

19



Octrooi Centrum
Nederland

11

2015824

12 B1 OCTROOI

21

Aanvraagnummer: **2015824**

22

Aanvraag ingediend: **20/11/2015**

51

Int. Cl.:

H01G 11/06 (2016.01) **H01M 4/133** (2016.01) **H01M 10/0525** (2016.01) **H01M 12/00** (2016.01) **H01M 2/16** (2016.01) **H01G 11/86** (2016.01) **H01G 11/50** (2016.01) **H01G 11/14** (2016.01) **H01G 11/60** (2016.01) **H01G 11/62** (2016.01)

30

Voorrang:

12/12/2014 CN 201410764686.1

43

Aanvraag gepubliceerd:

21/09/2016

47

Octrooi verleend:

15/02/2017

45

Octrooischrift uitgegeven:

27/03/2017

73

Octrooihouder(s):

NINGBO CSR NEW ENERGY TECHNOLOGY CO., LTD te Zhejiang Ningbo City, China, CN.

72

Uitvinder(s):

Dianbo Ruan te Ningbo City (CN).
Fudi Zeng te Ningbo City (CN).
Guansheng Fu te Ningbo City (CN).

74

Gemachtigde:

dr. J. van Straaten te Uden.

54

Pre-embedment method for Li-ion capacitors.

57

The present invention provides a novel pre-embedment method for a Li-ion capacitor, comprising the following steps of: (1) assembling a cell, and immersing the cell into an organic solution containing lithium salt; (2) connecting the anode and the cathode to a charge-discharge tester, respectively, to perform total 1 to 100 cycles each comprising one charge followed by one discharge, to finish the pre-embedment into the cathode; and (3) taking out the cell after the pre-embedment and putting the cell into a packaging shell, and injecting electrolyte into the packaging shell to form a single lithium ion capacitor. With the novel pre-embedment method of the preset invention, high cost resulted from the metal lithium and porous current collectors is effectively solved. The safety may be improved and the technological process may be simplified. The novel pre-embedment method of the preset invention is suitable for industrial production.

PRE-EMBEDMENT METHOD FOR LI-ION CAPACITORS

Technical Field of the Invention

The present invention relates to the field of Li-ion capacitors, and in particular to
5 a novel pre-embedment method for a Li-ion capacitor.

Background of the Invention

Li-ion capacitors are novel classic hybrid energy storage devices incorporating
Li-ion batteries into electric double-layer super capacitors. With both high specific
10 energy of Li-ion capacitors and high specific power, long service life and the like of
super capacitors together, such Li-ion capacitors have wide prospect of application in
fields such as military aerospace and green energy. At present, the pre-embedment
method for Li-ion capacitors is generally as that shown in Patent CN101138058B
owned by Fuji Heavy Industries. That is, lithium metal is used as a lithium source and
15 metal foil with through holes as a current collector; the lithium metal is placed in a
position opposite to cathode; and by connecting the lithium metal to the cathode in
short circuit, discharge is achieved due to a difference in potential between the lithium
metal and the cathode, thus to embed the Li-ion into the cathode. By this method, it is
possible to obtain a large-capacitance large-scale power storage device which has
20 high energy density and output density and has an excellent charge-discharge
characteristic. However, there are the following problems: first, since the chemical
properties of lithium and foil are highly active, the production of Li-ion capacitors
propose quite high requirements on the environment; second, it is required to
precisely control the amount of lithium to be used because too less lithium will not
25 achieve the expected effect while too much lithium will bring great safety risk to a
single capacitor, resulting in poor consistency in single capacitors; and third, Li-ion
capacitors are complex in manufacturing process, and the use of crucial raw materials
such as lithium metal and porous current collector results in high cost of Li-ion
capacitors.

30 In the prior art, there is a case where the short-circuit discharge and lithium

doping manner by connection of the cathode to lithium metal in short circuit is changed to connection of a charge-discharge tester between the cathode and the lithium metal, so that the Li-ion is embedded into the cathode carbon material by discharge or charge-discharge cycles. Although this method may allow for somewhat improvement to the performance of a single Li-ion capacitor, it fails to solve safety, production cost and other problems.

Chinese Patent Application CN102385991A disclosed a method for manufacturing a Li-ion capacitor and an application of the manufactured Li-ion capacitor, wherein the disclosed pre-embedment method was to form a lithium film on a surface of a diaphragm by vacuum vapor deposition, bring the lithium film to be opposite to the cathode, and pre-embed the Li^+ in the lithium film into the cathode. Compared with the method disclosed by Fuji Heavy Industries, this method has the following advantages: first, since the lithium film is in direct contact with the cathode for pre-embedment in a subsequent process, there is no need to use any through-hole current collector and this may decrease the internal resistance of the products; second, by this method, it may be convenient to control the amount of lithium to be used so that the safety is improved to some extent; and third, since each layer of the cathode is in direct contact with the lithium film for lithium doping, the time required by lithium pre-doping may be greatly shortened. This method is feasible theoretically. However, its practical feasibility remains to be proven.

J.P. Zheng team (W.J. Cao, J.P. Zheng, Li-ion capacitors with carbon cathode and hard carbon/stabilized lithium metal powder anode electrodes, Journal of Power Sources, 213(2012) 180-185.) mixed nanoscale lithium metal powder having a passivation layer on its surface, as a lithium source, with hard carbon to prepare a cathode by a dry process, and then used activated carbon as an anode to form a single Li-ion capacitor. Compared with the structure proposed by Fuji Heavy Industries where lithium foil is used, a Li-ion capacitor of this structure may be manufactured in a dry room, without requiring a severe glovebox environment, thereby greatly increasing the operability.

Summary of the Invention

In order to solve problems of high pre-embedment and production cost, high safety risk, and complex process of a Li-ion capacitor, a novel pre-embedment method for a Li-ion capacitor is proposed. With the novel pre-embedment method of the preset invention, high cost resulted from the lithium metal and porous current collectors is effectively solved. The safety may be improved and the technological process may be simplified. The novel pre-embedment method of the preset invention is suitable for industrial production. The present invention is realized through the following technical solutions: in order to realize the objective, the present invention provides a novel pre-embedment method for a Li-ion capacitor, including the following steps of:

(1) stacking or winding a cathode, a diaphragm, an anode and a diaphragm successively and then securing with an adhesive tape to form a cell, and immersing the cell into an organic solution containing lithium salt;

(2) connecting the anode and the cathode to a charge-discharge tester, respectively, to perform a number of times, preferably a total 1 to 100 cycles, each including one charge followed by one discharge, to finish the pre-embedment into the cathode; and

(3) taking out the cell after the pre-embedment and putting the cell into a packaging shell, and injecting electrolyte into the packaging shell to form a single Li-ion capacitor. Preferably, the anode current collector may be a foil or mesh of metals such as aluminous, stainless steel, iron and nickel, and the foil may be with or without pores.

Preferably, the cathode current collector may be foil or mesh of metals such as copper, stainless steel, iron and nickel, and the foil may be with or without pores.

Preferably, the lithium salt may be one of lithium salts, which are soluble in the organic solution, selected from LiPF_6 , LiBF_4 , LiClO_4 , LiAlO_4 , LiOH , Li_2CO_3 , CH_3COOLi , LiNO_3 , $\text{LiB}(\text{C}_2\text{O}_4)_2$, $\text{LiP}(\text{C}_6\text{H}_4\text{O}_2)_3$, $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$ and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$.

PC (polycarbonate), EC (ethylene carbonate), DEC (diethyl carbonate), DMC (dimethyl carbonate), DMF (dimethyl Fumarate), DME (1,2-dimethoxy-ethan) and

THF (tetrahydrofuran).

Preferably, the way of connecting the anode to the cathode is connecting the anode to the cathode by charge-discharge equipment. In the whole loop, resistors may be added for connection in series, or direct connection may be realized without
5 any resistors.

