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(54) Title: IMPROVEMENTS IN LEAD-ACID BATTERY CONSTRUCTION

(57) Abstract: A lead-acid battery or cell comprises electrode(s) of with current collector(s) of a fibrous material with an average interfibre spacing of less than 50 microns. The current collector material may be a carbon fibre material which has been thermally treated by electric arc discharge. The fibrous current collector material may comprise an impregnated paste comprising a mixture of lead sulphate particles and dilute sulfuric acid.

"IMPROVEMENTS IN LEAD-ACID BATTERY CONSTRUCTION"

FIELD OF THE INVENTION

The invention relates to an improved battery construction for lead-acid batteries.

BACKGROUND

A battery stores and releases energy by electrochemical reaction(s) at the surfaces of its electrodes. Each cell of a lead-acid battery in the fully charged state contains electrodes of elemental lead (Pb) and lead (IV) dioxide (PbO_2) in an electrolyte of dilute sulfuric acid (H_2SO_4). In the discharged state both electrodes turn into lead(II) sulfate ($PbSO_4$) and the electrolyte loses its dissolved sulfuric acid and becomes primarily water. In the pasted-plate construction each plate consists of a lead grid initially filled with a paste comprising a mixture of leady oxide (Pb and PbO) and dilute sulfuric acid. This construction allows the acid in the paste to react with the leady oxide inside the plate during cell formation (first charge and discharge cycle during which linkages between neighbouring particles, increasing the electrical conductivity and active surface area and thus the battery capacity. The paste may also contain carbon black, blanc fixe (fine barium sulfate), and lignosulfonate. The blanc fixe acts as a seed crystal for the lead to lead sulfate reaction. The lignosulfonate prevents the negative plate from forming a solid mass of lead sulfate during discharge. Carbon black counteracts the effect of inhibiting formation caused by the lignosulfonates.

SUMMARY OF INVENTION

In broad terms in one aspect the invention comprises a lead-acid battery or cell including at least one electrode comprising as a current collector a conductive fibrous material comprising:

filaments comprising fibres with an average interfibre spacing between fibres of less than 50 microns, and/or

filaments which are monofibres and in which the average interfibre spacing between monofibres is less than 50 microns.

In broad terms in another aspect the invention comprises a method for manufacturing a lead-acid battery or cell which includes forming at least one electrode comprising as current collector a conductive fibrous material comprising:

filaments comprising fibres with an average interfibre spacing between fibres of less than 50 microns, and/or

filaments which are monofibres and in which the average interfibre spacing between monofibres is less than 50 microns.

In broad terms the another aspect the invention comprises a lead-acid battery or cell comprising as a current collector a conductive fibrous material having length and width dimensions in a major plane of the material and depth perpendicular to said major plane of the material and comprising:

filaments comprising fibres with an average interfibre spacing between fibres of less than 50 microns, and/or

filaments which are monofibres and in which the average interfibre spacing between monofibres is less than 50 microns.

In some embodiments the average interfibre spacing is less than 20 microns.

Preferably said average interfibre spacing is over at least a major fraction of the material and more preferably over substantially all of the material.

The current collector fibrous material may have an average depth of the material of at least 0.2mm or at least 1mm.

The current collector may comprise multiple layers of the conductive fibrous material.

Preferably the current collector material has bulk resistivity less than 10 Ω mm and preferably less than 1 Ω mm or 0.1 Ω mm.

The electrode material may be a woven material (comprising intersecting warp and weft fibres), a knitted material, or a non-woven material, such as a woven or knitted or non-woven fabric.

The positive electrode or electrodes, the negative electrode or electrodes, or both, may be formed of one or more layers of the conductive fibrous material.

Preferably the conductive fibrous material is also lighter than lead.

The current collector material may comprise a carbon fibre material such as a woven or knitted or non-woven carbon fibre fabric.

Carbon fibre current collector material may be heat treated to sufficient temperature to increase its electrical conductivity.

In broad terms in another aspect the invention comprises a lead-acid battery or cell including at least one electrode comprising as a current collector a carbon fibre material thermally treated to reduce the resistivity thereof. The thermal treatment may be by electric arc discharge.

In the microscale electrode construction of the invention the average interfibre distance between fibres of the conductive fibrous current collector material is less than 50 microns and may be less than 20 microns, either between individual fibres of multifibre filaments such as carbon multifilament yarn used for example to weave or knit the material, or between monofilaments of a material for example woven or knitted from a monofilament. During formation and subsequent discharge and re-charge cycling of a battery or cell, each particle must connect electrically directly or indirectly with neighbouring particles and to the electrode current collector before it can receive charge or deliver charge by reaction. In the microscale electrode construction of the invention relatively fewer particles must link to connect to near current collector fibres. For example the farthest distance of any active particle in a conducting chain of particles to the nearest current collector fibre surface may be less than 25 microns or less than 10 microns. This may increase utilisation and capacity, and also reduce the time required for initial cell formation, and reduce the chance of electrical isolation of active particles (particles can be isolated by adjacent particles converting to $PbSO_4$ before they do - $PbSO_4$ is electrically insulating).

During cell or battery construction the current collector material such as carbon fibre material may be impregnated under pressure with a paste, such as a paste comprising a mixture of lead sulphate particles and dilute sulfuric acid.

In broad terms in another aspect the invention comprises a method for manufacturing a battery or cell comprising applying to at least one electrode comprising as current collector a conductive fibrous material, a paste which comprises a mixture of lead sulphate particles and dilute sulfuric acid. In preferred embodiments lead sulphate paste is substantially the sole source of lead in the active material paste.

The term "comprising" as used in this specification means "consisting at least in part of". When interpreting each statement in this specification that includes the term "comprising", features other than that or those prefaced by the term may also be present. Related terms such as "comprise" and "comprises" are to be interpreted in the same manner.

BRIEF DESCRIPTION OF THE FIGURES

The invention is further described with reference to the accompanying Figures by way of example wherein:

Figure 1 schematically illustrates one form of reactor for the continuous or semi-continuous activation of a carbon fibre material for use as a current collector material according to the invention, and

Figure 2 is a close up schematic view of the electrodes and the material path between the electrodes of the reactor of Figure 1,

Figure 3 is a photo micrograph of a section of the woven carbon fibre material referred to in subsequent experimental Example 1,

Figure 4 is a SEM image of a single multifibre filament of the carbon fibre material of Figure 3,

Figures 5 and 6 are "Ragone" type plots of specific capacity in Ah/kg Pb in the negative active mass versus specific current A/kg Pb in the negative active mass referred to in subsequent experimental Example 4,

Figure 7 is a cycle end-of-discharge cell voltage plot referred to in subsequent experimental Examples 6 and 7, and

Figure 8 is a plot of charge current against number of cycles referred to in experimental Example 8.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The invention includes a lead-acid battery including at least one electrode comprising as a current collector a microscale conductive fibrous material in which the average interfibre spacing thereof is less than 50 microns or less than 20 microns.

The current collector material may be a woven material, a knitted material, or a non-woven material, such as a woven or knitted or non-woven fabric. The material may comprise filaments extending unidirectionally in a major plane of the material with each filament composed of multiple fibres, with optionally connecting threads extending transversely across the filaments to mechanically connect the filaments.

The negative electrode or electrodes, the positive electrode or electrodes, or both, of a cell or battery may be formed with one or two or more layers of the conductive fibrous material as the current collector(s) of each electrode.

