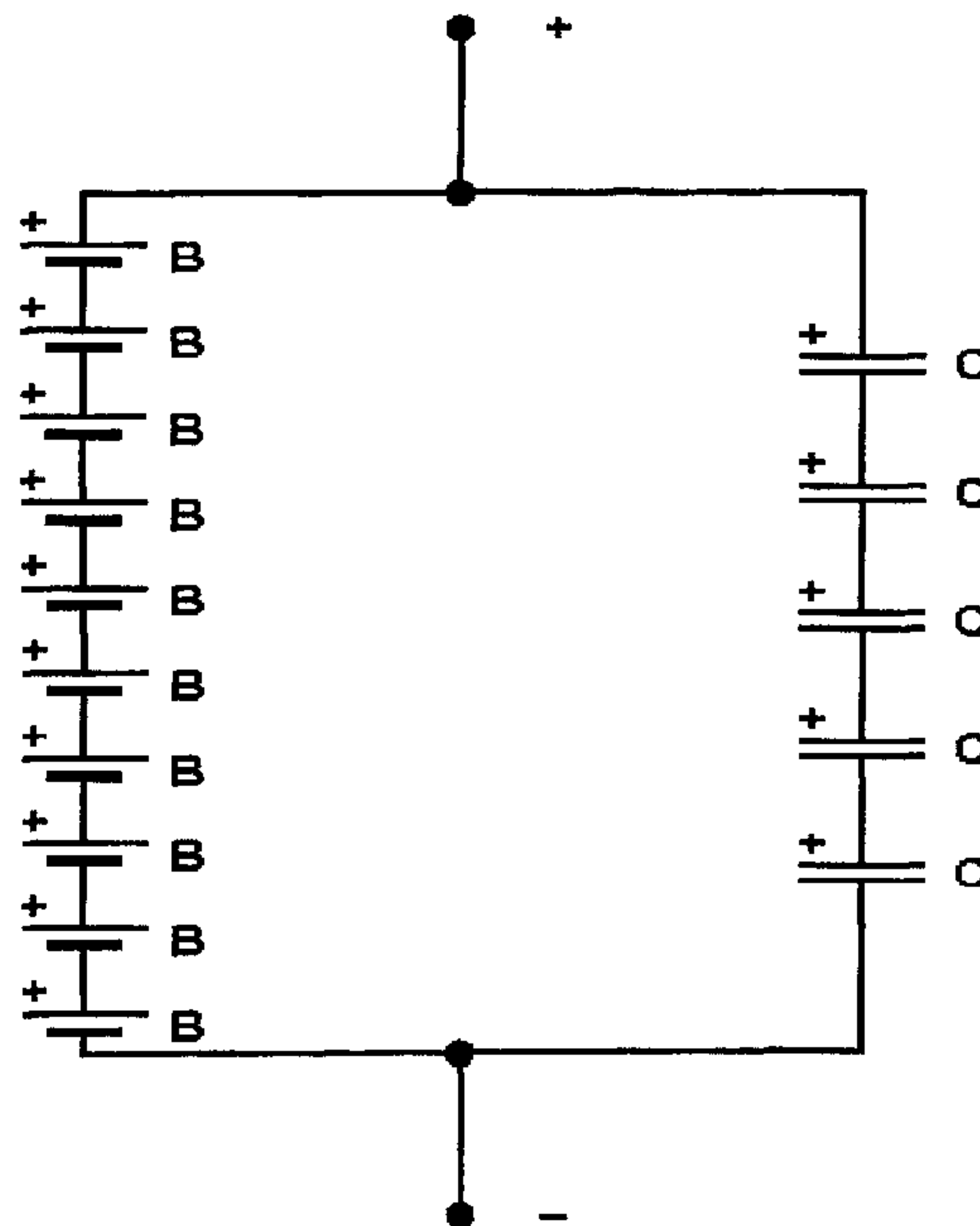




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 (72) Inventeurs/Inventors:
WENDEL, SOREN, CZ;
BIZA, VLADIMIR, CZ
 (73) Propriétaire/Owner:
KINITOLO CONSULTING LIMITED, CY
 (74) Agent: GELSING, SANDER R.

(54) Titre : BATTERIE D'ACCUMULATEURS DE DEMARRAGE SANS PLOMB, PROCEDE DE TRAITEMENT ET SON UTILISATION, EN PARTICULIER POUR LES MOTEURS A COMBUSTION ET LES VEHICULES A MOTEUR
 (54) Title: LEADLESS STARTING ACCUMULATOR BATTERY, PROCESSING METHOD AND ITS USE, PARTICULARLY FOR COMBUSTION ENGINES AND MOTOR VEHICLES



(57) **Abrégé/Abstract:**

Accumulator battery, the processing method and its use, especially for combustion engines and motor vehicles, consist in serial-parallel connection of at least one or more NiMH - Nickel-metal hydride cells and or Li-Ion Lithium-Ion cells and or Li-Pol - Lithium polymer cells and ultracapacitors.

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(71) Applicant (for all designated States except US): YDUN S.R.O. [CZ/CZ]; hrozenkovská 12, 155 21 Praha 5-Zlicin (CZ).

(72) Inventors; and

(75) Inventors/Applicants (for US only): WENDEL, Soren [DK/CZ]; K háji 889, 16500 Praha 6 (CZ). BIZA, Vladimír [CZ/CZ]; Jetelova 1723, 28601 Caslav (CZ).

(74) Agent: DANEK, Vilém; Vinohradská 45, 120 00 Prague (CZ).