Preferably, the cell immersed into an organic solution containing lithium salt is subject to a cycle of charge $\rightarrow$ discharge or charge $\rightarrow$ self-discharge, and both the charge current and the discharge current are constant currents. Specifically, the constant current may be a current value corresponding to a rate of 0.01 C -10 C
10 calculated based on the mass of the anode, the cathode or the cell.

Preferably, there is 1 to 100 charge-discharge cycles, the highest cut-off for the charge ranges from 3.6 V to 4.2 V, and the charge cut-off voltage in each of the cycles may be the same or different.

Preferably, the charge current in each of the cycles may be the same or different;
15 and the discharge current in each of the cycles may be the same or different. There may be or may not be a constant voltage process followed by each charge process.

Preferably, the self-discharge in each of the cycles lasts 1 min to 10 h, and the self-discharge duration in each of the cycles may be the same or different.

Preferably, the cyclic charge-discharge processing is performed at a constant
20 temperature ranging from 0°C to 60°C.

The Li-ion capacitor will produce a certain amount of heat during the charge-discharge process to rise the temperature of the cell of the capacitor. If the temperature of the cell of the capacitor is not controlled and when the temperature rises to a certain degree, electrolyte in the cell of the capacitor will decompose to
25 generate a large amount of gas which will shock the cell of the well assembled Li-ion capacitor to damage the diaphragms and plates of the cell. Performing the charge-discharge process at a lower temperature may effectively inhibit the decomposition of the electrolyte in the cell of the capacitor, reduce or even eliminate the generation of gas, and thus protect the diaphragms and plates of the cell of the
30 capacitor against damage.

Preferably, a charge regime in the cyclic discharge process is as follows:

(1) at a pre-charge stage: charging with a low current of 0.01-0.05 C when the voltage of the capacitor is lower than 3 V;

(2) at a constant-current high-rate charge stage: charging with a current having a charge rate of 0.1-0.5 C when the voltage of the capacitor is greater than 3 V and lower than 3.5 V;

(3) at a constant-current low-rate charge stage: charging with a current having a charge rate of 0.05-0.1 C when the voltage of the capacitor is greater than 3.5 V and lower than the highest cut-off voltage; and

(4) at a constant voltage charge stage: charging under a constant voltage when the voltage of the capacitor reaches the highest cut-off voltage, until the charge current is lower than 10-20 mA, and then stopping charging, the constant voltage being the highest cut-off voltage;

a discharge regime is as follows:

(1) at a first discharge stage: discharging with a discharge current having a discharge rate of 1-2 C when the voltage of the capacitor is greater than 3.5V and lower than or equal to the highest cut-off voltage;

(2) at a second discharge stage: discharging with a discharge current having a discharge rate of 0.5-1 C when the voltage of the capacitor is greater than 3V and lower than or equal to 3.5 V; and

(3) at a third discharge stage: discharging with a discharge current having a low discharge rate of 0.1-0.5 C when the voltage of the capacitor is lower than 3V.

Charging with a low current at the pre-charge stage may enable the capacitor to reach a high voltage in a stable state. The constant-current high-rate charging may enable the capacitor to reach a high voltage quickly. Since the cut-off voltage of the Li-ion capacitor ranges from 3.6 V to 4.2 V, after reaching 3.5 V by the high-rate constant-current charging, charging with a current having a low rate may prevent the voltage of the Li-ion capacitor from exceeding the cut-off voltage thus to prevent degradation of the performance of the capacitor. After the voltage of the capacitor reaches the cut-off voltage, charging under a constant voltage is required to continue

to increase the capacity of the capacitor, while preventing over-voltage.

At an initial discharge stage of the capacitor, discharging in a high discharge rate may discharge as soon as possible if the performance of the capacitor permits; at a final discharge stage, discharging in a low rate may prevent, during the discharge process, the voltage of the capacitor from falling below the lowest acceptable voltage of the capacitor, thereby preventing the capacitor from being damaged by excessive discharge and too low voltage.

Preferably, the diaphragm is a composite diaphragm having polypropylene as a matrix, and the composite diaphragm having polypropylene as a matrix is prepared from the following substance by the following steps: uniformly mixing 80-85 wt% of polypropylene, 10-15 wt% of natural cellulose pulp, 3-5 wt% of kaolin powder and 0.5-1.5 wt% of silane coupling agent, and then processing by a dry process.

Preferably, the natural cellulose pulp in the polypropylene-based composite diaphragm is made by the following steps of:

(1) adding bamboo fiber as raw material to a sodium hydroxide solution, and then steaming the sodium hydroxide solution in vacuum at 300°C for 2 h, wherein the mass ratio of the bamboo fiber to the sodium hydroxide solution is 1:4, and the concentration of the sodium hydroxide solution is 10 wt%;

(2) taking out and washing the steamed bamboo fiber with water, then immersing the bamboo fiber into hot water at a temperature of 80-90°C for grinding followed by filtering, and then collecting the filtered solid; and

(3) pulping the filtered solid by a pulping machine and concentrating to obtain the natural cellulose pulp having a solid content of 60-70 wt%.

The natural cellulose pulp manufactured by this method contains a large amount of natural cellulose which has advantages of good moisture absorption and excellent thermal stability. The moisture absorption and thermal stability of the polypropylene may be improved after mixing a small amount of the natural cellulose with polypropylene so that the absorption retention of the diaphragm to the electrolyte is enhanced, thereby improving the rate performance and cycle performance of products.

Additionally, the natural cellulose generates cross-linking after being mixed with

polypropylene and this enhances the tensile strength and puncture resistance strength of the diaphragm.

Compared with the prior art, the present invention has the following beneficial effects:

5 (1) replacing the lithium foil or nanoscale lithium metal with the organic solution containing lithium salt reduces the cost, and meanwhile the use of non-porous current collectors also significantly reduces the cost;

(2) replacing the lithium foil with the organic solution containing lithium salt requires no processing in an extreme environment, and as a result, the safety of
10 processing is improved;

(3) connecting the anode and the cathode with the charge-discharge tester may shorten the time required by the pre-embedment and improve the effect thereof; and

(4) the simplification of the technological process may be suitable for mass industrial production.

15

Brief Description of the Drawings

Fig.1 is a schematic diagram of tests of the specific capacity of a capacitor;
in which:

the vertical axis represents specific capabilities of the capacitor tested at different
20 discharge currents, and the horizontal axis represents discharge currents.

Detailed Description of the Invention

The content of the present invention will be described more specifically in conjunction with embodiments. It should be understood that the implementations of
25 the present invention are not limited to the following embodiments, and instead, variations and changes in any form to the present invention will all fall into the protection scope of the present invention; and all methods in the following embodiments are conventional methods in the art, otherwise specifically stated.

Embodiment 1

30 A pre-embedment method for a lithium ion capacitor includes the following steps

of:

(1) adhering pulp containing activated carbon as active material to non-porous aluminum foil to serve as an anode, and adhering pulp containing mesophase carbon micro beads as active material to non-porous copper foil to serve as a cathode; by using a PP(Polypropylene)/PE(polyethylene)/PP tri-layer polymer as a diaphragm, stacking the diaphragm, the anode, the diaphragm and the cathode successively to form a cell, and then securing with an adhesive tape; and welding current collectors of both the anode and the cathode to tabs or leading-out terminals of both the anode and the cathode, respectively;

(2) drying, and immersing the dried cell into a beaker containing a $\text{LiPF}_6\text{-EC/PC/DEC}$ solution;

(3) connecting an anode and a cathode of a charge-discharge tester to the anode and the cathode, respectively, charging with a constant current of approximately 0.1 C until the voltage reaches 3.8 V and keeping at 3.8 V for 1 h, turning the circuit off and standing for 1 h so that a single capacitor discharges naturally, turning the circuit on again after 1 h later and charging with a constant current of 0.1 C until the voltage reaches 3.8 V, and then turning the circuit off again so that the single capacitor discharges naturally for 1 h, all of which steps are repeated for three charge/self-discharge pulse periods; and

(4) taking the cell obtained in step (3) out and putting the cell into an aluminum-plastic shell, and injecting electrolyte into the aluminum-plastic shell to form a single flexibly packaged capacitor.