In preferred embodiments the electrode fibres are inherently conductive without requiring coating with a more conductive material such as a metal to increase conductivity, and may be carbon fibres which may in some embodiments be treated to increase conductivity, but in other embodiments the electrode fibres may be a less conductive microscale material the fibres of which are coated with a conductive or more conductive coating. In some embodiments the fibres of the current collector material may be coated with Pb or a Pb-based material. For example the negative electrode or electrodes may be coated with Pb and the positive electrode(s) coated with Pb and then thereon PbO_2.

Carbon fibre material for use as the electrode current collector material may be thermally treated at an elevated temperature sufficient to increase electrical conductivity. Thermal treatment may also increase the thermal conductivity of the material, which should be sufficient to prevent local hot spots on the electrode in use. Carbon fibres are generally hydrocarbon-based and during manufacture heated to around 1100°C or more ("carbonised"). For use as current collector material in batteries or cells of the invention, carbon fibre material may be heated further, generally in the range 2200 to 2800°C, to enlarge regions in the carbon that are already aromatic or graphitic, increasing electrical conductivity, by evaporating off at least some or a major fraction of non-graphitic carbon from the carbon fibres, and no more than a minor fraction of graphitic carbon.

Thermal treatment to increase electrical and/or thermal conductivity may be by electric arc discharge, or in a resistively heated furnace for example.

The microscale current collector material may be treated to increase its surface area to increase capacitance. In some embodiments carbon fibre electrode material is activated to increase the surface area of the material to increase internal capacitance with the battery. The material may be heated to a surface temperature for example above about 3600K. Also applying and then drying an $Ni(NO_3)_2$ solution onto carbon fibre material before arc treatment may increase surface area development (apparently through oxidation). The material may be thermally treated by electric arc discharge. Alternatively the material may be activated by physical activation such as by steam or carbon dioxide at temperatures around 1000°C, or by chemical activation by for example alkali solutions. Activation typically creates pores of nanoscale and most typically up to 50 nm in diameter, in the material, or on the surface of the material. Materials with extensive pores smaller than around 1 nm may not good electronic conductors. Pores from 1 nm to around 10 nm may provide the surface area required for significant capacity, but pores well distributed above 10 nm are also needed to provide easy diffusional access of ions for adequate electrolyte conductivity. Also required is sufficient electrical conductivity within the solid.

In some embodiments carbon fibre material has carbon nanotubes (CNTs) attached thereto. The CNTs bearing material may be produced by electric arc discharge treatment of the carbon fibre material, or alternatively by chemical vapour deposition at lower temperatures in the presence of a catalyst.

Preferably the current collector material and the fibres thereof are flexible, which will assist in accommodating volume changes of the active material attached to the current collector material during battery cycling, and the microscale fibres may also reinforce the active material, both assisting to reduce breaking off ("shedding") of active material from the electrode in use.

The current collector material may be supported mechanically and a supporting mechanical frame may also provide electrical connection of each electrode or plate to the battery terminals. For example one or more square or rectangular adjacent layers of the current collector material may be supported to form a planar battery plate by a peripheral metal frame on all sides or between opposite metal frame elements on two opposite sides. Alternatively for example concentric cylindrical positive and negative plates of each cell may comprise cylindrical sections of the microscale current collector supported at either cylindrical end by circular metal frames.

Preferably substantially all or at least a majority of filaments/fibres of the electrode material extend continuously across the electrode between or to a metal frame or frame elements to which both ends or at least one end of the fibres is/are electrically connected. A woven fabric of continuous fibres may be optimal. The electrical connection between the carbon fibres and the conductive frame should be a minimum resistance join and in a preferred form each fibre end is surrounded with a molten metal which physically fixes and electrically connects the fibre end to the metal frame, during battery or cell construction. The metal frame or frame elements may themselves be formed by cooling molten metal strips along one or more edges of the electrode material to surround and embed the fibre ends. Optionally the fibres or fabric can continue beyond one or more frame elements at one or more edges to form another adjacent electrode or electrode section. Preferably substantially all or at least a majority of electrode fibres in one direction or in plane axis of the material are electrically connected to a metal frame element not more than 100 mm to 10 mm away from where the fibre starts in the active material or at both opposite edges of the material. This distance or the size or area of each current collector material section is mainly determined by the bulk resistivity of the current collector material in the most conducting direction. If only one edge of the fabric is electrically connected to a metal frame element, preferably this most conducting direction in the fabric is aligned perpendicular to the connected edge to minimize the overall resistance. To allow highest current density in an electrode without significant capacity loss, the length of the fabric from the connected edge may be up to about 50 to 100 mm. A metal frame may alternatively comprise a metal sheet with apertures, on one or both sides of the material, leaving the apertures or windows with solely carbon fibres carrying the current and collecting from the active material that they carry. For example an electrode frame of height 200 mm, may comprise three windows of height each 60 mm, with a conducting web left around the edge. For each of these window regions, carbon fabric can be spread and attached at the metal cross-bars and at the edges.

Typically during battery or cell construction the microscale current collector material is impregnated under pressure with a paste, which in a preferred form comprises a mixture of lead sulphate ($PbSO_4$) particles and dilute sulfuric acid. The lead sulphate particles may comprise milled or chemically formed particles which may have a mean size of 10 microns or less, and the size distribution may be optimised for charge generation or charge acceptance rather than forming a conductive network. In preferred embodiments lead sulphate paste is substantially the sole source of lead in the active material paste. Alternatively the paste may include some Pb and PbO. Alternatively again, in other embodiments the paste may comprise a mixture of Pb and PbO and

dilute sulfuric acid. The paste may optionally also contain other additives such as carbon black, barium sulphate and sulphonate. It may also be optimised for electrolyte diffusion.

During initial cell formation (first charge and discharge cycle during which active particle linkages form) after cell or battery construction, in a conventional pasted-plate battery or cell where the paste comprises a mix of Pb oxides, cell formation occurs first by building the conducting framework, taking up most of the Pb in the negative active material, normally over lengths of several millimetres (connecting strings of perhaps a thousand or more micron sized particles end to end). This stage also produces small $PbSO_4$ particles. Second, these smaller particles attach to this conductive framework to provide and receive current. In accordance with this aspect of the invention the Pb framework is replaced with a microscale fibrous current collector and the paste comprises $PbSO_4$ particles, requiring during formation substantially only attaching these $PbSO_4$ particles to the nearest fibres in the microscale conductive current collector material. It may be advantageous that during formation the charging current is pulsed periodically. The fibre surfaces of the current collector material may be surface treated to enhance attachment of the $PbSO_4$ particles (at least the first particle in a chain) by processing to attach oxide particles or oxygen bearing chemical groups to the fibres. Anodic oxidation of electric arc-treated carbon fibre fabric also may convert it to a hydrophilic material. This may assist an even distribution of the active particles through the material and initial attraction of the Pb (covered with oxide groups) to the carbon, by dipole-dipole attractions.

A microscale electrode in accordance with the invention with an internal surface area may provide capacitance sufficient to add to charge acceptance over and above the electrochemical contribution. An electrode area that is well wetted by and accessible to the acid electrolyte may contribute an order of magnitude larger capacitance than that given by the total surface area of a conventional active material in the negative electrode of a lead-acid battery. It may have sufficient electrolytic double-layer capacity to absorb or deliver several seconds of high current. Alternatively a battery of the invention may comprise a separate high surface area electrode, which may comprise arc-treated carbon fibre material as described herein, in parallel to the or each negative or positive cell electrode, to add or increase capacitance.

