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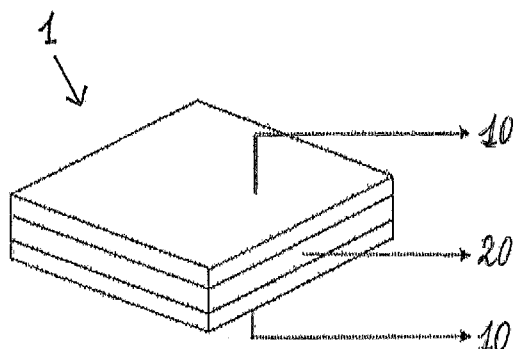


Fig. 1

(57) Abstract: The invention relates to an active material comprising at least one oxygen-containing compound selected from the group consisting of MgO, ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂, at least one thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose, and arabic gum, and at least one plasticizer additive. The invention concerns also an electric power generator (EPG) comprising at least a first electrode (11) and a second electrode (12), wherein the electric power generator comprises the active material between said electrodes (11, 12).



“ACTIVE MATERIAL AND ELECTRIC POWER GENERATOR CONTAINING IT”**FIELD OF THE INVENTION**

The present invention relates to an active material to be used for the manufacturing
5 of an electric generator and to a method for obtaining such medium. The present
invention hence relates also to an electric generator comprising said active material.

STATE OF THE ART

It is widely known the use of thermoelectric power generators and thermionic power
generators for the conversion of thermal energy directly into electrical energy.

10 The thermoelectric power generators are devices based on a thermoelectric effect,
namely the Seebeck effect, involving interactions between the flow of heat and of
electricity between solid bodies. Examples of such devices are disclosed in the
patent EP 2521192 and in the patent application EP 2277209. In broad terms,
thermoelectric power generators consist of three main components: thermoelectric
15 material, thermoelectric modules and thermoelectric system that interface with a
heat source.

Thermoelectric materials generate power directly from heat by converting
temperature differences into electric voltage. In particular, these materials typically
have both high electrical conductivity and low thermal conductivity. The low thermal
20 conductivity ensures that when one side is made hot, the other side stays cold. This
helps to generate a large voltage while in a temperature gradient.

A thermoelectric module is a circuit containing thermoelectric materials which
generate electricity from heat directly. A module consists of two dissimilar
thermoelectric materials joining at their ends, namely a negatively charged
25 semiconductor and a positively charged semiconductor. A direct electric current will
flow in the circuit when there is a temperature gradient between the two materials.
Such gradient is provided by the thermoelectric system which typically comprise
heat exchangers used on both sides on the module to supply respectively heating
and cooling.

30 A thermionic power generators, also called thermionic power converters, convert
heat directly into electricity. A thermionic power generator typically comprises two
electrodes arranged in a containment. One of these is raised to a sufficiently high

temperature to become a thermionic electron emitter or "hot plate". The other electrode is called collector because it receives the emitted electrons. The collector is operated at significantly lower temperature. The space between the electrodes can be vacuum or alternatively filled with a vapour gas at low pressure. The thermal energy may be supplied by chemical, solar or nuclear sources.

Thermoelectric power generators as well as thermionic power generators have many drawbacks, among which the low conversion efficiency and the need of providing a temperature gradient. In addition, such generators, requires relatively constant thermal source.

Therefore, it is the primary object of the present invention to provide an electric power generator capable to convert part of the thermal energy in electric energy and allowing to overcome the drawbacks of the devices of the prior art-

SUMMARY OF THE INVENTION

The inventors surprisingly found out a new active material capable to be applied on one electrode and to generate current when comprised between at least two electrodes without initial charging and dependently on the temperature.

Therefore, the present invention relates to an active material comprising at least one oxygen-containing compound selected from the group consisting of MgO, ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂, at least one thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose, and arabic gum, and at least one plasticizer additive.

In the present invention when the term "plasticizer additive" is used, it is meant a substance capable to produce or promote plasticity when added, for example silicone, siloxanes or Carnauba Wax.

In a preferred embodiment of the invention the active material comprises MgO, ZnO and ZrO₂ as oxygen-containing compounds, agar agar, Xanthan gum, methylcellulose as thickener additives and silicone as plasticizer additive.

In another aspect the invention concerns a process for preparing the active material comprising the following steps:

a) preparing a solution with a solvent selected from the group consisting of water, ethylene glycol, glycerin, dimethyl sulfoxide and relative mixtures of at least one oxygen-containing compound selected from the group consisting of MgO, ZnO,

ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂;

b) heating the solution of step a) at a temperature in the range from 75 to 90°;

c) adding at least one thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose and arabic gum, thus obtaining a homogeneous solution;

d) cooling down the homogenous solution of step c) to a temperature in the range from 30 °C to 15 °C allowing gelation, thus obtaining a gelled material;

e) adding at least one plasticizer to the gelled material, thus obtaining the active material.

In a still another aspect the invention concerns an alternative process for preparing the active material comprising the following steps

i) preparing a first solution with a solvent selected from the group consisting of water, ethylene glycol, glycerin, dimethyl sulfoxide and relative mixtures of at least one oxygen-containing compound selected from the group consisting of MgO, ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂;

ii) heating the first solution of step i) at a temperature in the range from 90 to 110 °C;

iii) cooling down the homogenous solution of step ii) to a temperature in the range from 50 °C to 30 °C;

iv) preparing a second solution with a solvent selected from the group consisting of water, ethylene glycol, glycerin, dimethyl sulfoxide and relative mixtures of at least one thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose, and arabic gum

v) heating the second solution of step iv) at a temperature in the range from 90 to 120 °C;

vi) mixing the first solution at 45 °C with the solution at step v),

vii) cooling down the homogenous solution of step vi) to a temperature in the range from 30 °C to 20 °C and subjecting it to cooling cycles from ambient temperature to -18 °C,;

ix) adding at least one plasticizer additive to the solution of step vii), thus obtaining an homogenous material solution;

x) optionally removing the solvent, and obtaining the active material.

In another aspect, the invention relates to an electric power generator (EPG)

comprising at least two electrodes, placed at a suitable distance from each other and preferably made of different material. The EPG comprises active material according to the invention between the at least two electrodes. The electrodes are made of metals, alloys and/or carbon-based materials like graphite. Electrodes thickness ranges preferably from 0.1 to 3000 μm , more preferably from 50 to 1000 μm , still more preferably from 300 to 600 μm . In a preferred embodiment of the EPG according to the invention, the at least two electrodes are made of Cu and Al, preferably in form of plates or foils substantially parallel. In case of flexible EPG both self-standing flexible materials (among the previous listed materials) and metallized polymers can be considered as electrodes.

The present invention also relates to a power generator module (PGM) comprising a plurality of EPG which can be connected in series or parallel without comprising the EPG characteristics (voltage and current).

DESCRIPTION OF FIGURES

Further features and advantages of the invention will be more apparent in light of the detailed description of the active material and of the preferred embodiments of the electric power generator with the aid of enclosed drawings in which:

- Figure 1 shows the sandwich structure of the electric power generator comprising the active material according to the present invention;

- Figures 1A and 1B show examples of electrical circuits comprising a plurality of electric power generators according to the present invention;

- Figure 2 shows an example of an electrical circuit comprising the electric power generator according to the present invention;

- Figure 3 shows the curve of the result of the tests carried out in example 4;

- Figure 4 shows the curve of the results of the test carried out in example 4;

- Figure 5 shows the curve of the result of the tests carried out in example 5;

- Figure 6 shows the curve of the results of the test carried out in example 5;

- Figure 7 shows the curve current temperature dependence in the test carried out in Example 5.

- Figure 8 shows the curve of the results of the test carried out in example 6;

- Figure 9 shows the curve of the results of the test carried out in example 7;

- Figure 10 shows the curve of the results of the test carried out in example 8;

- Figure 11 shows the curves of the results of the test carried out in example 9;
The same numbers in the Figures correspond to the same elements or components.

DETAILED DESCRIPTION OF THE INVENTION

The present invention hence relates to an active material comprising at least one
5 oxygen-containing compound selected from the group consisting of MgO, ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂, at least one thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose, and arabic gum, and at least one plasticizer additive.

10 In the active material of the invention the at least one oxygen-containing compound selected from the group consisting of MgO, ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂ is present.

Particles size of oxygen-based compounds have preferably an average diameter in the range from 5 nm to 100 µm, preferably in the range of 15 nm-10 µm, more preferably 20 nm-5 µm. More preferably, the particles size of oxygen-based
15 compounds have an average diameter in the range from 10-200 nm, still more preferably in the range of 15-100 nm, still more preferably 20-40 nm.

The active material comprises preferably magnesium oxide as oxygen-containing compound, more preferably in the weight percentage in the range from 3% and 17%, preferably 10% with respect to the total weight of the active material.

20 The active material preferably comprises MgO together with both ZnO and ZrO₂ as oxygen-containing compounds, more preferably each one in the weight percentage in the range from 0.7% and 10%, still more preferably 3.7% with respect to the total weight of the active material.

The active material comprises at least one thickener additive selected from the
25 group consisting of agar agar, xanthan gum, methylcellulose, and arabic gum. Preferably, the active material comprises agar agar, Xanthan gum, and/or methylcellulose as thickener additives, more preferably each one in the weight percentage in the range from 0.19% and 6.5 %, still more preferably 0.84 with respect to the total weight of the active material.