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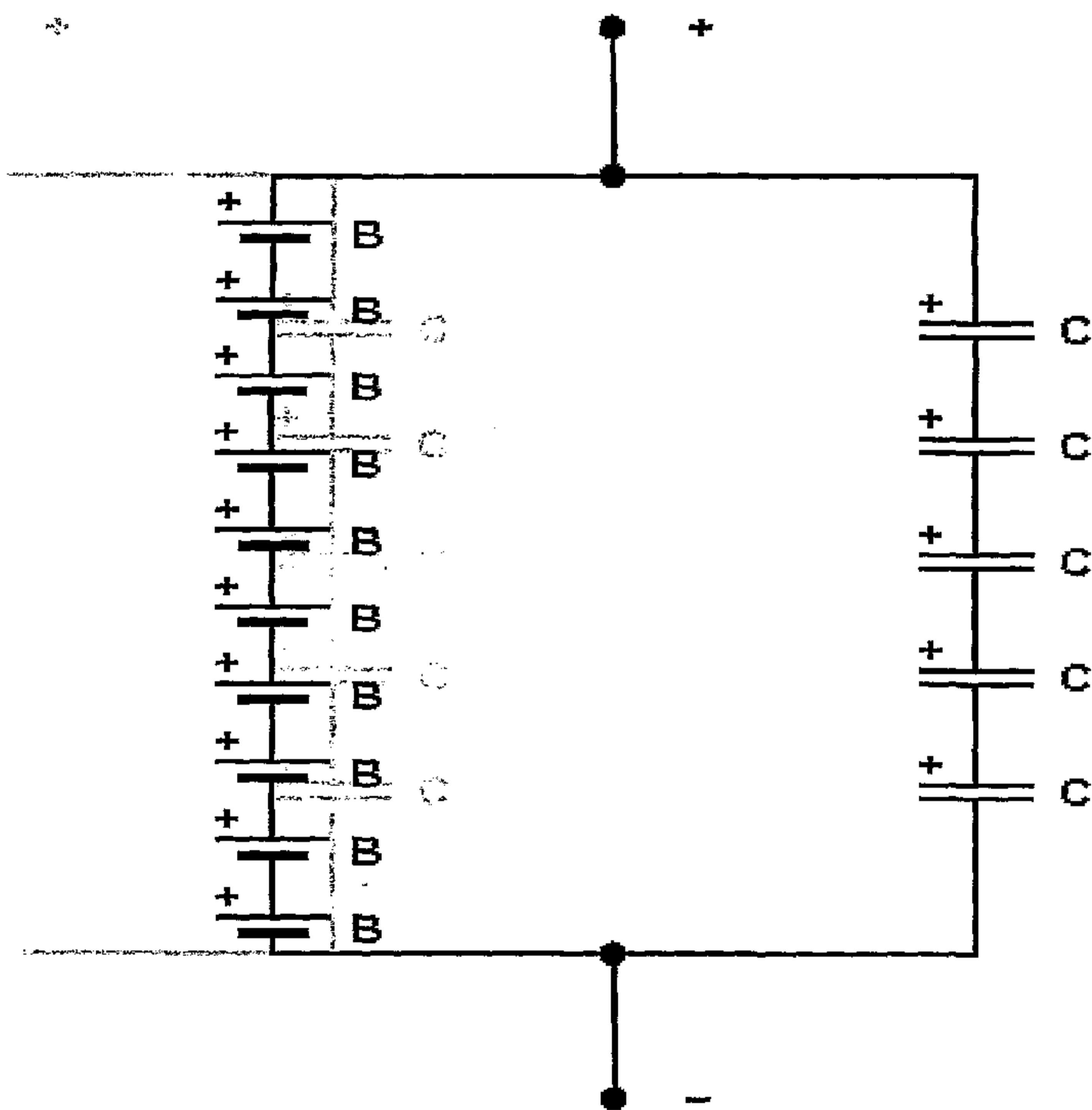
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[Continued on next page]

(54) Title: LEADLESS STARTING ACCUMULATOR BATTERY, PROCESSING METHOD AND ITS USE, PARTICULARLY FOR COMBUSTION ENGINES AND MOTOR VEHICLES



(57) Abstract: Accumulator battery, the processing method and its use, especially for combustion engines and motor vehicles, consist in serial-parallel connection of at least one or more NiMH - Nickel-metal hydride cells and or Li-Ion Lithium-Ion cells and or Li-Pol - Lithium polymer cells and ultracapacitors.

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Leadless starting accumulator battery, processing method and its use, particularly for combustion engines and motor vehicles

Technical Field

This invention relates to the new type of accumulator batteries with use for initiation of compression-ignition and spark-ignition combustion engines and batteries for all types of motor vehicles.

Background Art

All known types of initiation batteries for combustion engines and motor vehicles (hereinafter called "auto batteries") are based on electrochemical reaction of secondary lead-acid cell (hereinafter called "lead battery"). All types of lead auto batteries contain lead as electrodes and sulphuric acid H_2SO_4 solution as electrolyte, and during discharging and charging the known chemical process is occurring. These different types of lead auto batteries vary only in cell construction (shape and method of electrodes manufacture, cell shape, degasification channels and valves, etc.), material of lead paste decreasing lead consumption during manufacture, separators, electrolyte additives, etc. None of today known types is fully hermetically closed, the partial release of substances contained in the battery to the surrounding environment is always occurring during the operation. With the most modern types, co called AGM and gel lead batteries, this

effect can occur only when overcharging the battery. All today known types contain toxic (lead Pb) and dangerous (sulfuric acid H_2SO_4 solution) substances according to the meaning of Directive 2002/95/EC RoHS. Today known types of lead auto batteries have guaranteed the operating temperature ranging between $-18^{\circ} C.$ to $40^{\circ} C.$

Contemporary NiMH, Li-Ion and Li-Pol cells are not capable of delivering or receiving sufficient high currents and are not capable of delivering or receiving effectively the energy in temperatures below $-20^{\circ} C.$

Nickel-Cadmium Accumulators (NiCd)

The nickel is positive electrode, cadmium is the negative and potassium hydroxide fixed in separator and electrodes is the electrolyte. They are popular thanks to their favorable characteristics such weight - capacity ratio, are convenient even for high current load - have smaller inner resistance, provide greater current, can be charged quickly and are more resistant to improper use (overcharging or deep discharging), work even under extreme climatic conditions (to $-40^{\circ} C.$). They can be stored discharged without loss in electric properties practically for any time. The disadvantage is that it contains cadmium, which is a poisonous heavy metal with ability to cumulate in organism and can cause serious, fatal diseases. They have smaller capacity (up to ~

about 1100 mAh) and greater self-discharging (the inner resistance is raising).