In certain embodiments carbon fibre material may be treated by arc discharge by moving the carbon fibre material within a reaction chamber either through an electric arc in a gap between two electrodes or past an electrode so that an electric arc exists between the electrode and the material at a temperature effective to activate the material. In Figure 1, reference numeral 1 indicates a

reactor chamber in which the discharge arc is created. Electrodes 2 and 3 project into the reactor chamber 1 and are typically mounted by electrode-feeding mechanisms 4 as are known in the art, so that the position of electrode 3, which maybe the anode, and electrode 2, which may be the cathode (the positions of the anode and cathode may be reversed), may be adjusted to create the arc, and in operation to maintain or if required adjust the arc. A cooling system 5 consisting of copper tube coils wound around each electrodes through which water is circulated may also be arranged to cool the electrode(s). Carbon fibre material 8 passes between electrodes 2 and 3 and through the arc during operation of the reactor, as shown. This is shown in more detail in Figure 2. The current should be sufficient to vaporise non-graphitic carbon but not trigger the destructive localised arc attachment mode Operation between 10 A and 20 A is recommended. The material may enter the reactor chamber through a slit 12 in the reactor chamber and leave through a similar exit slit 13 in the reactor chamber on the other side of the electrodes. A mechanism is provided to feed the material through the reactor chamber. For example during operation of the reactor the substrate may be unwound from a spool 9 driven by a gearbox which is coupled to an electric motor with an appropriate control system. During operation the interior of the reactor is preferably at or slightly above atmospheric pressure, and the gas flow exiting the reactor through slit 13 is extracted via a fume hood or similar. An inert gas such as nitrogen, argon or helium for example is flushed through the reaction chamber, for example by introducing a controlled gas flow inside the reaction chamber 1 through one of the openings 11 at the base of the reactor. Additionally or alternatively a gas flow may also be directed through the tungsten tube 7 via a porous carbon anode 3 to flush away carbon vapour and/or cool the substrate during arc treatment. The cooling flow through porous carbon 3 assists in avoiding burn-through of the material and removal of excessive carbon vapour during arc discharge, whereas the operation of the other inlet 11 serves to control oxidation. The anode as well as the spool which drives the tape are preferably earthed. Any take-up mechanism for collecting the substrate after it has passed through the reactor chamber is also preferably earthed, as is also the reactor shell. Referring to Figure 2, it may be preferable for one electrode, which in the figure is the anode 3, to be positioned to impinge on the substrate 8 such that the substrate is tensioned against that electrode as the substrate moves past it as schematically shown. A gas flow 10 to cool the substrate may be directed through the carbon anode plug 3 housed inside a cylindrical carbon anode support 6 fixed on a tungten tube 7.

The method may be carried out in the presence of an introduced metal additive. Suitable additives may be Ni-Co, Co-Y, Ni-Y or alternatively lower cost additives such as Fe or B additive for example or a Pb additive.

EXPERIMENTAL

The invention is further illustrated by the following description of experimental work which is given by way of example and without intending to be limiting.

Example 1 - Production of Arc Treated Carbon Fibre Electrode Material

A polyacrylonitrite (PAN) based woven carbon fibre tape CW1001 manufactured by TaiCarbon, Taiwan sold under the brand name KoTHmex of the specific weight 220 g/m^2, thickness was 0.7 mm, and a carbon content of 99.98 % was cut into strips of width 25 mm. Figure 3 is a photomicrograph of a section of the material. The material was woven from filaments, each comprising many carbon fibres of average diameter of 6 – 7 μm. Figure 4 is a SEM image across a part of a single multifibre filament of the material.

The material strips were fed into a reactor through a slit 12 from a spool 9 similar to that described with reference to Figures 1 and 2, into the reaction chamber 1. The tape exited the reactor through an outlet slit 13. The graphite cathode diameter was 3 mm. The distance between the electrode tips was set to about 5 – 6 mm. During operation the reactor was flushed with nitrogen at a rate set to 10 L/min, and cooling water was circulated through cooling coils around the electrode supports. To strike the arc, the cathode was moved forward until the discharge took place, then the cathode was withdrawn slightly to establish the arc. The current was set to approximately 16 A. The material was fed through at a speed of 3 mm/s. An additional cooling gas was introduced through a porous carbon anode 3 to cool the material close to the arc attachment zone (as shown in Figure 2). After the desired length of the carbon material had been run through the reactor the discharge was stopped by shutting off the power supply. Gas was flushed through the reactor for a further five minutes to remove exhaust gases.

Example 2 – Effect of Arc Treatment on Resistivity of Carbon Fibre Electrode Material

Woven carbon fibre material as described in Example 1 was treated in an electric arc reactor also as described in Example 1 for 3 seconds. The measured treatment temperature in the arc was in the interval 3700-3800K. The resistivity of the fabric was measured by increasing the resistance of two different lengths of a 10 mm wide strip of the material using two spring-loaded clips with flat contacts 10 mm long, attached to the probes of a multi-meter set to resistance. By eliminating the

contact resistances by difference the resistance per unit length could be calculated. By multiplying this by the thickness of the material and by the width of the strip the resistivity was obtained. The fabric before arc treatment had resistivities of 1.18 Ω m, and 0.135 Ω m respectively, for the untreated fabric and fibre. The arc treated fabric had a fabric resistivity of 0.1 Ω m, resulting in a fibre resistivity of 0.010 Ω m (the fabric resistivity is based on the total volume of the fabric, whereas the fibre resistivity is based on the volume of the carbon in the fabric).

Example 3 – Effect of Arc Treatment on Capacitive Potential of Carbon Fibre Electrode Material

Carbon fibre material as described in Example 1 and arc-treated also as in Example 1 was investigated for internal surface area and for effective electrolytic capacity.

Aromatic vapour adsorption: A benzene adsorbtion analysis with 5 ppm benzene vapour in atmospheric pressure nitrogen at room temperature, gave 3.5 μmole/g of the carbon fabric consistent with that adsorbed by an activated carbon of 100 m^2/g BET surface area. A comparative benzene adsorption analysis for the same carbon fabric without arc treatment gave 0.5 μmole benzene / g carbon fabric.

Nitrogen adsorption (BET): The material without arc treatment showed a BET surface area of around 220 m^2/g, but with almost unmeasureable pore volume and very fine pores (< 1 nm). BET measurements of the arc-treated fabric gave values in the range 50 to 100 m^2/g carbon.

Effective electrolytic capacity: Cyclic voltammetry on two identical carbon fabric electrodes immersed in 1.28 s.g. sulphuric acid gave the effective capacitance per unit mass of the carbon fabric immersed stated below. Sweeping the individual potential of the negative electrode between -0.7 and -1.3 V with respect to a $Hg/HgSO_4$ reference electrode, the charging and then discharging current was integrated around the cycle, and divided by 2X total voltage sweep range of the cell to obtain the electrode capacitance. This was done for sweep voltage rates between 0.5 mV/s to 1000 mV/s. For sweep voltage rates equal to or larger than 10 mV/s, the charge over discharge ratio was 1.13. Then to obtain the specific electrode capacitance, the electrode capacitance was divided by the average mass of the carbon per electrode. The resulting electrode capacitance values are listed below:

Sample	10 mV/s	100 mV/s	1000 mV/s
Without arc treatment	25.2	3.9	0.5
Arc treated	37	7.3	1.2
Time per cycle in seconds	60	6	0.6

The arc-treated fabric had larger capacitance. Also the ratio of the arc-treated to non-treated increases as the sweep rate increases, reflecting the larger pore size found in the BET measurements.

