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(54) Title: CAPACITOR-BATTERY HYBRID FORMED BY PLASMA POWDER ELECTRODE COATING

(57) Abstract: Atmospheric plasma spray devices and methods are used in the making of the electrodes for both a lithium-ion battery and a lithium-ion utilizing capacitor structure, which are to be placed in a common container and infiltrated with a common lithium-ion transporting, liquid electrolyte. The lithium-ion-utilizing capacitor and lithium-ion cell battery are combined such that the respective electrodes may be electrically connected, either in series or parallel connection for in energy storage and management in an automotive vehicle or other electrical power supply application.



CAPACITOR-BATTERY HYBRID FORMED BY PLASMA POWDER ELECTRODE COATING

5 TECHNICAL FIELD

A combination of a lithium-utilizing capacitor and a lithium-ion battery is made in which each member of the combination comprises porous electrode layers prepared by using atmospheric plasma coating devices and processes. The layered, electrochemical, capacitor and battery are assembled in a common pouch and
10 electrically interconnected as a hybridized capacitor-battery, suitable for providing balanced energy and power to electrical load demanding devices.

BACKGROUND OF THE INVENTION

Electric powered automotive vehicles use multi-cell batteries to provide
15 electrical energy for providing electrical power for driving the vehicle and for providing electrical energy to many devices on the vehicle. Batteries comprising many lithium-ion electrochemical cells are examples of such electrical power sources. And such batteries are used in many non-automotive applications.

In some applications it may be useful to combine a lithium-ion battery
20 with an electrochemical capacitor which also uses lithium ions. For example, such capacitors may be charged during braking of the vehicle and the stored electrical charge used later in recharging cells of a lithium-ion battery.

There is a need for manufacturing practices to jointly prepare cells for lithium-ion batteries and such electrochemical capacitors for efficiency in their mutual
25 interconnection and interaction.

SUMMARY OF THE INVENTION

It is believed that there are applications in electrically powered automotive vehicles (and in non-automotive applications) in which suitable lithium-containing
30 capacitor structures and suitable lithium-ion battery structures may be placed close to each other, as in a common pouch or like container, and share a common volume of a

lithium-ion conducting electrolyte, with a suitable amount of electrolyte constituents for both devices. A hybridized combination of capacitor and battery is thus provided. The capacitor and battery each use lithium, and a lithium-ion conducting electrolyte, in its electrochemical function.

5 Here the capacitors include (1) electric double layer capacitors (ELDC), (2) supercapacitors, and (3) hybridcapacitors. An ELDC-type capacitor is based on the formation of electric double layers on the surfaces of electrodes, where cations and anions of an electrolyte form Helmholtz layers on the surfaces of both electrodes. During cell charge-discharge, positive ions such as lithium cations in the electrolyte
10 adsorb on one electrode while the negative ions, anions such as $(\text{PF}_6)^-$ adsorb on the other electrode. The fundamental process is adsorption and desorption, which enables the faster rate of charging and discharging. Supercapacitors utilize the hybridization of electric double layer capacitance with redox capacitance, where the composite electrode material is prepared to consist of porous carbon and fine metal particles.
15 Hybridcapacitors (or asymmetric supercapacitors) are proposed to get high capacitance and high energy density using different material at the two electrodes, anode and cathode, such as graphitized carbon at the anode and activated carbon at the cathode, where the intercalation/de-intercalation of Li^+ at the anode and the formation of electric double layers at the cathode are intended to occur.

20 In the lithium-ion battery cell, the negative electrode (anode) releases lithium ions (de-intercalates lithium ions) during discharging of the cell, and the positive electrode absorbs lithium ions. The negative electrode releases electrons to the external circuit and the positive electrode receives them. The reverse electrochemical process occurs when the battery is charged. The close proximity of
25 the separate capacitor and lithium-ion battery cell structures simplifies electrical connections and facilitates their interaction in providing electrical energy to nearby electrical loads.

 In such hybrid applications, the outline shapes of the respective current collectors, porous electrode material layers, and porous separators may be similar and
30 complementary so as to suggest the simultaneous manufacture of both the capacitor electrodes and the battery electrodes and their interrelated functions. The manufacturing process of this invention is particularly useful in making hybrid combinations of a lithium-using capacitor and lithium-ion battery cell.

In accordance with practices of this invention, atmospheric plasma spray devices and methods are used to form the porous particulate electrodes of both a capacitor and a lithium-ion cell. The plasma-spray methods of forming porous layered electrodes of the capacitor are comparable and compatible with plasma-spray methods that may be used for forming the porous layered electrodes of a lithium-ion battery. In some preferred embodiments of this invention, the electrodes and separator for a capacitor and the electrodes and separator for a lithium-ion cell may be prepared contemporaneously, but separately, and a capacitor and a lithium-ion cell may be placed, spaced-apart, in a suitable pouch module or other container and the porous electrodes and separators infiltrated with a lithium-ion transporting, non-aqueous, liquid electrolyte.

In an illustrative example, each member of the capacitor and battery may be prepared in a rectangular shape of suitable predetermined dimensions for assembly of the complementary, hybridized members in operating units. Pre-formed current collector foils for each of the positive and negative electrodes of the capacitor and battery may serve as substrates for the plasma deposition of porous layers of the respective electrode materials. Such current collector foils are typically flat and are sized with opposing rectangular surfaces (faces) of suitable area for the deposit of a suitable layer of selected electrode material on each side (major face) of the foil. The foil may have an uncoated tab extending from one side for electrical connection of the electrode material with other electrodes or with an electrical circuit.

In another embodiment of the invention, a porous polymer separator may serve as a substrate for the plasma deposition of particulate electrode material. A layer of positive capacitor electrode material may be deposited by plasma deposition on one side of a suitably sized, rectangular porous separator and a porous layer of negative capacitor electrode material is deposited by plasma deposition on the other side of the separator. In each embodiment, the deposited electrode material and its substrate are assembled with other members of the capacitor structure. A complementary lithium battery may be made using a like process.

Atmospheric plasma spray devices are commercially available, and practices for their use in the deposition of capacitor electrode materials and battery electrode materials will be described and illustrated in more detail below. The

deposition process will be initially described with reference to a capacitor. But substantially the same practices may be used to make the members of the battery.

In summary, a quantity of small particles of electrode material is prepared. Suitable portions are continually introduced into a confined stream of unheated air (or
5 other suitable carrier gas) flowing in a suitable duct or housing. The confined air stream is directed through a plasma generator, within the housing, in which the stream-borne particles are momentarily, rapidly heated. The energized stream of electrode material particles is passed through a suitable nozzle and directed so as to progressively form an adherent, porous, particulate coating on a major surface of a
10 current collector foil or on a major surface of a separator. A porous layer of the particles is formed having a generally predetermined uniform thickness. The thickness of the electrode material layer for the capacitor, which is often in the range of about 100-200 micrometers, is determined to provide a porous electrode layer for infiltration with a lithium-ion conducting electrolyte, to provide suitable lithium ion
15 transporting properties for the capacitor.

Examples of suitable anode materials for the capacitor include graphite, activated carbon, and lithium-titanium containing oxides and phosphates. Examples of suitable cathode materials include certain lithium-metal oxides and phosphates, activated carbon, graphite, and additional materials which will be identified below in
20 this specification. It may also be helpful to coat some of the respective electrode material particles with small metal particles (or other binder materials) which are at least partially melted or softened in the plasma and serve to bond the electrode material particles to each other and to their current collector or separator substrate.

After the electrode materials for the capacitor have been suitably deposited
25 on and bonded in a porous layer to their current collector foils or separators, the assembly of the elements for formation of a layered capacitor is completed for placement in a suitable pouch or other module container. Both the capacitor and the lithium-ion battery may have several layers of electrodes (with interspersed porous separators) with their respective current collectors. The current collectors are suitably
30 connected so that the capacitor and lithium-ion battery each have two terminals. In preferred embodiments of the invention, an assembly of like-sized elements of both the capacitor member and the lithium-ion cell member are placed in the pouch, but the capacitor is separated from the battery cell. The pores of the electrode members of

the capacitor and the lithium-ion cell, and their respective separators, are infiltrated with a common lithium ion transporting, non-aqueous lithium electrolyte solution.