Nickel-metal hydride Accumulators (NiMH)

They appear from nickel-cadmium accumulators, but are designed to have higher capacity while having the same volume, and to be less dangerous for environment. The positive electrode is nickel again, but the negative one is hydride of metal compound, for example nickel oxide Ni(OH)_2 hydroxide and the electrolyte is again potassium hydroxide. They have nominal voltage (1,2 - 1,25 V) and identical charging regime as NiCd, capacity is 40% higher and they have flat discharging characteristics, ergo smaller self-discharging, but their use under extreme climatic conditions is problematic - down to -10°C (some may resist -20°C) and the possibility of high discharging currents is now limited to tenth of the capacity. They can be stored charged and discharged, but it is vital to charge and discharge them a few times at least once a year, or, due to the chemical reactions, the accumulator electrodes damage and irreversible loss of capacity will occur.

Lithium-Ion Accumulators (Li-Ion)

They come from primary lithium cells. The positive electrode comprises of the compound of lithium oxides and another metal (usually lithium cobalt (III) oxide $+\text{Li}_2\text{O} \cdot \text{Co}_2\text{O}_3$), the negative is carbon mixed with other chemicals and compound of esters is the

electrolyte (exact composition is protected by particular producers, the commonly used is lithium tetrafluoroborate LiBF_4). They have voltage rating 3,6 V. These cannot be charged and discharged with excessive current and the disadvantage the demand of power protection of individual cells during charging and discharging. Final voltage during charging cannot be exceeded and the discharge under certain limit must be refrained, which is on the work of protection circuits of every single cell. Operation conditions of Li-Ion accumulators are similar as with NiMH, and, when stored for longer time, is required to charge them at least once a year to avoid the discharge under certain limit as the battery is self-discharging. The energy density is ranging from 120 to 130 Wh/kg or from 200 to 250 Wh/dm³.

Lithium Polymer Accumulators (Li-Pol)

These cells come from Li-Ion cells; they have similar characteristics including nominal voltage, capacity and current. Contrary to Li-Ion, they are lighter with prismatic construction, but are mechanically little durable. Much like the Li-Ion, the disadvantage is the need of power protection of individual cells when charging and discharging, and low discharging currents.

Ultracapacitors

In principle, the ultracapacitor is an electrolytic condenser manufactured with special technology, with goal to reach high capacity of thousands of farads while keeping the characteristics

of condenser, particularly the ability of fast charging and discharging. The capacity of condenser is directly proportional to surface of electrodes and indirectly proportional to distance electrodes (charges). Electrodes of ultracapacitor comprises of powder carbon, deposited on aluminum foil. Grains of powder have surface of up to 2000m^2 per 1 gram of powder. Two electrodes are separated by separation sheet made of polypropylene; the space between electrodes is filled with liquid electrolyte. Large surface of electrode and very small distance of particular carbon grains (10^{-10}m of series) creates the capacity of series of farads. The carbon grains distance also reduces the operation voltage of the condenser to the amount of approx. 2,5 V. The result is a polarized condenser with very high capacity and very low series resistance, convenient for fast electric energy supply and storage. Electric parameters of ultracapacitors are comparable with parameters of electrochemical sources (batteries, accumulators). The energy stored in ultracapacitor is, in series, 10 times higher than energy stored in common condenser. Low inner resistance enables fast discharging; superb power supply delivered by ultracapacitor reaches the values of series of kilowatts per 1kg of weight of the ultracapacitor. Electric parameters of ultracapacitor are preserved even under low temperatures down to -40°C .

Disclosure of Invention

Presented invention relates to the new type of accumulator battery, which is based on serial-parallel connection of leadless types of NiMH, Li-Ion, Li-Pol secondary cells and ultracapacitors with possible advantageous use of electronic control unit. Accumulator battery according to this invention also has the same qualitative characteristics without use of electronic control unit. This invention consists in finding convenient alternative of -and improvement of existing lead batteries. Battery according to this invention is a new type of connection of known parts, with reaching better quantitative and qualitative characteristics than existing lead batteries.

The principle of new accumulator battery lies in serial-parallel connection of NiMH, Li-Ion, Li-Pol cells and ultracapacitors, with purpose to eliminate existing lead accumulators. By permanent connection of those components into one solid complex, it is guaranteed following: the preservation of deserved characteristics (size of inner resistance of particular connection branches, joints and their transition resistance, thermal conduction and heat removal from conductors, electric conductivity of connection conductors and terminals electric isolation and mechanical solidity and individual components positioning stability) during entire operation time in any conditions, chemical and mechanical resistance in otherwise malign environment (excessive humidity, corrosion elements in the atmosphere, joints oxidation, etc.), corresponding temperature environment during operation (use of

different filling agents in epoxy container, providing - according to actual needs - heat conductivity or, respectively, heat isolation), eventually their combination for various parts of new type auto battery for maximum utilization of advantageous characteristics of particular components such as high capacity of NiMH, Li-Ion or Li-Pol cells, ability to charge rapidly, ability to provide current even if deeply discharged, their relatively small inner resistance and possibility to provide currents in size that is minimally treble than their nominal capacity and during entire operation time without degradation of joints affected by the environment; ultracapacitors are used for their ability to provide, for a short term, high currents of series of thousands of farads without damage caused by thermal loss, have small inner resistance thanks to which they provide high energy output, can be charged from used cells - or eventually from connected power supply - in a very short time. Their disadvantages, which is not possible with common connection, can be eliminated as well, namely their small mechanical durability (significant for Li-Pol cells), etc. The number of cells is given by requisite capacity and final voltage of new type of accumulator battery.