Embodiment 2

A pre-embedment method for a lithium ion capacitor includes the following steps

of:

(1) adhering pulp containing activated carbon as active material to non-porous aluminum foil to serve as an anode, and adhering pulp containing artificial graphite as active material to non-porous copper foil to serve as a cathode; by using a PP/PE/PP tri-layer polymer as a diaphragm, stacking the diaphragm, the cathode, the diaphragm and the anode successively to form a cell, and then securing with an adhesive tape;

and welding current collectors of both the anode and the cathode to tabs or leading-out terminals of both the anode and the cathode, respectively;

(2) drying, and immersing the dried cell into a beaker containing a $\text{LiBF}_4\text{-PC/DMF}$ solution;

5 (3) connecting an anode and a cathode of a charge-discharge tester to the anode and the cathode, respectively, charging with a constant current of approximately 0.1 C until the voltage reaches 3.8 V, turning the circuit off and standing for 2 h so that a single capacitor discharges naturally, turning the circuit on again after 2 h later and charging with a constant current of 0.1 C until the voltage reaches 3.8 V, and then
10 turning the circuit off again so that the single capacitor discharges naturally for 2 h, all of which steps are repeated for ten charge/self-discharge pulse periods; and

(4) taking the cell obtained in step (3) out, putting the cell into a square aluminum shell, and injecting electrolyte into the square aluminum shell to form a single square capacitor.

15 Embodiment 3

A pre-embedment method for a lithium ion capacitor includes the following steps of:

(1) adhering pulp containing activated carbon as active material to porous aluminum foil to serve as an anode, and adhering pulp containing hard carbon as
20 active material to porous copper foil to serve as a cathode; by using a single-PP polymer as a diaphragm, winding the diaphragm, the cathode, the diaphragm and the anode successively to form a cell, and then securing with an adhesive tape; and welding current collectors of both the anode and the cathode to tabs or leading-out terminals of both the anode and the cathode, respectively;

25 (2) drying, and immersing the dried cell into a beaker containing a Li_2CO_3 organic solution;

(3) connecting an anode and a cathode of a charge-discharge tester to the anode and the cathode, respectively, charging with a constant current of approximately 0.2 C until the voltage reaches 3.8 V, turning the circuit off and standing for a certain period
30 of time so that a single capacitor discharges naturally, turning the circuit on again and

charging with a constant current of 0.2 C until the voltage reaches 3.8 V, and then turning the circuit off again so that the single capacitor discharges naturally for a certain period of time, all of which steps are repeated for fifty charge/self-discharge pulse periods (wherein the self-discharge lasts for 0.5 h in the first to tenth periods, the self-discharge lasts for 1 h in the eleventh to twentieth periods, the self-discharge lasts for 1.5 h in the twenty first to thirtieth periods, the self-discharge lasts for 2 h in the thirty first to fortieth periods, and the self-discharge lasts for 3 h in the fortieth to fiftieth periods); and

(4) taking the cell obtained in step (3) out and putting the cell into a round aluminum shell, and injecting electrolyte into the round aluminum shell to form a single round capacitor.

Embodiment 4

A pre-embedment method for a lithium ion capacitor includes the following steps of:

(1) adhering pulp containing activated carbon as active material to non-porous aluminum foil to serve as an anode, and adhering pulp containing mesophase carbon micro beads as active material to non-porous copper foil to serve as a cathode; by using polypropylene-based natural fiber composite material as a diaphragm, stacking the diaphragm, the cathode, the diaphragm and the anode successively to form a cell, and then securing with an adhesive tape; and welding current collectors of both the anode and the cathode to tabs or leading-out terminals of both the anode and the cathode, respectively;

(2) drying, and immersing the dried cell into a beaker containing a $\text{LiPF}_6\text{-EC/PC/DEC}$ solution;

(3) connecting an anode and a cathode of a charge-discharge tester to the anode and the cathode, respectively, performing three charge/discharge periods at a constant temperature of 0°C according to the following regimes:

a charge regime:

a) at a pre-charge stage: charging with a low current of 0.01 C when the voltage of the capacitor is lower than 3 V;

b) at a constant-current high-rate charge stage: charging with a current having a charge rate of 0.1 C when the voltage of the capacitor is greater than 3 V and lower than 3.5 V;

c) at a constant-current low-rate charge stage: charging with a current having a charge rate of 0.05 C when the voltage of the capacitor is greater than 3.5 V and lower than 4.2 V; and

d) at a constant voltage charge stage: charging under a constant voltage of 4.2 V when the voltage of the capacitor reaches 4.2 V, until the charge current is lower than 10 mA, and then stopping charging; and

10 a discharge regime:

a) at a first discharge stage: discharging with a discharge current having a discharge rate of 1 C when the voltage of the capacitor is greater than 3.5V and lower than or equal to 4.2 V;

b) at a second discharge stage: discharging with a discharge current having a discharge rate of 0.5 C when the voltage of the capacitor is greater than 3V and lower than or equal to 3.5V; and

c) at a third discharge stage: discharging with a discharge current having a low discharge rate of 0.1 C when the voltage of the capacitor is lower than 3V; and

(4) taking the cell obtained in step (3) out, putting the cell into an aluminum-plastic shell, and injecting electrolyte into the aluminum-plastic shell to form a single flexibly packaged capacitor.

Embodiment 5

A pre-embedment method for a lithium ion capacitor includes the following steps of:

25 (1) adhering pulp containing activated carbon as active material to non-porous aluminum foil to serve as an anode, and adhering pulp containing artificial graphite as active material to non-porous copper foil to serve as a cathode; by using polypropylene-based natural fiber composite material as a diaphragm, stacking the diaphragm, the cathode, the diaphragm and the anode successively to form a cell, and then securing with an adhesive tape; and welding current collectors of both the

30

anode and the cathode to tabs or leading-out terminals of both the anode and the cathode, respectively;

(2) drying, and immersing the dried cell into a beaker containing a $\text{LiBF}_4\text{-PC/DMF}$ solution;

5 (3) connecting an anode and a cathode of a charge-discharge tester to the anode and the cathode, respectively, performing ten charge/discharge periods at a constant temperature of 30°C according to the following regimes:

a charge regime:

10 a) at a pre-charge stage: charging with a low current of 0.03 C when the voltage of the capacitor is lower than 3 V;

b) at a constant-current high-rate charge stage: charging with a current having a charge rate of 0.3 C when the voltage of the capacitor is greater than 3 V and lower than 3.5 V; c) at a constant-current low-rate charge stage: charging with a current having a charge rate of 0.075 C when the voltage of the capacitor is greater than 3.5

15 V and lower than 4.2 V; and

d) at a constant voltage charge stage: charging under a constant voltage of 4.2 V when the voltage of the capacitor reaches 4.2 V, until the charge current is lower than 15 mA, and then stopping charging; and

a discharge regime:

20 a) at a first discharge stage: discharging with a discharge current having a discharge rate of 1.5 C when the voltage of the capacitor is greater than 3.5V and lower than or equal to 4.2 V;

b) at a second discharge stage: discharging with a discharge current having a discharge rate of 0.75 C when the voltage of the capacitor is greater than 3V and lower than or equal to 3.5V; and

25 c) at a third discharge stage: discharging with a discharge current having a low discharge rate of 0.3 C when the voltage of the capacitor is lower than 3V; and

(4) taking the cell obtained in step (3) out, putting the cell into a square aluminum shell, and injecting electrolyte into the square aluminum shell to form a single square capacitor.