30 The active material comprises also at least one plasticizer additive. The at least one plasticizer additive is preferably selected from the group consisting of silicone, siloxanes and Carnauba Wax. More preferably it is silicone, still more preferably in

an amount in the range from 5 to 40%, preferably 12.5% and 37.5%, still more preferably 33.3% by weight with respect to the total weight of the gelled material. The active material comprises also at least one plasticizer additive with respect to the weight of the gelled material in the range from 1:4 to 3:2, still more preferably in a ratio of 1:3.

The active material can be anhydrous or can contain a certain amount of the water deriving from the process for preparing it.

The active material can also contain further additives. Additives may be water coordination additives, casein can be cited.

In a preferred embodiment of the invention, the active material comprises MgO, ZnO, ZrO₂ as oxygen-compounds, agar agar, Xanthan gum, methylcellulose as thickener additives and silicone as plasticizer additive.

In another aspect, the invention concerns a process for preparing the active material comprising the following steps:

- a) preparing a solution with a solvent selected from the group consisting of water, ethylene glycol, glycerin, dimethyl sulfoxide and relative mixtures of at least one oxygen-containing compound selected from the group consisting of MgO, ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂;
- b) heating the solution of step a) at a temperature in the range from 75 to 90 °C;
- c) adding at least one thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose, and arabic gum thus obtaining a homogeneous solution;
- d) cooling down the homogenous solution of step c) to a temperature in the range from 30 °C to 15 °C, thus obtaining a gelled material;
- e) adding at least one plasticizer additive selected from the group consisting of silicone, thus obtaining the active material.

Step a) of the process of the invention provides for preparing a solution of a solvent selected from the group consisting of water, ethylene glycol, glycerin, dimethyl sulfoxide and relative mixtures, preferably water, of at least one oxygen-containing compound selected from the group consisting of MgO ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂ preferably by stirring during the addition of the components. More preferably the addition of the components, while stirring is carried out in

sequence.

In step b) the solution of step a) is heated at a temperature range from 75 to 90 °C. After the heating in step c) at least one thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose, and arabic gum is added.

- 5 Further additives can be also added, for example casein. In the preferred embodiment of the invention step c) provides for the addition of agar agar, Xanthan gum and methylcellulose, advantageously in a simultaneous way. After the addition of the at least one thickener additive a homogenous solution is obtained preferably by stirring.

- 10 In step d) the homogenous solution of step c) is cooled down to a temperature in the range from 30 °C to 15 °C, thus obtaining a gelled material.

In step e) the at least one plasticizer additive, for instance silicone, siloxanes or Carnauba Wax, is added, preferably by stirring to the gelled material.

- 15 In a still another aspect the invention concerns an alternative process for preparing the active material comprising the following steps

i) preparing a first solution with a solvent selected from the group consisting of water, ethylene glycol, glycerin, dimethyl sulfoxide and relative mixtures of at least one oxygen-containing compound selected from the group consisting of MgO, ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂;

- 20 ii) heating the first solution of step i) at a temperature in the range from 90 to 110 °C;
iii) cooling down the homogenous solution of step ii) to a temperature in the range from 50 °C to 30 °C;

- iv) preparing a second solution with a solvent selected from the group consisting of water, ethylene glycol, glycerin, dimethyl sulfoxide and relative mixtures of at least one thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose and arabic gum;

25 v) heating the second solution of step iv) at a temperature in the range from 90 to 120 °C;

vi) mixing the first solution at 45 °C with solution at step v);

- 30 vii) cooling down the homogenous solution of step vi) to a temperature in the range from 30 °C to 20 °C and subjecting it to cooling cycles from ambient temperature to -18 °C;

viii) adding at least one plasticizer additive to the solution of step vii), thus obtaining an homogenous material solution;

x) optionally removing the solvent, and obtaining the active material.

The steps iv), v) and vi) can optionally be repeated before the mixing step (vii) by
5 preparing a third or more solutions with the addition of a further thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose, and arabic gum.

Optional additives such as casein can be added in anyone of the solutions above cited in the process.

10 The process of the invention allows to obtain the active material having a viscosity in the range from 5000 to 100000 centipoise, preferably from 5000 to 40000 centipoise, more preferably from 10000 to 20000 centipoise, as measured with the rotatory viscometer Viscotester VTR5 at rpm =20 at T=25 °C.

In another aspect, the invention relates to an electric power generator (EPG)
15 comprising at least two electrodes, placed at a suitable distance from each other. The EPG comprises the active material according to the invention between the at least two electrodes.

The active material and/or the oxygen-based compounds can be placed on at least one electrode according to any suitable known application method in the art, for
20 example doctor blade, electrophoresis, spin-coating, inkjet printing, sol-gel, thermal spray, sputtering, plasma and any physical or chemical vapour deposition techniques.

The electrodes are made of metals, alloys and/or carbon-based materials like graphite. Electrodes thickness ranges preferably from 0.1 to 3000 µm, more
25 preferably from 50 to 1000 µm, still more preferably from 300 to 600 µm. In a preferred embodiment of the EPG according to the invention, the at least two electrodes are made of Cu and Al, preferably in form of plates or foils substantially parallel. In case of flexible EPG both self-standing flexible materials (among the previous listed materials) and metallized polymers can be considered as electrodes.

30 In a preferred embodiment of the EPG 1 schematically shown in Fig. 1, the at least two electrodes have a plate-shape. The two plates 10 are arranged substantially parallel each other so as to define a gap filled with the active material 20 of the

invention according to a "*sandwich structure*". The distance of the plates 10 depends directly on the desired thickness of the active material to be applied.

The shape of the electrodes is not binding. In an alternative embodiment, for example, the EPG could comprise two coaxial cylindrical electrodes that define an annular space filled with the active material according to the invention. According to
5 the invention, the EPG could comprise more than two electrodes wherein two adjacent electrodes define a gap filled with the active material.

According to a preferred embodiment, the at least two electrodes are made of different material, preferably of Cu and Al. The two at least electrodes are preferably
10 subjected to cleaning and etching prior to be used in the electric power generator of the invention.

The active material is preferably applied on the electrode, by depositing the active material in a thickness from 100 nm to 5 mm. To now, the best results, using a load of 100 Ohm, have been observed with a thickness of 2 mm. On the other hand, the
15 optimal thickness varies depending on the energy required from the device.

The active material can be deposited on the surface of the electrode with doctor blade technique or similar. Once the EPG is assembled with the active material comprised between the at least two electrodes, the EPG is preferably subjected to a heating step, more preferably at about 80°C, in order to obtain a solid sandwich
20 structure.

In a further aspect, the invention relates to a power generator module (PGM) comprising a plurality of EPG which can be connected in series or parallel. On this regards, Figure 1A shows a circuit comprising a PGM wherein the two EPG are connected in parallel, while Figure 1B shows a circuit comprising a PGM having two
25 EPG connected in series. Both the circuits of Figures 1A and 1B comprise a load resistance R_L . The voltage relative to the PGM can be monitored, for example, by connecting a galvanostat parallel to the load resistance R_L .

As it will be evident from the following experimental part the EPG of the invention is capable to generate current as soon as it has been assembled, thus being a different
30 device from a conventional capacitor. Furthermore and surprisingly, the performances of the EPG of the invention have a strongly dependence on temperature, i.e. potential difference increases with the temperature. In particular,

with respect to the traditional power generators of the prior art, the EPC according to the invention does not require a temperature gradient. Indeed, the electric power generator of the invention is able to convert part of the thermal energy in electric energy even an isotherm condition. Specifically and advantageously, the current measured by the electric power generator of the invention increased by a factor of 6-10, increasing the temperature from 20 to 80 °C.

The invention will now be illustrated by some not limitative examples of the active material and of electric power generator of the invention.

Examples

Example 1:

Preparation of the active material of the invention

In order to prepare the active material the following components in the respective amounts reported in the below Table 1 were used. Particles size of oxygen-based compounds (MgO, ZnO, ZrO₂) had an average diameter in the range from 1-100 µm, preferably in the range of 1-10 µm, more preferably 2-5 µm as sold by Sigma-Aldrich.

Components		Amount
1. Demineralized H ₂ O		60-90 % by weight with respect to the total weight of components 1-7
2. MgO	Oxygen-containing compound	5-20% by weight with respect to the total weight of components 1-7
3. ZnO	Oxygen-containing compound	1-7% by weight with respect to the total weight of components 1-7
4. ZrO ₂	Oxygen-containing compound	0.1-5% by weight with respect to the total weight of components 1-7
5. Agar Agar	Thickener additive	0.1-3.5% by weight with respect to the total weight of components 1-7

6. Xanthan Gum	Thickener additive	0.1-2% by weight with respect to the total weight of components 1-7
7. Methyl cellulose	Thickener additive	0.1-2% by weight with respect to the total weight of components 1-7
8. Silicone	Plasticizer additive	20-60% by weight with respect to the total weight of the gelled material obtained after step d)

In a Becker demineralized water was poured and stirring was set between 200 and 400 rpm. The stirrer used was "AREX 630W", WELP SCIENTIFICA. In the becker MgO, ZnO and ZrO₂ were added in sequence, by waiting 5 minutes after adding each component. A final homogeneous aqueous solution was obtained. The solution was then heated up to a temperature in the range from 80 to 90°C. Components Agar Agar, xanthan gum and methyl cellulose were added simultaneously and the stirring was manually continued until an homogeneous solution was obtained. The latter was then left to cool down to ambient temperature at T in the range from 15 to 30°C under manual stirring. A gelled material was obtained. Silicone was then added, and the product was manually stirred until an homogenous active material was obtained.