When high discharging current is required, this is provided mainly by ultracapacitors. The NiMH (Li-Ion, Li-Pol) cells, due to value of inner resistance and connection conductors and individual branches terminals, eventually due to electronic control unit if such is used, are not overcharged. Particular branches and joints

have selective resistance specified regarding the type of cells (mainly due to their maximum discharging current).

For NiMH branch, Li-Ion or Li-Pol cells, the resistance is 3-10 times higher than for the branch of ultracapacitors. The resistance ratio and absolute size of those resistances is dependent on type and characteristics of particular components.

This new type of accumulator battery can be discharged for a short-term by current reaching the value of its nominal capacity multiplied 20 - 30 times.

During decrease of discharging current under the level of permanent discharging current of NiMH (Li-Ion, Li-Pol) cells, the ultracapacitors turn into electrical appliances and their charging proceeds. The current by which the ultracapacitors are charged is dependent on the charge, level of NiMH (Li-Ion, Li-Pol) cells, surrounding temperature and total amount of demanded energy, and exponentially decreasing. Here described system enables to use NiMH (Li-Ion, Li-Pol) cells in facilities that demands the energy permanently, up to the tenth (when using NiMH cells) or treble (when using Li-Ion or Li-Pol cells) of capacity of used accumulator and, along with that, they fitfully demand a few seconds lasting currents of size up to 30 times of the nominal capacity of used accumulator, which was not possible so far. In temperatures below -20° C, where the maximum discharging current

of NiMH (Li-Ion, Li-Pol) cells is decreasing to approx. 30% of the value reached in 20° C, the ultracapacitor is capable of delivering sufficient amount of current and so the functionality of the accumulator is guaranteed in temperatures down to -40° C. In respect to flat discharging characteristics of NiMH (Li-Ion, Li-Pol) cells and accumulator construction, this type of accumulator is able to deliver the currents up to times of the value of nominal capacity, even if deeply discharged under 10% of the nominal capacity.

The main advantages of present invention:

- The new type of accumulator battery does not contain lead, sulphuric acid solution or any other dangerous or toxic substances in the meaning of Directive 2002/95/EC RoHS in unbound form and therefore is ecologically harmless (toxic and dangerous substances in unbound form during storage and operation that is fully and hermetically separated from surrounding environment).
- The new type of accumulator battery is utilizable in wider range (-40 to 60° C.) of operating temperatures.
- Due to use of ultracapacitors and flat discharging characteristics of NiMH (Li-Ion, Li-Pol) cells, it is possible to start combustion engines even by accumulator battery that is discharged by 90% of its nominal capacity. Compared to the lead battery capacity, the accumulator battery with just half the capacity of first mentioned can be used for corresponding apparatus.

- Described type of accumulator battery, due to its composition and combination of NiMH (Li-Ion, Li-Pol) cells and ultracapacitors, is lighter and smaller in size than lead batteries. The density of stored energy, according to the construction mode and election of NiMH (Li-Ion, Li-Pol) cells, starts at 150Wh/dm³ (lead accumulators typically 50Wh/dm³).
- Due to construction of used NiMH (Li-Ion, Li-Pol) cells, ultracapacitors and monolithic construction of the accumulator battery itself, it is much more resistant to damage and vibrations. By virtue of the fact that ultracapacitors take part of the invention, it is possible to provide in series higher initiation current in full range of operating temperatures.

On the disadvantage side and in comparison with lead battery, we can consider the sensitivity to reversal of poles of the accumulator battery (if convenient compensational electronics is not applied) and generally higher discharge of NiMH (Li-Ion, Li-Pol) cells in temperatures over 40° C, which, on the other hand, can be eliminated by using, different NiMH (Li-Ion, Li-Pol) cells, but only at the price of limiting lower level of operating temperature ranging between -25° C and -30° C. When selecting Li-Pol (Li-Ion) cells as NiMH (Li-Ion, Li-Pol) cells, it is necessary to consider the use of electronic protection for control of charging and discharging currents.

New type of accumulator battery consist in serial-parallel

connection of NiMH, Li-Pol, eventually Li-Ion secondary cells or block of cells (on schemes marked as "B") and ultracapacitors (on schemes marked as "C"), placed into blocks with or without electronic control unit (on schemes marked as "E"). The required characteristics of individual blocks can be adjusted by suitable combination of different types of NiMH (Li-Ion, Li-Pol) cells, ultracapacitors and by electronic control unit setting. By said procedure the advantages of NiMH (Li-Ion, Li-Pol) can be taken, namely their high capacity comparing to their volume to weight ratio and, at the same time, the disadvantageous lower discharging current can be eliminated. To continue, the ultracapacitors advantages are, in particular, the high discharging currents (approx. 1000 A) and low inner resistance (approx. 1m Ω), and their disadvantageous low capacity can be eliminated. These block, according to needs on nominal voltage, required capacity, or eventually other demands, separately or together connected and with electronic control unit connection, are consequently embedded with convenient material getting monolithic product provided with terminals, and after hardening are prepared for use as a direct substitute of existing lead batteries and auto batteries.

The method of production of the battery according to this invention is characterized by that the serial-parallel connection of NiMH, Li-Pol, eventually Li-Ion secondary cells or blocks of cells and ultracapacitors into blocks, is realized. Consequently,

better qualitative and, regarding the capacity, also quantitative characteristics of a new type battery are achieved.

The primary benefit of this invention is the possibility of using NiMH, Li-Pol, eventually Li-Ion secondary cells or blocks of cells and ultracapacitors into blocks, for initiation of compression-ignition and spark-ignition combustion engines and all types of motor vehicles, by serial-parallel connection of those above-identified components.

The battery according to this invention consist of at least one NiMH or Li-Pol accumulator, eventually Li-Ion secondary cells, eventually of blocks of cells and ultracapacitors, by using serial or parallel or serial-parallel connection.