Other aspects and features of our invention will be further understood following a more detailed description of illustrated examples of forming electrodes
5 for capacitors which are to be used in combination with a lithium-ion cell or group of cells.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic, side view of a positive electrode, porous separator,
10 and negative electrode of a capacitor placed in a common pouch with a positive electrode, porous separator, and negative electrode for a lithium-ion battery cell. In practice, each of the capacitor and lithium-ion battery would have many layers of electrode materials deposited on current collectors. The current collector tabs of the positive electrodes would be suitably interconnected at a positive terminal and the
15 current collector tabs of the negative electrodes would be likewise connected at a negative terminal. The illustrations of the capacitor and lithium ion battery have been simplified in Figure 1 by depicting only one of the seven-layer sets of the electrode and separator elements of each capacitor unit and lithium-ion battery unit.

In Figure 1, a side of the pouch has been removed to show the layered
20 structures of the capacitor and lithium-ion cell. The respective electrode materials have been deposited as porous particulate layers from a plasma spray device onto metal current collector foils. Each element is a thin rectangular body. The current collector foils have connector tabs extending from their upper sides and are arranged for a series-type electric connection between a hybrid combination of the capacitor
25 and its associated lithium-ion battery cell. In the series-type connection of Figure 1 there are four separate current collector leads extending from the top of the pouch, representing the four terminals of the hybridized capacitor and lithium-ion battery.

Figure 2 is a simplified, schematic side view, with a portion of the pouch container removed, similar to Figure 1, of the hybrid combination of a capacitor and
30 lithium-ion cell. In this hybrid combination, the capacitor and lithium-ion cell are positioned in a common pouch in an arrangement in which they are in electrical parallel-connection for co-delivery of electrical power to an external circuit. In Figure 2, only two terminals emerge from the pouch because the positive electrode

tabs of the capacitor and battery have been connected, as have their negative electrode tabs.

Figure 3A is a schematic illustration of an atmospheric plasma device, a plasma nozzle supported and adapted to progressively apply particles of cathode material onto the upper side of an aluminum current collector foil. The device and coating process may be used in making electrodes for both capacitors and lithium ion cells. The aluminum current collector foil is carried on a conveyor belt or the like. The particles of cathode material may, for example, be particles of activated carbon for a capacitor cathode or particles of LiMn_2O_4 for a cathode of a lithium-ion battery. The particles of electrode material may be coated with small particles of a metal or of a suitable resin which, when heated in the plasma device, melt and re-solidify to serve as a binder to bond the electrode material particles to each other and to the current collector foil.

Figure 3B is an enlarged side view of an aluminum current collector foil which has been coated on both of its opposing sides or faces with a bonded layer of positive electrode (cathode) particles for a lithium-containing capacitor.

Figure 3C is an enlarged side view of a copper current collector foil which has been coated on both of its opposing sides or faces with a bonded layer of negative electrode (anode) particles for a lithium-containing capacitor.

Figure 4 is an enlarged schematic side view illustration of a seven layer capacitor structure that is produced using the plasma spray process illustrated in Figure 3A. The center layer of the capacitor structure is a porous polymer separator. Three layers of materials for the capacitor have been applied, progressively, to each side of the porous plasma separator. A layer of capacitor cathode material has been applied to the upper surface of the separator (as it is shown in Figure 4), followed by a current collector foil layer, and a second layer of capacitor cathode material. Likewise, three layers of material for the anode have been applied, progressively, to the bottom side of the capacitor as illustrated in Figure 4. A lithium-ion battery structure could be prepared and illustrated in a similar manner.

DESCRIPTION OF PREFERRED EMBODIMENTS

In accordance with practices of this invention, hybrid electrochemical capacitors are prepared, consisting of a capacitor and a lithium-ion battery which are

fabricated by plasma powder electrode coating technology, delivering a balanced energy-power performance. Both the capacitor and the battery will adsorb or intercalate lithium ions and both the capacitor and battery will be combined in a common pouch or other suitable container. Accordingly, electrode members for both the capacitor and the battery may be prepared using atmospheric plasma spray devices or like plasma deposition devices. As stated, a uniform layer of particulate electrode material may be deposited over a selected surface area of a metal foil current collector or over a selected surface area of a porous separator member. The formation of electrode layers on current collectors and separator surfaces may be conducted in sequential or complementary steps to accommodate the assembly of positive and negative electrodes on opposite sides of a compatible separator. The positive electrode-separator-negative electrode structures for a capacitor and a lithium-ion cell may thus be prepared separately, but contemporaneously, for assembly into a pouch and infiltration with a common volume of a non-aqueous, lithium-ion conducting electrolyte.

In accordance with practices of this invention, it is intended that selected electrode materials, for both the electrochemical capacitor positive and negative electrodes be prepared in the form of micrometer size particles for deposition on a selected substrate. The selected electrode material compositions are deposited on compatible metal current collector foils, or on a sheet of porous separator material, using one or more atmospheric plasma spray devices. The particles of electrode materials, prepared for the plasma deposition, may have been coated with smaller particles of a metal or of other suitable binder material. Electrode materials for the lithium-ion cell are likewise separately prepared and plasma deposited on selected cell substrates for assembly into lithium-ion cells and placement with a compatible lithium-ion absorbing capacitor in a container.

Suitable materials for plasma deposition as cathode (positive electrode) particles for the capacitor include:

Metal oxides, MO_x , where M is one or more of Pb, Ge, Co, Ni, Cu, Fe, Mn, Ru, Rh, Pd, Cr, Mo, W, and Nb.

A lithium-metal-oxide including: Li_xMO_2 in which M is Co, Ni, Mn, Cr, or V.

$\text{Li}_x\text{M}_2\text{O}_4$, in which M is Co, Ni, Mn, Cr, or V.

$\text{Li}_x\text{Ni}_y\text{M}_{1-y}\text{O}_2$, in which M is Fe or Mn.

$\text{LiNi}_{1-x-y-z}\text{Co}_x\text{M1}_y\text{M2}_z\text{O}_2$, in which M1, M2 are different metals selected from Al, Ni, Co, Fe, Mn, V, Cr, Ti, W, Ta, or Mo.

$\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ in which M is one of Co, Ni, Fe, Cu, Cr, V.

5 One of LiNiVO_4 , LiNbO_3 , LiFePO_4 , $\text{LiTi}_2(\text{PO}_4)_3$, or $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

LiMPO_4 in which M is one of Ti, Ge, Zr, Hf.

One or more of $\text{Li}_3\text{FeV}(\text{PO}_4)_3$, $\text{LiFeNb}(\text{PO}_4)_3$, $\text{Li}_2\text{FeNb}(\text{PO}_4)_3$, $\text{Li}_x\text{Fe}_y\text{Mn}_{1-y}\text{PO}_4$, LiMSiO_4 (M= Mn, Fe), $\text{Li}_x\text{Fe}_2(\text{WO}_4)_3$, $\text{Li}_x\text{Fe}_2(\text{SO}_4)_3$, and LiFeO_2 .

A metal sulfide: NiS, $\text{Ag}_4\text{Hf}_3\text{S}_8$, CuS, FeS, and FeS_2 .

10 Activated carbon.

A polymer such as: poly (3-methyl thiophene), polyaniline, polypyrrole, poly (para-phenylene), or polyacene.

As further described in this specification, cathode particles for the capacitor are usually plasma-deposited on an aluminum current collector foil or on a porous polymer separator.

Suitable materials for plasma deposition as anode (negative electrode) particles for the capacitor include:

$\text{Li}_4\text{Ti}_5\text{O}_{12}$, LiTi_2O_4 , LiCrTiO_4 , $\text{LiTi}_2(\text{PO}_4)_3$, and graphite or activated carbon.