30

Embodiment 6

A pre-embedment method for a lithium ion capacitor includes the following steps of:

(1) adhering pulp containing activated carbon as active material to porous aluminum foil to serve as an anode, and adhering pulp containing hard carbon as active material to porous copper foil to serve as a cathode; by using polypropylene-based natural fiber composite material as a diaphragm, winding the diaphragm, the cathode, the diaphragm and the anode successively to form a cell, and then securing with an adhesive tape; and welding current collectors of both the anode and the cathode to tabs or leading-out terminals of both the anode and the cathode, respectively;

(2) drying, and immersing the dried cell into a beaker containing a Li_2CO_3 organic solution; and

(3) connecting an anode and a cathode of a charge-discharge tester to the anode and the cathode, respectively, performing fifty charge/discharge periods at a constant temperature of 60°C according to the following regimes:

a charge regime:

a) at a pre-charge stage: charging with a low current of 0.05 C when the voltage of the capacitor is lower than 3 V;

b) at a constant-current high-rate charge stage: charging with a current having a charge rate of 0.5 C when the voltage of the capacitor is greater than 3 V and lower than 3.5 V;

c) at a constant-current low-rate charge stage: charging with a current having a charge rate of 0.1 C when the voltage of the capacitor is greater than 3.5 V and lower than 4.2 V; and

d) at a constant voltage charge stage: charging under a constant voltage of 4.2 V when the voltage of the capacitor reaches 4.2 V, until the charge current is lower than 20mA, and then stopping charging; and

a discharge regime:

a) at a first discharge stage: discharging with a discharge current having a

discharge rate of 2 C when the voltage of the capacitor is greater than 3.5V and lower than or equal to 4.2 V;

b) at a second discharge stage: discharging with a discharge current having a discharge rate of 1 C when the voltage of the capacitor is greater than 3V and lower than or equal to 3.5V; and

c) at a third discharge stage: discharging with a discharge current having a low discharge rate of 0.5 C when the voltage of the capacitor is lower than 3V; and

(4) taking the cell obtained in step (3) out, putting the cell into a round aluminum shell, and injecting electrolyte into the round aluminum shell to form a single round capacitor.

Comparative Example 1

A method for manufacturing a Li-ion capacitor includes the following steps of:

(1) adhering pulp containing activated carbon as active material to porous aluminum foil to serve as an anode, and adhering pulp containing hard carbon as active material to porous copper foil to serve as a cathode; by using a PP/PE/PP tri-layer polymer as a diaphragm and by closely compressing the lithium foil onto the copper foil as a lithium electrode, stacking the diaphragm, the anode, the diaphragm, the cathode, the diaphragm, the lithium electrode and the diaphragm successively to form a cell, and then securing with an adhesive tape; and welding current collectors of all the anode, the cathode and the lithium electrode to tabs or leading-out terminals of both the anode and the cathode, respectively;

(2) putting the cell into an aluminum-plastic shell, and injecting electrolyte of a $\text{LiPF}_6\text{-EC/PC/DEC}$ solution into the aluminum-plastic shell to form a single flexibly packaged capacitor; and

(3) short-circuit embedding: directly connecting the cathode to the lithium electrode in short circuit by leads for discharge pre-embedment.

Comparative Example 2

A pre-embedment method for a lithium ion capacitor includes the following steps of:

(1) adhering pulp containing activated carbon as active material to porous

aluminum foil to serve as an anode, and adhering pulp containing artificial graphite as active material to porous copper foil to serve as a cathode; by using a PP/PE/PP tri-layer polymer as a diaphragm and by closely compressing the lithium foil onto the copper foil as a lithium electrode, stacking the diaphragm, the anode, the diaphragm, the cathode, the diaphragm, the lithium electrode and the diaphragm successively to form a cell, and then securing with an adhesive tape; and welding current collectors of all the anode, the cathode and the lithium electrode to tabs or leading-out terminals of both the anode and the cathode, respectively;

(2) putting the cell into a square aluminum shell, and injecting electrolyte of a $\text{LiBF}_4\text{-PC/DMF}$ solution into the square aluminum shell to form a single square capacitor; and

(3) short-circuit embedding: directly connecting the cathode to the lithium electrode in short circuit by leads for discharge pre-embedding.

Comparative Example 3

A method for manufacturing a Li-ion capacitor includes the following steps of:

(1) adhering pulp containing activated carbon as active material to porous aluminum foil to serve as an anode, and adhering pulp containing hard carbon as active material to porous copper foil to serve as a cathode; by using a Single-PP polymer as a diaphragm and by closely compressing the lithium foil onto the copper foil as a lithium electrode, winding the diaphragm, the anode, the diaphragm, the cathode, the diaphragm, the lithium electrode and the diaphragm successively to form a cell, and then securing with an adhesive tape; and welding current collectors of all the anode, the cathode and the lithium electrode to tabs or leading-out terminals of both the anode and the cathode, respectively;

(2) putting the cell into a round aluminum shell, and injecting a Li_2CO_3 organic solution into the round aluminum shell to form a single flexibly packaged round capacitor; and

(3) short-circuit embedding: directly connecting the cathode to the lithium electrode in short circuit by leads for discharge pre-embedding.

Comparative Example 4

Super capacitor FB series are commercially available from NEC-tokin.

Detection methods and results

1. Specific capacity of capacitors

A comprehensive battery performance detector LRBT-02 is utilized to test the specific discharge capacities of Embodiments 1, 2 and 3 and Comparative Examples at currents of 1 C, 5 C and 10 C, respectively. The results are as shown in Fig. 1.

2. Capacity retention ratio

As for Embodiments 1, 2 and 3 and Comparative Examples, charge and discharge are performed at currents of 1 C, 5 C and 10 C, and as for the correspondingly embodiments, charge and discharge are performed in a same manner as that described in Embodiments 4, 5 and 6. The capacity retention ratios are recorded, and the results are as shown in Table 1.

3. The initial amount of lithium to be embedded is detected by an externally connected charge-discharge tester which may monitor the embedment amount of lithium in real time. The results are as shown in Table 2.

As can be known from Fig. 1, a Li-ion capacitor manufactured by this pre-embedment method of the present invention has a significantly high specific capacity and a low drop in the specific capacity of the capacitor while discharging at a high current when compared with a Li-ion capacitor manufactured by a conventional process.

Table 1

	Charge-discharge current	Initial discharge capacity (mAh/g)	100 cycles	500 cycles
Embodiment 1	1C	48 ± 2	$98.9 \pm 0.3\%$	$97.8 \pm 0.4\%$
	5C	47 ± 3	$98.3 \pm 0.6\%$	$97.5 \pm 0.6\%$
	10C	46 ± 3	$98.0 \pm 0.7\%$	$97.2 \pm 0.5\%$

Embodiment 2	1C	48 ± 2	$99.0 \pm 0.2\%$	$97.9 \pm 0.5\%$
	5C	48 ± 2	$98.5 \pm 0.4\%$	$97.7 \pm 0.4\%$
	10C	46 ± 3	$98.2 \pm 0.7\%$	$97.3 \pm 0.7\%$
Embodiment 3	1C	49 ± 2	$99.1 \pm 0.2\%$	$98.0 \pm 0.3\%$
	5C	48 ± 3	$98.6 \pm 0.4\%$	$97.8 \pm 0.4\%$
	10C	48 ± 3	$98.3 \pm 0.8\%$	$97.3 \pm 0.8\%$
Embodiment 4	The charge-discharge process follows those described in Embodiment 4.	49 ± 2	$98.5 \pm 0.2\%$	$97.5 \pm 0.3\%$
Embodiment 5	The charge-discharge process follows those described in Embodiment 5.	52 ± 4	$99.1 \pm 0.2\%$	$98.3 \pm 0.5\%$
Embodiment 6	The charge-discharge process follows those described in Embodiment 6.	51 ± 6	$98.7 \pm 0.3\%$	$97.6 \pm 0.6\%$
Comparative Example 1	1C	46 ± 2	$97.8 \pm 0.5\%$	$93.7 \pm 0.9\%$
	5C	45 ± 3	$97.3 \pm 0.8\%$	$93.4 \pm 0.8\%$
	10C	42 ± 5	$97.1 \pm 1.0\%$	$93.0 \pm 0.9\%$
Comparative Example 2	1C	46 ± 2	$97.9 \pm 0.3\%$	$93.8 \pm 1.0\%$
	5C	44 ± 4	$97.5 \pm 0.7\%$	$93.1 \pm 1.1\%$
	10C	42 ± 5	$97.3 \pm 0.6\%$	$93.4 \pm 0.9\%$