In the below presented samples are shown technical parameters of the apparatus, depending on selection of used components, materials and type of construction.

Brief Description of Drawings

Fig. 1 - The battery created by serial-parallel connection of 10 NiMH cells B with nominal capacity 22 Ah, nominal voltage 1,2V and maximum discharging current 2C, and 5 ultracapacitors C with capacity 400F, nominal voltage 2,7V and maximum current 500A.

Fig. 2 - Specification of accumulator battery charging and discharging, according to Sample 1

Fig. 3 - Shows a circuit for an electronic control unit.

Fig. 4 - The battery created by serial-parallel connection of 110 NiMH cells B with nominal capacity 4,5Ah, nominal voltage 1,2V and maximum discharging current 10C, and 10 ultracapacitors C with capacity 400F, nominal, voltage 2,7V and maximum current 500A.

Fig. 5 - Specification of accumulator battery discharging, according to Sample 2

The apparatus shown in Fig. 3 consist of safety fuse P with nominal current 40mA, Zener diode D with working voltage 15V, and connection conductors of sufficient cross section size.

The apparatus shown in Fig. 3, in addition to previous installation, has voltage stabilizer S with working voltage 8V, and voltmeter M module that is able to measure and display the electric voltage between 0 to 20V.

The description of function of chosen samples of electronic control unit units E:

The unit E shown in Fig. 4 is composed of Zener diode D for 15V and safety fuse P with nominal current 40mA, connected into series. When reversing the polarity of the battery, the Zener

diode D is opening and the current flows through the safety fuse P which causes its interruption. When connection to power source whose voltage is higher than 15V the Zener diode D is channeled in inverse direction so that the voltage is stabilized. If the voltage of the power source rises over approx. 17V, the current flowing through the safety fuse P exceeds 40mA and the fuse is consequently interrupted. The condition of safety fuse P, or eventually of Zener diode D, is indicating whether the change of accumulator battery polarity has occurred, or if it has been connected to the power source with higher voltage than specified in the documentation.

The unit E shown in Fig. 4 consists of above described block shown in Fig. 3 and the voltmeter M module, supplied with power through the voltage, stabilizer S set to measuring range of 20V, is shunted to this unit. Except the information whether the change of polarity occurred in the past or whether it was connected to power source with higher voltage than specified in the documentation, this unit also shows actual voltage status of the battery.

In added figures and schemes the characteristics and electronic connections for particular samples of invention are displayed.

Industrial Utilization

This type of accumulator battery is primarily designed for

initiation of compression-ignition and spark-ignition combustion engines and batteries for all types; above all it is ecologic, modern and maintenance-free substitution of existing lead batteries used in motor vehicles.

Further it may be used as a "drive battery" in electro mobiles, electric scooters, wheelchairs, etc. Moreover, the utilization is possible in back-up power supply systems and the like.

Examples of the Embodiment of the Technical Solution

Sample 1

According to scheme 1, the battery is created by serial-parallel connection of 10 NiMH cells B with nominal capacity 22Ah, nominal voltage 1,2V and maximum discharging current 2C, and 5 ultracapacitors C with capacity 400F, nominal voltage 2,7V and maximum current 500A. This pack of batteries and cells, after connection completion, is potted with epoxy into monolithic unit. Technical features of this apparatus are shown in Tab. 1. The process of charging, long term discharging and short term initiation discharging by high current is shown in Fig. 1. This battery is primarily designed for initiation of spark-ignition engines up to 100kW and may replace ordinary lead, auto batteries of capacity ranging between 36 and 45Ah. This battery does not contain any electronic control or master units.

The cross sections of conductors in all inner joints have respective surface 10 mm^2 , are made of copper and particular parts are coupled with SnAg3 solder.

The final mechanic embodiment, the size, type of epoxy, filling agent, shape; output distribution and cross sections of conductors are subject to desired utilization.

For use in motor vehicles, the chosen size is $207 \times 175 \times 175 \text{ mm}$ (LxWxH), output poles are of type 1 and the battery polarity is 0. The epoxy contains thermally conductive filling agent based on aluminum.

Sample 2

According to scheme 2, the battery is created by serial-parallel connection of 110 NiMH cells B with nominal capacity 4500mAh, nominal voltage 1,2V and maximum discharging current 40C, and 10 ultracapacitors C with capacity 400F, nominal voltage 2,7V and maximum, current 500A. This pack of batteries and cells, after connection completion, is potted with epoxy into monolithic unit. Technical features of this apparatus are shown in Tab. 2. The process of charging, long term discharging and short term initiation discharging by high current is shown in Fig. 2. This battery is primarily designed for initiation of spark-ignition and

compression-ignition engines up to 200kW and may replace ordinary lead auto batteries of capacity up to 100Ah. This battery contains electronic control unit E (Fig. 3, see description below) Indicating whether the change of accumulator battery polarity has occurred in the past or if it has been-connected to the power source with higher voltage than 15V.

The cross sections of conductors connecting cells B in series have respective surface 10 mm^2 , the cross sections of conductors connecting ultracapacitors C in series have surface 20 mm^2 and connection terminals shunting all branches have surface 25 mm^2 . All conductors and terminals are made of copper and particular parts are coupled with SnAg3 solder.

The final mechanic embodiment, the size, type of epoxy, filling agent, shape output distribution and cross sections of conductors are subject to desired utilization. For use in motor vehicles, the chosen size is $207 \times 175 \times 175 \text{ mm}$ (LxWxH), output poles are of type 1 and the battery, polarity is 0. The epoxy contains thermally conductive filling agent based on aluminum.