20 Positive electrode material for the capacitor is preferably plasma deposited on an aluminum current collector foil or on a polymeric separator such as a porous layer of polyethylene, polypropylene, or an ethylene-propylene copolymer.

After the assembling of electrodes and separator and filling their pores with the electrolyte, the hybrid capacitor and battery undergo a formation cycle and are then degassed. The plasma powder coating method can optimize the surface area of the material layers coated on the foil or the separator, and can also control the porosity of the respective electrodes, in order to improve both the energy and power performance of the hybrid capacitor-battery.

30 Recently, a lithium and titanium containing spinel structure, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, listed above, has been demonstrated as a promising negative electrode material for use in combination with activated carbon as the positive electrode material for hybrid capacitor applications. Accordingly, the power density depends on the rate capability of the intercalated compound $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which is associated with the Li-ion diffusion

coefficient and the diffusion distance in the intercalated compound particle. To obtain a high rate capability, plasma powder electrode coating technology can be introduced to develop a nanosize- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode with well controlled porosity, in which conductive metal particle and no polymer binder will benefit the rate performance. In addition, the energy density of the capacitor is critically dependent on the energy density of the carbon positive electrode material. Plasma powder electrode coating technology can be used to enlarge the surface area of carbon material in the electrode by size and porosity optimization to improve the specific capacity.

The lithium-ion cell component of this capacitor-cell combination may be formed of like current collector foils and like porous separator materials.

Examples of suitable particulate materials for positive electrodes for lithium-ion cells include lithium manganese nickel cobalt oxide, lithium manganese oxide, lithium cobalt oxide, lithium nickel aluminum cobalt oxide, lithium iron phosphate, and other lithium oxides and phosphates. Examples of particulate negative electrode materials for lithium-ion cells include lithium titanate, graphite, activated carbon, and silicon-based materials such as silicon, silicon-based alloys, SiO_x , silicon-tin composites, and lithium-silicon alloys.

The common electrolyte for the capacitor cell and the lithium-ion cell may be a lithium salt dissolved in one or more organic liquid solvents. Examples of salts include lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), lithium perchlorate (LiClO_4), lithium hexafluoroarsenate (LiAsF_6), and lithium trifluoroethanesulfonimide. Some examples of solvents that may be used to dissolve the electrolyte salt include ethylene carbonate, dimethyl carbonate, methylethyl carbonate, and propylene carbonate. There are other lithium salts that may be used and other solvents. But a combination of lithium salt and non-aqueous liquid solvent is selected for providing suitable mobility and transport of lithium ions between the opposing electrodes in the operation of the cell. The electrolyte is carefully dispersed into and between closely spaced layers of the electrode elements and separator layers of each of the capacitor cell and the battery cell. The electrolyte is not illustrated in the following drawing figures because it is difficult to illustrate the electrolyte between tightly compacted electrode layers pressing on an interposed separator.

A thin porous separator layer is interposed between the major outer face of the negative electrode material layer and the major outer face of the positive electrode

material layer of each of the capacitor and the battery unit. The porous separator may be formed of a porous film or of porous interwoven fibers of suitable polymer material, or of ceramic particles, or a polymer material filled with ceramic particles. In the assembly of the hybrid capacitor and separated lithium-ion cell units, the porous separator layer is filled with a liquid lithium-ion containing electrolyte and enables the transport of lithium ions between the porous electrode members. But the separator layer is used to prevent direct electrical contact between each of the negative and positive electrode material layers in each unit, and is shaped and sized to serve this function.

Figure 1 is a schematic illustration of a pouch-contained assembly 10 of the elements of an electrochemical capacitor 12, a lithium-ion battery cell 14, and a polymer-coated, metal foil pouch 16 to contain the combined capacitor and cell elements for electrical series connection to each other and/or to other members of an electrical circuit. One side of the pouch 16, including the closure seam of its sides, has been cut-away in the figure to show the relative positions of the electrochemical capacitor 12 and the lithium-ion cell 14.

As stated above in this specification, in actual practice each capacitor will be formed of several layers of positive electrodes, negative electrodes, and separators, prepared as described in the following paragraphs. The like-charged electrode layers are connected by tabs on their current collectors, respectively, in a positive terminal and a negative terminal for the capacitor. The positive and negative tabs for the groups of positive and negative capacitor electrodes may be connected with other devices in an electrical circuit as desired. Lithium-ion batteries are also typically formed of many positive electrodes connected to a positive terminal and many negative electrodes connected to a negative terminal. But since the focus of this specification is on the use of plasma deposition methods and devices to make such electrodes and separators, the illustrations of Figures 1 and 2 have been simplified to depict the single set of electrodes for capacitor 12 and lithium-ion cell 14.

The illustrated electrochemical, capacitor 12 comprises a positive electrode, which in this example comprises a rectangular aluminum foil current collector 18 with a connector tab 18' extending from its top side and through the overlapping surface of pouch 16. The positive electrode of the capacitor further comprises porous particulate layers of electrode material 20 which have been

deposited by atmospheric plasma deposition on each face of the aluminum foil current collector 18. The positive electrode material for the capacitor may, for example, be activated carbon. The thickness of the current collector foil 18 may be, for example, about ten micrometers and the lengths of the sides of the foil may, for example be in the range of 75 mm to 100 mm, not including the tab 18'. The porous layers of electrode material 20 may, for example, be about 10 to 500 micrometers in thickness and applied to substantially cover the rectangular faces of current collector foil 18, but not tab 18'.

The electrochemical capacitor 12 further comprises a negative electrode, which in this example comprises a rectangular copper foil current collector 22 with a connector tab 22' extending from its top side and through the overlying surface of pouch 16. The negative electrode of the capacitor further comprises porous particulate layers of electrode material 24 which have also been deposited by atmospheric plasma deposition on each face of the copper foil current collector 22, but not on tab 22'. The negative electrode material for the capacitor may, for example, also be activated carbon. The side lengths and thickness of the copper current collector foil 22 are suitably like the dimensions of the positive electrode current collector foil. The porous layers of negative electrode material 24 may, for example, be of complementary thickness to that of the positive electrode materials and applied to substantially cover the rectangular faces of current collector foil 22, but not tab 22'.

As illustrated in Figure 1, the outer surface of one side of the positive electrode material 20 is placed close against one face of a porous separator layer 26 and the outer surface of one side of the negative electrode material is pressed against the opposite face of the porous separator 26. Porous separator 26 may be formed, for example, of polyethylene fibers. Separator 26 has a two-dimensional shape and a thickness. In this example, the rectangular shape of separator is determined to cover the contacting surfaces of the respective electrode materials 20, 24 and to physically separate them. The shape and thickness of the porous separator 26 also serves to retain liquid electrolyte for lithium absorption and desorption by the electrode layers 20, 24 of the capacitor. In the assembled device, the pores of the electrode materials 20, 24 are infiltrated with liquid lithium-ion conducting electrolyte, as well as the pores of separator 26.

The liquid electrolyte is not illustrated in Figure 1, but it is present in the porous electrode layers and the separators of each of the assembled capacitor 12 and battery 14. In the capacitor 12, lithium ions are transported between the electrode materials 20 and 24 through the electrolyte.

5 The structure of the lithium-ion cell or battery 14 is similar to that of capacitor 12 and the outline sizes and thickness of the respective current collector foils, electrode material layers and separator of battery 14 are comparable to the similar structural elements of capacitor 12. But the electrode materials may be different and the electrochemical reactions are different.