Example 2

Preparation of the active material of the invention

In order to prepare the active material the following components in the respective amounts reported in the below Table 1 were used. Particles size of oxygen-based compounds (MgO, ZnO, ZrO₂) had an average diameter in the range from 10-200 nm, preferably in the range of 15-100 nm, more preferably 20-40 nm as sold by US Research Nanomaterials, Inc.

Components		Amount
1. Demineralized H ₂ O		60-90 % by weight with respect to the total weight of components 1-7
2. MgO	Oxygen-containing compound	5-20% by weight with respect to the total weight of components 1-7
3. ZnO	Oxygen-containing compound	1-7% by weight with respect to the total weight of components 1-7
4. ZrO ₂	Oxygen-containing compound	0.1-5% by weight with respect to the total weight of components 1-7
5. Agar Agar	Thickener additive	0.1-3.5% by weight with respect to the total weight of components 1-7
6. Xanthan Gum	Thickener additive	0.1-2% by weight with respect to the total weight of components 1-7
7. Methyl cellulose	Thickener additive	0.1-2% by weight with respect to the total weight of components 1-7
8. Silicone	Plasticizer additive	20-60% by weight with respect to the total weight of the gelled material obtained after step d)

In a Becker demineralized water was poured and stirring was set between 200 and 400 rpm. The stirrer used was "AREX 630W", WELP SCIENTIFICA. In the becker

5 MgO, ZnO and ZrO₂ were added in sequence, by waiting 5 minutes after adding each component. A final homogeneous aqueous solution was obtained. The solution was then heated up to a temperature in the range from 80 to 90°C. Components Agar Agar, xanthan gum and methyl cellulose were added

simultaneously and the stirring was manually continued until an homogeneous solution was obtained. The latter was then left to cool down to ambient temperature at T in the range from 15 to 30°C under manual stirring. A gelled material was obtained. Silicone was then added, and the product was manually stirred until an

5 homogenous active material was obtained.

Example 3: Preparation of the active material of the invention and preparation of the electric power generator (EPG)

In order to prepare the active material the following components in the respective amounts reported in the below Table 2 were used.

10 Table 2

Components		Amount
1. Demineralized H ₂ O		60-90% by weight with respect to the total weight of components 1-7
2. MgO	Oxygen-containing compound	3-20% by weight with respect to the total weight of components 1-7
3. Casein	Water coordination additive	0.1-20% by weight with respect to the total weight of components 1-7
4. Gum Arabic	Thickener additive	0.1-5% by weight with respect to the total weight of components 1-7
5. Agar Agar	Thickener additive	0.1-8% by weight with respect to the total weight of components 1-7
6. Xanthan Gum	Thickener additive	0.1-4% by weight with respect to the total weight of components 1-7
7. Methyl cellulose	Thickener additive	0.1-4% by weight with respect to the total weight of components 1-7

8. Silicone	Plasticizer additive	20-60% by weight with respect to the total weight of the gelled material
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Here below the detailed description of the operating procedure taking into consideration intermediate amount of each chemical shown in table 2.

A solution 1 was prepared with the ingredients in the following table 3

5

Table 3: ingredients of solution 1

Chemical	Amount [g]
MgO	150
Casein	150
Demineralized Water	1500

MgO e casein reported in table 3 were mixed at ambient temperature until a homogeneous distribution between two solid state substances is reached. After that, demineralized water was added and the solution was heated up to 100°C in a range of time varying from 20 to 40 minutes. The solution was mixed during this procedure to guarantee a complete and proper homogenization. Once the temperature of 100°C is reached, the solution is maintained at this temperature for 5-10 min. The solution was then gradually cooled down to 40°C.

15 A solution 2 was prepared with ingredients of Table 4

Table 4: ingredients of solution 2

Chemical	Amount [g]
Arabic gum	50
Demineralized water	500

The solution 2 was heated up to 120°C until the Gum Arabic was completely dissolved. After that, the solution was cooled up to 90°C in order to add agar agar. A solution 2b whose ingredients are reported in Table 5 was obtained.

20

Table 5: ingredients of solution 2b

Chemical	Amount [g]
Gum Arabic	50
Demineralized water	500
Agar Agar	100

The Solution 1 at 40°C was then mixed with Solution 2b at 90°C, thus obtaining Solution 3 (whose ingredients are reported in table 6).

5

Table 6: ingredients of solution 3

Chemical	Temperature [°C]
Solution 1	40
Solution 2b	90

Solution 3 was mixed in order to blend properly the two solutions. This mixture was maintained at 45°C in order to avoid gelation phenomena.

10 To the solution 3 methyl cellulose and xanthan gum were added, thus obtaining the Solution 4, whose ingredients are reported in table 7:

Table 7: ingredients of solution 4

Chemical	Amount [g]
MgO	150
Casein	150
Demineralized Water	2000
Gum Arabic	50
Agar Agar	100
Methyl cellulose	30
Xanthan gum	20

This solution 4 was mixed for a minimum of 15 min. After that, Solution 4 was cooled down to ambient temperature for a minimum time period of 4 hours, thus removing
15 any type of mixing action.

As soon as the temperature of 25 °C was reached, the Solution 4 was subjected to cooling cycles starting from ambient temperature to -18 °C. Once this temperature was reached, Solution 4 was stabilized and maintained at 4 °C. After that the solution 4 was weighted and an amount of 50% of its weight of silicone was added and manual agitation was performed in order to obtain an homogenous distribution of the plasticizer. A solution 5 reported in Table 7b was obtained.

Table 7b: ingredients of solution 5

Chemical	Amount [g]
MgO	150
Casein	150
Demineralized Water	2000
Gum Arabic	50
Agar Agar	100
Methyl cellulose	30
Xanthan gum	20
Silicone	1250

The solution 5 was used directly to prepare the electric power generator into a beaker containing the solution 5 (table 7b), two aluminum plates (10cm x 10cm) were immersed, at a distance of 1 cm between them. The plates were connected to a 150W power generator which provides 30V. The applied potential was maintained until the current reaches a value below 30% of the initial value (5A for an ideal case), after that the generator was switched off. This procedure allowed to obtain a uniform and homogeneous layer of active material on the aluminum plate connected to the positive pole. This plate was cooled then down to -18 °C for 1h and then kept at 4 °C for 1h.

In order to remove the residual water, the plate was heated up in an oven at 80 °C.

After this step the EPG was built up adding to the aluminum plate, treated as above described, the copper plate. Keeping the EPG at ambient temperature, a small

pressure was exerted on it in order to favor the adhesion between each plate and the active material.

Example 4:

Preparation of the active material of the invention and preparation of the electric power generator (EPG)

5

In order to prepare the dry active material the following components in the respective amounts reported in the below Table 8 were used.

Table 8: ingredients of example 3

Components		Amount
1. Demineralized H ₂ O		60-90% by weight with respect to the total weight of components 1-7
2. MgO	Oxygen-containing compound	4-20% by weight with respect to the total weight of components 1-7
3. Casein	Water coordination additive	0.1-20% by weight with respect to the total weight of components 1-7
4. Gum Arabic	Thickener additive	0.1-5% by weight with respect to the total weight of components 1-7
5. Agar Agar	Thickener additive	0,1-8% by weight with respect to the total weight of components 1-7
6. Xanthan Gum	Thickener additive	0,1-4% by weight with respect to the total weight of components 1-7
7. Methyl cellulose	Thickener additive	0.1-4% by weight with respect to the total weight of components 1-7
8. Carnauba Wax	Plasticizer additive	15-50% by weight with respect to the total weight of the gelled material

Here below the detailed description of the operating procedure taking into consideration intermediate amount of each chemical shown in table.

The Solution 1 was prepared with the ingredients reported in Table 9:

5

Table 9: ingredients of solution 1

Chemical	Amount [g]
MgO	150
Casein	150
Demineralized Water	1500

10

MgO and casein were mixed at ambient temperature until a homogeneous distribution between two solid state substances was reached. Demineralized water was then added and the solution was heated up to 100°C in a range of time varying from 20 to 40 minutes. The solution was mixed during this procedure to guarantee a complete and proper homogenization. Once the temperature of 100°C was reached, the solution was maintained at this temperature for 5-10 min. The solution was gradually cooled down to 40°C.

The Solution 2 was prepared with the ingredients reported in Table 10.

15

Table 10: ingredients of solution 2

Chemical	Amount [g]
Arabic gum	50
Demineralized water	500

20

The solution 2 was heated up to 120°C until the gum Arabic was completely dissolved. After that, the solution was cooled up to 90°C in order to add agar agar. The solution 2b as reported in Table 11 was so obtained.

Table 11: ingredients of solution 2b

Chemical	Amount [g]
Gum Arabic	50
Demineralized water	500
Agar Agar	100

The solution 1 at 40 °C was mixed with solution 2b at 90 °C, thus obtaining solution 3 (as reported in table 12).

5

Table 12: ingredients of solution3

Chemical	Temperature [°C]
Solution 1	40
Solution 2b	90

Solution 3 was mixed in order to blend properly the two solutions. This mixture was maintained at 45 °C in order to avoid gelation phenomena.

10 methyl cellulose and xanthan gum were then added to the Solution 3, thus obtaining the solution 4:

Table 13: ingredients of solution 4

Chemical	Amount [g]
MgO	150
Casein	150
Demineralized Water	2000
Gum Arabic	50
Agar Agar	100
Methyl cellulose	30
Xanthan gum	20

15 The solution 4 (as reported in table 13) was mixed for a minimum of 15 min. After that, Solution 4 was cooled down to ambient temperature for a minimum of 4 hours, removing any type of mixing action.