Table 1

Nominal capacity at 20° C	22 Ah
Nominal voltage	12 V
Initiation current equivalent to EN	390 A
Interruption current	600 A
Reserve capacity RC	40 min
Maximum discharging current (max 1s)	500 A
Maximum permanent discharging current	25 A
Operative temperatures range	-40 to 60° C
Ultracapacitor capacity	80 F
Energy density	6 Ah/kg

Table 2

Nominal capacity at 20°C	48 Ah
Nominal voltage	12 V
Initiation current equivalent to EN	800 A
Interruption current	2000 A
Reserve capacity RC	107 min
Maximum discharging current (max 1s)	1800 A
Maximum permanent discharging current	500 A
Operative temperatures range	-40 to 60° C
Ultracapacitor capacity	160 F
Energy density	7 Ah/kg

List of reference marks

B - NiMH cell;

C - Ultracapacitor;

P - Safety fuse;

D - Zener diode;

S - Voltage stabilizer

E - Electronic control unit

Claims

1. An automotive battery, having:

at least one NiMH cell, at least one Li-Ion cell and/or at least one lithium polymer cell; and

at least one ultracapacitor;

the at least one cell and at least one ultracapacitor electrically connected;

the at least one cell and at least one ultracapacitor permanently connected into a solid monolithic block;

the automotive battery further characterized in that it is leadless; and

characterized in that the solid monolithic block is formed by potting with epoxy.

2. An automotive battery as claimed in claim 1, further having an electronic control unit.

3. An automotive battery as claimed in claim 2, characterized in that the electronic control unit consists of a Zener diode, a voltage stabilizer and/or a voltmeter module.

4. An automotive battery as claimed in claim 1 wherein the epoxy contains a thermally conductive filling agent.

5. An automotive battery as claimed in claim 4 wherein the filling agent is based on aluminum.

6. An automotive battery comprising:

an anode battery terminal and a cathode battery terminal;

a plurality of serially connected cells each cell selected from a group consisting of NiMH - Nickel metal hydride cells; Li-Ion - Lithium-Ion cells, and Li-Pol-Lithium polymer cells, the cells being connected between the anode battery terminal and the cathode battery terminal thereby referencing the voltages of the anode battery and the cathode battery terminals; and a plurality of serially connected ultracapacitors connected between the anode battery terminal and the cathode battery terminal thereby referencing the voltages of the anode and the cathode terminals, wherein the automotive battery is leadless, wherein the serially connected cells and the serially connected ultracapacitors are parallel-connected between the anode battery terminal and the cathode battery terminal to define a parallel circuit between the anode battery terminal and the cathode battery terminal, and wherein the anode and cathode battery terminals are terminals of the automotive battery,

wherein resistance of the plurality of the serially connected cells is three to ten times resistance of the plurality of serially connected ultracapacitors,

wherein the cells and the ultracapacitors are connected to charge and discharge through the cathode battery terminal,

wherein the automotive battery is made as a solid monolithic block, and

wherein the solid monolithic block includes the cells and the ultracapacitors potted with epoxy.

7. Automotive battery according to claim 6, wherein said plurality of serially connected cells and said plurality of serially connected ultracapacitors are connected to form a monolithic block between the anode and the cathode terminals.

8. Automotive battery according to claim 7, further comprising an electronic control unit connected between the serially connected ultracapacitors, the serially connected cells and one of the two terminals and configured for interruption if polarity of the battery is reversed.

9. Automotive battery according to claim 8, wherein the electronic control unit comprises at least a Zener diode;

a voltage stabilizer; and

a voltmeter module.

10. Automotive battery according to claim 6, wherein the epoxy contains a thermally conducting filling agent based on aluminum.

11. Automotive battery according to claim 10, further comprising a controller unit that includes a safety fuse connected between the

serially connected cells and the serially connected ultracapacitor and is interrupted when the polarity of the battery is reversed.

12. Automotive battery according to claim 11, further comprising a zener diode connected to the safety fuse to provide current to the safety fuse when the polarity of the battery is reversed.

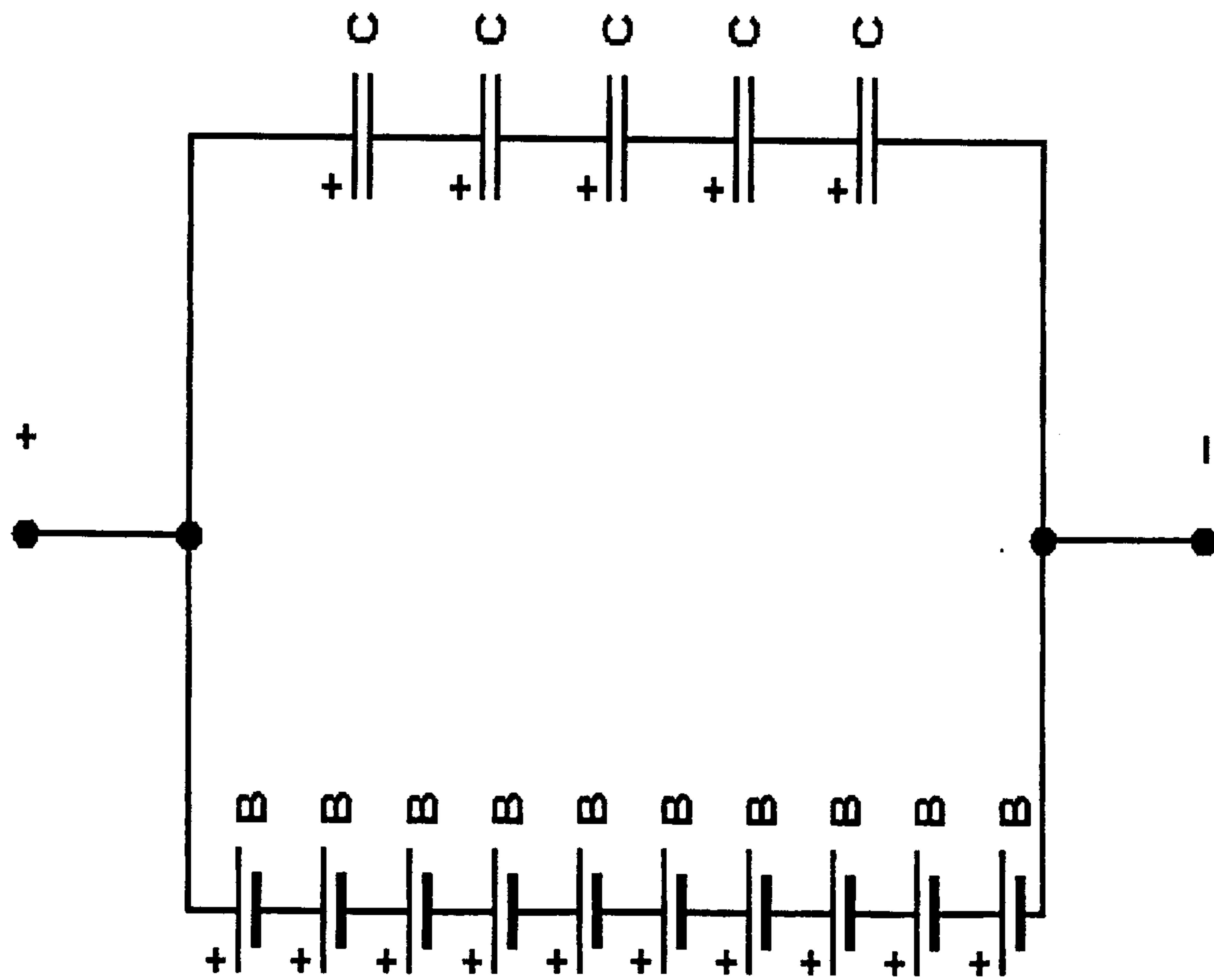


Fig. 1

Fig. 2

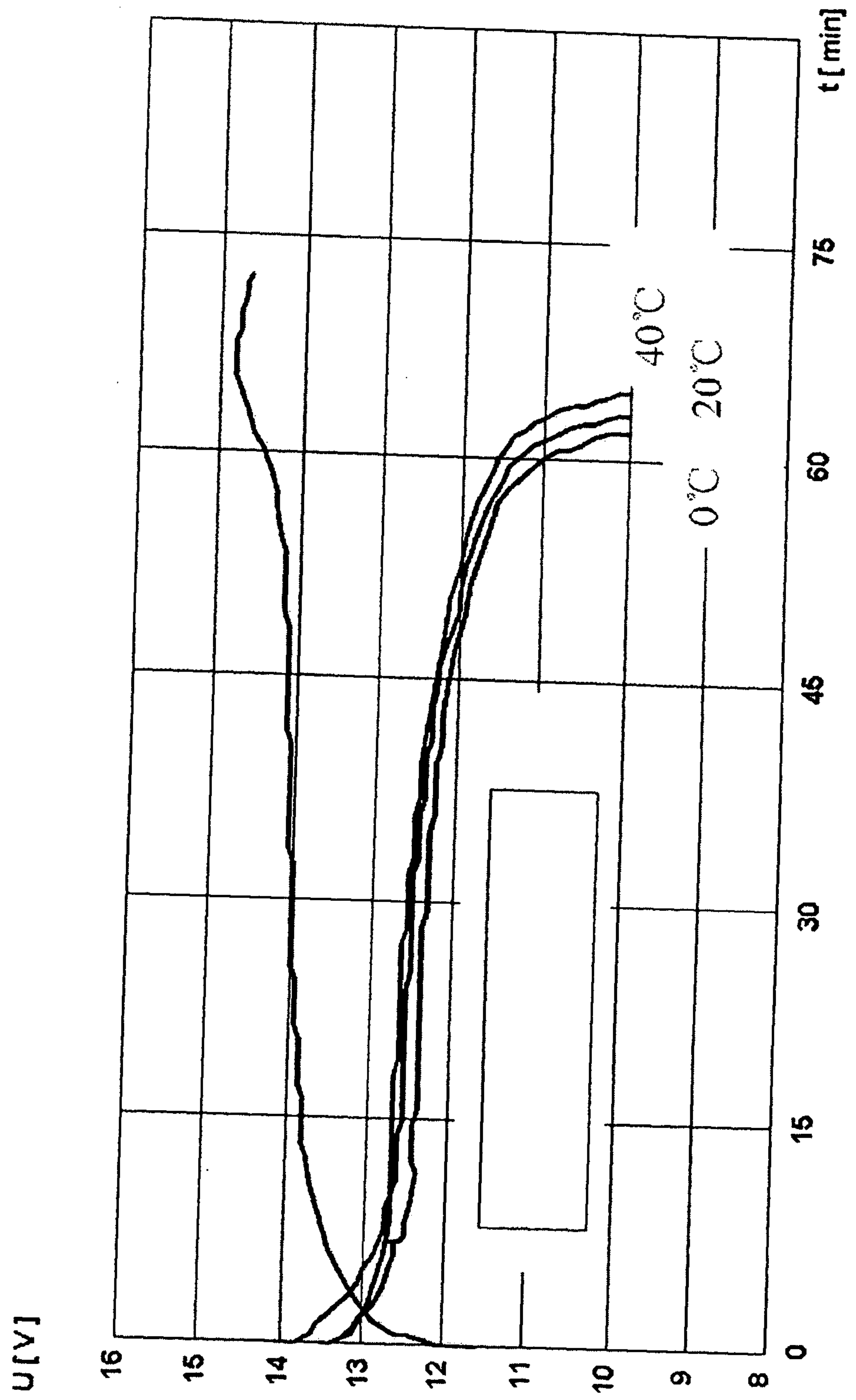
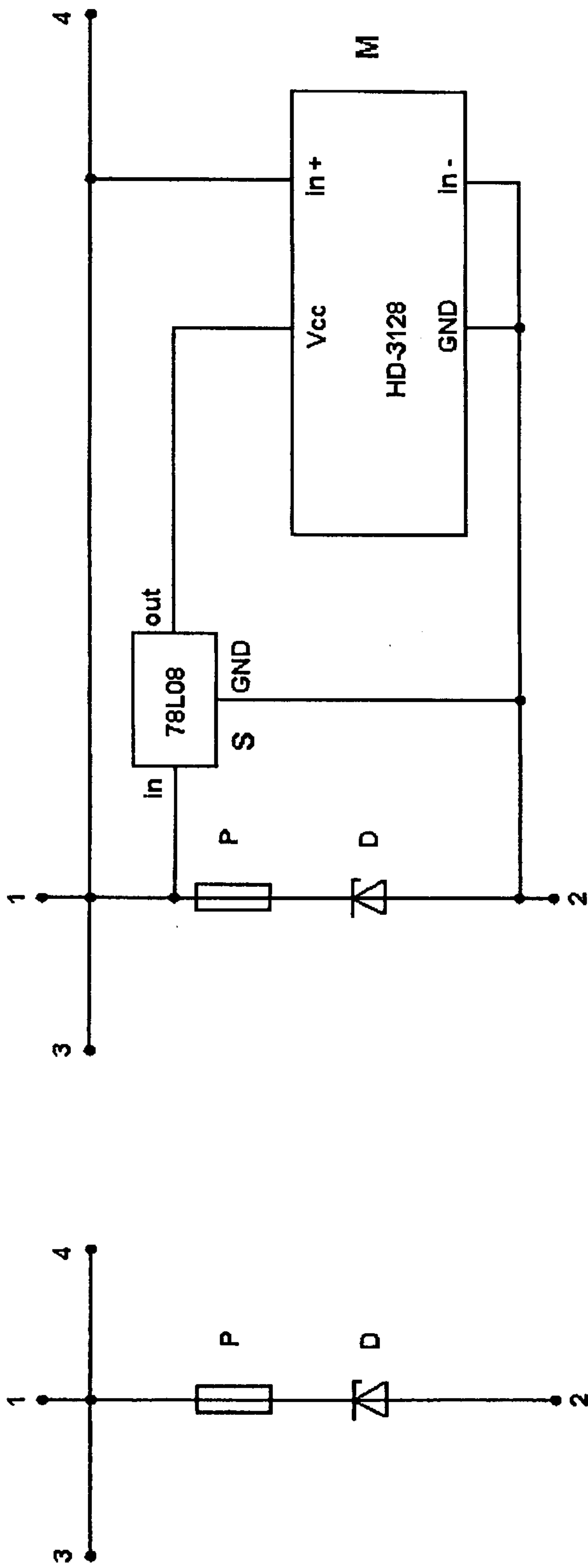