10 In this example and simplified illustration, battery 14 includes an aluminum positive electrode current collector foil 30 with a connector tab 30' extending through the overlying pouch material 16. Plasma deposited positive electrode layers 32 (e.g., activated carbon) are formed on both major faces of the aluminum current collector foil 30. The positive electrode material 32 for the battery 14 may, for example, be
15 particles of LiFePO_4 . A copper negative current collector foil 34 with tab 34' is plasma coated on both of its major faces with layers of negative electrode material 36. The particle layers of negative electrode material 36 may comprise activated carbon or resin-bonded activated carbon. The facing porous layers of positive electrode material 32 and of negative electrode material 36 are kept apart by porous polymer
20 separator 38. In the assembled battery 14, placed in pouch 16, the pores of separator 38 and of electrode layers 32 and 36 are filled with a suitable non-aqueous, lithium-ion conducting electrolyte. The electrolyte may, for example, comprise lithium hexafluorophosphate (LiPF_6) dissolved in a mixture of dimethyl carbonate and methylethyl carbonate as solvent.

25 In Figure 1, the current collector tab leads 18' and 22' for capacitor 12 and the current collector tab leads 30', 34' for battery 14, each extend through the adjoining pouch material and are positioned for serial electrical connections. In a typical hybrid capacitor, these current collector leads would be the four terminal posts for the series-connected assembly in pouch 16. Such an arrangement offers many
30 possibilities for interconnection of the capacitor electrodes and battery electrodes with each other and with other members of an electrical power-requiring system. The electrical connections between capacitor 12 and lithium-ion battery 14 may, for example, be through a DC-DC converter. This type of electrical interconnection

could enable the capacitor 12 to store energy, for example, when an automotive vehicle is braking, and to later release energy to the adjacent lithium-ion battery 14 during vehicle starting or acceleration.

Figure 2 illustrates a pouch-contained assembly 110 of a capacitor 112 and
5 battery 114 which are arranged and oriented in pouch 116 for parallel electrical connection between capacitor 112 and battery 114. Again, in this simplified illustration only single electrode structures are illustrated for each of capacitor 112 and battery 114. In practice, a capacitor and battery would each comprise many connected positive electrodes with current collector tabs connected in a single positive
10 terminal and many negative electrodes with current collector tabs electrically connected in a single negative terminal.

In this example and illustration, the electrodes and separator of capacitor 112 may be substantially identical in shapes and compositions with respect to the corresponding elements of capacitor 12 as shown in Figure 1. And the electrodes and
15 separator of battery 114 may be substantially identical in shapes and compositions with respect to the corresponding elements of battery 14 shown in Figure 1. Accordingly, the corresponding current collector foils, electrode layers and separators of Figure 2 are identified by numerals 1xx (or 1xx') with respect to the same parts of Figure 1 which are identified as xx or xx'.

20 The main difference between Figure 1 and Figure 2 is that capacitor 112 and battery 114 are arranged and oriented in pouch 116 for parallel electrical connection between capacitor 112 and battery 114, and for series connection with these combined elements and electrical power-requiring devices outside pouch 116. Accordingly, positive electrode tab 118' of capacitor 112 and positive electrode tab
25 130' of battery 114 are connected as a single positive (+) terminal 140 which extends through the top of pouch 116. In a similar arrangement, negative electrode tab 122' of capacitor 112 and negative electrode tab 134' of battery 114 are connected as a single negative (-) terminal 142 which extends through the top of pouch 116.

Thus, in the parallel connection arrangement of the electrodes of capacitor
30 112 and battery 114, the two components may be designed to operate in a common voltage window and to achieve a higher power in their common voltage range.

Figure 3A is presented to illustrate the plasma deposition of heated particles of active positive electrode (cathode during capacitor discharge) material for

a capacitor onto one major face of an aluminum current collector foil. For example, the capacitor elements may be shaped and composed like those of capacitor 12 in Figure 1, or capacitor 112 in Figure 2, with its aluminum current collector foil 18 and positive electrode material 20.

5 Figure 3A illustrates the practice of using an atmospheric plasma application device 200 to deposit active positive electrode material particles for a capacitor in a porous layer on a surface of a metal current collector foil. In this embodiment, the finished capacitor is intended to be like capacitor 12 as illustrated in Figure 1. Figure 3A is intended to illustrate the method of applying particles of
10 positive electrode material as electrode material layer 20 on one side of current collector foil 18. Thus, the substrate is the upper surface 17 of a copper current collector foil 18 with its connection tab 18'. Connection tab 18' is not coated with the electrode material. The active positive electrode material is particles of commercially available activated carbon with their extraordinary porosity and surface area. The
15 activated carbon particles may be coated with a suitable amount of a polymer binder for bonding of the particles to each other and to surface 17 of the current collector 18.

 In this example, the current collector foil 18 is placed and carried on a movable work surface 202, such as a conveyor belt, or the like, for locating the current collector foil 18, with its upper surface 17, under the plasma application
20 device. This process may be conducted in air and in a normal ambient workplace atmosphere.

 In this example, the copper current collector foil 18 is illustrated in the form of a thin, square layer of about 100 millimeters length on each side, but the capacitor elements are also often made in other rectangular shapes and dimensions
25 depending on the intended size of the capacitor elements and assembled capacitor modules. The copper current collector foil layer 18 is often about ten to twelve micrometers in thickness. The substrate 202 is moved and placed in a flat position at ambient conditions under a suitable atmospheric plasma spray generator apparatus 200 with a nozzle for directing its flow stream of electrode material particles. The
30 spray device(s) and/or workpiece may be carried on a suitable support and moved under suitable programmable controls for sequential deposition of particulate electrode material on the surface 17 of one or more copper current collectors 18.

In practices of this invention, and with reference to Figure 3 , an atmospheric plasma apparatus 200 may comprise an upstream round flow chamber 204 (shown partly broken-off in Figure 3) for the introduction and conduct of a flowing stream of suitable working gas, such as air, nitrogen, or an inert gas such as helium or argon. The flow of the working gas would be introduced above the broken-off illustration of flow chamber 204 and proceed in a downward direction. In this embodiment, this illustrative initial flow chamber 204 is tapered inwardly to smaller round flow chamber 206. Active positive electrode material particles 208 for the capacitor (for example, activated carbon particles) are delivered through opposing supply tubes 210, 212 into round flow chamber 206. Supply tube 208 is shown partially broken-away to illustrate delivery of the positive capacitor electrode material particles 208. The electrode material particles 208 are suitably introduced from opposing sides of the apparatus 200 into the working gas stream in chamber 206 and then carried into a plasma nozzle 214 in which the air (or other working gas) is converted to a plasma stream at atmospheric pressure. As the electrode material particles 208 enter the gas stream in chamber 206 they are dispersed and mixed in the stream and carried by it. As the stream flows through the downstream plasma-generator nozzle 214, the electrode material particles 208 are heated by the formed plasma of predetermined and controlled energy to a precursor processing temperature. The momentary thermal impact on the electrode material particles may be a temperature of from about 300°C up to about 3500°C. The plasma activated electrode material particles exit nozzle 214 as stream 216.

In this example, the stream 216 of air-based plasma and suspended, plasma-activated, activated carbon electrode material particles is progressively directed by the nozzle 214 to deposit particles as a layer of electrode material 20 onto the surface of the upper surface 17 of the copper foil current collector 18. The nozzle 214 and stream 216 of suspended electrode material is moved in a suitable path and at a suitable rate such that the particulate activated carbon electrode material 208 is deposited as a porous layer 20 of specified thickness of the electrode particles on the surface 17 of the current collector foil 18.

The relative movement of the plasma spray stream 216 and/or the substrate 202 is continues until the entire face 17 of current collector foil 18 (but not tab 18') is covered with a generally uniformly thick layer of capacitor positive electrode material

20. The current collector foil may then be turned over so that its opposing face is likewise coated with a layer of positive electrode material 20.

Figure 3B is a schematic illustration of a representative positive electrode for a capacitor, like capacitor 12 in Figure 1 or capacitor 112 in Figure 2. Both major sides of aluminum current collector foil 18 have been coated, using an atmospheric plasma spray device, with substantially identical adherent layers of positive capacitor electrode material 20. Current collector tab 18' remains exposed for desired inter-connection with other capacitor electrodes or with battery electrodes or with other electrical devices.