Example 4 - Battery with negative electrode current collectors of arc-treated carbon arc treated fibre material

A small 3 cell 6V lead acid motorcycle battery of 2 Ah capacity (Bike Master 6N2 2A1) at the beginning of its life was disassembled by first cutting off the polypropylene top. Each cell was made up of one positive electrode between two negative electrodes. The positive electrode had active material loaded in its grid with access to electrolyte either side. Each negative electrode was likewise constructed and was separated from the positive by a fibrous separator. The size of each original electrode was 56 mm wide and 44 mm high giving an area of 26.4 cm^2. With two active surfaces acting in parallel, the total negative-positive area for each cell was (2)(26.4) = 52.8 cm^2. The thickness of each original active layer was around 2 mm.

One of the negative electrodes of one cell was removed and replaced by a smaller negative electrode made up as described below. The other negative electrode was disconnected from the charging circuit.

The smaller negative electrode was made up of four layers each 10 mm x 45 mm x 0.5 mm thick of a woven carbon fabric as described in Example 1 arc treated also as described in Example 1 (resulting in properties 150 g/m^2, 0.5 mm thick, 0.23 Ω / sq along roll, 0.37 Ω / sq across roll). The layers were cut from a roll of the carbon fabric with the long side in the direction of the width of the unwound roll. Of these layers, 35 mm length was used as an active area and 10 mm used as an electrical contact area. Prior to arc treatment the material was fully wetted with $Pb(NO_3)_2$ aqueous solution, dried overnight so that 2 mass % Pb was deposited. The arc treatment graphitised the material and distributed the lead in a smooth coating over all fibres. SEM

micrographs showed a uniform layer of around 100 nm thick on the fibres, shown by microprobe elemental analysis to be PbO2.

Four such layers were then assembled one beneath the other so that they were all bonded to lead shim to form a connecting lug at one of their ends. A 0.8 mm dia lead solder wire (60 % Sn, 40 % Pb) that incorporated a resin flux core was laid in zig-zag form in the three gaps between the four layers. A 20 mm wide ribbon of metallic lead (0.6 mm thick) was then wrapped around the outside of the ends of the four layers, covering the top 10 mm section of each layer. The lead coverings were squeezed between the two electrodes of a spot-welder while current was passed to melt the ensemble, providing good contact between the carbon fibres and solder and lead. In this way, a lug was formed on the top end of the electrode, connecting and holding the carbon fabric layers that could be flexibly moved about for further treatment.

To make the active material, $PbSO_4$ powder (mean size 4-5 μm after milling) was mixed in with low concentration sulphuric acid (s.g. < 1.05) to make a paste of 78 mass % $PbSO_4$ (0.37 volume fraction). This paste was squeezed with a spatula into the free exposed part (35 mm length) of each layer of carbon fabric, while that layer was pressed against the flat bottom of a glass vessel immersed in an ultrasound cleaning bath (180 W, 4 L, 53 kHz). Each pasted layer was then scraped clean of superfluous paste. These pasted layers were also lightly squeezed together at this point to make good contact with each other while still wet.

The whole electrode had a superficial active area of 3.5 cm^2 (where the $PbSO_4$ had been loaded) and was 2 mm thick. This electrode was dried to allow the dry mass of $PbSO_4$ to be measured, and then inserted in place of a larger negative of the original battery, and the cell then became limited only by the new 3.5 cm^2 electrode, opposite a single 26.4 cm^2 conventional positive.

After insertion of the negative electrode into the cell, charging was immediately started using a Cadex C7200-C battery analyser (Cadex Electronics, British Columbia, Canada) using a period of controlled 45 mA current followed by a period of controlled cell voltage at 2.4 V. After the formation charge and discharge, a further 4 complete cycles with 45 mA initial charging current and 17 mA discharge current were carried out to stabilize the electrode capacity. Further cycles were charged at 45 mA (around 39 A / kg Pb in the negative active mass) and discharged at successively higher currents of 40, 195, 256, 655, 800 mA and then stepped down over the same values. The current during discharge was integrated with the respect to time to estimate the

capacity for each cycle in mAh. These capacities and currents were divided by the mass of lead in the electrode (estimated from the dry mass of PbSO4). Figure 5 is a "Ragone" type plot of the return sequence points specific current A/kg Pb in the negative active mass (NAM) versus specific capacity Al/kg Pb in the NAM – triangle data points.

Figure 6 is a plot similar to Figure 5 for a battery made up as described above but with three carbon fibre layers in the carbon fibre negative electrode instead of four layers and with all of the cut edge of two of three the layers completely surrounded by solder at the connecting lug. The higher capacity may be due to lower resistance at this connection.

Example 5 - Battery with negative electrode current collector of non-arc treated carbon fibre material

A battery was constructed as described in Example 4 but without first arc treating the carbon fibre material. Capacities were measured as described in Example 4. These capacity – current measurements were again divided by the lead mass in the active material of the negative, and were plotted in Figure 5 – square data points.

The battery of Example 4 with arc-treated fabric electrodes had superior capacity performance particularly at high current densities.

Example 6 - Negative electrode current collector of arc-treated carbon fibre material – cycle life

An electrode was constructed with arc-treated PAN-based carbon fibre fabric as described in Example 4 with no additives in the paste, and subjected to an accelerated lifetime test which approximated the partial state of charge (PSOC) duty in mild hybrid vehicles, beginning with a fully charged battery, then discharging at 50 A for 1 minute, then charging for 1 minute, and continuing until the cell voltage at the end of the discharge time drops below around 1.75 V per cell. The charge began at a constant 50 A, until the cell voltage rose to 2.35 V, dropping after this to maintain the charging voltage constant. The Cadex C7200-C battery tester was also used for this test. The end-of-discharge cell voltage is plotted in Figure 6 against cycle number – darker plot, and it can be seen that almost 11,000 cycles were achieved before failure. The sudden drop just after 6000 cycles was due to an earthquake turning off power for 10 days. Typical lifetimes are also indicated for typical conventional lead-acid battery, an ISS battery, and an "Ultrabattery".

Example 7 - Negative electrode current collector of non-arc treated carbon fibre material – cycle life

An electrode was constructed from non-arc treated carbon fibre as described in Example 6 and was subjected to the same accelerated lifetime test as described in Example 6, but with more active material. The end-of-discharge cell voltage is plotted on Figure 7 against cycle number – lighter plot, showing a lifetime of just more than 9000 cycles.

The arc-treated fabric electrode of Example 6 had a higher lifetime (despite having higher current density).

Example 8 - Negative electrode current collector of arc-treated carbon fibre material – charge acceptance

The battery of Example 4 was tested for charge acceptance over a range of currents prior to the tests of Example 4. The charging tests followed the cycle of charge and discharge described in Example 7, but the currents were reduced below and raised above the 167 mA chosen for that test. The battery was near fully charged. The charge and discharge periods used were again 1 minute. The Cadex C7200-C was again used. The timing of the one measurement of charge current varied according to the current. The charge current set at the beginning of the test was 120 mA for the first 450 cycles, 180 mA for the second set of 200 cycles and 240 mA for the last set of 1000 cycles. It took some seconds for the current to rise to the set level, as observed from the digital current meter. The measured current is plotted in Figure 8 against total number of cycles. The current was measured at almost 60 s after the start of charging for the 120 mA cycles (measured at 90 mA), 19 s after the start for the 180 mA cycles (at 180 mA) and 23 s after the start for the 240 mA (at 238 mA). Thus the charging current dropped from 120 to 90 mA over the full minute, and dropped negligibly from 180 mA over 19 s, and dropped just 2 mA over 23 from 240 mA.

The maximum specific charging rate tested for was (240 mA)/(0.81 g) = 295 A / kg of lead in the active mass, and the electrode can accept this at least for around 20 s (enough for regenerative charging in a hybrid vehicle). Probably the charging current continued high for the full minute even for the highest current. As the test progressed the state of charge will have decreased somewhat, allowing more charge to be accepted.