Fig. 3



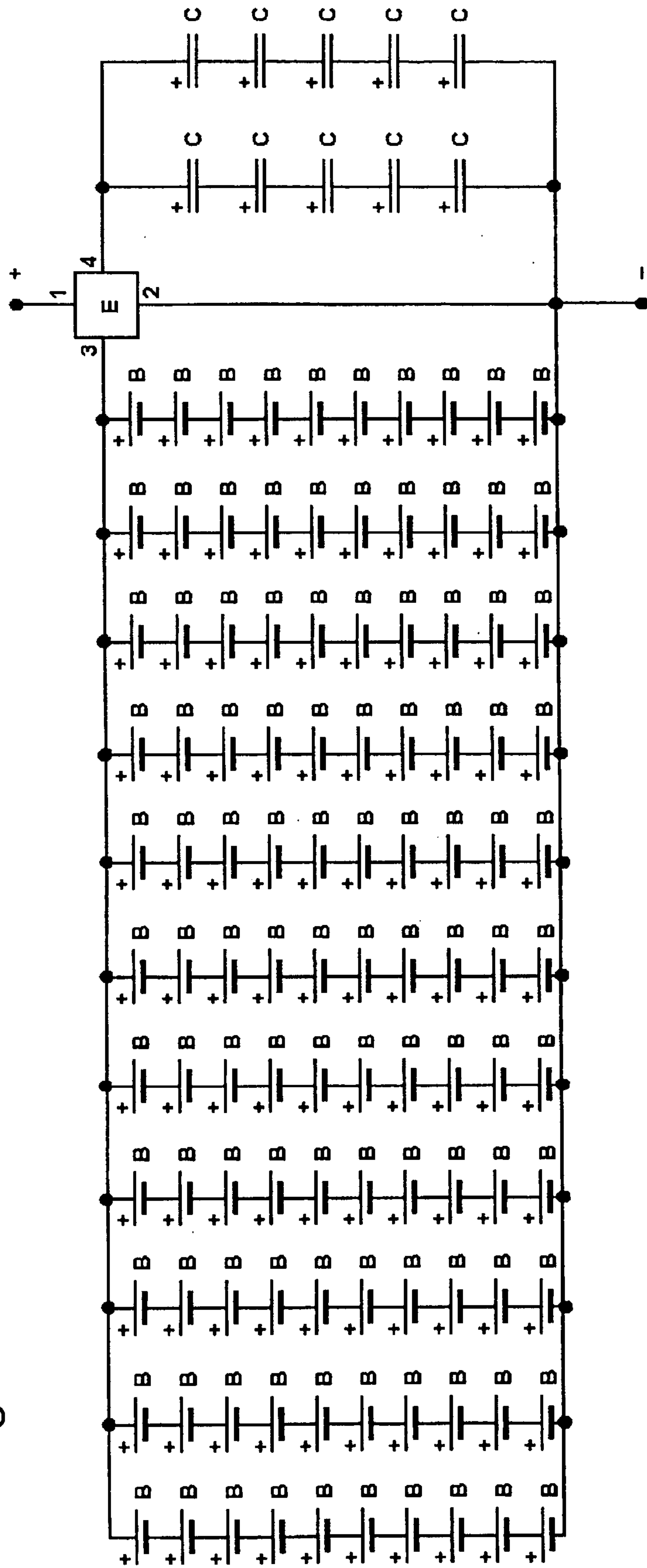


Fig. 4