The above described plasma spray deposition device and method may be used to deposit porous layers of particulate negative capacitor electrode material on a suitable metal foil current collector material. For example, Figure 3C illustrates a negative capacitor electrode that, in this example, consists of a copper current collector foil 22 (with extended tab 22') coated on both major faces with generally uniformly thick layers of plasma deposited negative electrode material 24. For example, the negative electrode material for the capacitor may also be suitably sized particles of a commercially-available activated carbon.

In the above described process, both the positive electrode and the negative electrode for a capacitor cell were prepared by plasma deposition of particles of the electrode material onto both sides of a suitable metal current collector. The assembly of the capacitor elements is then advanced by placing one face of positive electrode material against one side of a porous separator and one face of a negative electrode material against the opposite face of the separator. The assembled capacitor is illustrated in Figure 4. In Figure 4, the capacitor is identified by numeral 12 because it is intended to illustrate in perspective view, the capacitor structures illustrated in side view in Figures 1 and 2. As seen in Figure 4, and described in downward order from top surface, the seven layers of capacitor 12 comprise porous layer 20 of positive capacitor electrode material, copper positive electrode current collector foil 18 with its uncoated connector tab 18', the opposing layer of porous positive electrode material 20, porous separator 26, a layer of porous negative capacitor electrode material 24, aluminum negative electrode current collector foil 22 with its uncoated connector tab 22', and an opposing layer of porous positive electrode material 24. It is seen that a layer of positive electrode material 20 and a

layer negative electrode material 24 are pressed against the corresponding faces of the porous separator 26.

When capacitor 12 has been assembled with a like-shaped and like-made battery (e.g., battery 14) in a suitable container, like pouch 16, both the capacitor and
5 battery will be suitably infiltrated with a shared lithium-ion transporting electrolyte.

In the above described plasma application process, particulate cathode material was plasma coated on both sides of an aluminum current collector foil to form a capacitor cathode, and particulate anode material was plasma coated onto both sides of a copper current collector foil to form a capacitor anode. The assembly of the
10 capacitor cell was then completed by placing a cathode on one side of a suitable porous separator and a cathode on the other side of the separator. A like plasma deposition process, using suitable electrode materials, may be used to make and assemble a lithium-ion battery cell for the hybrid combination.

In a second plasma deposition process, similar to that illustrated in Figure
15 3a, particles of cathode electrode material are deposited on one side of a suitable separator. Then particles of a current collector metal (e.g., Al) are plasma deposited onto the particulate cathode layer. Then, a second layer of particulate cathode material may be plasma deposited on the current collector layer. Particles of anode electrode material, metal current collector material, and anode electrode material are
20 then sequentially plasma deposited onto the opposite side of the separator. The result of the six layers of plasma-deposited is equivalent to the seven layer capacitor structure illustrated in Figure 4.

As stated, either plasma deposition process, using appropriate particulate electrode materials and current collector material may be used to make the
25 electrochemical cell structures of either a lithium-ion using capacitor or a lithium-ion battery. The plasma deposition process can be conducted, for example, in parallel or other complementary manufacturing lines to simultaneously produce complementary capacitors and batteries for assembly into suitable containers for hybrid combination. The porous elements of the combined assembly are then infiltrated or impregnated
30 with a suitable lithium ion containing electrolyte. And capacitor and battery members of the combination may be charged or otherwise prepared for their respective electrochemical functions.

As stated, the layers of the respective electrode material particles is pre-deposited on a compatible current collector surface or a compatible separator surface using one or more atmospheric plasma nozzles or deposition devices. Such plasma nozzles for this application are commercially available and may also be carried and used on robot arms, under multi-directional computer control, to apply suitable electrode particles to coat the surfaces of each metal current collector foil or separator surface for a lithium-using capacitor and, separately, for a lithium-ion cell. Multiple nozzles may be required and arranged in such a way that a desired coating speed may be achieved in terms coated area per unit of time.

The atmospheric plasma nozzle typically has a metallic tubular housing which provides a flow path of suitable length for receiving the flow of working gas, receiving and dispersing particles of electrode material, and for enabling the formation of the plasma stream in an electromagnetic field established within the flow path of the tubular housing. The tubular housing terminates in a conically tapered outlet, shaped to direct a suitably shaped plasma stream toward an intended substrate to be coated. An electrically insulating ceramic tube is typically inserted at the inlet of the tubular housing such that it extends along a portion of the flow passage. A stream of a working gas, such as air (or nitrogen or argon), and carrying dispersed particles of a specified electrode material, is introduced into the inlet of the nozzle. The flow of the air-particle mixture may be caused to swirl turbulently in its flow path by use of a swirl piece with flow openings, also inserted near the inlet end of the nozzle. A linear (pin-like) electrode is placed at the ceramic tube site, along the flow axis of the nozzle at the upstream end of the flow tube. During plasma generation the electrode is powered by a suitable generator at a frequency in the 0.1 hertz to gigahertz range and to a suitable potential of a few kilovolts. Plasma generation technology such as corona discharge, radio wave, and microwave sources, and the like, may be employed. The metallic housing of the plasma nozzle is grounded. Thus, an electrical discharge can be generated between the axial pin electrode and the housing. No vacuum chamber is used.

When the generator voltage is applied, the frequency of the applied voltage and the dielectric properties of the ceramic tube produce a corona discharge at the stream inlet and the electrode. As a result of the corona discharge, an arc discharge from the electrode tip to the housing is formed. This arc discharge is carried by the

turbulent flow of the air/particulate electrode material stream to the outlet of the nozzle. A reactive plasma of the air (or other carrier gas) and dispersed electrode particles is formed at a relatively low temperature. A copper nozzle at the outlet of the plasma container is shaped to direct the plasma stream in a suitably confined path
5 against the surfaces of the current collector substrates for the lithium-ion cell electrode members. The energy of the plasma may be determined and managed for the material to be applied.

Thus, specific examples have been presented for the use of plasma spray deposition devices and methods in the preparation of lithium-ion incorporating
10 capacitors and batteries for assembly into a common container to serve as hybrid electrochemical devices for provision of electrical power in many devices consuming electrical energy. The examples are intended to illustrate practices of the invention and not the scope of the following claims.

15

CLAIMS

1. A method of forming a hybrid combination of a (i) lithium-ion battery and (ii) a capacitor that both use a common lithium ion conducting electrolyte; the method comprising:

5 forming porous positive and negative electrode material layers for the capacitor by separately using an atmospheric plasma stream to deposit particles of capacitor positive electrode material as a porous positive electrode layer bonded to a one side of a porous separator member or to a metal positive electrode current collector, and, separately, to deposit particles of capacitor negative electrode material
10 as a porous negative electrode layer bonded to the opposing side of a porous separator member or to a metal negative electrode current collector, at least one of the positive and negative electrode materials being of a composition to work with the electrolyte used with the lithium-ion battery;

 assembling one or more pairs of capacitor positive and negative electrodes
15 as a capacitor with each positive electrode layer bonded to a porous separator on one of its layer sides and to a positive electrode current collector on the other of its layer sides, and with one layer side of each negative electrode layer bonded to the opposite side of a porous separator from a positive electrode layer and to a negative electrode current collector on the other of its negative electrode layer sides;

20 placing the assembled capacitor in a container with a lithium-ion battery comprising one or more pairs of porous layer, positive and negative electrode members with corresponding porous separators ; and

 infiltrating the porous electrodes and separators of the capacitor and the porous layer electrodes and separators of the lithium-ion battery with the same lithium
25 ion conducting liquid electrolyte composition.

2. A method of forming a hybrid combination of a (i) lithium-ion battery and (ii) a capacitor as stated in claim 1 in which porous layer electrodes and separators of the lithium-ion battery are formed with like sizes and shapes as the
30 electrodes and separators for the capacitor.

3. A method of forming a hybrid combination of a (i) lithium-ion battery and (ii) as recited in claim 1 in which particles of capacitor positive electrode material

are deposited as a positive capacitor electrode layer on one side of a porous separator and particles of a capacitor negative electrode layer are deposited as a negative capacitor electrode layer on the other side of the porous separator layer.

5 4. A method of forming a hybrid combination of a (i) lithium-ion battery and (ii) as recited in claim 3 in which particles of metal current collector material are deposited on the sides of each of the positive electrode layer and the negative electrode layer that are not bonded to the porous separator.

10 5. A method of forming a hybrid combination of a (i) lithium-ion battery and (ii) as recited in claim 4 in which a layer of positive electrode material is deposited on the exposed side of the positive electrode current collector and a layer of negative electrode material is deposited on the exposed side of the negative electrode current collector.

15 6. A method of forming a hybrid combination of a (i) lithium-ion battery and (ii) as recited in claim 1 in which layers of capacitor positive electrode material are deposited on both sides of a positive current collector foil to form a positive capacitor electrode, layers of capacitor negative electrode material are deposited on
20 both sides of a negative current collector foil to form a capacitor negative electrode, and the capacitor electrodes are placed on opposite sides of a porous separator.

 7. A method of forming a hybrid combination of a (i) lithium-ion battery and (ii) as recited in claim 6 in which the positive current collector foil is an
25 aluminum foil and the negative current collector foil is a copper foil.

 8. A method of forming a hybrid combination of a (i) lithium-ion battery and (ii) as recited in claim 1 in which the capacitor positive electrode material comprises activated carbon or graphite.

30 9. A method of forming a hybrid combination of a (i) lithium-ion battery and (ii) as recited in claim 1 in which the capacitor negative electrode material comprises activated carbon or graphite.

10. A method of forming a hybrid combination of a (i) lithium-ion battery and (ii) as recited in claim 1 in which the capacitor positive electrode material comprises activated carbon and the capacitor negative electrode material comprises
5 $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

11. A method of making a combination of (i) a lithium-ion battery and (ii) a capacitor comprising an electrode that uses the lithium-containing electrolyte composition of the lithium-ion battery, for placement of the capacitor and battery in a
10 common container for use with a common lithium ion conducting electrolyte; the capacitor comprising a plurality of positive capacitor electrode layers and of negative capacitor electrode layers, one side of each positive electrode layer facing one side of a negative electrode layer with the facing sides of the electrode layers being physically separated by a porous separator layer, and the opposing sides of the
15 electrode layers being bonded to current collector foils; the method comprising:

heating particles of positive capacitor electrode material in an atmospheric plasma stream and depositing the heated particles as a porous positive capacitor electrode layer, either on the surface of a metal current collector foil for the positive electrode material or on one surface of a porous capacitor separator with two
20 opposing surfaces;

heating particles of negative capacitor electrode material in an atmospheric plasma stream and depositing the heated particles as a porous negative capacitor electrode layer, either on the surface of a metal current collector foil for the negative electrode material or on the opposing surface of the porous capacitor separator;

25 completing the formation of the capacitor with a surface of each of the atmospheric plasma-deposited positive and negative electrode layers separated from electrical contact by a porous separator and with the opposite surface of each capacitor electrode being covered and bonded for electrical contact with a metal current collector shaped with a connector tab for electrical contact with another
30 electrode member;

placing the capacitor in a common container with a lithium-ion battery comprising porous battery electrodes and separators, but with the capacitor and lithium-ion battery separated from physical contact with each other; and

infiltrating the electrodes and separators of the capacitor and battery with a common lithium ion-conducting electrolyte.

12. A method of making a combination of (i) a lithium-ion battery and (ii) a capacitor as recited in claim 11 in which particles of capacitor positive electrode material are plasma deposited on both sides of a metal current collector to form a capacitor positive electrode, particles of capacitor negative electrode material are plasma deposited on both sides of a metal current collector to form a capacitor negative electrode, and the positive and negative electrodes are placed on opposite sides of a porous separator.

13. A method of making a combination of (i) a lithium-ion battery and (ii) a capacitor as recited in claim 11 in which particles of capacitor positive electrode material are plasma deposited as a positive electrode layer on one side of a porous capacitor separator, particles of capacitor negative electrode material are plasma deposited as a negative electrode layer on the opposite side of a porous capacitor separator, and metallic current collectors with connector tabs are formed on the exposed sides of the positive electrode layer and the negative electrode layer.

14. A method of making electrode materials for a positive electrode-separator-negative electrode structure of a capacitor which is to be used in combination with a positive electrode-separator-negative electrode structure of a lithium-ion battery, the capacitor electrode materials being compatible with like-made electrode materials for the lithium-ion battery, the capacitor electrode materials and lithium-ion battery electrode materials being made for use with a common lithium-conducting electrolyte and placement in a common container as a hybridized combination, the method comprising:

depositing particles, which are dispersed and heated in an atmospheric plasma stream, as a porous layer of capacitor positive electrode material, deposited, either on a surface of a metal current collector foil for the positive electrode material or on a surface of a porous capacitor separator with two opposing surfaces, to form a porous layer of positive electrode material with one layer side contacting the current

collector foil, or the surface of the separator, and with an opposing positive electrode material layer side;

- separately depositing particles, which are dispersed and heated in an atmospheric plasma stream, as a layer of capacitor negative electrode material, either
5 on the surface of a metal current collector foil for the negative electrode material or on one surface of a porous capacitor separator with two opposing surfaces, to form a porous layer of negative electrode material with one layer side contacting the negative current collector foil, or the surface of the separator, and an opposing negative electrode material layer side; and
10 using the plasma deposited layer of capacitor positive electrode material and the plasma deposited layer of capacitor negative electrode material in an assembly of a layered capacitor structure comprising a porous separator with a layer of capacitor positive electrode material on one separator surface and a layer of capacitor negative electrode material on the opposing separator surface, and each of the layers
15 of capacitor electrode material having a current collector foil on their opposing material layer side.

15. A method of making electrode materials for a capacitor as recited in claim 14 in which

- 20 a layer of capacitor positive electrode particles are plasma deposited on each side of a metallic current collector foil to form a positive capacitor electrode;
a layer of capacitor negative electrode materials are plasma deposited on each side of a metallic current collector foil to form a negative capacitor electrode; and
25 the positive capacitor electrode is placed with one of its layers of electrode particles against one side of a porous separator and the negative electrode is placed with one of its layers of electrode particles against the opposite side of the porous separator to form the positive electrode-separator-negative electrode structure of a capacitor.

- 30 16. A method of making electrode materials for a capacitor as recited in claim 14 in which

a layer of capacitor positive electrode particles are plasma deposited on one side of a porous separator; a layer of particles of a metallic current collector are deposited on the layer of particles of capacitor positive electrode material, and a layer of capacitor positive electrode particles are plasma deposited on the metallic current collector layer; and

a layer of capacitor negative electrode particles are plasma deposited on the opposite side of the porous separator; a layer of particles of a metallic current collector are deposited on the layer of particles of capacitor negative electrode material, and a layer of capacitor negative electrode particles are plasma deposited on the metallic current collector layer to form the positive electrode-separator-negative electrode structure of a capacitor.

17. A method of making electrode materials for a capacitor as recited in claim 15 and further comprising placing the positive electrode-separator-negative electrode structure of the capacitor into a common container with, but spaced from, the positive electrode-separator-negative electrode structure of a lithium battery and impregnating the electrodes and separators of both the capacitor and lithium-ion battery with a liquid, lithium-conducting electrolyte.

18. A method of making electrode materials for a capacitor as recited in claim 16 and further comprising placing the positive electrode-separator-negative electrode structure of the capacitor into a common container with, but spaced from, the positive electrode-separator-negative electrode structure of a lithium battery and impregnating the electrodes and separators of both the capacitor and lithium-ion battery with a liquid, lithium-conducting electrolyte.

19. A method of making electrode materials for a capacitor as recited in claim 17 in which a plurality of positive electrode-separator-negative electrode structures are placed in the common container with intervening separators and with the positive electrodes connected to a positive electrode terminal and the negative electrodes connected to a negative electrode terminal.

20. A method of making electrode materials for a capacitor as recited in claim 18 in which a plurality of positive electrode-separator-negative electrode structures are placed in the common container with intervening separators and with the positive electrodes connected to a positive electrode terminal and the negative
- 5 electrodes connected to a negative electrode terminal.

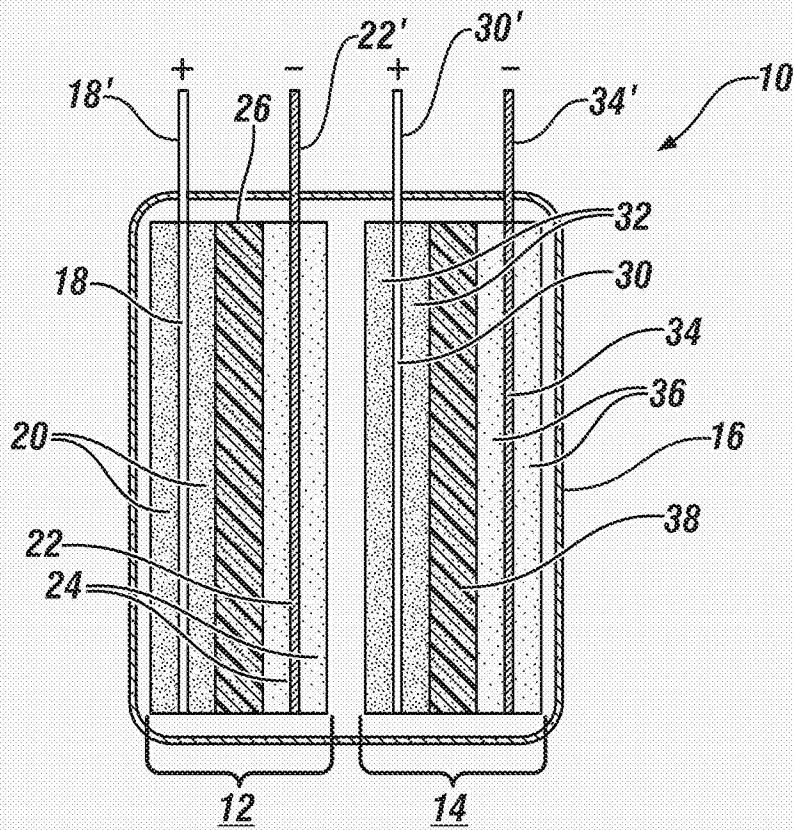


FIG. 1

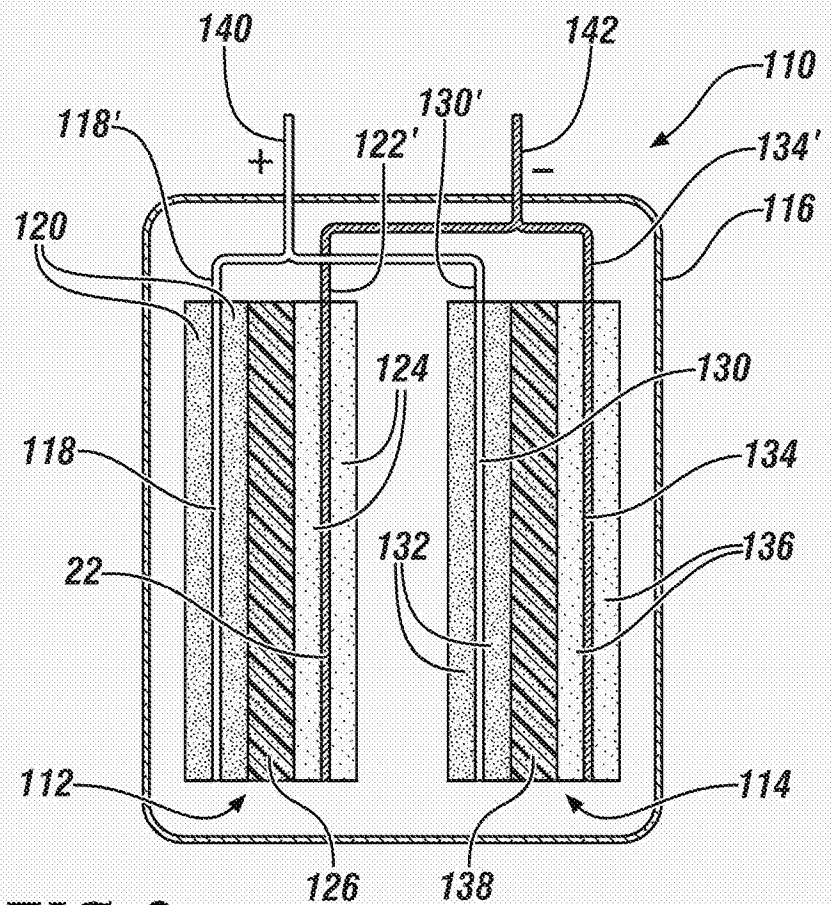
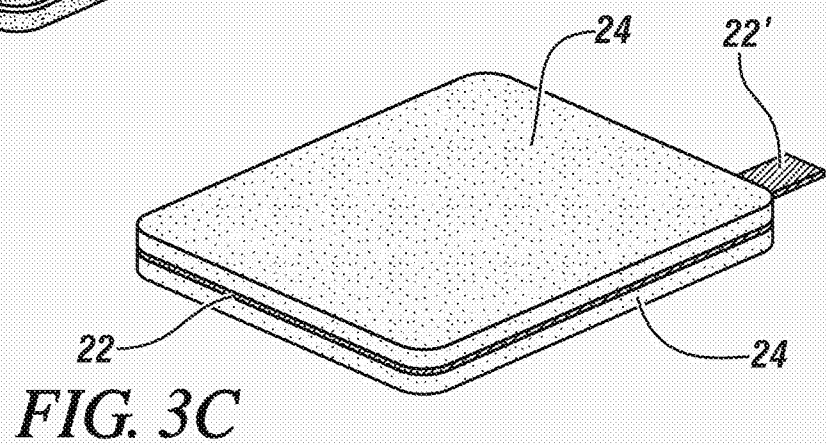
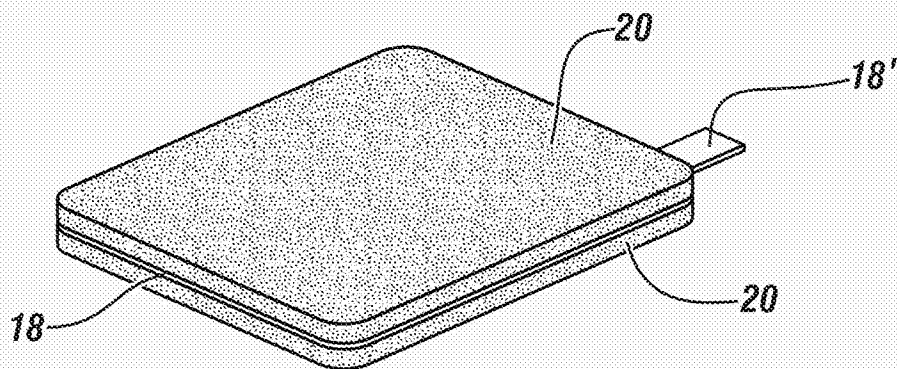
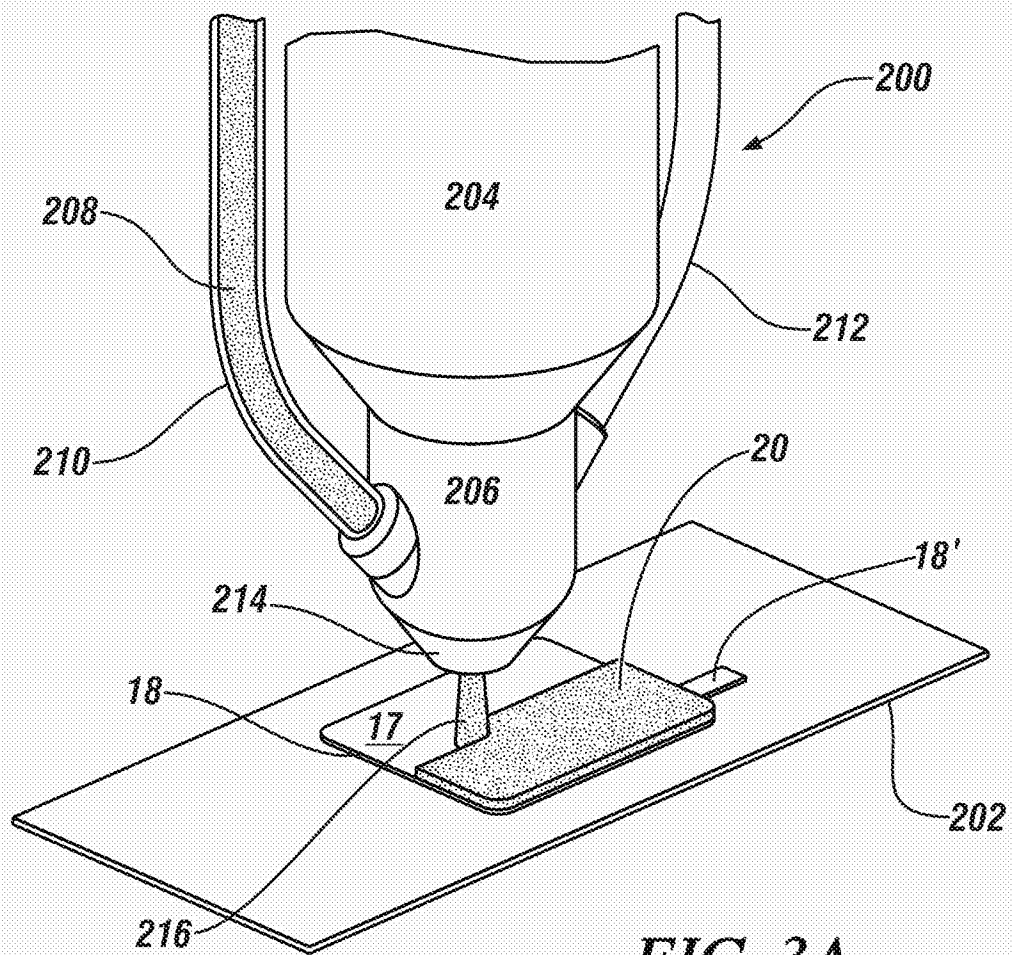


FIG. 2



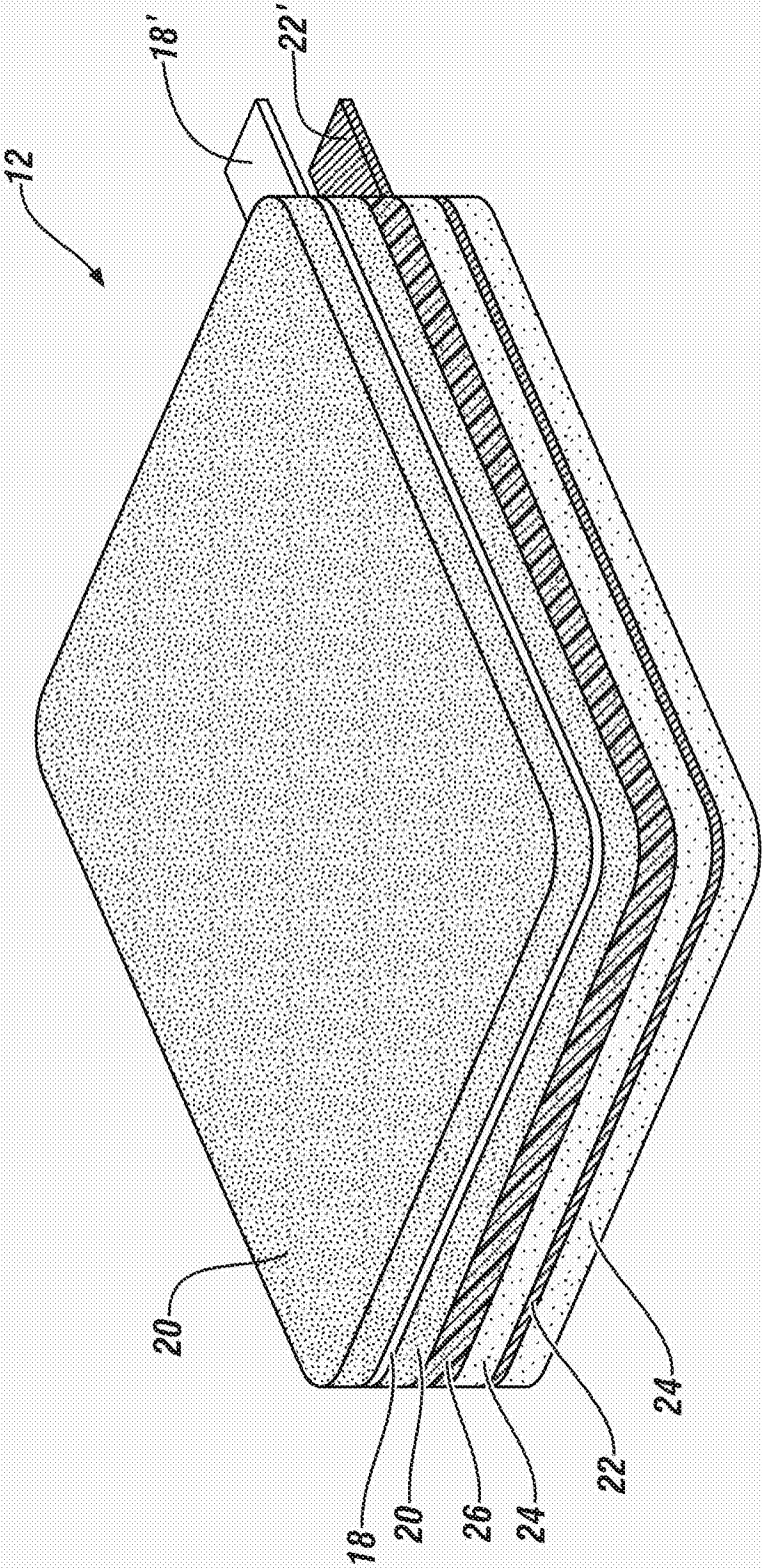


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/075046**A. CLASSIFICATION OF SUBJECT MATTER**

H01G 11/08(2013.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01G; H01M

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

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

WPI;EPODOC;lithium,deposit,thermal spray,plasma,electrode,atmosphere,connector tab, capacitor, battery

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101517817 A (LG CHEM., LTD.) 26 August 2009 (2009-08-26) description, page 3, line 2 to page 9, line 21, figures 1-3	1-20
A	CN 103280334 A (WANG, ZIQI) 04 September 2013 (2013-09-04) the whole document	1-20
A	CN 102306755 A (ZIBO QISHENG NEW ENERGY TECHNOLOGY CO.) 04 January 2012 (2012-01-04) the whole document	1-20

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

“A”	document defining the general state of the art which is not considered to be of particular relevance	“T”	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“E”	earlier application or patent but published on or after the international filing date	“X”	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“L”	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“Y”	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“O”	document referring to an oral disclosure, use, exhibition or other means	“&”	document member of the same patent family
“P”	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

12 June 2015

Date of mailing of the international search report

29 June 2015

Name and mailing address of the ISA/CN

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2015/075046

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				US	8574736	B2	05 November 2013
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