Comparative Example 3	1C	46 ± 3	$97.9 \pm 0.2\%$	$93.8 \pm 0.7\%$
	5C	46 ± 4	$97.5 \pm 0.7\%$	$93.3 \pm 0.5\%$
	10C	41 ± 8	$97.0 \pm 0.9\%$	$93.0 \pm 0.9\%$
Comparative Example 4	1C	48 ± 2	$98.3 \pm 0.5\%$	$94.5 \pm 0.7\%$
	5C	47 ± 4	$98.0 \pm 0.8\%$	$94.1 \pm 0.8\%$
	10C	47 ± 4	$97.6 \pm 1.2\%$	$93.9 \pm 0.9\%$

As can be known from Table 1, both a Li-ion capacitor manufactured by this method of the present invention and a Li-ion capacitor manufactured by connecting the cathode to the lithium electrode in short circuit as a pre-embedment method may ensure, at various charge-discharge currents, a high capacity by a few cycles, and however, after many charge-discharge cycles, the Li-ion capacitor manufactured by this method of the present invention exhibits a higher capacity retention ratio, and stable results at various different currents. The service life and use effect of a capacitor are limited by the degree of embedment. It is indicated by Table 1 that the pre-embedment way used in the present invention benefits a capacitor to allow the capacitor to show more stable long-term use performance while ensuring the fundamental functions of the capacitor, and prolongs the service life of the capacitor.

Table 2

	Embodiment 1	Embodiment 2	Embodiment 3	Embodiment 4	Embodiment 5	Embodiment 6
Initial embedment amount (mAh/g)	112.3 ± 5.7	114.2 ± 6.1	114.5 ± 9.4	112.3 ± 9.2	118.5 ± 9.6	116.4 ± 5.6

As can be known from Table 2, different durations and different currents for

charge-discharge cycles have little influence on the initial embedment amount of a capacitor. Temperature, at which the embedment is performed, has certain influence on the initial embedment amount. Too low temperature will hinder the process of embedment, and lower current will require longer charge-discharge duration. The embedment amount of the capacitor may be increased slightly, so that the service life and the charge-discharge efficiency of the capacitor may be improved. Charging/discharging with a low current is more effective to the increase in the embedment amount of the capacitor.

The invention can be described as follows:

10 A pre-embedment method for a lithium ion capacitor, comprising the following steps of: stacking or winding a cathode, a diaphragm, an anode and a diaphragm successively and then securing with an adhesive tape to form a cell, and immersing the cell into an organic solution containing lithium salt; (2) connecting the anode and the cathode to a charge-discharge tester, respectively, to perform a number of cycles each comprising one charge followed by one discharge, to finish the pre-embedment into the cathode; and (3) taking out the cell after the pre-embedment and putting the cell into a packaging shell, and injecting electrolyte into the packaging shell to form a single lithium ion capacitor.

One or more of the following additional preferred features can be part of preferred embodiments of the invention, alone or in any combination of features:

- current collectors in the anode and the cathode are current collectors with or without pores;
- the lithium salt is at least one of lithium salts, which are soluble in the organic solution, selected from LiPF_6 、 LiBF_4 , LiClO_4 , LiAlO_4 , LiOH , Li_2CO_3 , CH_3COOLi , LiNO_3 , $\text{LiB}(\text{C}_2\text{O}_4)_2$, $\text{LiP}(\text{C}_6\text{H}_4\text{O}_2)_3$, $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$ and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, and the organic solution is at least one of PC, EC, DEC, DMC, DMF, DME, THF and SL;
- the discharge in the cycle is discharge of the tester or self-discharge of the cell;
- the charge and the discharge are of constant current, and the charge-discharge rate ranges from 0.01 C to 10 C;

- the highest cut-off voltage for the charge ranges from 3.6 V to 4.2 V;
- currents and voltages separately for the charge and discharge in each of the cycles may be the same or different wherein preferably the discharge in each of the cycles lasts for 1 min to 10 h;

5

- the number of cycles totals 1 to 100;
- the charge and discharge in each of the cycles are performed at a constant temperature ranging from 0°C to 60°C;

- the charge regime is as follows:

at a pre-charge stage: charging with a low current of 0.01-0.05 C when the
10 voltage of the capacitor is lower than 3 V;

(2) at a constant-current high-rate charge stage: charging with a current having a charge rate of 0.1-0.5 C when the voltage of the capacitor is greater than 3 V and lower than 3.5 V;

(3) at a constant-current low-rate charge stage: charging with a current having a
15 charge rate of 0.05-0.1 C when the voltage of the capacitor is greater than 3V and lower than the highest cut-off voltage; and

(4) at a constant-voltage charge stage: charging under a constant voltage when the voltage of the capacitor reaches the highest cut-off voltage, until the charge current is lower than 10-20 mA, and then stopping charging, the constant voltage
20 being the highest cut-off voltage;

a discharge regime is as follows:

at a first discharge stage: discharging with a discharge current having a discharge rate of 1-2 C when the voltage of the capacitor is greater than 3.5V and lower than or equal to the highest cut-off voltage;

25 (2) at a second discharge stage: discharging with a discharge current having a discharge rate of 0.5-1 C when the voltage of the capacitor is greater than 3V and lower than or equal to 3.5V; and

(3) at a third discharge stage: discharging with a discharge current having a low discharge rate of 0.1-0.5 C when the voltage of the capacitor is lower than 3V;

30 - the diaphragm is a composite diaphragm having polypropylene as a matrix,

and the composite diaphragm having polypropylene as a matrix is prepared from the following substance by the following steps: uniformly mixing 80-85 wt% of polypropylene, 10-15 wt% of natural cellulose pulp, 3-5 wt% of kaolin powder and 0.5-1.5 wt% of silane coupling agent, and then processing by a dry process, wherein

5 preferably the natural cellulose pulp is made by the following steps of: (1) adding bamboo fiber as raw material to a sodium hydroxide solution, and then steaming the sodium hydroxide solution in vacuum at 300°C for 2 h, wherein the mass ratio of the bamboo fiber to the sodium hydroxide solution is 1:4, and the concentration of the sodium hydroxide solution is 10 wt%; (2) taking out and washing the steamed bamboo

10 fiber with water, then soaking the bamboo fiber in hot water at a temperature of 80-90 °C for grinding followed by filtering, and then collecting the filtered solid; and (3) pulping the filtered solid by a pulping machine and concentrating to obtain the natural cellulose pulp having a solid content of 60-70 wt%.

Conclusies

1. Voor-inbeddingswerkwijze voor een lithium ion condensator, bevattende de volgende stappen:

- 5 - stapelen of wikkelen van successievelijk een kathode, een diafragma, een anode en een diafragma and dan
 - vastzetten door plakband om een cel te vormen en
 - onderdompelen van de cel in een organische oplossing bevattende een lithium zout
- 10 - verbinden van de kathode en de anode met respectievelijk een oplading-ontlading tester om een aantal maal een cyclus te voltooien elke cyclus bevatten een oplading gevolgd door een ontlading om de voor-inbedding te voltooien en
 - uithalen van de cel na de voor-inbedding en
- 15 - plaatsen van de cel in een verpakkingssomhulsel en
 - injecteren van een elektrolyt in het verpakkingssomhulsel om een enkele lithium ion condensator te vormen.

2. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens conclusie 1, met het kernmerk, dat de stroomcollectoren in de anode en de kathode stroomcollectoren met of zonder poriën zijn.

3. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens conclusie 1 of 2, met het kenmerk, dat het lithium zout ten minste een van lithium zouten, oplosbaar in de organische oplossing, is gekozen uit LiPF_6 , LiBF_4 , LiClO_4 , LiAlO_4 , LiOH , Li_2CO_3 , CH_3COOLi , LiNO_3 , $\text{LiB}(\text{C}_2\text{O}_4)_2$, $\text{LiP}(\text{C}_6\text{H}_4\text{O}_2)_3$, $\text{LiPF}_3(\text{C}_2\text{F}_5)_3$ and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ en het organisch oplosmiddel ten minste een van PC, EC, DEC, DMC, DMF, DME, THF and SL is.

4. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens een der voorgaande conclusies, met het kenmerk, dat de ontlading in de cyclus een ontlading van de tester of een zelf-ontlading van de cel is.

5. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens een der voorgaande conclusies, met het kenmerk, dat de cyclus in totaal 1 tot 100 maal voltooid wordt.

6. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens een der
5 voorgaande conclusies, met het kenmerk, dat de oplading en de ontlading met constant stroom gebeuren en de oplading-ontlading niveau tussen 0.01 C en 10C ligt.

7. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens een der voorgaande conclusies, met het kenmerk, dat de hoogste cut-off spanning voor de oplading tussen 3.6 V en 4.2 V ligt.

10 8. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens conclusie 1, 4, 6 of 7, met het kenmerk, dat de stromen en spanningen afzonderlijk voor de oplading en ontlading in elk van de cycli gelijk of ongelijk kunnen zijn.

9. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens conclusie 8, met het kenmerk, dat de ontlading in elk van de cycli 1 tot 10 minuten duurt.

15 10. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens een der voorgaande conclusies, met het kenmerk, dat de ontlading en oplading in elk van de cycli plaatsvinden bij een constante temperatuur tussen 0 °C en 60 °C.

11. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens een der voorgaande conclusies, met het kenmerk, dat het opladingschema als volgt is:

20 - tijdens de voor-opladingfase: opladen met een lage stroom van 0,01 tot 0,05 C wanneer de spanning op de condensator lager is dan 3Volt

- (2) tijdens een constante-stroom hoog-niveau opladingfase: opladen met een stroom met een oplading van 0,1-0,5 C wanneer de spanning op de condensator lager is dan 3,5 Volt

25 - (3) tijdens een constante-stroom lage-snelheid oplaadfase: opladen met een stroom met een oplading van 0,05-0,1 C wanneer de spanning op de condensator lager is dan 3 Volt en lager dan de hoogste cut-off spanning

- (4) tijdens een constante-spanning oplaadfase: opladen onder een constante spanning wanneer de spanning van de condensator de hoogste cut-off spanning
30 bereikt, totdat de oplaadstroom lager is dan 10-20 mA, dan stoppen met laden, de

constante spanning zijnde de hoogste cut-off spanning

en dat een ontladingschema als volgt is:

- tijdens een eerste ontladingsfase: ontladen met een ontlaadstroom met een ontlading van 1-2 C wanneer de spanning van de condensator hoger is dan 3,5 Volt en lager of gelijk aan de hoogste cut-off spanning;
- (2) tijdens een tweede ontladingsfase: ontladen met een ontlaadstroom met een ontlading van 0,5-1 C wanneer de spanning van de condensator hoger is dan 3 Volt en lager dan 3,5 Volt
- (3) tijdens een derde ontladingsfase: ontladen met een ontlaadstroom met een ontlading van 0,1-0,5 C wanneer de spanning van de condensator lager is dan 3 Volt.

12. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens een der voorgaande conclusies, met het kenmerk, dat het diafragma een samengestelde diafragma is met polypropyleen als matrix, en het samengestelde diafragma met polypropyleen als matrix vervaardigd wordt uit de volgende substantie door de volgende stappen: het gelijkmatig mengen van 80-85 gewichtsprocent van polypropyleen, 10-15% gewichtsprocent van natuurlijke cellulose pulp, 3-5 gewichtsprocent kaolien poeder en 0,5-1,5 gewichtsprocent van een silaan verbindingsmiddel, en dan verwerken door een drogingsproces.

13. Voor-inbeddingswerkwijze voor een lithium ion condensator volgens conclusie 11, met het kenmerk, dat de natuurlijk cellulose pulp gemaakt is door de volgende stappen:

- (1) bamboe vezel als een grondstof toevoegen aan een natriumhydroxide oplossing en dan de natriumhydroxide oplossing 2 uur stomen op 300 °C waarbij de massaverhouding van bamboe vezel tot de natrium hydroxide oplossing 1: 4 is en het gehalte van de natriumhydroxide oplossing 10 gewichtsprocent bedraagt.
- (2) wegnemen en wassen van de gestoomde bamboe vezel met water, daarna weken van de bamboe vezel in heet water op een temperatuur van 80-90 °C voor malen gevolgd door filtreren en dan de gefilterde vaste stof verzamelen

en

- (3) de gefilterde vast stof verpulpen in door een pulpapparaat and concentreren om de natuurlijk cellulose pulp men een vast stof gehalte van 60-70 gewichtsprocent te verkrijgen.

5

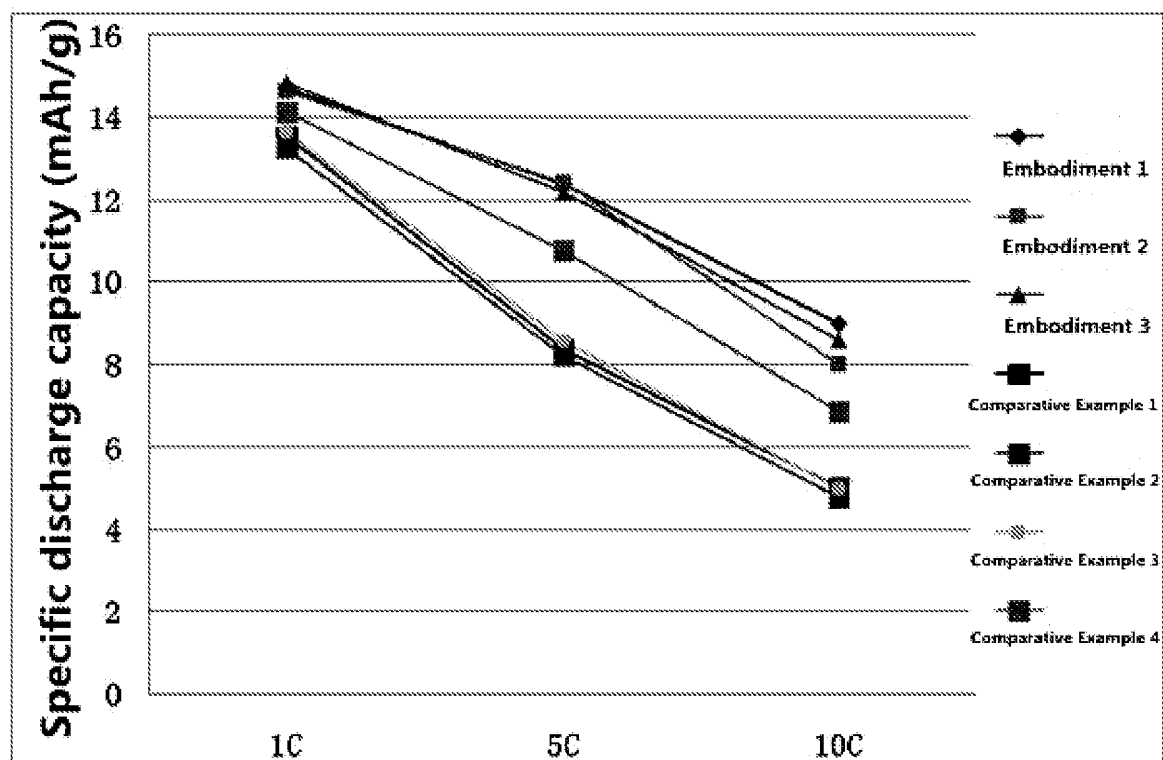
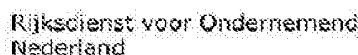


