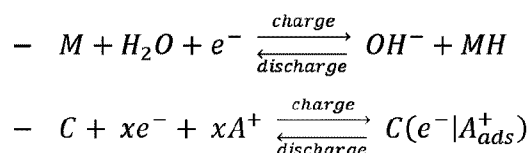
[0064] Similar to the fabrication of the Li-Ion based micro-hybrid electrochemical cell 32, the micro-hybrid electrochemical cell 70, based on either Ni-Cd or Ni-MH chemistries, in certain embodiments is integrated by growing porous positive and negative electrode materials on ICCN interdigitated patterns. An exemplary process for fabricating the micro-hybrid electrochemical cell 70 is schematically illustrated in Figure 7. Steps 100 and 102 are completed the same as shown in Figure 4. However, new steps are added after step 102 to accommodate the Ni-Cd or Ni-MH chemistries to sequentially electrodeposit anode and cathode materials on the ICCN scaffold. As with the fabrication of Li-Ion based micro-hybrid electrochemical cell 32, voltage-controlled and current-

controlled electrodeposition is used to ensure conformal coating of the active materials throughout the 3D structure of ICCN. A metal such as lanthanum nickel (LaNi_5) or palladium (Pd) is electrodeposited on ICCN microelectrodes making up the second battery electrode 80 that forms a portion of an anode (step 110). Next, $\text{Cd}(\text{OH})_2$ is added to the ICCN corresponding to the anode (step 112). To complete the micro-hybrid electrochemical cell 70, a drop of electrolyte 82 is added to provide ions that allow continuous electron flow when the micro-hybrid electrochemical cell 70 is under load (step 114).

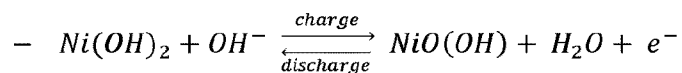
[0065] The electrochemical reactions of the Ni-MH and Ni-Cd based hybrid electrochemical cells are described in the following:

Ni-MH based hybrid electrochemical cell

- The negative electrode



- On the positive electrode

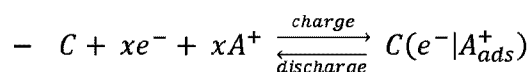
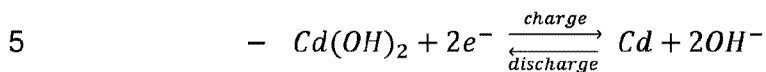


The metal, M, in the negative electrode of a Ni-MH cell, is actually a hydrogen storage alloy. It comes from a new group of intermetallic compounds which can reversibly store hydrogen. Many different compounds have been developed for this application, but the most extensively adopted is rare earth-based AB_5 -type alloys. In this type of alloy, the A component consists of one or more rare earth elements, and B is mainly composed of transition metals such as Ni, Co, Mn, and Al. The capacitor electrode stores charge in an electric double layer. $(e^-|A_{\text{ads}}^+)$ refers to an electric double layer (EDL) formed at the interface between the carbon electrode and electrolyte, where e^- is an electron from the electrode side and A_{ads}^+ is a cation from the electrolyte side. In the Ni-MH hybrid electrochemical cell, nickel oxyhydroxide (NiOOH), is the active material in the charged positive electrode. During discharge, it reduces to the lower valence state, nickel

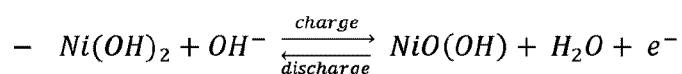
hydroxide, $\text{Ni}(\text{OH})_2$, by accepting electrons from the external circuit. These reactions reverse during charging of the cell.

Ni-Cd based hybrid electrochemical cell

- The negative electrode



- On the positive electrode



10 In the Ni-Cd based hybrid electrochemical cell, the negative electrode consists of cadmium metal and high surface area carbons. During charge, $\text{Ni}(\text{OH})_2$ is oxidized to the higher valence state and releases electrons to the external circuit. These electrons are stored in the negative electrode by reducing $\text{Cd}(\text{OH})_2$ to elemental cadmium and in electric double layers.

15 [0066] Figure 8A is a charge-discharge graph of voltage versus time for a prior art lithium ion capacitor. The charge rate and the discharge rate are relatively steep in comparison to a lithium ion battery charge rate and discharge rate shown in Figure 8B. Figure 8C is a non-limiting charge-discharge graph of voltage versus time for a hybrid electrochemical cell of the present disclosure. Notice that in this case, and in certain embodiments of the present disclosure, 20 the hybrid electrochemical cell has charge rates and discharge rates that are commensurate with both the lithium ion capacitor and the lithium ion battery. As a result, the hybrid electrochemical cells of this disclosure share the best properties of both the lithium ion capacitor and the lithium ion battery and therefore can be thought of as being “super-batteries.”

25 [0067] The shape of the charge-discharge graph of the hybrid electrochemical cell is controlled by the type of the second capacitor electrode. For example, Figure 8C describes the case when using a double layer capacitor electrode

such as ICCN 28 or activated carbon. However, when using redox active Nb_2O_5 , the behavior is illustrated in Figure 9. Other materials are also suitable.

[0068] Figure 10A is a graph depicting a charge-discharge curve for a prior art nickel-carbon supercapacitor. In contrast, Figure 10B is a graph depicting a charge-discharge curve for both a prior art Ni-Cd battery and a prior art Ni-MH battery. Figure 10C is a non-limiting illustration of a charge-discharge graph of voltage versus time for either of the Ni-Cd and the Ni-MH chemistries for embodiments comprising hybrid electrochemical cells of the present disclosure. In essence, the charge-discharge graph of Figure 10C can be thought of as the result of a combination of the electrochemical properties of nickel-carbon supercapacitor and Ni-Cd or Ni-MH battery.

[0069] A Ragone plot is useful to highlight the improved electrochemical storage ability of the hybrid electrochemical cells of the present disclosure. Figure 11 is a Ragone plot comparing the performance of hybrid electrochemical cells with different energy storage devices designed for high-power demanding loads. The Ragone plot shows the gravimetric energy density and power density of the packaged cells for all the devices tested. The Ragone plot reveals a significant increase in performance for energy density in comparison to traditional supercapacitors. Remarkably, compared with lithium ion supercapacitors, hybrid electrochemical cells of certain embodiments of the subject matter described herein store up to ten times more energy and around about the same to slightly greater power density than lithium ion supercapacitors. For example, the hybrid electrochemical cells of the present disclosure have an energy density that ranges between 20 watt-hour/kilogram (Wh/kg) to around about 200 Wh/kg. Furthermore, although lithium ion batteries can provide high energy density, they have limited power performance that is nearly two orders of magnitude lower than the hybrid electrochemical cells of the present disclosure. For example, the hybrid electrochemical cells of the present disclosure have a power density that ranges between nearly 10^3 watt/kilogram (W/kg) to about 10^4 W/kg. This superior energy and power performance of the hybrid electrochemical hybrids will compete, completely replace, and/or complement batteries and supercapacitors,

including lithium ion supercapacitors in a variety of applications. Moreover, a further miniaturization of the width of the micro-electrodes and the space between micro-electrodes in micro-hybrid electrochemical cells would reduce ionic diffusion pathways, thus leading to micro-hybrid electrochemical cells with even higher power density.

[0070] Applications for the disclosed embodiments of a micro-hybrid electrochemical cell are diverse. The following list is only exemplary. For example, Figure 12A is a non-limiting, illustrative depiction of an implantable medical device 84 having the micro-hybrid electrochemical cell 70 integrated within. Figure 12B is a non-limiting, illustrative depiction of a smart card 86 having the micro-hybrid electrochemical cell 70 integrated within. Figure 12C is a non-limiting, illustrative depiction of a radio frequency identification (RFID) tag 88 having the micro-hybrid electrochemical cell 70 of the present disclosure integrated within. Figure 12D is a non-limiting, illustrative depiction of a wireless sensor 90 having the micro-hybrid electrochemical cell 70 of the present disclosure integrated within. Figure 12E is a non-limiting, illustrative depiction of the wearable device 92 having a micro-hybrid electrochemical cell 70 of the present disclosure integrated within. Figure 12F is a non-limiting, illustrative depiction of a solar cell 94 having the micro-hybrid electrochemical cell 70 of the present disclosure integrated with the solar cell 94 to realize a self-powered system. Other self-powered systems that will benefit from integration with the present embodiments include but are not limited to vibrational type energy harvesting systems, wind energy harvesting systems, and temperature differential type energy harvesting systems.

[0071] Those skilled in the art will recognize improvements and modifications to the embodiments of the present disclosure. All such improvements and modifications are considered within the scope of the concepts disclosed herein and the claims that follow.