The foregoing describes the invention including preferred forms thereof and alterations and modifications as will be obvious to one skilled in the art are intended to be incorporated in the scope thereof as defined in the accompanying claims.

CLAIMS:

1. A lead-acid battery or cell including at least one electrode comprising as a current collector a conductive fibrous material comprising:

filaments comprising fibres with an average interfibre spacing between fibres of less than 50 microns, and/or

filaments which are monofibres and in which the average interfibre spacing between monofibres is less than 50 microns.

2. A lead-acid battery or cell comprising as a current collector a conductive fibrous material having length and width dimensions in a major plane of the material and depth perpendicular to said major plane of the material and comprising:

filaments comprising fibres with an average interfibre spacing between fibres of less than 50 microns, and/or

filaments which are monofibres and in which the average interfibre spacing between monofibres is less than 50 microns.

3. A lead-acid battery according to claim 2 in which the average depth of the material is at least 0.2 millimetres.

4. A lead-acid battery according to claim 2 in which the average depth of the material is at least 1 millimetre.

5. A lead-acid battery according to any one of claims 1 to 4 wherein the current collector material is composed substantially of filaments each composed of multiple fibres.

6. A lead-acid battery or cell according to any one of claims 1 to 5 wherein in the conductive fibrous material the average interfibre spacing is less than 20 microns.

7. A lead-acid battery according to any one of claims 1 to 6 wherein the average interfibre spacing is over at least a major fraction of the material.

8. A lead-acid battery according to any one of claims 1 to 6 wherein the average interfibre spacing is over substantially all of the material.

9. A lead-acid battery according to any one of claims 1 to 8 wherein the fibrous current collector material is a woven material.

10. A lead-acid battery according to any one of claims 1 to 8 wherein the fibrous current collector material is a knitted material.

11. A lead-acid battery according to any one of claims 1 to 8 wherein the fibrous current collector material comprises filaments extending unidirectionally in a major plane of the material and each composed of multiple fibres.

12. A lead-acid battery according to any one of claims 1 to 11 wherein the fibrous current collector material or the fibres thereof are flexible.

13. A lead-acid battery according to any one of claims 1 to 12 wherein the fibrous current collector material comprises a carbon fibre material.

14. A lead-acid battery according to claim 13 wherein the carbon fibre material is comprises or derived from a rayon, polyacrylonitrile, phenol resin, or pitch material.

15. A lead-acid battery according to any either claim 13 or claim 14 wherein the carbon fibre material has been thermally treated to increase the electrical conductivity thereof

16. A lead-acid battery according to any one of claims 13 to 15 wherein the carbon fibre material has been thermally treated by electric arc discharge.

17. A lead-acid battery according to claim 16 wherein the carbon fibre material has been thermally treated by electric arc discharge by causing relative movement between the carbon fibre material and an electric arc in a gap between two electrodes or past an electrode so that an electric arc exists between the electrode and the carbon fibre material.

18. A lead-acid battery according to claim either claim 16 or claim 17 wherein the carbon fibre material has been thermally treated by electric arc discharge to vaporise a major fraction of non-graphitic carbon and no more than a minor fraction of graphitic carbon of the carbon fibre material.

19. A lead-acid battery according to any one of claims 1 to 18 wherein the fibrous current collector material has bulk resistivity less than 10 Ω mm.

20. A lead-acid battery according to any one of claims 1 to 18 wherein the fibrous current collector material has bulk resistivity less than 1 Ω mm.

21. A lead-acid battery according to any one of claims 1 to 20 wherein the fibrous current collector material has been surface activated to increase its surface area to increase capacitance.

22. A lead-acid battery according to any one of claims 1 to 21 wherein said at least one electrode comprises a conductive frame or frame elements supporting the current collector material and to which the filaments of the current collector material are electrically connected.

23. A lead-acid battery according to claim 22 wherein the filaments of the current collector material are electrically connected to the metal frame or frame elements by a metal element in which ends or another portion of the filaments are embedded and which was molten on application to the filaments at manufacture.

24. A lead-acid battery according to any one of claims 1 to 21 wherein the current collector material is supported, and the filaments of the current collector material are electrically connected, by a metal element in which ends or another portion of the filaments are embedded and which was molten on application to the filaments at manufacture.

25. A lead-acid battery according to any one of claims 1 to 24 wherein the fibrous current collector material during battery or cell construction has been impregnated with a paste comprising a mixture of lead sulphate particles and dilute sulfuric acid.

26. A lead-acid battery according to claim 25 wherein the lead sulphate in the paste is substantially the sole source of lead in the active material of the battery or cell.

27. A lead-acid battery according to any one of claims 1 to 26 wherein said at least one electrode is a negative electrode.

28. A lead-acid battery according to any one of claims 1 to 27 wherein said at least one electrode comprises multiple layers of said fibrous current collector material.

29. A lead-acid battery or cell including at least one electrode comprising as a current collector a carbon fibre material thermally treated by electric arc discharge.

30. A lead-acid battery according to claim 29 wherein the carbon fibre material has been thermally treated by electric arc discharge by causing relative movement between the carbon fibre material and an electric arc in a gap between two electrodes or past an electrode so that an electric arc exists between the electrode and the carbon fibre material.

31. A lead-acid battery according to either claim 29 or claim 30 wherein the carbon fibre material has been thermally treated by electric arc discharge to vaporise a major fraction of non-graphitic carbon and no more than a minor fraction of graphitic carbon of the carbon fibre material.

32. A lead-acid battery according to any one of claims 29 to 31 wherein the carbon fibre material has bulk resistivity less than 10 Ω mm.

33. A lead-acid battery according to any one of claims 29 to 31 wherein the carbon fibre material less than 1 Ω mm.

34. A lead-acid battery according to any one of claims 29 to 33 wherein the carbon fibre material has been surface activated to increase its surface area to increase capacitance.

35. A lead-acid battery according to any one of claims 29 to 34 wherein the carbon fibre material is a woven material.

36. A lead-acid battery according to any one of claims 29 to 34 wherein the carbon fibre material is a knitted material.

37. A lead-acid battery according to any one of claims 29 to 36 wherein the carbon fibre material comprises or is derived from a rayon, polyacrylonitrile, phenol resin, or pitch material.

38. A lead-acid battery according to any one of claims 29 to 37 wherein the carbon fibre material during battery or cell construction has been impregnated with a paste comprising a mixture of lead sulphate particles and dilute sulfuric acid.

39. A lead-acid battery according to claim 38 wherein lead sulphate in the paste is substantially the sole source of lead in the active material of the battery or cell.

40. A lead-acid battery according to any one of claims 29 to 39 wherein said at least one electrode is a negative electrode.

41. A lead-acid battery according to any one of claims 29 to 40 said at least one electrode comprises multiple layers of said carbon fibre material.

42. A method for manufacturing a lead-acid battery or cell which includes forming at least one electrode comprising as current collector a conductive fibrous material comprising:

filaments comprising fibres with an average interfibre spacing between fibres of less than 50 microns, and/or

filaments which are monofibres and in which the average interfibre spacing between monofibres is less than 50 microns.

43. A method for manufacturing a lead-acid battery or cell which includes forming at least one electrode comprising as current collector a conductive fibrous material having length and width in a major plane of the material and depth perpendicular to said major plane of the material and comprising:

filaments comprising fibres with an average interfibre spacing between fibres of less than 50 microns, and/or

filaments which are monofibres and in which the average interfibre spacing between monofibres is less than 50 microns.