As soon as the temperature of 25 °C was reached, the solution 4 was subjected to cooling cycles starting from ambient temperature to -18 °C. Once this temperature was reached, the solution 4 was stabilized and maintained at 4 °C. After that Solution 4 was maintained at ambient temperature for 24 hours.

- 5 An amount of 25% by weight with respect to the weight of the solution 4 of properly crumbled carnauba wax was added at ambient temperature to Solution 4 in order to obtain the Solution 5 (table 14).

Table 14: ingredients of solution 5

Chemical	Amount [g]
MgO	150
Casein	150
Demineralized Water	2000
Gum Arabic	50
Agar Agar	100
Methyl cellulose	30
Xanthan gum	20
Carnauba Wax	625

10

The solution 5 (Table 14) was heated up to 78 °C providing both agitation and ultrasound application. Once solution became homogeneous, the solution 6 was poured on the aluminum plated heated at 78 °C too. After this step, the aluminum plate was immersed into a beaker containing Dimethyl Sulfoxide (DMSO) in order to remove the remaining water.

15

Keeping constant temperature at 78 °C, the EPG was built putting in contact the copper plate with the active material.

At this stage, a potential difference of 30V was applied on EPG for different value of time depending on the temperature:

20

- 5 minutes for T=78 °C
- 5 minutes for T=70 °C
- 10 minutes for T=60 °C

- 10 minutes for $T=50^{\circ}\text{C}$
- 10 minutes for $T=40^{\circ}\text{C}$
- 30 minutes for $T=30^{\circ}\text{C}$
- 10 minutes for $T=25^{\circ}\text{C}$
- 30 minutes for $T=-18^{\circ}\text{C}$

5

Example 5

Assembling of an electric power generator having two electrodes.

Two squared electrodes, respectively made of Cu and Al and having the same area (about 25cm^2) were cleaned and etched in order to be used for assembling the electric power generator. The active material obtained by the Example 1 was then deposited on the surface of Cu electrode with doctor blade technique. The thickness of the active material was about 2mm and the electrode of Al was placed on top of the deposited active material in a parallel way with respect to the Cu electrode. The two electrodes were gently pressed together assuring a uniform contact of the active material with their own surface. The product so obtained was baked for 20 minutes at 80°C in order to dry the active material, thus obtaining a solid electric power generator. The generator of the invention so obtained was then stored at a temperature from 15 to 18°C for a time period of 12-24 hours before testing it.

Example 6

Electrical characterization of the electric power generator.

The EPG of Example 5 was electrically characterized by using AMEL2553 potentiostat/galvanostat. The electrical circuit is reported in Figure 2.

From Figure 2, it is shown the EPG is a generator, providing a current in, coupled with its own internal resistance (R_i). The latter is normally defined as a ratio between the open circuit potential and the short circuit current. The load resistance (R_L) was connected in series to the electric power generator of Example 2. The voltage was monitored by connecting the galvanostat parallel to the load resistance. The source resistance (R_i) is strongly dependent on the components of the active material. The internal resistance was measured following the "*voltage divider procedure*": Different load resistances were applied to the EPG until a voltage of an half with respect to the open circuit one was reached after some minutes. In this way, a

“voltage divider” is created with two equal series load resistances, namely the internal one (R_i) and the load resistance (R_L). Through this procedure, the internal resistance (R_i) was estimated to be between 1 and 100 K Ω m. The resistance R_{EPG} measured between the electrodes had an average value of 1.2-1.6 M Ω . The active material resulted to have a low conductivity. The electric power generator was characterized by running a potentiometric analysis setting a null current (open voltage). On the contrary, closing the circuit the current flowed through the load resistance (R_L). The amount of current was measured from the value of the voltage measured divided by $R_L=100\Omega$.

Example 7

Thermal characterization of the electric power generator.

The circuit scheme reported in Figure 2 comprising the electric power generator of Example 5 was tested at ambient temperature (18-20°C). The test consisted in a 5 minutes open voltage measurement followed by two hour with the circuit closed.

The curves reported in Figure 3 and 4 were obtained. With reference to Figures 3 and 4, three different regions were observed:

- 1) a first region characteristic of a condition of “*open circuit*”; in such region, the voltage was constant and the average open circuit voltage (OCV) measured for all EPGs fabricated was 1.2-1.4 V prior to testing. No current was measured (open circuit);
- 2) a second region characteristic of a “*transition*” between the open circuit condition and a closed circuit condition; as soon as the circuit was closed the voltage dropped abruptly and constantly reduced in time until a minimum was reached (transition region); in the transition region the current increased to a maximum value (1-1,2 mA);
- 3) a third region characteristic of a condition of “*closed circuit*”; in the third region the current generated by the EPG increased with time although the EPG was “discharging” and stabilized to a given value, i.e. $I=0.5-1\text{ mA}$.

Example 8

Thermal characterization of the electric power generator.

The circuit scheme reported in Figure 2 comprising the electric power generator of Example 5 was tested for temperature dependence (20-90°C). The test consisted

in heating the EPG with the aid of a heater or by immersing the electric power generator in a liquid under stirring. Temperature was monitored with a thermographic camera (FLIR Exx series) or with a mercury-in-glass thermometer in case of a heating bath. In this example, mercury-in-glass thermometer was chosen.

- 5 The electric power generator was heated up to 90°C after having let the electric power generator for 1 hour at 20 °C with a 100Ω load in order to stabilize the current. The curves reported in Figure 5 and 6 were obtained.

After 1 hour at 20 °C under load, the EPG stabilized at about 0.57 mA; the current reached about 3.5 mA at T=90°C.

- 10 The circuit scheme reported in Figure 2 comprising the electric power generator of Example 5 was tested at different temperature conditions. Temperature was constantly monitored and the curve current temperature dependence reported in Figure 7 was obtained. More precisely, the curve in Figure 7 shows the values of currents measured at different temperature conditions with the circuit scheme of
15 Figure 2 in a closed condition.

Example 9

An electric power generator EPG as reported in Example 5 was assembled by using electrodes made of the same material, namely Cu-Cu. Active medium as in the Example 1 has been used with a 2 mm thickness. The electrodes area was 9 cm².

- 20 Figure 8 shows the current evolution as a function of the temperature. It is worth to notice that also this test shows an increase of the current generated by the EPG with the temperature. However, such an increase is in the order of μA and not of mA as in the Example 8.

Example 10

- 25 An EPG as reported in Example 5 was assembled by using electrodes having higher area (1.5, 6.25, 25 and 100 cm²). The current generated was proportional to the electrode area: the bigger the area, the higher the current produced. Figure 9 shows a curve of the EPG performance depending on the electrodes area. The other parameters of the EPG (thickness, active medium composition, electrodes material)
30 are kept constant as in Example 5.

Example 11

The possibility of working with alternate discharge has been evaluated for an EPG

having the features as in the Example 5, namely thickness, active medium, composition, electrodes material, electrodes area as in the Example 5. In Figure 10, a continuous discharge (curve C1) is compared with an alternate discharge (curve 30-30). Both the curves refer to the tested EPG. The alternate discharge comprises 30 seconds of working and 30 seconds of rest. In the 30 seconds of working, an external load resistance is applied and the circuit is closed. In the 30 seconds of rest, the circuit is open and the load resistance is removed. In both cases (continuous and alternate discharge) a load resistance of 100 Ω has been applied. An evaluation is performed comparing both the "active working times" (ON states) and the effective times of each tests. The expression "ON STATE" wants to indicate a working period in which the load resistance is applied. In the specific case, this condition occurred cyclically every 30 seconds. For the following 30 seconds, the load resistance was disconnected (OFF STATE) from the EPG by means of a releé. Alternate discharge was evaluated also for different ON and OFF times in the range of 2-60 seconds.

Figure 10 shows that the performances (in term of current discharged) are greatly improved with the alternate discharge. During the rest phase, the EPG partially shows a recovery effect, namely a temporary recover of voltage (V) when the load resistance is not applied to the EPG. It is worth to notice that, during the OFF STATE, it was possible to apply a voltage and/or current at the EPG electrodes so as to increase the voltage and consequently the current discharge thereby. Such a procedure can be actually used after each test or anytime the EPG is disconnected from the load resistance.

Example 12

The EPG shows a strong sensibility to the working condition e.g. environment. The presence of water and oxygen seemed to decrease the lifetime of the EPG. Preliminary tests have been performed on EPGs prepared according to the Example 5 to evaluate the requirement of a proper sealing to extend the device lifetime. For this purpose, the EPGs have been tested with a potentiostat/galvanostat AMEL2553. The test consists in applying a discharge current of 100 μA ; EPGs have been discharge from the nominal voltage to 0.8V subsequently followed by 45 minutes of rest $I=0 \mu\text{A}$ to evaluate the recovery. With exception of the sealing step,

the two EPGs have been fabricated with the same route as in Example 5 with standard electrodes dimensions 25 cm². In the first case, the EPG has not been sealed allowing the interaction with the atmosphere; in the second case the EPG has been completely sealed by immersion in silicone.

- 5 Figure 11 shows the curves of the EPG performance depending on the sealing. On the tested EPGs a relative lifetime extension of 400% is observed; higher OCV voltage is measured for the sealed EPG prior the application of a discharge current. It is important to notice that these tests have been carried on a standard formulation, containing a relatively high water content. Sealing effect is expected to be higher on
10 an optimized one, containing a lower amount of water. In addition, large improvements in sealing quality is expected.

Example 13

- Particle size of the oxygen-based compounds (MgO, ZnO, ZrO₂) affects the overall performances of the EPG. In fact, the smaller the particles dimension the higher the
15 active surface area for a given material volume. The effect of particle dimension has been investigated comparing EPGs performances for micrometric and nanometric oxygen-based particles as obtained according to the formulation of Example 1 and Example 2 and following the procedure of Example 5, EPG electrodes area is 25 cm². For this purpose, the EPGs have been tested with a potentiostat/galvanostat
20 AMEL2553. The test consisted in applying a discharge current of 100μA; EPGs have been discharge from the nominal voltage to 0.8V subsequently followed by 45 minutes of rest I=0 μA to evaluate the recovery.

- The use of nanoparticle extends the EPG relative lifetime more than 200% with respect to the micrometric formulation. A higher OCV voltage has been also
25 observed.

Example 14

- Assembling multiples EPGs according to specific configurations as in the Example 5 results in the enhancement of the power generated above at least of 10%. In the test considered, the current is measured using a multimeter. In this experiment, ten
30 EPGs connected in series are considered. In the first configuration, the EPGs are disposed side by side; the electrodes of different EPGs are not in physical contact but are electrically connected by means of a copper wire. In the second

configuration, the EPGs are piled up preferably maintaining the connection wires, preferably putting in contact the surface of copper and aluminum of adjacent EPGs. The latter configuration has shown a current of $I=15$ mA while for the former $I=13$ mA has been measured.

CLAIMS

1. An active material comprising at least one oxygen-containing compound selected from the group consisting of MgO, ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂, at least one thickener additive selected from the group consisting of agar agar,
5 xanthan gum, methylcellulose, and arabic gum, and at least one plasticizer additive.
2. The active material of claim 1, wherein the at least one oxygen-containing compound has particle average diameter in the range from 5 nm to 100 μm, preferably in the range of 15 nm-10 μm, more preferably 20 nm-5 μm.
3. The active material of claim 2, wherein the at least one oxygen-containing
10 compound has particle average diameter in the range from 10 to 200 nm, preferably in the range of 15-100 nm, more preferably 20-40 nm.
4. The active material of anyone of claims 1-3, wherein the at least one oxygen-containing compound is MgO, in the range from 3% and 17%, preferably 10% with respect to the total weight of the active material.
- 15 5. The active material of anyone of claims 1-3, wherein the at least one oxygen-containing compound is ZnO or ZrO₂.
6. The active material of claim 5, wherein the at least one oxygen-containing compound is in the range from 0.7% and 10%, preferably 3.7% with respect to the total weight of the active material.
- 20 7. The active material of anyone of claims 1-6, wherein the at least one thickener additive is selected from the group consisting of agar agar, xanthan gum, and methylcellulose.
8. The active material of claim 7, wherein the at least one thickener additive is in the range from 0.19% and 6.5 %, preferably 0.84 % with respect to the total weight of
25 the active material.
9. The active material of anyone of claims 1-8, wherein the at least one plasticizer additive is selected from the group consisting of silicone, siloxanes and carnauba wax.
10. The active material of anyone of claims 1-9, wherein the active material
30 comprises silicone in an amount in the range from 5% to 40%, preferably 12.5% and 37.5%, more preferably 33.3% with respect to the total weight of the active material.
11. The active material according to anyone of claims 1-3, wherein it comprises

MgO, ZnO, ZrOCl₂, agar agar, xanthan gum, methylcellulose and silicone.

12. A process for preparing the active material according to anyone of claims 1-11, comprising the following steps:

a) preparing a solution with a solvent selected from the group consisting of water, ethylene glycol, glycerin, dimethyl sulfoxide and relative mixtures of at least one oxygen-containing compound selected from the group consisting of MgO, ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂;

b) heating the solution of step a) at a temperature in the range from 75 to 90 °C;

c) adding at least one thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose and arabic gum, thus obtaining a homogeneous solution;

d) cooling down the homogenous solution of step c) to a temperature in the range from 30 °C to 15 °C allowing gelation, thus obtaining a gelled material;

e) adding at least one plasticizer to the gelled material, thus obtaining the active material.

13. A process for preparing the active material according to anyone of claims 1-11, comprising the following steps:

i) preparing a first solution with a solvent selected from the group consisting of water, ethylene glycol, glycerin, dimethyl sulfoxide and relative mixtures of at least one oxygen-containing compound selected from the group consisting of MgO, ZnO, ZrOCl₂, ZrO₂, SiO₂, Bi₂O₃, Al₂O₃ and TiO₂;

ii) heating the first solution of step i) at a temperature in the range from 90 to 110 °C;

iii) cooling down the homogenous solution of step ii) to a temperature in the range from 50 °C to 30 °C;

iv) preparing a second solution with a solvent selected from the group consisting of water, ethylene glycol, glycerin, dimethyl sulfoxide and relative mixtures of at least one thickener additive selected from the group consisting of agar agar, xanthan gum, methylcellulose, and arabic gum

v) heating the second solution of step iv) at a temperature in the range from 90 to 120 °C;

vi) mixing the first solution at 45 °C with the solution at step v);

vii) cooling down the homogenous solution of step vi) to a temperature in the range

from 30 °C to 20 °C and subjecting it to cooling cycles from ambient temperature to - 18 °C;

viii) adding at least one plasticizer additive to the solution of step vii), thus obtaining an homogenous material solution;

5 x) optionally removing the solvent, and obtaining the active material.

14. An electric power generator (EPG) comprising at least a first electrode (11) and a second electrode (12), wherein the electric power generator comprises an active material, according to any one of the claims 1-11, between said electrodes (11,12).

10 15. The electric power generator (EPG) according to Claim 14, wherein said electrodes are made of the different materials.

16. The electric power generator (EPG) according to Claim 14, wherein said electrodes are made of the same material.

15 17. The electric power generator (EPG) according to Claim 15, wherein said first electrode (11) is made of copper and wherein said second electrode is made of aluminum.

18. The electric power generator (EPG) according to Claim 16, wherein said electrodes are made of copper.

20 19. The electric power generator (EPG) according to Claim 14, wherein said electrodes are made of a material selected in a group consisting of metals, alloys and carbon based materials.

20. A power generator module (PWG) characterized in that it comprises a plurality of electric power generators (EPGs) according to any one of the claims 14-18, wherein said generators are connected in parallel or in series.

25 21. A power generator module (PWG) according to Claim 20, wherein when said EPGs are connected in series, the electrodes of different EPGs are electrically connected by a conductive wire.

22. A power generator module (PWG) according to Claim 20, wherein when said EPGs are connected in series, the EPGs are piled up so that the surface of an electrode of a first EPG is in contact with a surface of a second EPG.

30

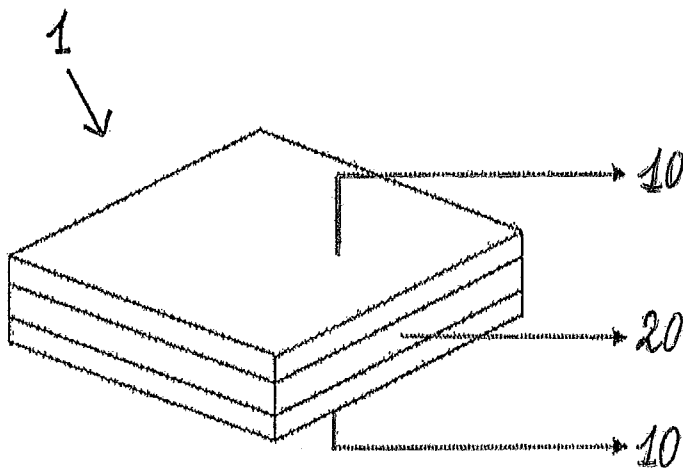


Fig. 1

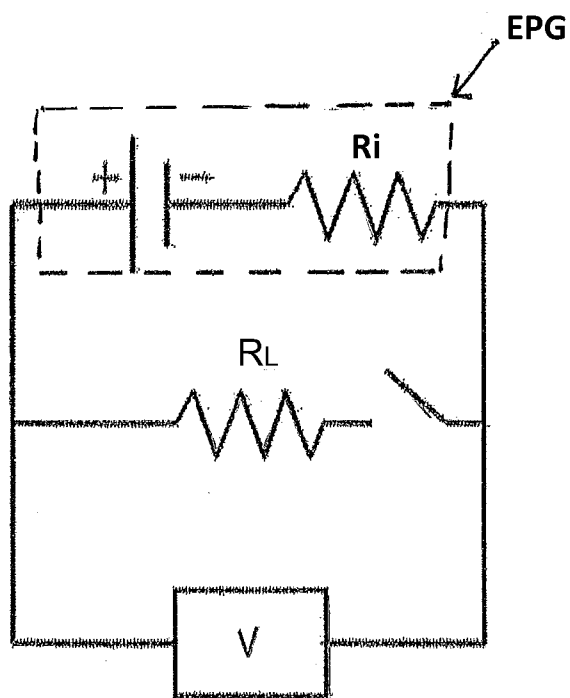


Fig. 2

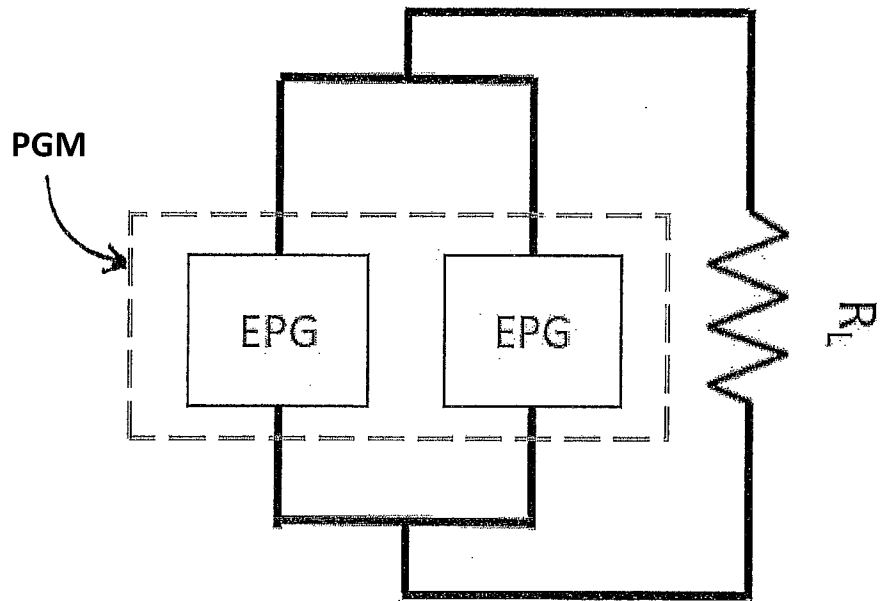


Fig. 1A

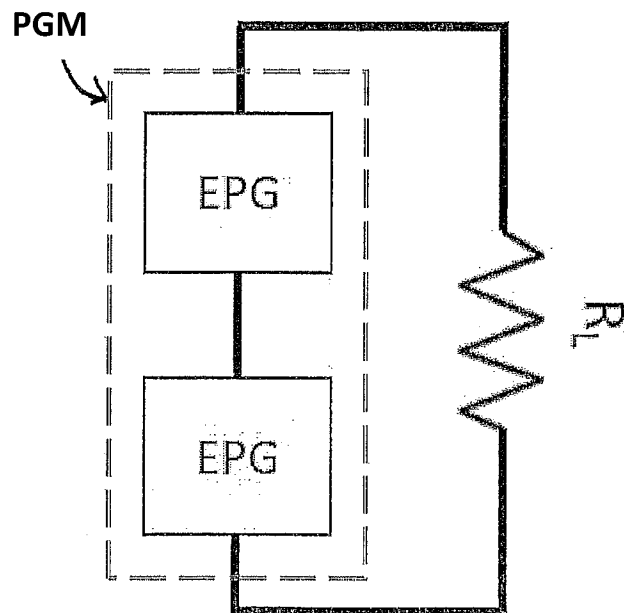


Fig. 1B

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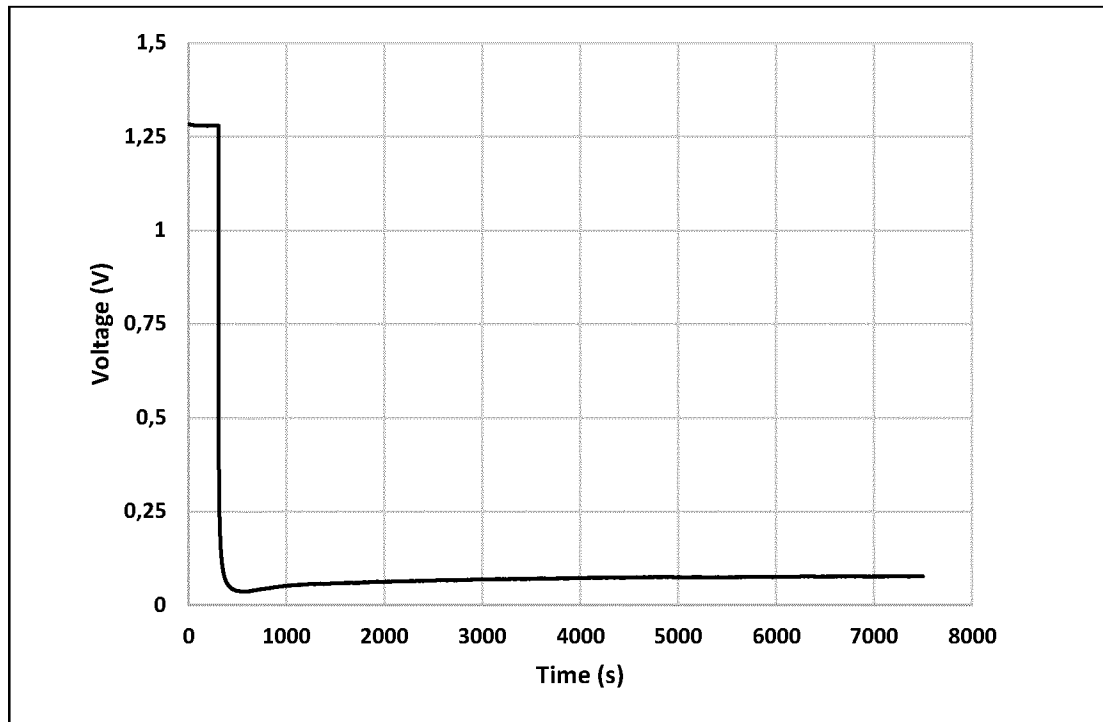


Fig. 3

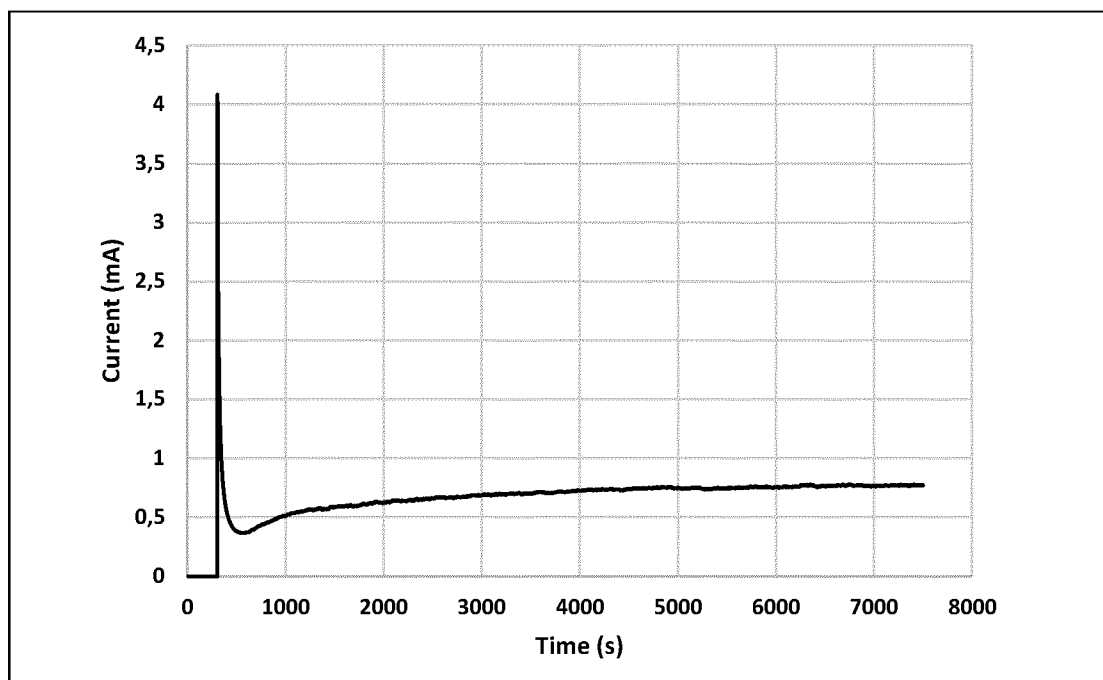


Fig. 4

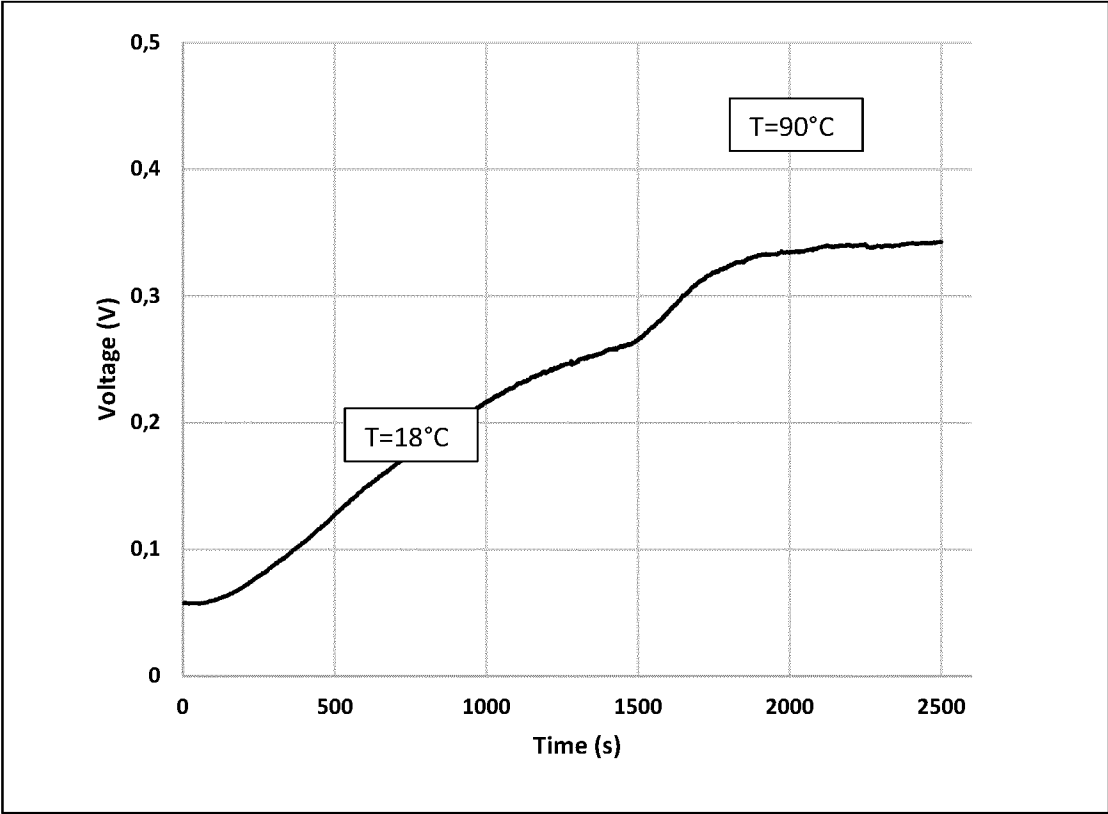


Fig. 5

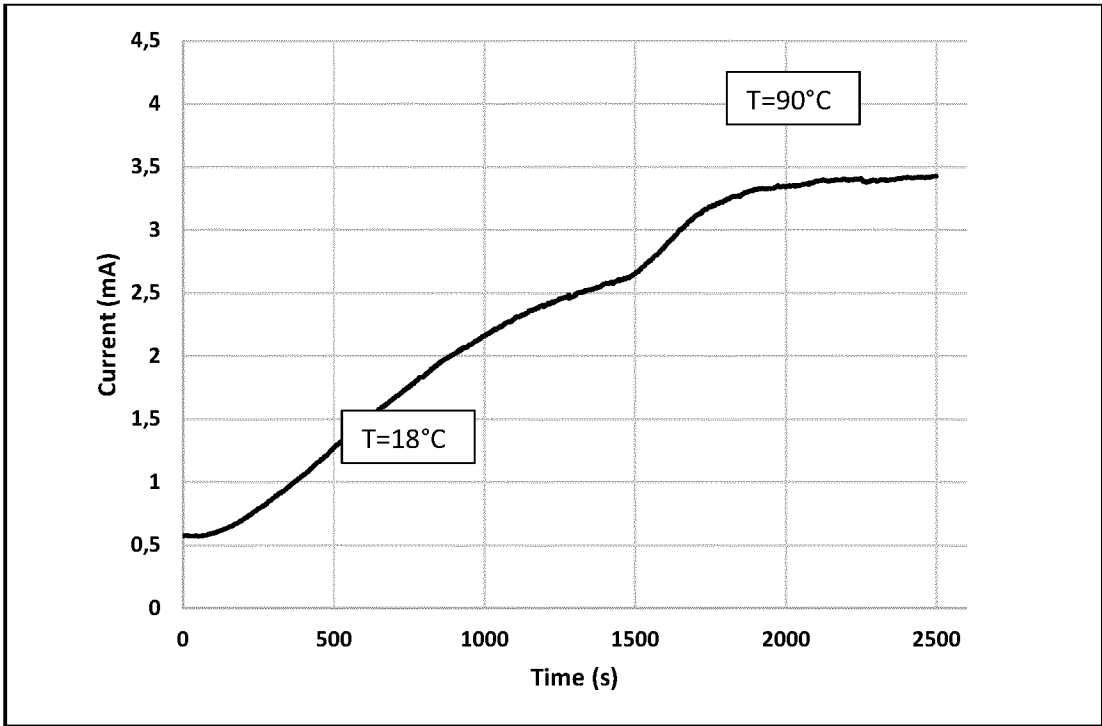


Fig. 6

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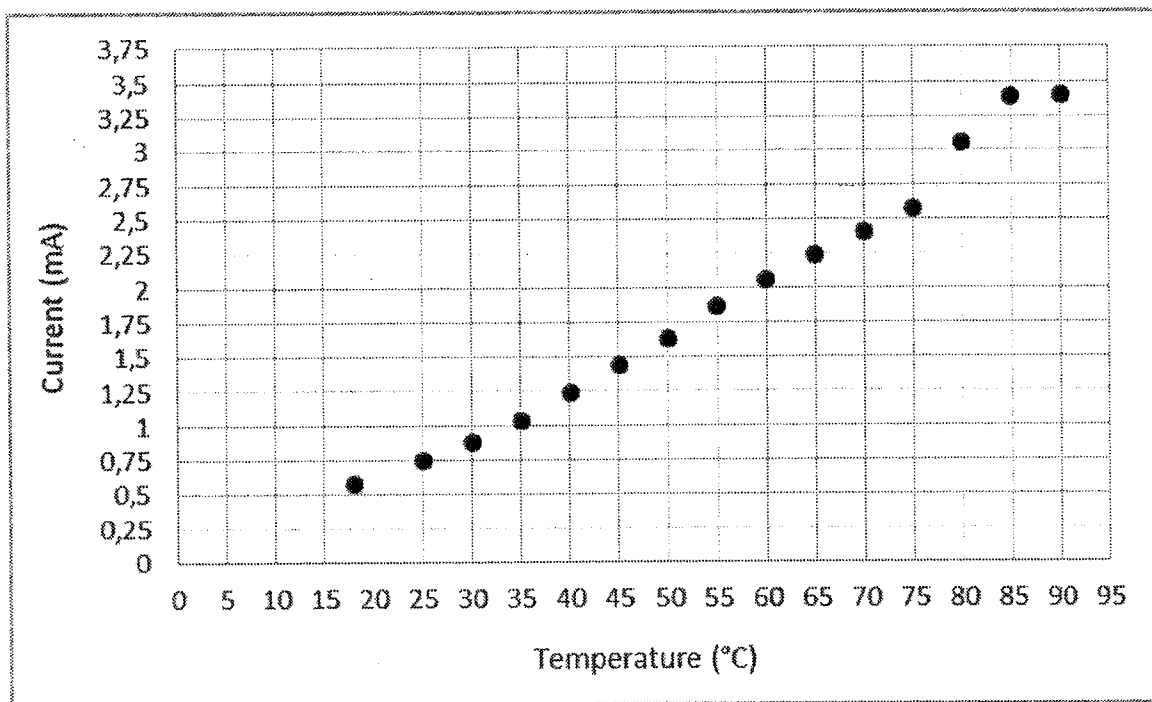


Fig. 7

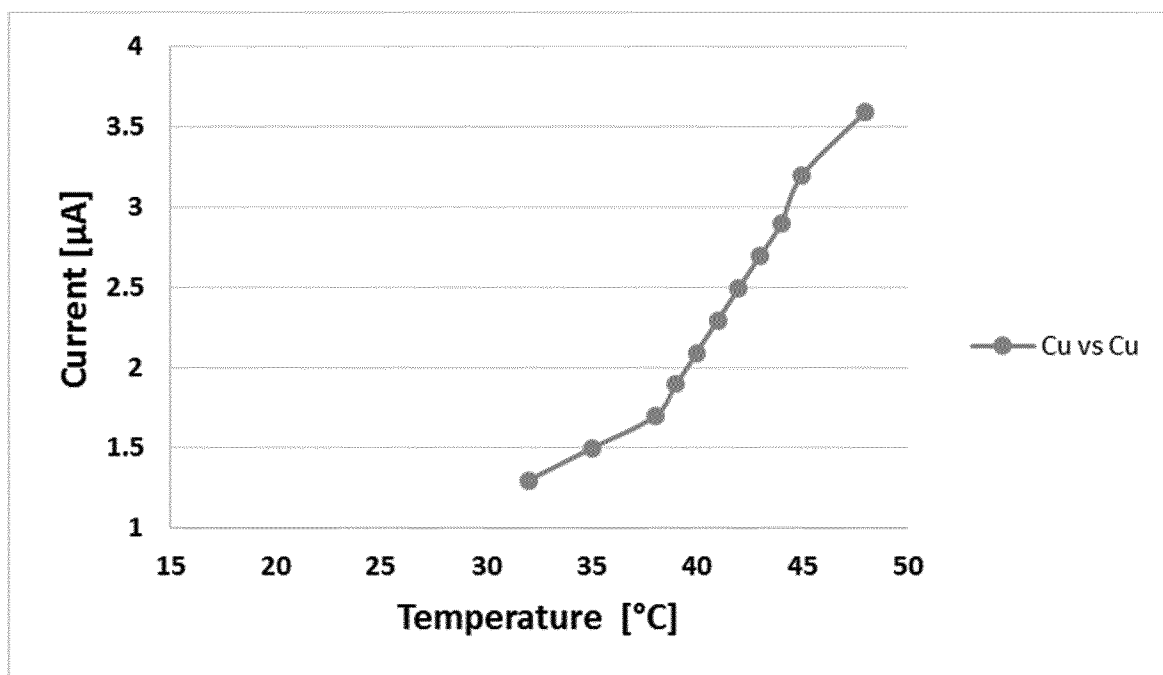


Fig. 8

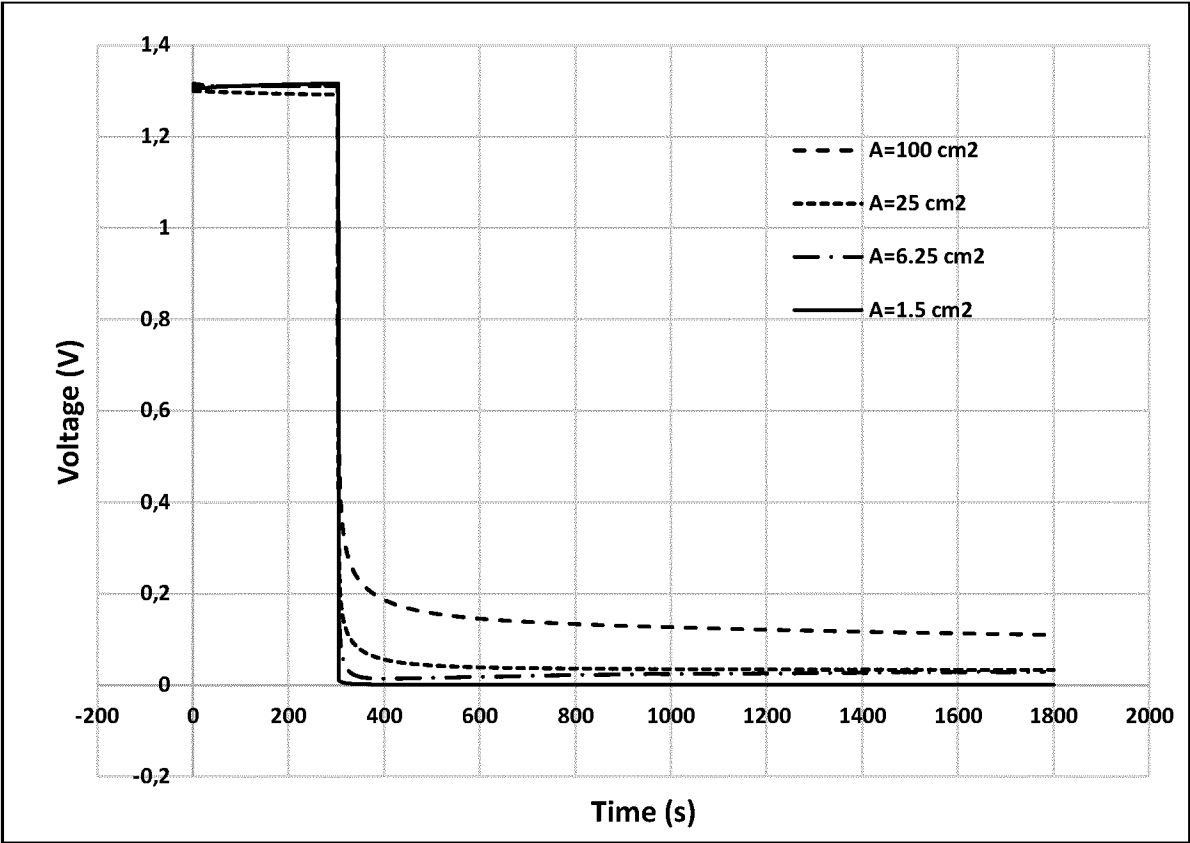


Fig. 9

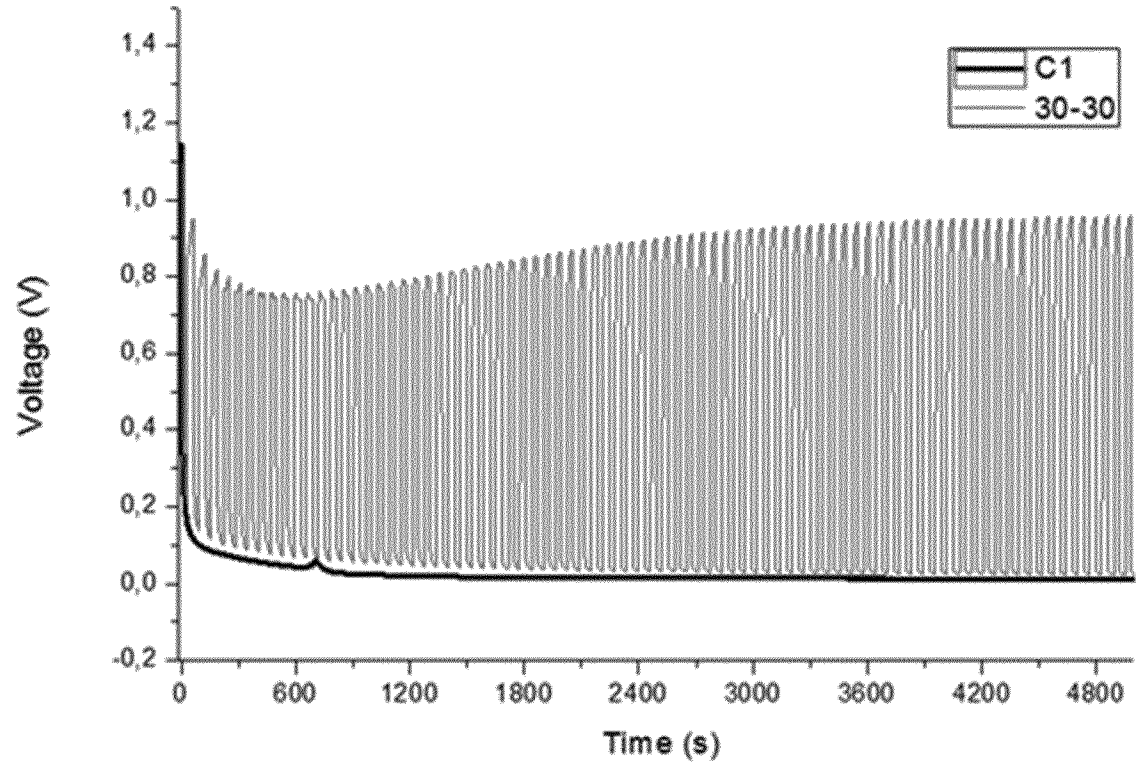


Fig. 10

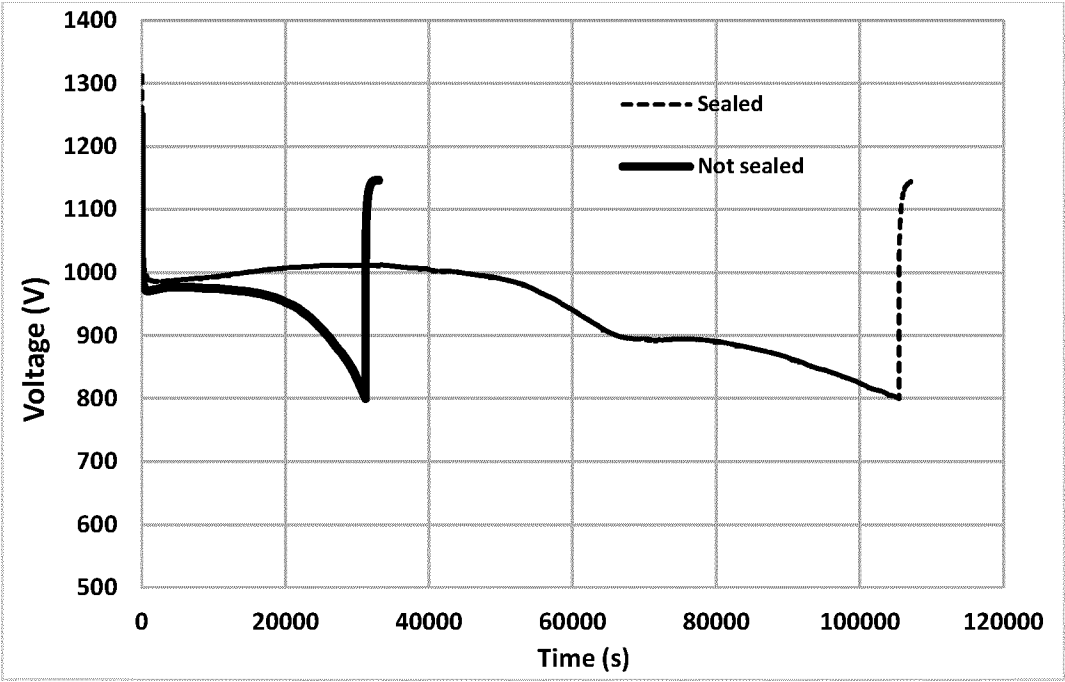


Fig. 11

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/069030

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L35/22 H01L35/34
ADD.

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)

H01L

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/268382 A1 (TANAKA AKIHIKO [JP] ET AL) 30 October 2008 (2008-10-30)	1,2,5,7, 9,10, 14-22
A	abstract paragraphs [0029], [0031] paragraphs [0048] - [0050] paragraph [0043] paragraph [0095]	3,4,6,8, 11-13
A	----- JP 2016 079348 A (SOMAR CORP) 16 May 2016 (2016-05-16) abstract	1,11
A	----- WO 2016/035454 A1 (FUJIFILM CORP [JP]) 10 March 2016 (2016-03-10) abstract paragraph [0071] -----	1



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

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

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

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

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Date of the actual completion of the international search

22 December 2016

Date of mailing of the international search report

09/01/2017

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Authorized officer

Deconinck, Eric

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/069030

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
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			KR 20080071579 A	04-08-2008
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JP 2016079348	A	16-05-2016	NONE	

WO 2016035454	A1	10-03-2016	NONE	