What is claimed is:

1. A hybrid electrochemical cell comprising:
 - (a) a first conductor having at least a one portion that is both a first capacitor electrode and a first battery electrode;
 - (b) a second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode, wherein the second capacitor electrode comprises an interconnected corrugated carbon-based network (ICCN) having a three-dimensional (3D) structure, wherein a metal oxide is deposited throughout the 3D structure of the ICCN; and
 - (c) an electrolyte in contact with both the first conductor and the second conductor.
2. The hybrid electrochemical cell of claim 1 further comprising a separator between the first conductor and the second conductor that is configured in a manner to prevent physical contact between the first conductor and the second conductor and that facilitates *ion* transport between the first conductor and the second conductor.
3. The hybrid electrochemical cell of claim 1 wherein the hybrid electrochemical cell comprises lithium-ion (Li-Ion) material or chemistry.
4. The hybrid electrochemical cell of claim 3 wherein the first conductor is negative and is doped with lithium ions.
5. The hybrid electrochemical cell of claim 3 wherein the first conductor comprises a graphite negative electrode.
6. The hybrid electrochemical cell of claim 3 wherein the first battery electrode comprises hard carbon.

7. The hybrid electrochemical cell of claim 3 wherein the first battery electrode comprises silicon alloy.
8. The hybrid electrochemical cell of claim 3 wherein the first battery electrode comprises composite alloy.
9. The hybrid electrochemical cell of claim 3 wherein the second capacitor electrode comprises a layered metal oxide positive electrode, and the second battery electrode comprises an activated carbon positive electrode.
10. The hybrid electrochemical cell of claim 3 wherein the second battery electrode comprises lithium cobalt oxide.
11. The hybrid electrochemical cell of claim 3 wherein the second battery electrode comprises lithium manganese oxide.
12. The hybrid electrochemical cell of claim 3 wherein the second battery electrode comprises lithium nickel oxide.
13. The hybrid electrochemical cell of claim 3 wherein the second battery electrode comprises lithium nickel manganese cobalt oxide.
14. The hybrid electrochemical cell of claim 3 wherein the second battery electrode comprises lithium nickel cobalt aluminum oxide.
15. The hybrid electrochemical cell of claim 3 wherein the second battery electrode comprises lithium titanium oxide.

16. The hybrid electrochemical cell of claim 3 wherein the second battery electrode comprises lithium iron phosphate.
17. The hybrid electrochemical cell of claim 3 wherein the second capacitor electrode and the second battery electrode are connected internally in parallel on one cell.
18. The hybrid electrochemical cell of claim 3 wherein the second capacitor electrode and the second battery electrode are connected internally in parallel on one cell, and wherein the second capacitor electrode provides buffering to prevent or reduce high rate charge and discharge of the hybrid electrochemical cell.
19. The hybrid electrochemical cell of claim 3 wherein the second capacitor electrode comprises an electric double layer capacitor (EDLC) in which charge is stored in double layers.
20. The hybrid electrochemical cell of claim 3 wherein the second capacitor electrode comprises activated carbon.
21. The hybrid electrochemical cell of claim 3 wherein the second capacitor electrode comprises the interconnected corrugated carbon-based network (ICCN), wherein the ICCN comprises the metal oxide in a conformal coating of an active material throughout the three-dimensional (3D) structure of the ICCN.
22. The hybrid electrochemical cell of claim 21 wherein the interconnected corrugated carbon-based network (ICCN) electrode comprises a plurality of expanded and interconnected carbon layers that include a corrugated carbon layer.

23. The hybrid electrochemical cell of claim 22 wherein each expanded and interconnected carbon layer comprises at least one corrugated carbon sheet that is at most one atom thick.
24. The hybrid electrochemical cell of claim 22 wherein each expanded and interconnected carbon layer comprises a plurality of corrugated carbon sheets.
25. The hybrid electrochemical cell of claim 22 wherein thickness of the ICCN, as measured from cross-sectional scanning electron microscopy (SEM) and profilometry, ranges from about 7 μm to about 8 μm .
26. The hybrid electrochemical cell of claim 22 wherein a range of thicknesses of the plurality of expanded and interconnected carbon layers making up the ICCN is from about 5 μm to about 100 μm .
27. The hybrid electrochemical cell of claim 3 wherein the second capacitor electrode is redox active to store charge via intercalation pseudo-capacitance.
28. The hybrid electrochemical cell of claim 27 where in the second capacitor electrode comprises niobium pentoxide.
29. The hybrid electrochemical cell of claim 3 integrated as a micro-hybrid electrochemical cell with an implantable medical device.
30. The hybrid electrochemical cell of claim 3 integrated as a micro-hybrid electrochemical cell with a smart card.
31. The hybrid electrochemical cell of claim 3 integrated as a micro-hybrid electrochemical cell with a radio frequency identification (RFID) tag.

32. The hybrid electrochemical cell of claim 3 integrated as a micro-hybrid electrochemical cell with a wireless sensor.
33. The hybrid electrochemical cell of claim 3 integrated as a micro-hybrid electrochemical cell with a wearable electronic device.
34. The hybrid electrochemical cell of claim 3 integrated as a micro-hybrid electrochemical cell integrated with an energy harvester.
35. The hybrid electrochemical cell of claim 3 integrated with a solar cell.
36. The hybrid electrochemical cell of claim 3 wherein the second capacitor electrode and the second battery electrode have electrode digits with a length L , a width W , and an interspace I .
37. The hybrid electrochemical cell of claim 36, wherein the length L is about 4000 μm to about 5000 μm , the width is about 300 μm to about 1800 μm , and the interspace I is about 100 μm to about 200 μm .
38. The hybrid electrochemical cell of claim 36, wherein the length L is about 0.5 cm to about 1.5 cm, the width W ranges from about 0.05 cm to about 0.2 cm, and the interspace I is about 0.01 cm to about 0.05 cm.
39. The hybrid electrochemical cell of claim 36 wherein a miniaturization of the width W of the electrode digits and the interspace I between the electrode digits in the hybrid electrochemical cell reduces ionic diffusion pathways.

40. The hybrid electrochemical cell of claim 1 wherein the hybrid electrochemical cell comprises nickel-cadmium (Ni-Cd) and/or nickel-metal hydride (Ni-MH) chemistries.

41. The hybrid electrochemical cell of claim 40, wherein the second conductor is positive and includes nickel oxyhydroxide (NiOOH) that reduces to nickel hydroxide (Ni(OH)₂) during discharge.

42. The hybrid electrochemical cell of claim 40 wherein the second capacitor electrode and the second battery electrode are positive electrodes.

43. The hybrid electrochemical cell of claim 40 wherein the second capacitor electrode and the second battery electrode are connected internally in parallel on one cell.

44. The hybrid electrochemical cell of claim 40 wherein the second capacitor electrode and the second battery electrode each have electrode digits with a length L, a width W, and an interspace I.

45. The hybrid electrochemical cell of claim 44, wherein the length L is about 4000 μm to about 5000 μm , the width W ranges from about 300 μm to about 1800 μm , and the interspace I ranges from about 100 μm to about 200 μm .

46. The hybrid electrochemical cell of claim 44, wherein the length L is about 0.5 cm to about 1.5 cm, the width W ranges from about 0.05 cm to about 0.2 cm, and the interspace I is about 0.01 cm to about 0.05 cm.

47. The hybrid electrochemical cell of claim 44 wherein a miniaturization of the width W of the electrode digits and the interspace I between the electrode digits in the hybrid electrochemical cell reduces ionic diffusion pathways.

48. The hybrid electrochemical cell of claim 1 wherein energy density of the hybrid electrochemical cell ranges between about 20 watt-hour/kilogram (Wh/kg) to about 200 Wh/kg.
49. The hybrid electrochemical cell of claim 1 wherein power density of the hybrid electrochemical cell ranges between about 10^3 watt /kilogram (W/kg) to about 10^4 W/kg.
50. A method of producing a hybrid electrochemical cell comprising:
- fabricating a first conductor having a single portion that is both a first capacitor electrode and a first battery electrode;
 - fabricating a second conductor having at least one portion that is a second capacitor electrode and at least one other portion that is a second battery electrode, wherein the second capacitor electrode comprises an interconnected corrugated carbon-based network (ICCN) having a three-dimensional (3D) structure, wherein a metal oxide is deposited throughout the 3D structure of the ICCN; and
 - adding an electrolyte to both the first conductor and the second conductor,
 - wherein a power density of the hybrid electrochemical cell is from about 10^3 watt/kilogram to about 10^4 watt/kilogram (W/kg).
51. The method of producing the hybrid electrochemical cell of claim 50 wherein fabricating the second conductor comprises:
- receiving a substrate having a carbon-based oxide film; and
 - generating a light beam that reduces portions of the carbon-based oxide film to a plurality of expanded and interconnected carbon layers that are electrically conductive, thereby forming the interconnected corrugated carbon-based network (ICCN).

52. A method of manufacturing a micro-hybrid electrochemical cell comprising lithium-ion (Li-Ion) material, the method comprising growing porous positive and negative electrode materials on ICCN interdigitated patterns, wherein an ICCN pattern is created using a consumer-grade optical disc burner drive, comprising a series of steps of:

- (a) a first step, wherein a graphite oxide (GO) dispersion in water is dropcast onto an optical disc and dried in air to form a graphite oxide film;
- (b) a second step, wherein a micro-pattern made with imaging or drafting software is directly printed onto the GO-coated optical disc, and wherein the GO film absorbs energy from a laser and is converted into the ICCN pattern;
- (c) a third step, wherein anode and cathode materials are sequentially electrodeposited on the ICCN pattern, and voltage-controlled and current-controlled electrodeposition is used to ensure conformal coating of active materials throughout the three-dimensional (3D) structure of the ICCN;
- (d) a fourth step, wherein a nickel-tin alloy, silicon, or graphite micro-particles are electrodeposited onto the ICCN pattern corresponding to an anode; and
- (e) a fifth step, wherein a drop of electrolyte is added to provide ions that allow continuous electron flow when the micro-hybrid electrochemical cell is under load,

wherein the positive electrode comprises an interconnected corrugated carbon-based network (ICCN) having a three-dimensional (3D) structure, wherein a metal oxide is deposited throughout the 3D structure of the ICCN.

53. A method of manufacturing a micro-hybrid electrochemical cell relying on nickel-cadmium (Ni-Cd) and/or nickel-metal hydride (Ni-MH) chemistries, the method comprising growing porous positive and negative electrode materials on ICCN

interdigitated patterns, wherein an ICCN pattern is created using an optical disc burner drive, comprising a series of steps of:

- (a) a first step, wherein a graphite oxide (GO) dispersion in water is dropcast onto an optical disc and dried in air to form a graphite oxide film;
- (b) a second step, wherein a micro-pattern made with imaging or drafting software is directly printed onto the GO-coated optical disc, and wherein the GO film absorbs energy from a laser and is converted into the ICCN pattern;
- (c) a third step, wherein voltage-controlled and current-controlled electrodeposition is used to ensure conformal coating of active materials throughout the 3D structure of the ICCN, and a metal such as lanthanum nickel (LaNi_5) or palladium (Pd) is electrodeposited on ICCN microelectrodes making up a second battery electrode that forms a portion of an anode;
- (d) a fourth step, wherein cadmium hydroxide ($\text{Cd}(\text{OH})_2$) is added to the ICCN corresponding to the anode; and
- (e) a fifth step, wherein a drop of electrolyte is added to provide ions that allow continuous electron flow when the micro-hybrid electrochemical cell is under load,

wherein the positive electrode comprises an interconnected corrugated carbon based network (ICCN) having a three-dimensional (3D) structure, wherein a metal oxide is deposited throughout the 3D structure of the ICCN.

54. The method of claim 50, further comprising inserting a separator between the first conductor and the second conductor.

55. The method of claim 50, further comprising doping the first conductor with lithium ions.

56. The method of claim 50, wherein the hybrid electrochemical cell comprises lithium-ion (Li-Ion) material or chemistry.
57. The method of claim 50, wherein the hybrid electrochemical cell comprises a nickel-cadmium (Ni—Cd) chemistry, a nickel-metal hydride (Ni-MH) chemistry, or both.
58. The method of claim 50, wherein the first conductor comprises nickel oxyhydroxide (NiOOH), graphite, or both.
59. The method of claim 50, wherein the first battery electrode comprises hard carbon, silicon alloy, a composite alloy, or any combination thereof.
60. The method of claim 50, wherein the second capacitor electrode comprises an electric double layer capacitor.
61. The method of claim 50, wherein the second capacitor electrode is redox active and stores charge via intercalation pseudo-capacitance.
62. The method of claim 50, wherein the second capacitor electrode comprises a layered metal oxide, activated carbon, the interconnected corrugated carbon-based network, niobium pentoxide, or any combination thereof.
63. The method of claim 50, wherein the ICCN comprises the interconnected corrugated carbon-based network comprising a plurality of expanded and interconnected carbon layers.
64. The method of claim 63, wherein the plurality of expanded and interconnected carbon layers comprises at least one corrugated carbon sheet.

65. The method of claim 64, wherein each of the at least one corrugated carbon sheet has a thickness of 1 atom.

66. The method of claim 63, wherein each of the plurality of expanded and interconnected carbon layers has a thickness of about 5 μm to about 100 μm .

67. The method of claim 50, wherein the second battery electrode comprises activated carbon, lithium cobalt oxide, lithium manganese oxide, lithium nickel oxide, lithium nickel manganese cobalt oxide, lithium nickel cobalt aluminum oxide, lithium titanium oxide, lithium iron phosphate, or any combination thereof.

68. The method of claim 50, wherein a ratio in area between the at least one portion that is the second capacitor electrode and the at least one other portion that is the second battery electrode is about 1:10 to about 10:1.

69. The method of claim 50, wherein the hybrid electrochemical cell has an energy density of about 20 watt-hour/kilogram (Wh/kg) to about 200 Wh/kg.

70. The method of claim 50, wherein the hybrid electrochemical cell has a power density of about 10^3 watt/kilogram (W/kg) to about 10^4 W/kg.

71. The method of claim 50, wherein the first conductor and the second conductor are interdigitated.

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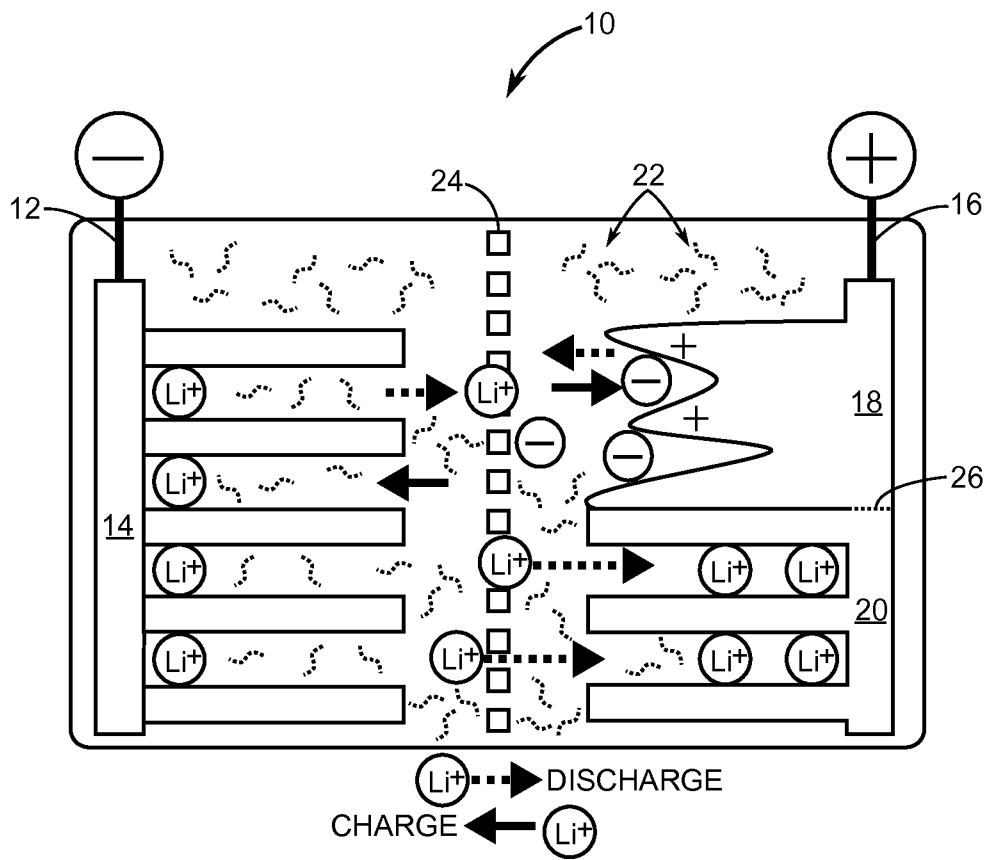


FIG. 1

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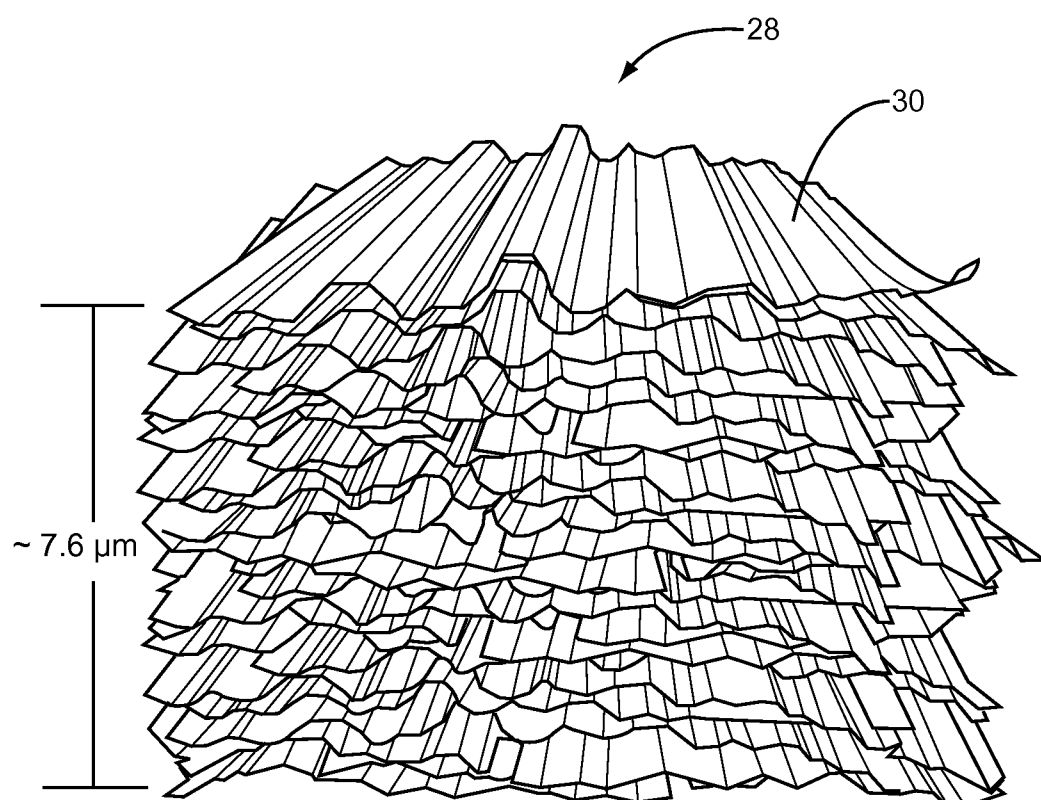


FIG. 2

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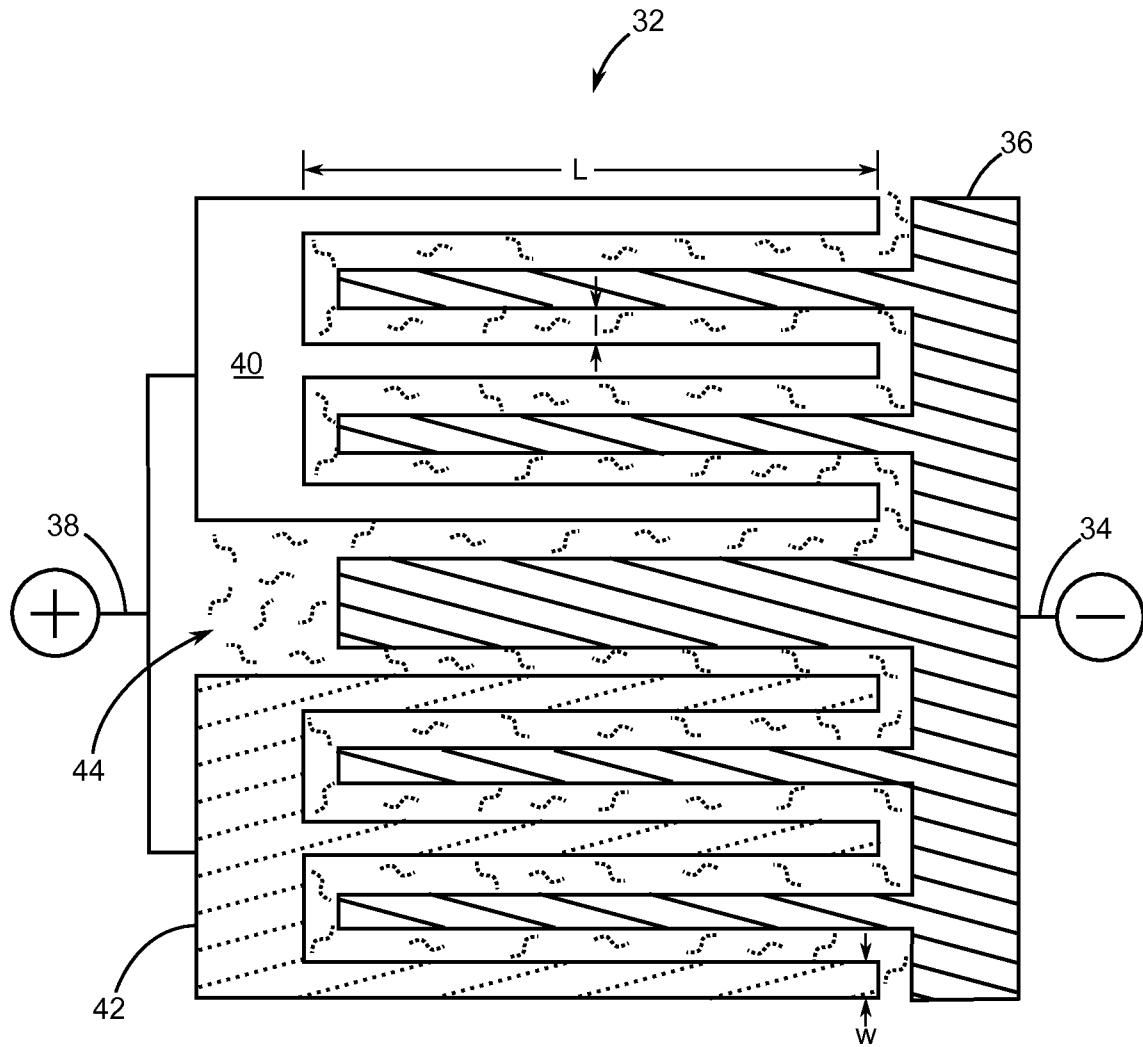


FIG. 3

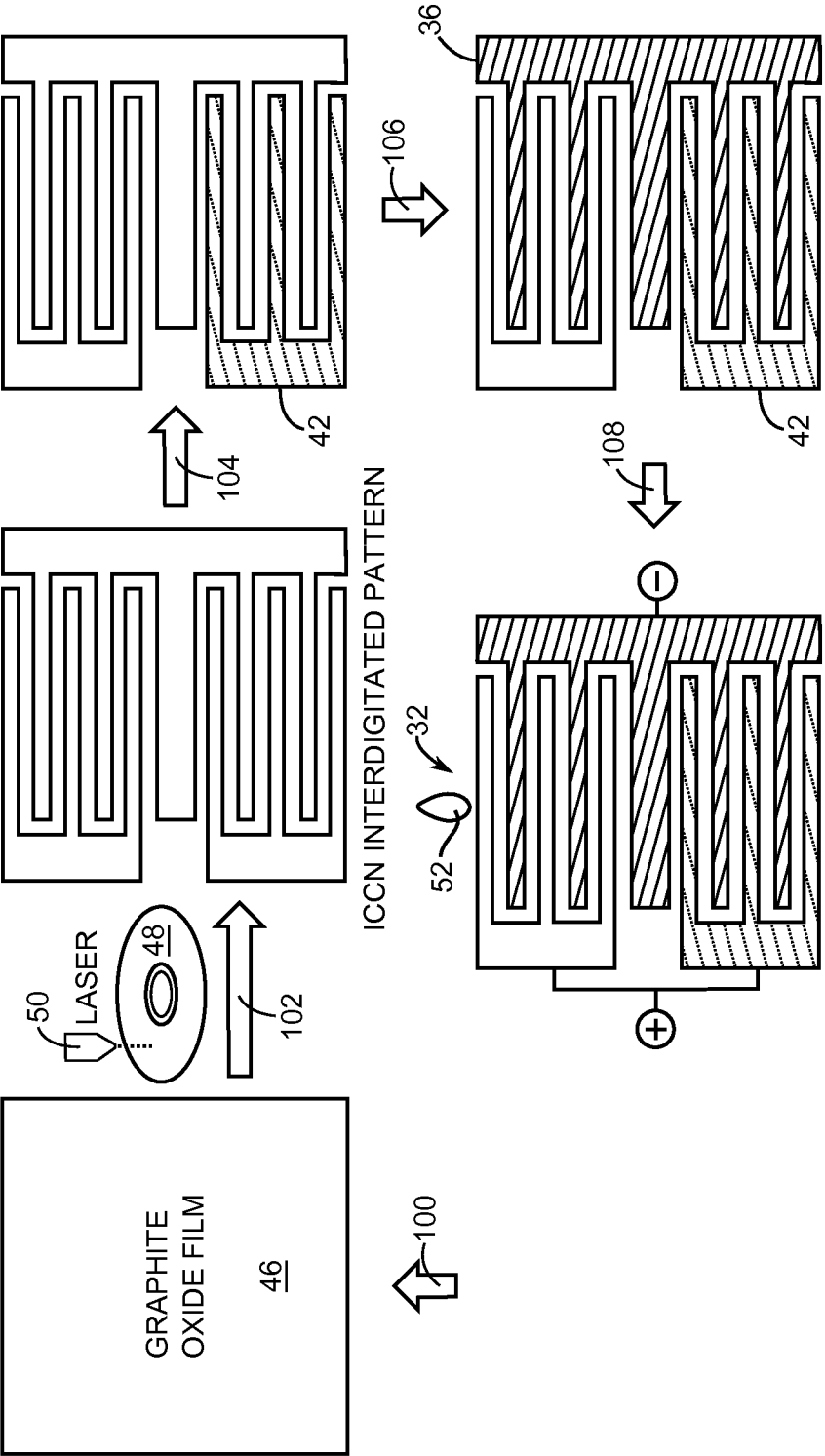


FIG. 4

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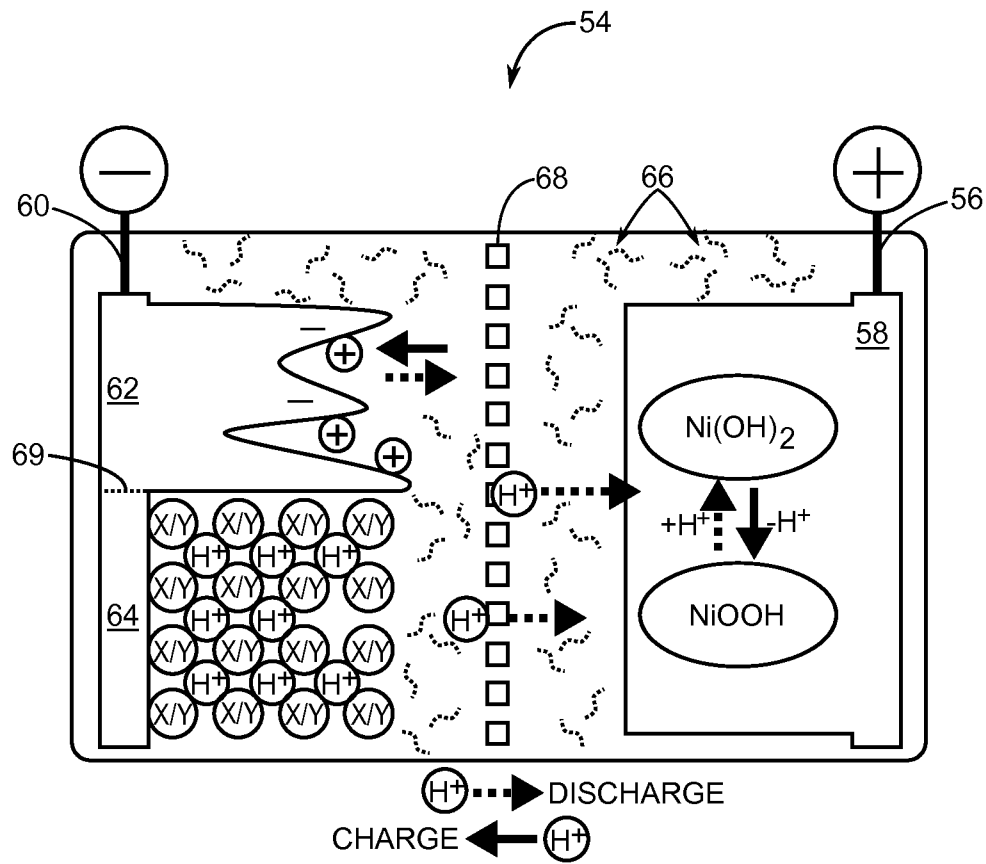


FIG. 5

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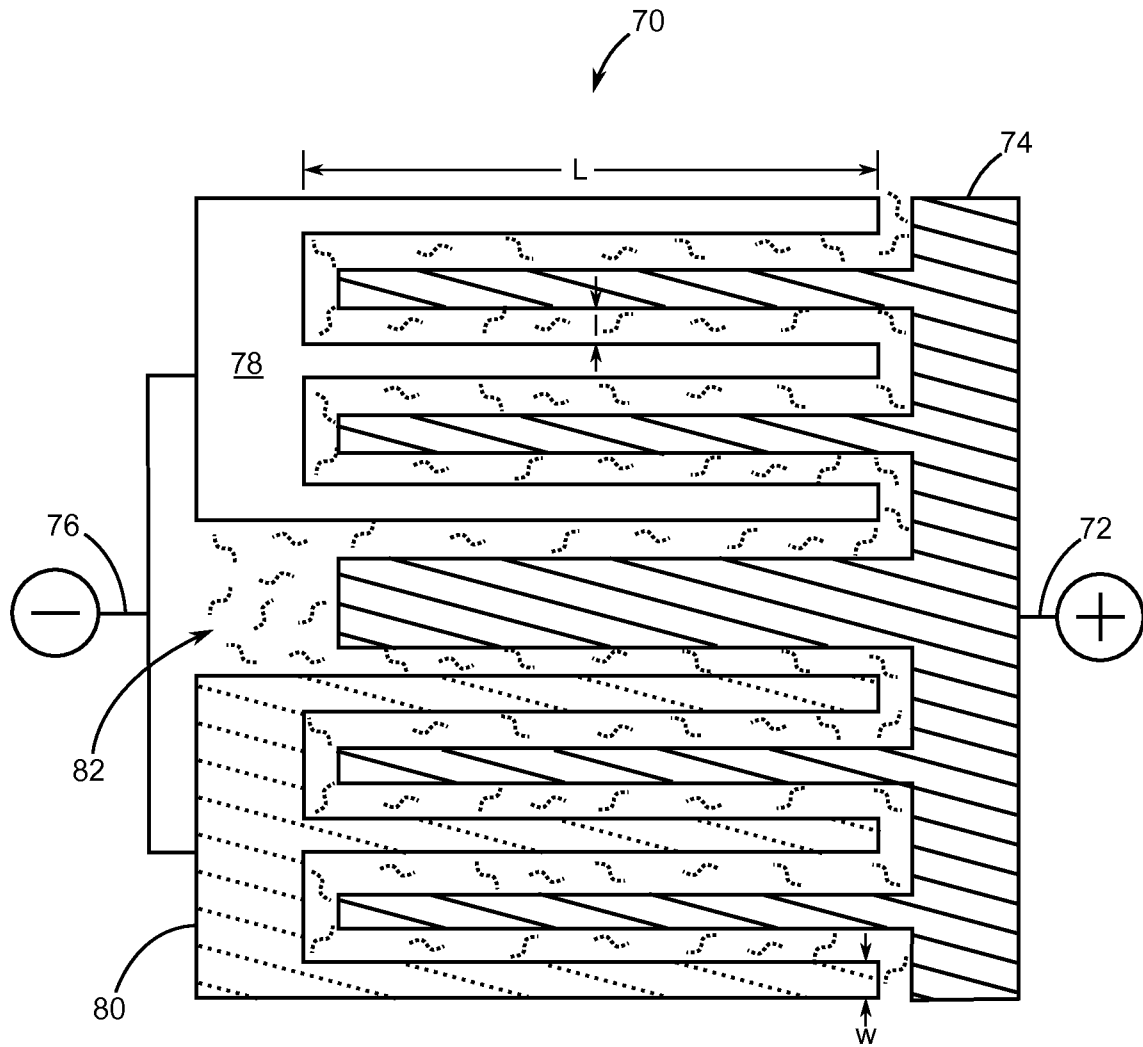


FIG. 6

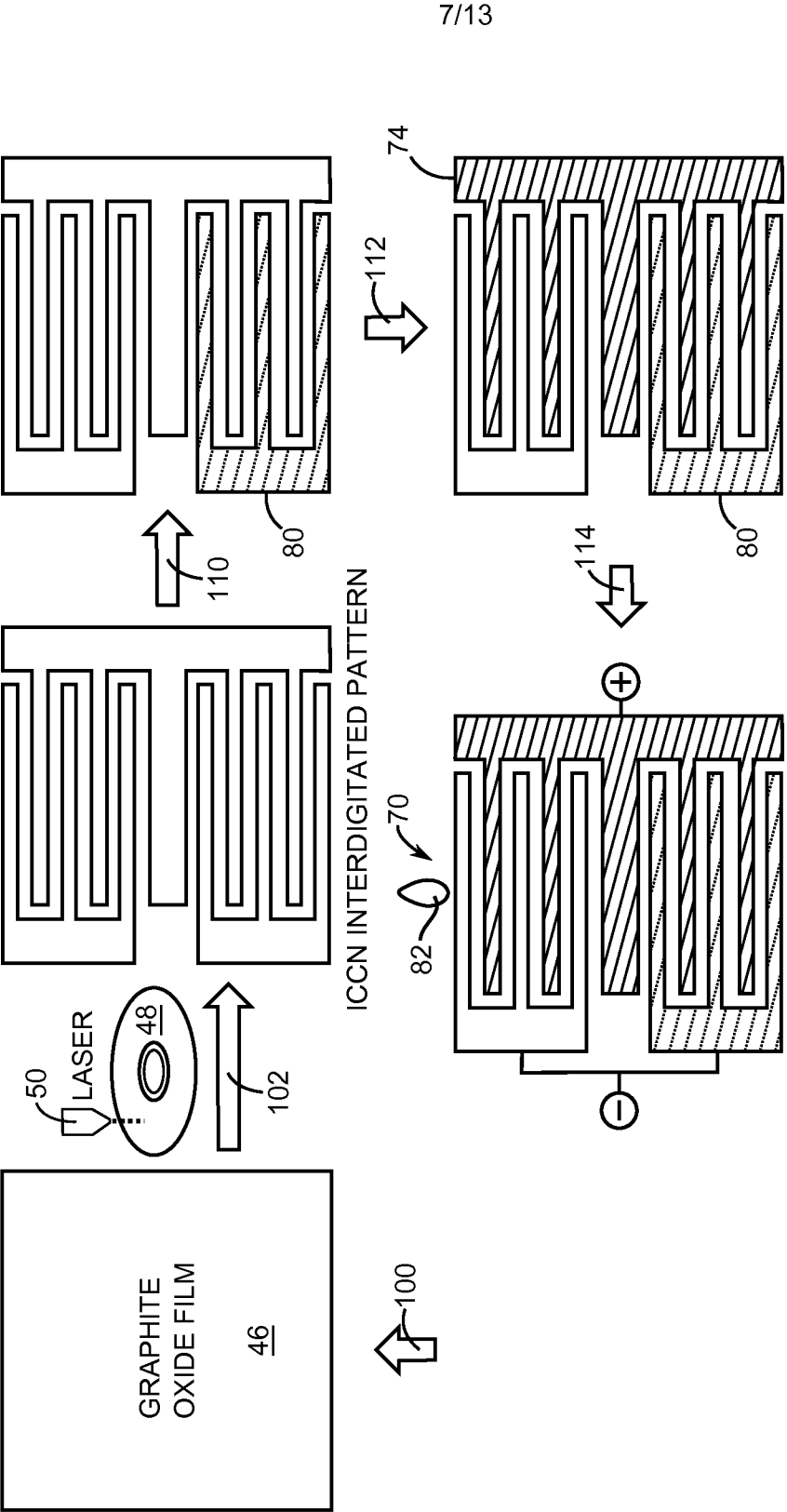


FIG. 7

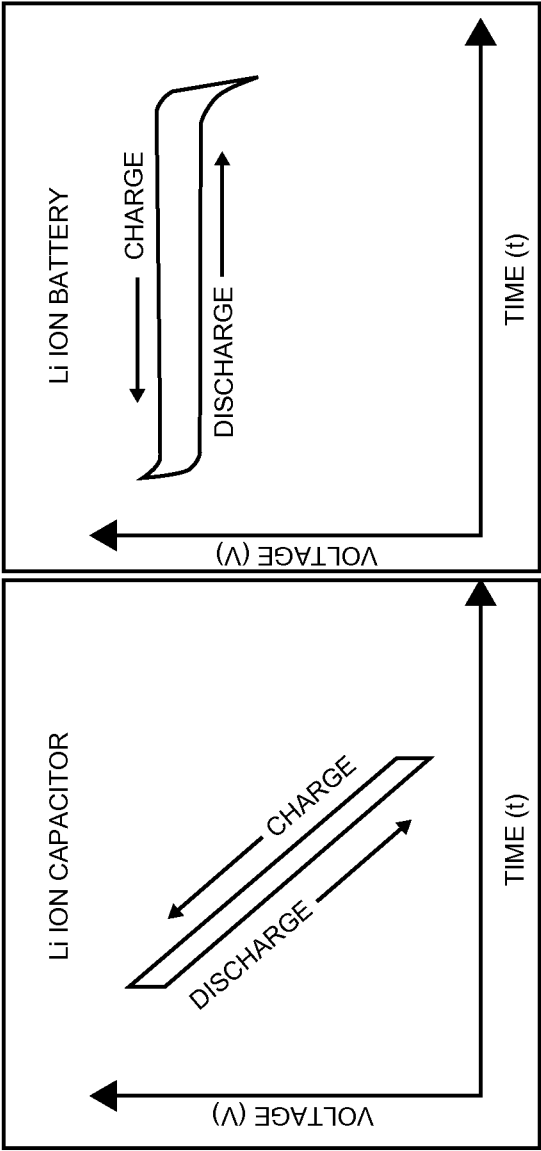


FIG. 8A (PRIOR ART) FIG. 8B (PRIOR ART)

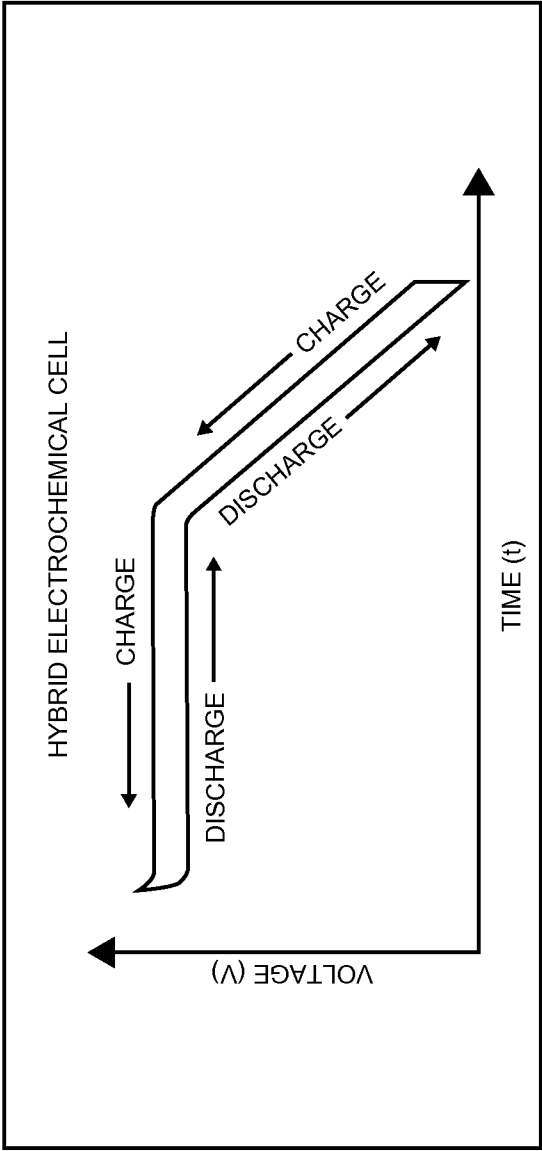


FIG. 8C

HYBRID ELECTROCHEMICAL CELL WITH NIOBIUM PENTOXIDE (Nb_2O_5)