44. A method according to claim 43 in which the average depth of the material is at least 0.2 millimetres.

45. A method according to claim 43 which the average depth of the material is at least 1 millimetre.

46. A lead-acid battery according to any one of claims 42 to 45 wherein the current collector is composed substantially of filaments each composed of multiple fibres.

47. A method according to any one of claims 42 to 46 wherein the average interfibre spacing is less than 20 microns.

48. A method according to any one of claims 42 to 47 wherein the average interfibre spacing is over at least a major fraction of the material.

49. A method according to any one of claims 42 to 47 wherein the average interfibre spacing is over substantially all of the material.

50. A method according to any one of claims 42 to 49 wherein the fibrous material is a woven material.

51. A method according to any one of claims 42 to 49 wherein the fibrous material is a knitted material.

52. A method according to any one of claims 42 to 49 wherein the conductive fibrous material comprises filaments extending unidirectionally in a major plane of the material and each composed of multiple fibres.

53. A method according to any one of claims 42 to 52 wherein the fibrous material or the fibres thereof are flexible.

54. A method according to any one of claims 42 to 53 wherein the fibrous material comprises a carbon fibre material.

55. A method according to claim 54 wherein the carbon fibre material comprises or is derived from a rayon, polyacrylonitrile, phenol resin, or pitch material.

56. A method according to either claim 54 or claim 55 including thermally treating the carbon fibre material to increase the electrical conductivity thereof

57. A method according to any one of claims 54 to 56 including thermally treating the carbon fibre material by electric arc discharge.

58. A method according to claim 57 including thermally treating the carbon fibre material by electric arc discharge by causing relative movement between the carbon fibre material and an electric arc in a gap between two electrodes or past an electrode so that an electric arc exists between the electrode and the carbon fibre material.

59. A method according to either claim 57 or claim 58 including thermally treating the carbon fibre material to vaporise a major fraction of non-graphitic carbon and no more than a minor fraction of graphitic carbon of the carbon fibre material.

60. A method according to any one of claims 42 to 59 wherein the conductive fibrous material has bulk resistivity less than 10 Ω mm.

61. A method according to any one of claims 42 to 59 wherein the conductive fibrous material has bulk resistivity less than 1 Ω mm.

62. A method according to any one of claims 42 to 61 including surface activating the fibrous material to increase its surface area to increase capacitance.

63. A method according to any one of claims 42 to 62 including impregnating the conductive fibrous material with a paste comprising a mixture of lead sulphate particles and dilute sulfuric acid.

64. A method according to claim 65 wherein the lead sulphate in the paste is the substantially sole source of lead in the active material of the battery or cell.

65. A method according to any one of claims 42 to 64 including placing the current collector material in a conductive frame or between conductive frame elements to support the current collector material and electrically connecting the filaments of the current collector material to the frame or frame elements.

66. A method according to claim 65 including electrically connecting the filaments of the current collector material to the metal frame or frame elements by embedding the ends or another portion of the filaments in a molten metal and allowing the molten metal to solidify.

67. A method according to any one of claims 42 to 64 including electrically connecting the filaments of the current collector material by embedding the ends or another portion of the filaments in a molten metal and allowing the molten metal to solidify.

68. A method for manufacturing a battery or cell which includes applying to at least one electrode comprising as current collector a conductive fibrous material, a paste which comprises a mixture of lead sulphate particles and dilute sulfuric acid.

69. A method according to claim 68 wherein the lead sulphate in the paste is substantially the sole source of lead in the active material of the battery or cell.