Fig. 1

Abstract

The present invention provides a novel pre-embedment method for a Li-ion capacitor, comprising the following steps of: (1) assembling a cell, and immersing the cell into an organic solution containing lithium salt; (2) connecting the anode and the cathode to a charge-discharge tester, respectively, to perform total 1 to 100 cycles each comprising one charge followed by one discharge, to finish the pre-embedment into the cathode; and (3) taking out the cell after the pre-embedment and putting the cell into a packaging shell, and injecting electrolyte into the packaging shell to form a single lithium ion capacitor. With the novel pre-embedment method of the preset invention, high cost resulted from the metal lithium and porous current collectors is effectively solved. The safety may be improved and the technological process may be simplified. The novel pre-embedment method of the preset invention is suitable for industrial production.



OCTROOIAANVRAAG NR.
NO 139562
NL 2015824

ONDERZOEKSRAPPORT

BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK

RELEVANTE LITERATUUR			
Categorie ¹	Literatuur met, voor zover nodig, aanduiding van speciaal van belang zijnde tekstgedeelten of figuren.	Van belang voor conclusie(s) nr:	Classificatie (IPC)
X	EP 2 541 566 A1 (SHANGHAI AOWEI TECHNOLOGY DEV [CN]) 2 januari 2013 (2013-01-02) * voorbeelden 1-5 * * alinea [0001] * * alinea [0009] ~ alinea [0011] * * alinea [0013] * * alinea [0014] * * alinea [0015] * * alinea [0017] * * alinea [0016] * * alinea [0018] * * alinea [0024] * * alinea [0026] * * alinea [0028] * * conclusies 1-11 * * alinea [0031] * * alinea [0023] * * alinea [0021] * ----- -/-	1-13	INV. H01M4/133 H01M10/0525 H01M12/00 H01M2/16 H01G11/86 H01G11/50 H01G11/06 H01G11/14 H01G11/60 H01G11/62
			Onderzochte gebieden van de techniek
			H01M H01G
Indien gewijzigde conclusies zijn ingediend, heeft dit rapport betrekking op de conclusies ingediend op:			
Plaats van onderzoek:	Datum waarop het onderzoek werd voltooid:	Bevoegd ambtenaar:	
München	15 november 2016	Kuhn, Tanja	

¹ CATEGORIE VAN DE VERMEDELDE LITERATUUR

X: de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur Y: de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht A: niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft O: niet-schriftelijke stand van de techniek P: tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur	T: na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvrage, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding E: eerdere octrooi(aanvraag), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven D: in de octrooiaanvraag vermeld L: om andere redenen vermelde literatuur S: lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie
--	--

RELEVANTE LITERATUUR		
Categorie ¹	Literatuur met, voor zover nodig, aanduiding van speciaal van belang zijnde tekstgedeelten of figuren.	Van belang voor conclusie(s) nr.
A	EP 1 865 521 A1 (FUJII HEAVY IND LTD [JP]) 12 december 2007 (2007-12-12) * alinea [0001] * * alinea [0004] * * alinea [0005] * * alinea [0008] - alinea [0009] * * alinea [0010] * * alinea [0011] * * alinea [0012] * * alinea [0013] * * alinea [0019] * * alinea [0020] * * alinea [0022] * * alinea [0024] * * alinea [0027] * * alinea [0040] - alinea [0042] * * conclusies 1-9 *	1-13
A	EP 2 647 662 A1 (TOKUSHU TOKAI PAPER CO LTD [JP]) 9 oktober 2013 (2013-10-09) * conclusies 13-15 * * alinea [0002] - alinea [0003] * * alinea [0031] - alinea [0034] * * alinea [0035] - alinea [0036] * * alinea [0038] * * alinea [0064] *	12,13
A	US 2012/047720 A1 (CHOI DONG HYEOK [KR] ET AL) 1 maart 2012 (2012-03-01) * alinea [0014] * * alinea [0017] * * alinea [0018] * * alinea [0020] * * conclusie 1 *	1-13

2

2025 FORM 12/20 (P214C)

¹ CATEGORIE VAN DE VERMELDE LITERATUUR

- X: de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur
- Y: de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht
- A: niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft
- O: niet-schriftelijke stand van de techniek
- P: tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur

- T: na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvraag, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding
- E: eerdere octrooi(aanvraag), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven
- D: in de octrooiaanvraag vermeld
- L: om andere redenen vermelde literatuur
- &: lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

**AANHANGSEL BEHORENDE BIJ HET RAPPORT BETREFFENDE
HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK,
UITGEVOERD IN DE OCTROOIAANVRAGE NR.**

NO 139562
NL 2015824

Het aanhangsel bevat een opgave van elders gepubliceerde octrooiaanvragen of octrooien (zogenaamde leden van dezelfde octroofamilie), die overeenkomen met octrooischriften genoemd in het rapport.

De opgave is samengesteld aan de hand van gegevens uit het computerbestand van het Europees Octrooibureau per

De juistheid en volledigheid van deze opgave wordt noch door het Europees Octrooibureau, noch door het Bureau voor de Industriële eigendom gegarandeerd; de gegevens worden verstrekt voor informatiedoeleinden.

15-11-2016

In het rapport genoemd octrooigeschrift		Datum van publicatie	Overeenkomend(e) geschrift(en)	Datum van publicatie
EP 2541566	A1	02-01-2013	CN 101847513 A	29-09-2010
			EP 2541566 A1	02-01-2013
			JP 5939990 B2	29-06-2016
			JP 2013520805 A	06-06-2013
			US 2012321913 A1	20-12-2012
			WO 2011103705 A1	01-09-2011
EP 1865521	A1	12-12-2007	CN 101138058 A	05-03-2008
			EP 1865521 A1	12-12-2007
			JP 4833065 B2	07-12-2011
			US 2009154064 A1	18-06-2009
			WO 2006112068 A1	26-10-2006
EP 2647662	A1	09-10-2013	BR 112013018606 A2	18-10-2016
			CA 2824632 A1	18-04-2013
			CN 103842418 A	04-06-2014
			EP 2647662 A1	09-10-2013
			JP 5461745 B2	02-04-2014
			JP WO2013054884 A1	30-03-2015
			KR 20130088901 A	08-08-2013
			RU 2013134484 A	27-01-2015
			TW 201332194 A	01-08-2013
			US 2013280615 A1	24-10-2013
			WO 2013054884 A1	18-04-2013
US 2012047720	A1	01-03-2012	JP 2012049500 A	08-03-2012
			KR 20120019849 A	07-03-2012
			US 2012047720 A1	01-03-2012

SCHRIFTELIJKE OPINIE

DOSSIER NUMMER NO139562	INDIENINGSDATUM 20.11.2015	VOORRANGSDATUM 12.12.2014	AANVRAAGNUMMER NL2015824
CLASSIFICATIE INV. H01M4/133 H01M10/0525 H01M12/00 H01M2/16 H01G11/86 H01G11/50 H01G11/06 H01G11/14 H01G11/60 H01G11/62			
AANVRAGER NINGBO CSR NEW ENERGY TECHNOLOGY CO., LTD			

Deze schriftelijke opinie bevat een toelichting op de volgende onderdelen:

- ☒ Onderdeel I Basis van de schriftelijke opinie
- ☐ Onderdeel II Voorrang
- ☐ Onderdeel III Vaststelling nieuwheid, inventiviteit en industriële toepasbaarheid niet mogelijk
- ☐ Onderdeel IV De aanvraag heeft betrekking op meer dan één uitvinding
- ☒ Onderdeel V Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid
- ☐ Onderdeel VI Andere geciteerde documenten
- ☐ Onderdeel VII Overige gebreken
- ☒ Onderdeel VIII Overige opmerkingen

	DE BEVOEGDE AMBTENAAR Kuhn, Tanja
--	--------------------------------------

SCHRIFTELIJKE OPINIE

Aanvraag nr. NL2015824

Onderdeel I Basis van de Schriftelijke Opinie

1. Deze schriftelijke opinie is opgesteld op basis van de meest recente conclusies ingediend voor aanvang van het onderzoek.
2. Met betrekking tot **nucleotide en/of aminozuur sequenties** die genoemd worden in de aanvraag en relevant zijn voor de uitvinding zoals beschreven in de conclusies, is dit onderzoek gedaan op basis van:
 - a. type materiaal:
 - ☐ sequentie opsomming
 - ☐ tabel met betrekking tot de sequentie lijst
 - b. vorm van het materiaal:
 - ☐ op papier
 - ☐ in elektronische vorm
 - c. moment van indiening/aanlevering:
 - ☐ opgenomen in de aanvraag zoals ingediend
 - ☐ samen met de aanvraag elektronisch ingediend
 - ☐ later aangeleverd voor het onderzoek
3. ☐ In geval er meer dan één versie of kopie van een sequentie opsomming of tabel met betrekking op een sequentie is ingediend of aangeleverd, zijn de benodigde verklaringen ingediend dat de informatie in de latere of additionele kopieën identiek is aan de aanvraag zoals ingediend of niet meer informatie bevatten dan de aanvraag zoals oorspronkelijk werd ingediend.
4. Overige opmerkingen:

SCHRIFTELIJKE OPINIE

Aanvraag nr. NL2015824

Onderdeel V Gemotiveerde verklaring ten aanzien van nieuwheid, inventiviteit en industriële toepasbaarheid

1. Verklaring

Nieuwheid	Ja: Conclusies 1-13 Nee: Conclusies
Inventiviteit	Ja: Conclusies Nee: Conclusies 1-13
Industriële toepasbaarheid	Ja: Conclusies 1-13 Nee: Conclusies

2. Citaties en toelichting:

Zie aparte bladzijde

Onderdeel VIII Overige opmerkingen

De volgende opmerkingen met betrekking tot de duidelijkheid van de conclusies, beschrijving, en figuren, of met betrekking tot de vraag of de conclusies nawerkbaar zijn, worden gemaakt:

Zie aparte bladzijde

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1

Reference is made to the following documents:

- D1 EP 2 541 566 A1 (SHANGHAI AOWEI TECHNOLOGY DEV [CN]) 2 januari 2013 (2013-01-02)
- D2 EP 1 865 521 A1 (FUJI HEAVY IND LTD [JP]) 12 december 2007 (2007-12-12)
- D3 EP 2 647 662 A1 (TOKUSHU TOKAI PAPER CO LTD [JP]) 9 oktober 2013 (2013-10-09)
- D4 US 2012/047720 A1 (CHOI DONG HYEOK [KR] ET AL) 1 maart 2012 (2012-03-01)

2 The present application does not meet the criteria of patentability, because the subject-matter of independent claim 1 does not involve an inventive step.

2.1 D1 may be regarded as being the prior art closest to the subject-matter of claim 1, and discloses (the references in parenthesis applying to this document):

Voor-inbeddingswerkwijze voor een lithium ion condensator, bevattende de volgende stappen:

- stapelen of wikkelen van successievelijk een kathode, een diafragma, een anode en een diafragma (Figure 1 paragraphs 21, 23 to 31) and dan
- vastzetten en
- onderdompelen van de cel in een organische oplossing bevattende een lithium zout door de elektrolyt in het verpakingsomhulsel om een enkele lithium ion condensator te vormen
- verbinden van de kathode en de anode met respectievelijk een oplading-ontlading tester om een aantal maal een cyclus te voltooien elke cyclus bevatten een oplading gevolgd door een ontlading om de voor-inbedding te voltooien (examples 1 to 5 and in particular paragraphs 35, 38, 44 and 47).

- 2.2 The subject-matter of claim 1 therefore differs from this known method known from D1 in that the following extra steps are performed:
- vastzetten door plakband om een cel te vormen
 - uithalen van de cel na de voor-inbedding en pas daarna
 - plaatsen van de cel in een verpakkingssomhulsel en
 - injecteren van een elektrolyt in het verpakkingssomhulsel om een enkele lithium ion condensator te vormen.
- 2.3 The problem to be solved by the present invention may therefore be regarded as to provide for an alternative method of making a lithium capacitor.
- 2.4 The solution proposed in claim 1 of the present application cannot be considered as involving an inventive step for the following reasons: To additionally fix an anode/separator/cathode unit by a tape is general knowledge in the art of lithium capacitors and batteries and can therefore not justify an inventive step. D1 discloses the charge/discharge cycling to improve the capacity retention rate. The application solves the same problem by the same means. The fact that the anode/separator/cathode unit of claim 1 undergoes the charge/discharge cycles in a lithium salt containing electrolyte outside the capacitor casing before being placed in a casing containing lithium salt electrolyte does not cause any (surprising) technical effect, thus the technical features not disclosed in document D1 do not lead to an inventive step over the document D1 and therefore claim 1 is not inventive.

Document D1 also discloses the additional technical features of dependent claims 2 (paragraph 17 and claim 11 anode and cathode collector with or without pores), 3 (paragraph 26), 4 (see the already cited passages with respect to the independent claim), 5 (paragraph 35 discloses 2000 cycles, but as D1 discloses same type of lithium capacitor as the application it implicitly yields an improved capacity retention also at a lower cycle rate), 6, 7 and 8 (paragraph 44: highest cut off voltage being 4.2V, thus implicitly yielding the charge/discharge level between 0.01C and 10C, here: constant current), 9 (as D1 discloses same type of lithium capacitor as the application and thus implicitly yields the claimed time span for discharge in every cycle), 10 (in D1 the room temperature at the time of cycling is an implicit technical feature and usual in the art of cycling capacitors).

As to dependent claim 11: D1 is silent about the cycle scheme of claim 11. However no surprising technical effect is presently substantiated in the application for the specific cycle scheme of claim 11. This is so as none the examples disclosed in the description of the application differs from the comparative examples disclosed in the description of the application only in

the cycling steps; e.g. example 1 differs from comparative example not only in the charge/discharge cycles but also in that mesophase carbon micro beads are used as active cathode material wherein in comparative example hard carbon is used as active cathode material. Thus the technical effect shown in table 1 of the application is not necessarily caused by the specific claimed cycling scheme. Further it appears that there is no surprising technical effect caused by the claimed charge/discharge cycle scheme in view of the charge/discharge cycle scheme disclosed in D1. Therefore an inventive step can not be acknowledged.

As to claims 12 and 13: polypropylene and cellulose pulp are known materials for the production of lithium ion capacitors. The precise method of claims 12 13 is however not disclosed in the available prior art document. Is it however not clear from the application, what technical effect is caused by these method steps and therefore an inventive step can presently not be acknowledged.

Thus claims 1 to 13 are considered to lack an inventive step

Re Item VIII

Certain observations on the application

Independent claim 1 is not clear and not supported.

The terms "*een aantal maal (how often?) een cyclus te voltooien*", used in claim 1 is vague and unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claim unclear.

Also the term "*elke cyclus bevatten een oplading gevolgd door een ontlading om de voor-inbedding te voltooien*", used in claim 1 is vague and unclear as it is not clear what is pre-embedded.

Claim 1 is also not supported by the description, as its scope is broader than justified by the description and drawings. The application does only support the pre-embedding of lithium.