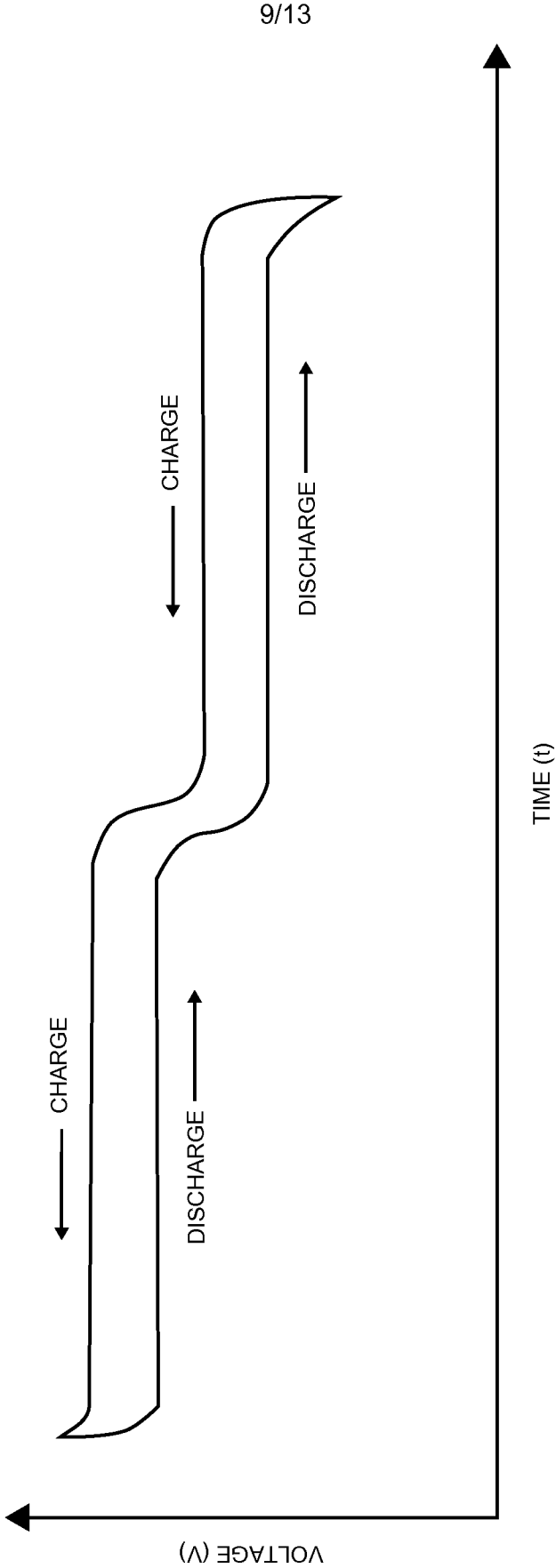


FIG. 9

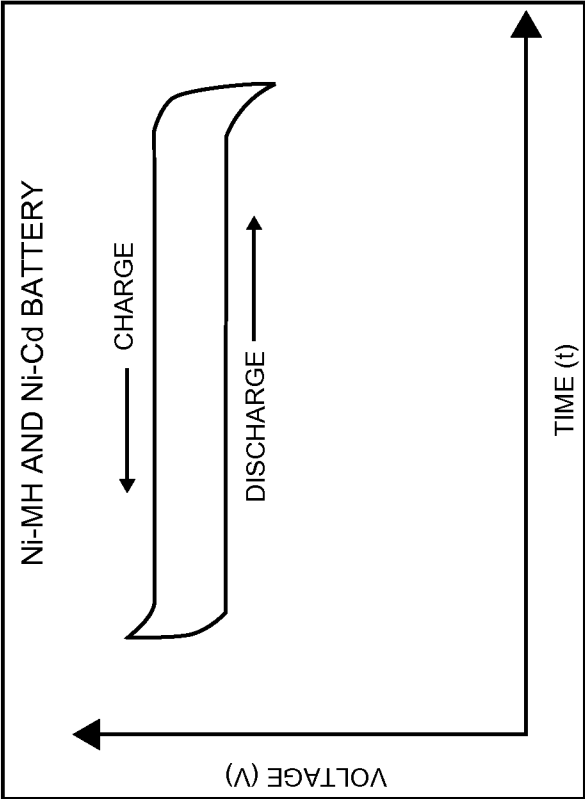


FIG. 10B (PRIOR ART)

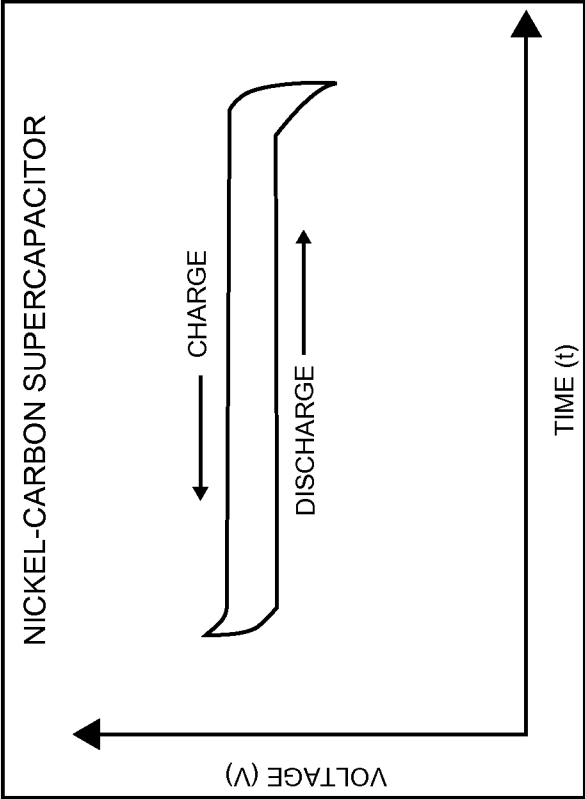


FIG. 10A (PRIOR ART)

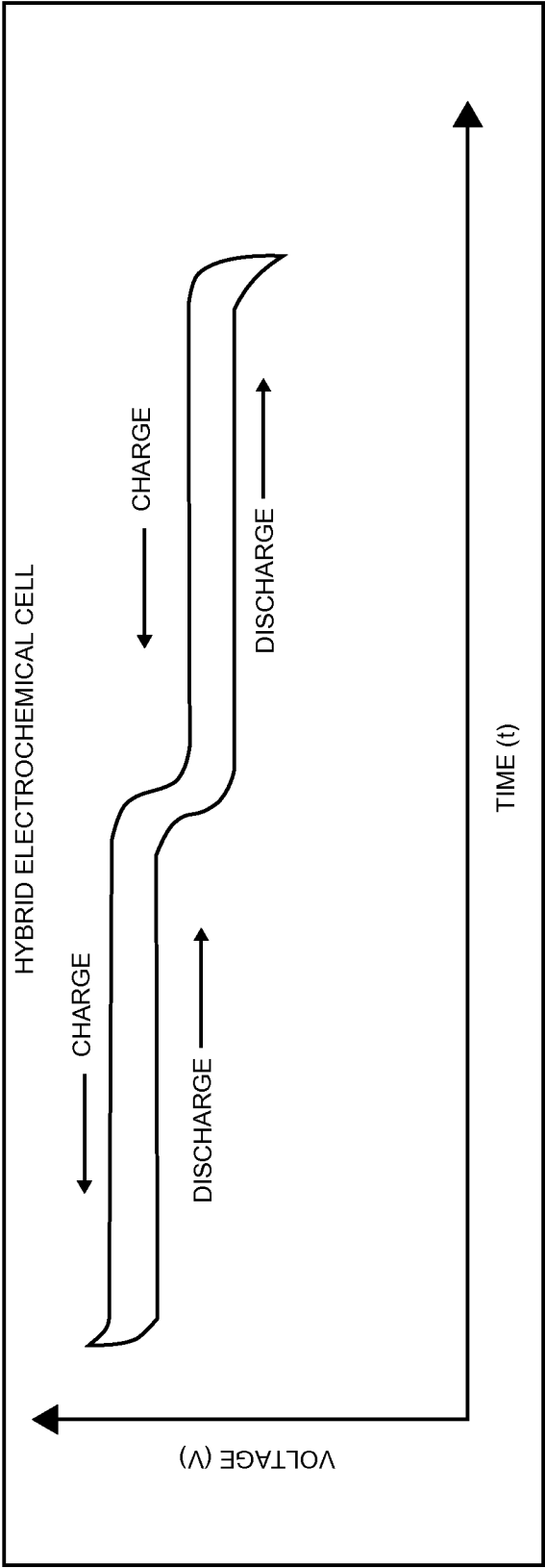


FIG. 10C

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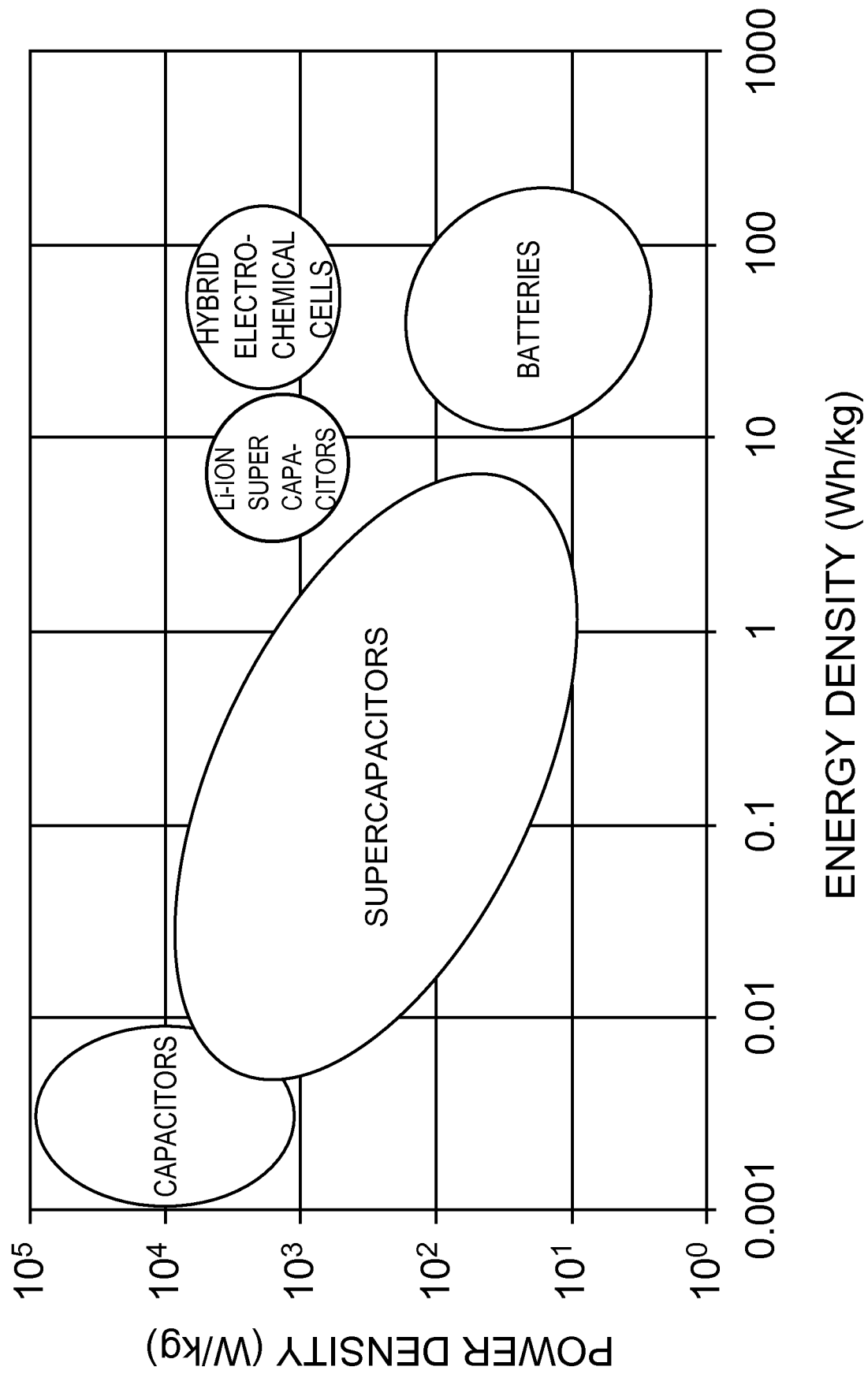
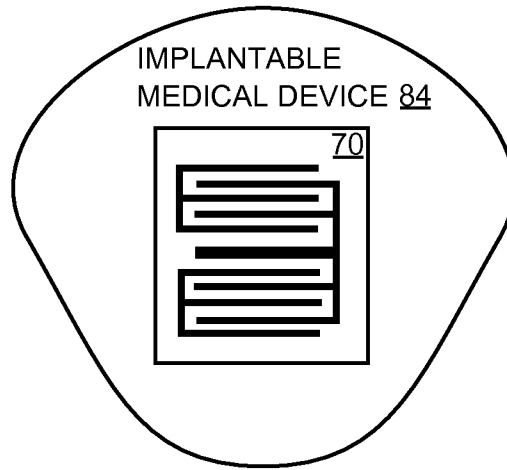
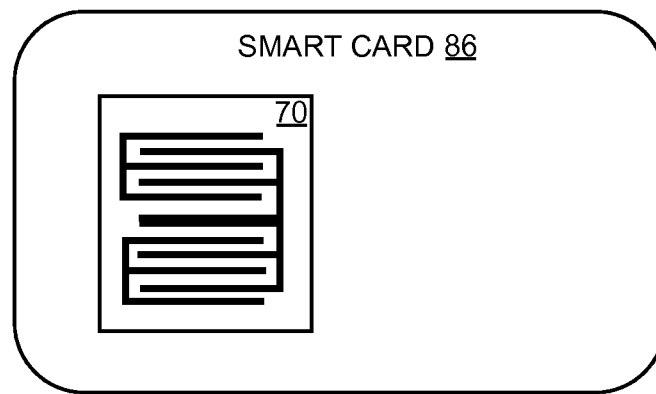
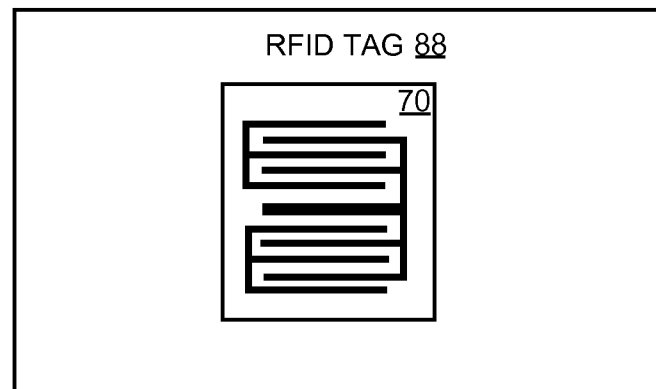


FIG. 11

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*FIG. 12A**FIG. 12B**FIG. 12C*

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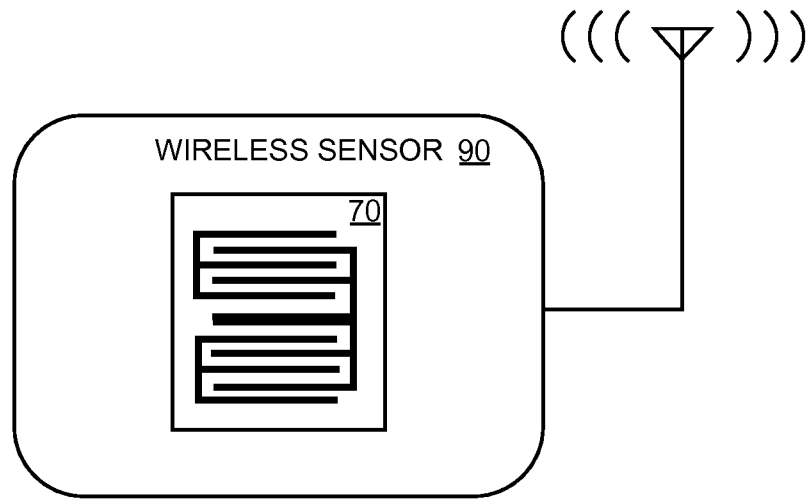


FIG. 12D

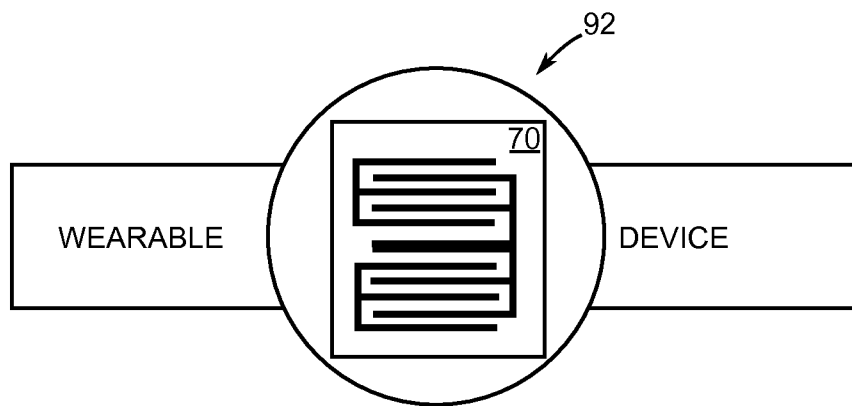


FIG. 12E

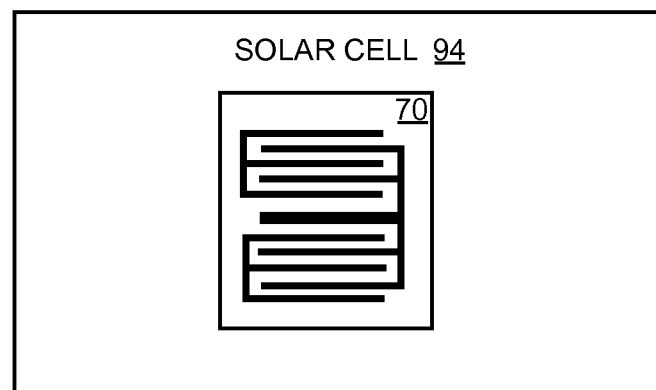


FIG. 12F