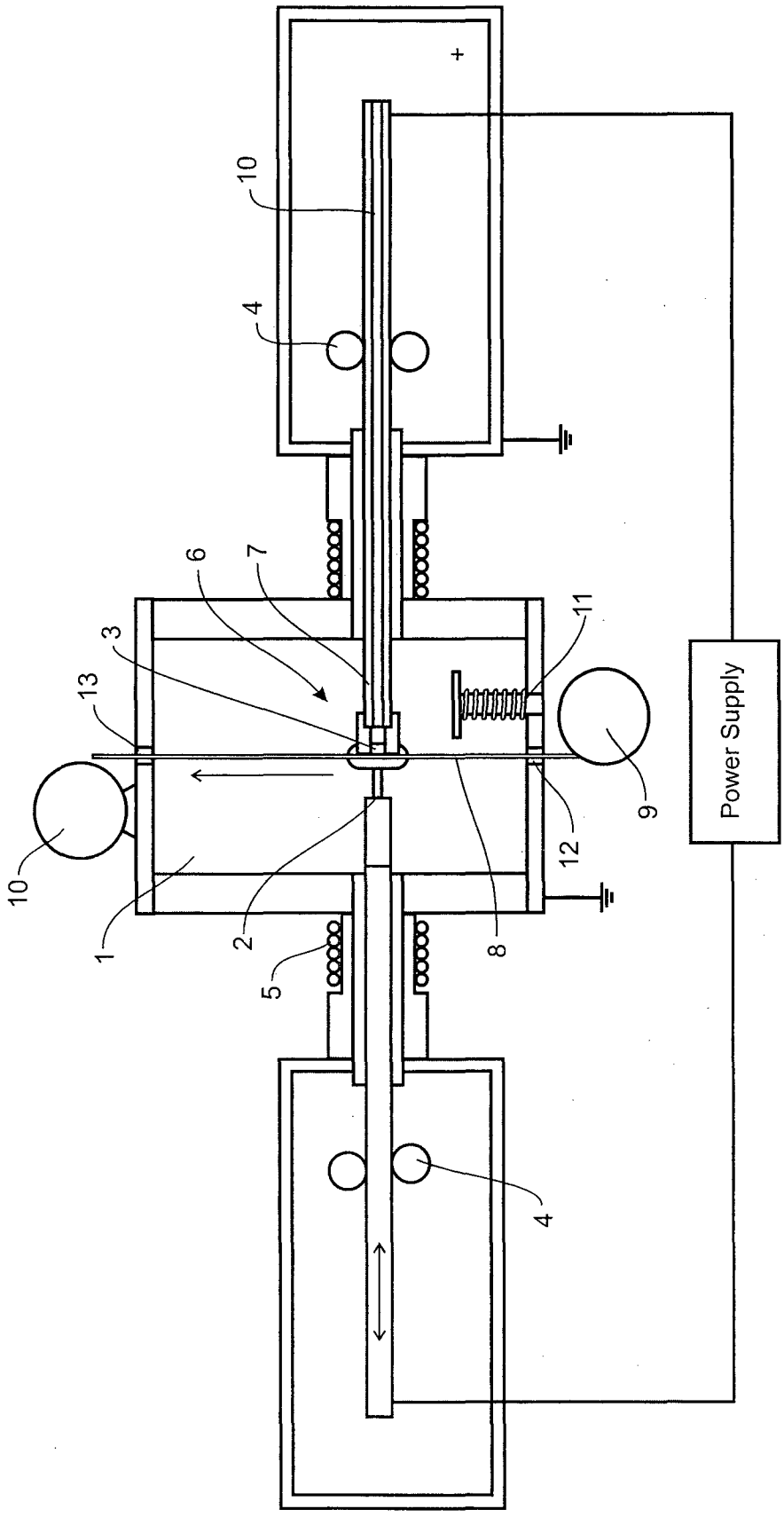


FIGURE 1

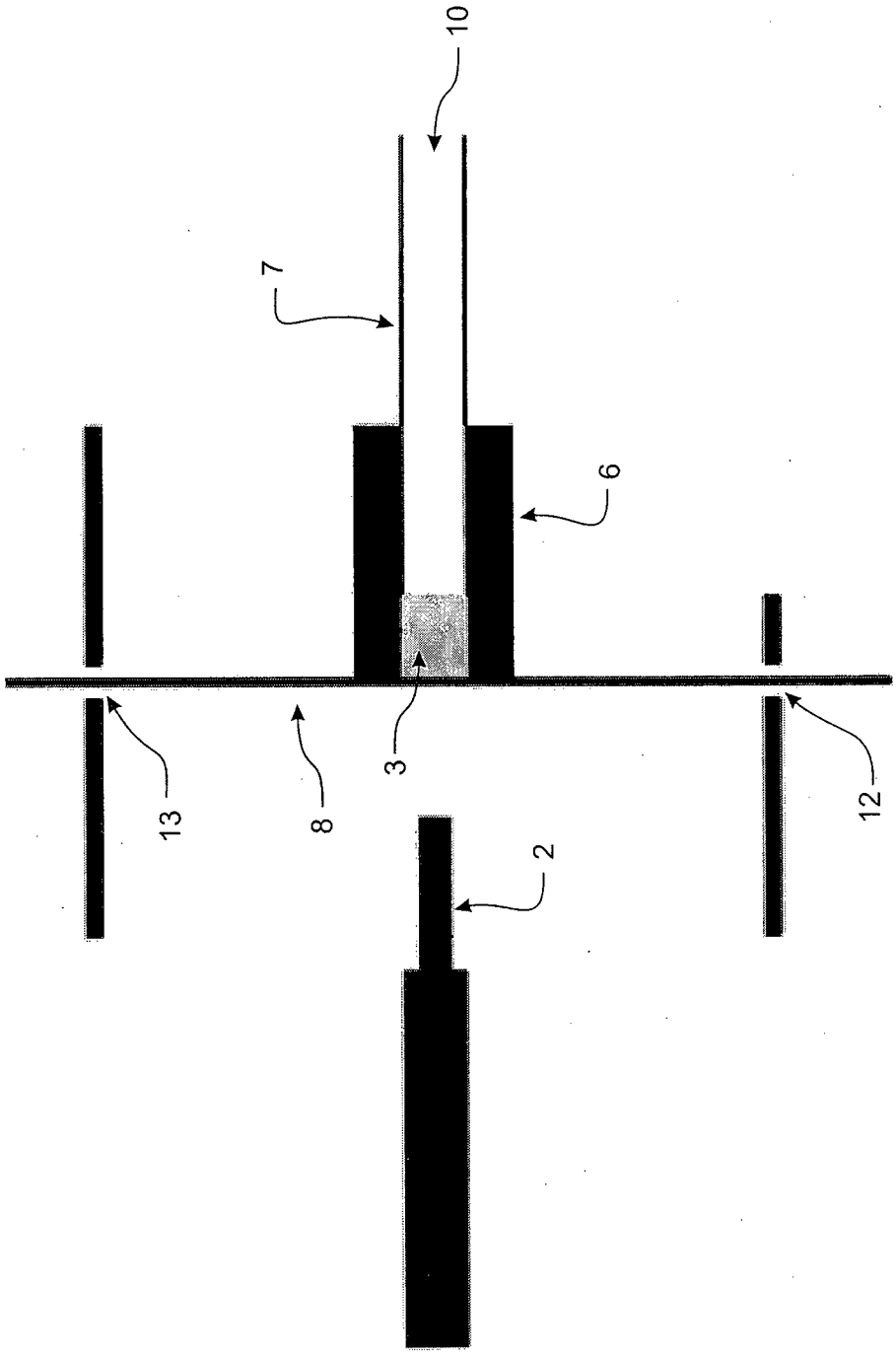


FIGURE 2



FIGURE 3



FIGURE 4

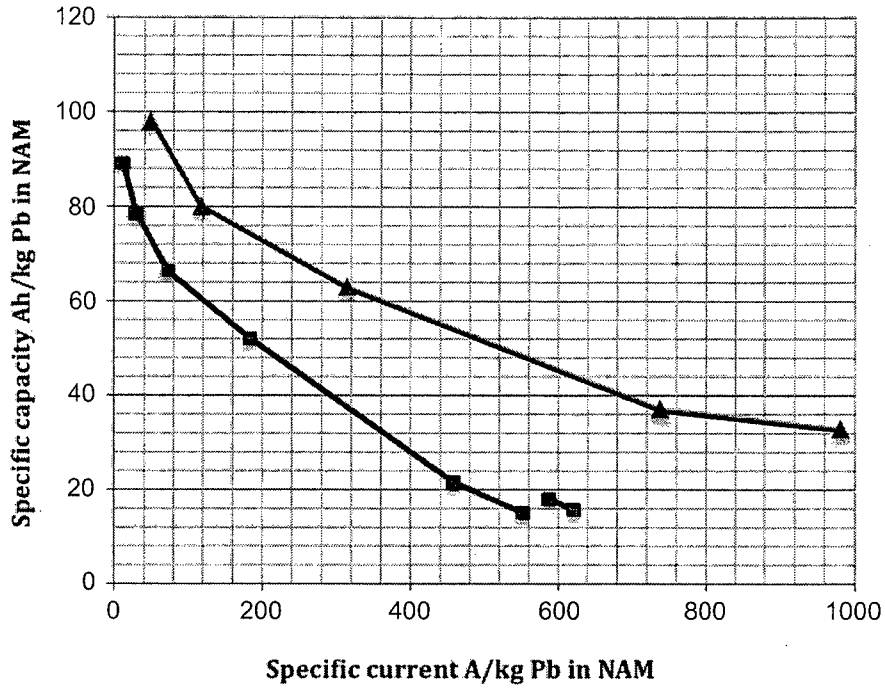


FIGURE 5

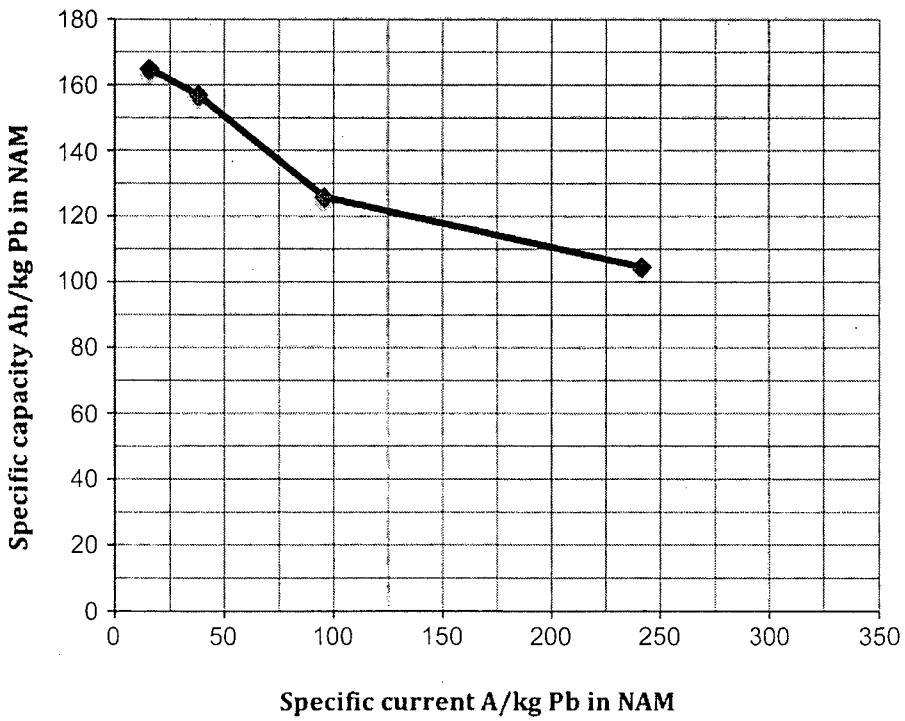


FIGURE 6

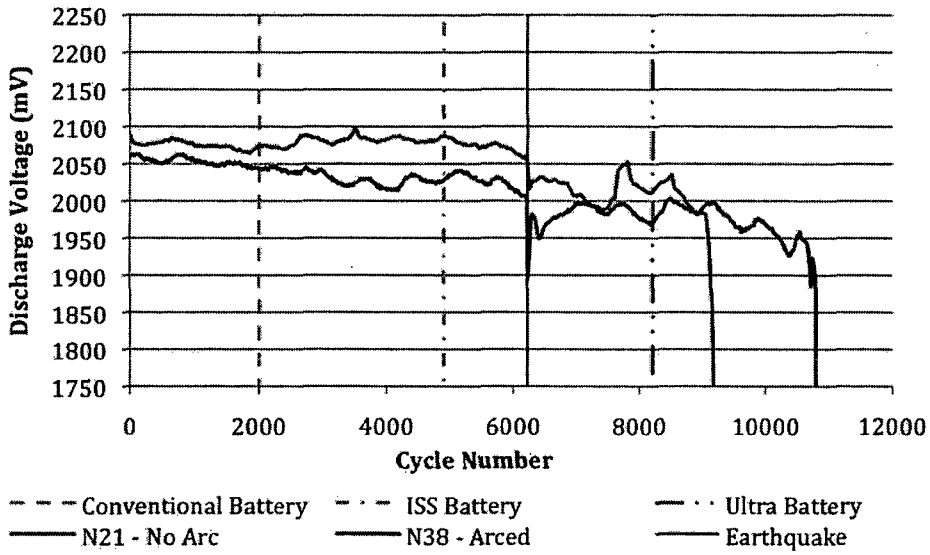


FIGURE 7

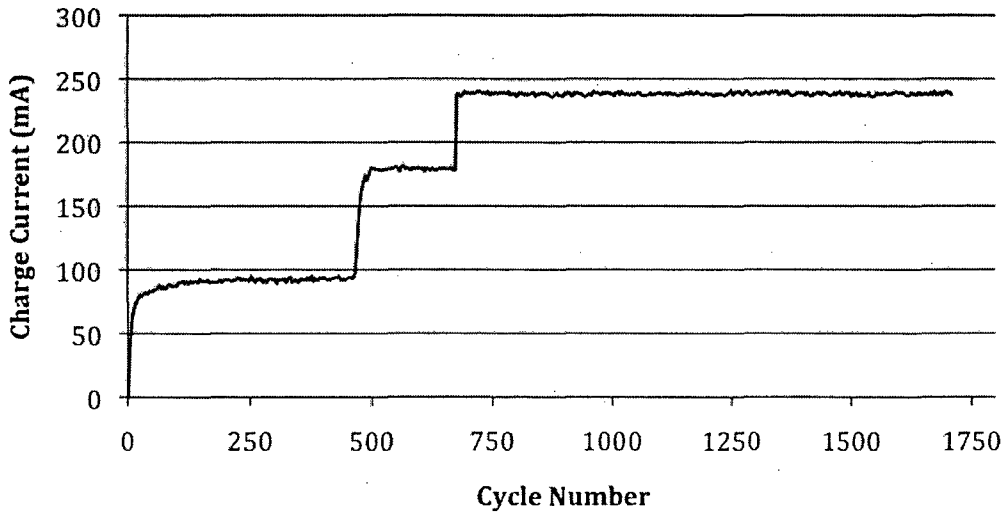


FIGURE 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2010/000264

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. ***H01M 4/20*** (2006.01) ***H01M 4/68*** (2006.01)

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)

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI & EPODOC – IPC & EC: D06F, D06F 9/-, D06F 11/-, H01M 2/26, 2/28, 4/14, 4/36, 4/56, 4/64, 4/68, 4/72, 4/73 & keywords (lead, acid, accumulator, collector, grid, carrier, fibre, fiber, fibrous, strand, thread, filament, fabric, cloth, knit, woven, weave, carbon, lead sulfate, lead sulphate, PbSO4, arc and like terms); Google & Google Patents – keywords (carbon, fibre, cloth, lead, acid, accumulator, collector, carrier, grid, arc, paste, slurry, interfibre, interfiber, thread count, bundle, dense, micron and like terms)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/0269666 A1 (LARA-CURZIO et al.) 29 October 2009 See: abstract, paragraphs [0010], [0013], [0014], [0017], [0018] & Fig. 3	1-4, 6, 7, 9-15, 19, 20, 22-25, 27, 28, 42-45, 48, 50-56, 60, 61, 63, 65-67
X	US 2005/0208382 A1 (DATTA et al.) 22 September 2005 See abstract, paragraphs [0008], [0075], [0076] and [0087]	1-15, 19, 20, 22-24, 27, 42-56, 60, 61, 65-67
X	US 4429442 A (THOMAS) 7 February 1984 See abstract, column 2 lines 5-16 and 36-62	68

[X] Further documents are listed in the continuation of Box C [X] 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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 May 2011	17 MAY 2011
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **RHYS MUNZEL** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 3 9935 9623

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2010/000264

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5156935 A (HOHJO et al.) 20 October 1992 See whole document	
A	Patent Abstracts of Japan JP 03-285263 A (SHIN KOBE ELECTRIC MACH CO LTD) 16 December 1991 See whole abstract	
A	WO 2006/105186 A2 (FIRE-FLY ENERGY INC.) 5 October 2006 See whole document	
A	US 6372192 B1 (PAULAUSKAS et al.) 16 April 2002 See whole document	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NZ2010/000264

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box 1.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box 1
(To be used when the space in any of Boxes I to IV is not sufficient)

Continuation of Box No: III

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept. In assessing whether there is more than one invention claimed, I have given consideration to those features which can be considered to potentially distinguish the claimed combination of features from the prior art.

This International Searching Authority has found that there are different inventions as follows:

- Claims 1-28 and 42-67 relate to a lead-acid cell comprising a current collector further comprising fibres/monofibres with an average interfibre spacing of less than 50 microns. It is considered that this group of claims define a first invention.
- Claims 29-41 relate to a lead-acid cell comprising as a current collector a carbon fibre material thermally treated by electric arc discharge. It is considered that this group of claims define a second invention.
- Claims 68 and 69 relate to a method for manufacturing a cell comprising applying a paste that comprises a mixture of lead sulphate particles and dilute sulphuric acid to a current collector formed of a conductive fibrous material. It is considered that this group of claims define a third invention.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

The only feature common to all of the claims is a lead-acid cell current collector formed of a fibrous material. However this common feature is generic in the art. This means that the common feature can not constitute a special technical feature within the meaning of PCT Rule 13.2, second sentence, since it makes no contribution over the prior art.

Because the common feature does not satisfy the requirement for being a special technical feature it follows that it cannot provide the necessary technical relationship between the identified inventions. Therefore the claims do not satisfy the requirement of unity of invention a posteriori.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/NZ2010/000264

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	2009269666	NONE					
US	2005208382	WO	2005091404				
US	4429442	BR	8006354	DE	3037304	FR	2466871
		GB	2062344	JP	56099976		
US	5156935	EP	0352115	JP	2033859	JP	2044658
		JP	2046653	JP	2177260		
JP	3285263	NONE					
WO	2006105186	CN	101167201	EP	1866988	US	2009233175
US	6372192	AU	59020/01	WO	0155487		

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX