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(54) Title: REDOX GEL BATTERY

(57) Abstract

A redox gel battery (10) consists of a positive redox gel electrolyte (13) a negative redox gel electrolyte (14) and a membrane (15) therebetween. A positive electrode (11) is electrically connected to the positive redox gel electrolyte (13) and a negative electrode (12) is electrically connected to the negative redox gel electrolyte (14). The operation of the redox gel battery can be enhanced by a battery management system which minimises the effects of polarisation.

REDOX GEL BATTERY

FIELD OF INVENTION

This invention relates to electric storage batteries and more
particularly to storage batteries having enhanded operating characteristics.

5   BACKGROUND ART

The battery industry has seen increased demand for battery
management technology, primarily due to the consumers' ever-increasing
appetite for the convenience of battery-powered portable equipment such
as cellular phones and laptop computers. Additionally, the battery industry

10   is seeing a movement toward an increased emphasis on electric motor-
driven tools and zero emission vehicles with the primary power source for
these new generation vehicles being batteries. This movement is due to
rapidly increasing government regulations and consumer concerns about air
and noise pollution. Another area which requires high efficiency batteries is

15   energy storage applications such as load-levelling, emergency/standby
power and power quality systems for sensitive electronic components.

As a result of the increasing demand of battery-powered equipment,
the battery industry is under competitive pressure to produce an ideal cell.
A cell that weighs almost nothing, takes up no space, provides excellent

20   cycle life and has ideal charge/discharge performance and does not itself
produce an environmental hazard at the end of its life. The most popular
technology utilised by the battery industry is the lead-acid battery, which is
being challenged to meet higher energy density, smaller size, better
performance levels, longer cycle life and guaranteed recyclability.

25   Conventional lead-acid batteries suffer from limited capacity
utilisation, low depth of discharge, short cycle life, low energy density,

thermal management problems and the need for constant boost charging to maintain cell equalisation.

The lead-acid batteries also require long charge times and high charge currents can only be used for a few minutes at very low states-of-charge. If high currents are used it normally results in higher than allowable voltages being reached leading to electrolyte loss and a reduction in the battery's capacity. The time to recharge a lead-acid battery with boost charging can be up to 4 hours at best if a proper charge profile is followed.

The cycle life of lead-acid batteries varies greatly depending on the Depth-of-Discharge (DOD) reached during cycling. For electric vehicle applications a 90-100% DOD may not be uncommon and at these DOD levels the cycle life of conventional deep cycle lead-acid batteries would be approximately 300 cycles. As most controllers function on the total battery voltage it is not uncommon for individual cells to be discharged below an acceptable limit as the overall battery voltage technique relies on the assumption that all cells are at the same state-of-charge, which is usually not the case in practise. Systems can be so far out of balance that under high loads individual cells can actually reverse and even gas during the discharge. This may seem extreme, however, when a large battery array is used to provide power at higher voltages cell reversal may occur without being detected initially.

Conventional NiMH batteries employ advanced processed and high purity materials. This leads to a very high cost for the battery systems. Expanded nickel foams with high purity nickel hydroxide compounds and processed metal alloy materials all need a very high degree of quality control in order to obtain a high performance battery.

NiMH hydride batteries can also suffer from self-discharge problems and can also be affected by temperature. On certain systems the extraction of high current can cause damage to the battery cells and care must be taken not to over charge the batteries. In this respect, advanced battery

5   chargers are needed to ensure proper charging.

Redox batteries have been under investigation for may years and have mainly been in the form of flow batteries. Redox flow batteries store energy in the liquid electrolytes which are stored separately to the battery stack. During operation the electrolytes are re-circulated through the

10   system and energy is transferred to and from the electrolytes. When charging, electricity is transferred to and stored by the electrolytes, upon discharge, the electrolyte release the stored energy to the load. Redox flow batteries typically have a low energy density and incur pumping losses associated with re-circulating the electrolyte through the system. In certain

15   cases, high self-discharge rates are possible depending on the membranes or the existence of internal leaks and shunt currents.

SUMMARY OF THE INVENTION

According to one aspect of the invention there is provided a redox gel battery comprising at least one cell consisting of a positive redox gel

20   electrolyte, a negative redox gel electrolyte, a membrane between the positive and negative redox gel electrolytes, a positive electrode electrically connected to the positive redox gel and a negative electrode electrically connected to the negative redox gel electrolyte.

BRIEF DESCRIPTION OF THE DRAWINGS

25   Fig.1 is a schematic diagram of a single cell redox gel battery according to one embodiment of the invention,

Fig. 2   is a schematic diagram of a multi-cell redox gel battery
          according to another embodiment of the invention,

Fig. 3 is a schematic diagram of a spirally formed single cell redox
          gel battery according to a still further embodiment of the
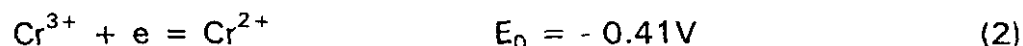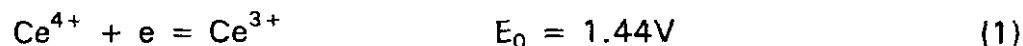5   invention,

Fig. 4 is a block diagram of a battery management system for a
          Redox Gel Battery according to the invention, and

Fig. 5 is a block diagram of the resistance control module of the
          battery management system shown in Fig. 4.
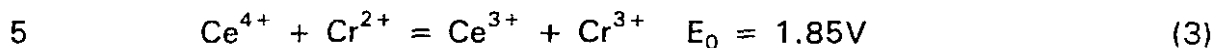
10   MODES FOR CARRYING OUT THE INVENTION

          Conventional battery systems employ some form of solid metal
electrodes that involve phase transfer reactions which leads to increased
weight and loss in efficiencies. The redox gel battery of the invention
employs super concentrated gels, which contain a high concentration of
15   positive and negative reactive ions in the respective gels. All reactive
species or reactants are contained in the gels and no phase transfer
reactions are involved which leads to high efficiencies due to minimal
losses.

          An example of a redox gel cell is the Cerium / Chromium battery
20   (typically Cerium Chloride $CeCl_3$ and Chromium Chloride $CrCl_3$) with the
typical reactions illustrated by equations 1 and 2 below:

$$Ce^{4+} + e = Ce^{3+} \qquad\qquad E_0 = 1.44V \qquad\qquad (1)$$

$$Cr^{3+} + e = Cr^{2+} \qquad\qquad E_0 = -0.41V \qquad\qquad (2)$$

          At a charged state the negative and positive gels are composed of
25   Ce^{4+} and Cr^{2+} respectively. When the battery is discharged the negative
gel electrolyte Cr^{2+} is oxidised to Cr^{3+} and the positive gel electrolyte Ce^{4+}
is reduced to Ce^{3+}.

The overall discharge reaction is given by equation 3 below, with the theoretical cell voltage based on the standard electrode potentials of equations 1 and 2, for aqueous solutions calculated at 25^0C vs NHE, being 1.85V. The charge reaction is the reverse reaction of equation 3.

5        $$Ce^{4+} + Cr^{2+} = Ce^{3+} + Cr^{3+} \quad E_0 = 1.85V \qquad (3)$$

The actual cell voltages will depend on the supporting electrolytes used for the reactants in the redox gel media.

A single cell redox gel battery 10 is shown in Fig 1 and includes an inert positive electrode 11, an inert negative electrode 12, a positive redox

10   gel electrolyte 13, a negative redox gel electrolyte 14 and a membrane 15 between the positive and negative redox gel electrolytes 13 and 14. The electrodes 11 and 12 are preferably non-metallic.

A membrane 15 which has a very low electrical resistance separates the redox gel electrolytes 13 and 14 with a very low electrical resistance.

15   The redox gel electrolytes 13 and 14 may be made of any metallic ion, metallic ion combination, inorganic and organic compounds that enable the gels to be conductive and produce a current when connected to a load at the characteristic voltage of the cell. The gels may also contain any additive that may enable their performance to be enhanced.

20   The gel electrolytes may also contain gelling agents such as silica or any other material which may assist in the formation of a stable gel without precipitation of the reactive species.

The redox gel battery differs from the redox flow principle in that the electrolytes do not need to be re-circulated since the electrolytes are super

25   concentrated gels and are contained within the battery as shown for a single cell in Fig. 1.

The redox gel cell may be constructed as a single cell as shown in Fig. 1, as a bipolar multicell assembly as shown in Fig. 2 or in a spiral wound cell design as illustrated in Fig. 3.

The bipolar multi-cell assembly 20 shown in Fig. 2 consists of cells 5   1, 2 .... N-1, and N. Each cell 1 to N has a positive redox gel electrolyte 13 and a negative redox gel electrolyte 14 separated by a membrane 15. Between each cell there is a common electrode 16. At the outer face of cell 1 there is an inert negative electrode 12 and at the outer face of cell N there is an inert positive electrode 11.

10   The single cell spiral wound redox gel 30 shown in Fig 3 includes a cell structure as shown in Fig. 1 and an insulating film 17 which separates the wound segments of the cell structure.

The redox gel cell can be used with a battery management system as 15   shown in Fig. 4 which contains a module that can be integrated into the battery pack to minimise the effects of polarisation. The operation of the redox gel cell is enhanced by the battery management system which limits polarisation and provides a high level of individual cell control due to the speed and monitoring of the battery management system.

20   As the gels are superconcentrated, polarisation tends to be higher when high loads are applied to the battery system. A battery management system specifically suited to the redox gel battery can alleviate many of the constraints in the design of the redox gel system.

A battery management system specifically designed for the redox gel 25   cell can also perform a number of monitoring functions, such as monitoring the individual cell voltages and temperatures. It can also monitor the internal pressure of the sealed battery pack and ascertain the allowable load

limits of the system at any given condition. The battery management system can also have the added ability to be able to take active steps in maintaining optimal battery performance at any state-of-charge. With this high degree of system control, the redox gel battery of the invention can

5   utilise its total capacity repeatedly and over a very long cycle life.

The preferred battery management system which is shown in Fig 4 in block form includes a microprocessor 40 and associated software 57 that manages all of the following described functions. In this instance the microprocessor is 8 bit running at 8MHz, however 4,16, 32 or 64 bit

10   processors can be used. The processor speed could be 4MHz to 166MHz. Alternatively a Digital Signal Processing Chip could be used depending on the individual battery requirements. The microprocessor has EEPROM, ROM and RAM Memory. Alternatively an ASIC (Application Specific Integrated Circuit) could be used.

15   The individual cell voltage measurement module 41 utilises a separate wire connected to the junction of each cell. This wire is used solely for the measurement of voltage. The voltage of each cell is measured with reference to ground for batteries up to 24 Volts. This can also be accomplished using direct measurement of each cell voltage as the

20   needs and accuracy requirements dictate.

Individual cell voltage measurement conditioning is achieved by module 42 which includes a circuit in which the cell voltages are divided by a resistor network and smoothed by a filter capacitor connected across the ground resistor in the divider. Active filtering using operational amplifiers or

25   other filtering means could be used. The voltages are scaled by the divider and filter to a voltage suitable for analog to digital conversion. In this case 4.95 Volts represents the expected maximum voltage of each connection

to the battery. A 12 bit analog to digital converter is used for each cell voltage to be measured. The analog to digital converter is controlled serially by the microprocessor which converts each measured voltage to the cell voltage by scaling each voltage and subtracting the voltage of the negative side of each cell from the voltage of the positive side of the cell. This is done for each cell and this method is applicable for cell voltages up to 24 Volts.

Above 24 Volts multiple stages of the above method can be used by transmitting the serial digital data by means of optically coupled serial communications thus isolating the cell voltages. Also applicable would be the use of a Voltage to Frequency Converter connected across each cell to directly measure the cell voltage and send this information as a frequency to the microprocessor. These Voltage to Frequency converters can be galvanically or optically coupled to the microprocessor which measures the frequency and converts this to a voltage.

The current measurement module 43 measures the voltage across a shunt resistor and scaling this value using a current sense amplifier with active filtering. An alternative to this would be to use a Hall effect device to measure the current with the appropriate signal conditioning.

Current measurement conditioning is achieved by circuit module 44 in which the voltage measured across the shunt is converted to a 0-5Volt signal irrespective of the direction of the current which is then fed to an input of the same 12 bit analog to digital converter used for the measurement of voltage described above. The conditioning circuitry also provides a digital input to the microprocessor indicating the direction of current flow. This is achieved via an integrated circuit with minimal external

components. Discrete component solutions would also be cost effective in this area.

Temperature is measured by circuit module 45 using an integrated circuit temperature sensor mounted on the circuit board. Any number of

5   these can be used and located in different areas for example the battery, individual cells or outside for ambient temperature.

Temperature Measurement conditioning is achieved by circuit module 46 in which:

the temperature value is a voltage output and a low offset voltage

10   operational amplifier is used to scale this value to a 0-5Volt value suitable for connection to an input of the same analog to digital converter used for voltage and current measurement.

A Liquid Crystal Display 47 is used to display information such as capacity remaining, kilometers remaining and any other information.

15   The display driver 48 is driven directly by the microprocessor 40 by writing the appropriate value to a memory location based on a lookup table stored inside the microprocessor 40. Depending on the microprocessor requirements and LCD complexity a separate integrated circuit driver may be used. A LED or gas plasma display could also be used. A Liquid Crystal

20   display module may also be used.

Audible indicator module 49 includes a piezo electric buzzer which provides audible signal to the user. This is ideally driven directly from the microprocessor or with a transistor driver if necessary.

A distance sensor 50 is mounted on the wheel should the battery be

25   used in a moving vehicle. This sensor 50 can take the form of either a magnetic pickup where the magnet is located on the wheel and a hall effect

pickup device is mounted on a stationary part of the vehicle or an optical
sensor.

Distance sensor conditioning is achieved by a circuit module 51 in
which the output of the distance sensor 50 is a frequency that is scaled

5   and measured by the microprocessor 40 which in turn converts this to a
speed or distance value.

Pressure sensor module 52 includes a pressure transducer with a low
voltage (in the order of 0-100mV) output is located in the battery.

Pressure sensor conditioning module 53 scales the output to

10   0-5Volts via a precision operational amplifier and fed to the analog to digital
converter.

The communications module 54 ensures that all control and
communications signals from the battery charger are communicated via a
serial bus direct from the microprocessor 40. This serial bus can also

15   access a PC for calibration purposes.

To ensure long battery life all components of the optimiser are
chosen for low current consumption. The microprocessor, analog to digital
converter, and all other circuitry can be placed in a low current
consumption mode by a signal from the microprocessor to the low current

20   mode module 55.

To achieve the required levels of accuracy the analog inputs to the
microprocessor are calibrated by the calibration module 56 and the
calibration factors and offsets are store in EEPROM memory.

The software 57 is preferably polling orientated as well as being

25   interrupt driven for time critical events such as current monitoring for
energy use integration. Preferably, the software can determine if an
individual cell is faulty and notify the battery charger.

The software may include a polynomial voltage current algorithm to prevent the battery from over-discharge by opening the switch. The software is adapted to:-

(a)   calculate the self discharge of the battery and can initiate the cell balancing process,

(b)   log the number of cycles and can send this information to the battery charger,

(iii)   monitor, communicate and initiate protective measures to prevent overvoltage or under voltage,

(iv)   sample current at regular time intervals and integrates current with respect to time to provide ampere hours used and remaining data, and

(v)   the amperehours used and remaining is corrected depending on loads during the current cycle.

The microprocessor 40 can also drive FETS or IGBT's to control the current to a motor 58. This can provide a single pulse width modulated control for a brushed type motor, or a quasi sinusoid control with multiple outputs for brushless multiple type motors such as reluctance motors or brushless DC motors.

A FET or IGBT switch 59 is used for security and protection of the battery. FETS with a low on resistance are used.

The switch 59 is controlled by switch control module 60 which is driven by the microprocessor 40 and the drive of the FETS or IGBT's utilises a switched power supply to boost the voltage to enable high side driving.

In the resistance control module 61, the microprocessor controls a FET the function of which is to periodically charge a capacitor to a voltage

above the battery voltage and discharge this capacitor into the battery whilst at the same time switch another capacitor whose charge can hold the load current.

The output of an energy gauge 62 is displayed on the LCD display as capacity remaining. This value is calculated by integrating the current over time. Current is sampled at regular intervals and this value is subtracted from an accumulator and then scaled to 100% to give a capacity remaining output.

The internal resistance/impedance module 63 calculated the internal resistance and impedance by means of measuring the change in voltage before and after a step change in current. This can occur both during charge and discharge. AC current or voltage may be injected into the battery and the resultant voltage or current is measured to calculate internal resistance and impedance.

The cell balancing module 64 operates so that when one cell is considered to be self discharged more than others in the group, power is taken from the entire group, converted to an appropriate voltage using a switched mode power converter and distributed to the weakest cell thus balancing the cells.

The electrodes employed in the redox gel cells function to allow the transfer of energy into and out of the gel electrolytes. The electrodes are inert and can be produced from specially developed non-metallic conducting materials, which can be formed or moulded to almost any specific shape.

The electrolytes are used to store all energy contained in the Redox-Gel battery. The specific ions contained within the gel are selected based on application and the energy density and can be either employ single or multi-electron half-cell reactions. The gel electrolyte can be produced with

and without an electrode matrix integrated into the gel. In either case the primary function of the gel to store the energy remains unchanged.

The redox gel cell has a very long cycle life due to the stability of the gel electrolytes, as in their fundamental form the electrolytes store energy

5   without phase transfer taking place, the electrolytes do not degrade and the system as a whole is very cost effective. With its lightweight and robustness it is well suited to the battery exchange process for the "rental energy" vehicles, emergency back-up applications and portable power packs.

10   The manner of controlling polarisation and hence battery output will now be further described with reference to Fig. 5.

The control system 100 shown in Fig. 5 is adapted to provide a predetermined power output from a redox battery system 111 at the terminals or output means 112 to which a load such as an electrical vehicle

15   is connected. Between the output terminals 112 and the terminals 113 of the redox gel battery system 111 there is a control means 114 which senses predetermined operating parameters of the redox gel battery system 111. The control means 114 supplies power from the battery system 111 to the output terminals 112 during a first mode of operation.

20   First capacitor means 115 connected between the battery system 111 and the control means 14 stores a predetermined quantity of power from the battery system 111 during the first mode of operation of the control means 114 and supplies its stored power to the battery system 111 in response to a command signal from the control means 114 when the

25   control means is in a second mode of operation.

Second capacitor means 116 which is connected between the output terminals 112 and the control means 114 stores a predetermined

amount of power from the battery system 111 when the control means

114 is in its first mode of operation and supplies its stored power to the

output terminals 112 in response to a command signal from the control

means 114 when the control means 114 is in its second mode of

5   operation.

Thus, the power control system incorporates two capacitor networks

and when the control means senses, for example, that the polarisation level

in the battery system 111 is too high or that a pre-set time interval has

elapsed since power was first supplied to the load, it initiates a back charge

10   to the battery system 111. In this discharge cycle, the control means 114

allows the energy stored in the first capacitor network 115 to charge the

battery system 111 and at the same time the second capacitor means 116

supplies uninterrupted power to the output terminals 112. The time

interval for this reverse cycle or discharge cycle is very small and as it is

15   very efficient it can be performed at regular intervals.

The reverse charge has the ability to disrupt and minimise the effects

and associated losses of polarisation within the battery system.

The power control system may also work in conjunction with a

charger to provide optimum performance and battery care at all times

20   during its operation. The power control system may be adapted to prevent

an unauthorised type of charger being connected to the battery system

thereby preventing a potential abuse and ensuring that the vehicle owner

does not attempt to charge the battery system with an incorrect charger at

home.

25   The power control system, the charger and the vehicle may

incorporate individual electronic signatures so that the entire system can be

tracked and monitored with a high degree of accuracy. Each time a battery

system is installed into a charger unit, the power control system will identify itself, the vehicle from which it has been removed as well as the user.

The charger unit may monitor the energy level of the battery and
5   credit the users for this value, add the cost of the exchange, the electricity and a monthly rental for the battery. Upon receipt of this payment either by cash or credit card, a new battery is released and installed into the vehicle. If the client has abused or tampered with the battery anyway this will be identified by the charger.

10   The control system can be adapted to not only identify the energy level of the battery, but it can also assess the driving range left based on current energy usage levels. Thus, the vehicle driver will know how many kilometres can be travelled on the remaining level of energy.

Each charger unit may be linked via a telemetry system to an
15   operation centre which enables constant monitoring of all stations in the network of charging stations.

The power control system may include the functions and features of speed control modules which means that the vehicle manager can eliminate a speed control device from the vehicle and simply control the output via
20   the power control system. This reduces vehicle costs, reduces manufacturer warranty exposure and can provide continuous performance monitoring via the telemetry communication system.

The power control system may be applied to various battery systems such as valve-regulated lead acid batteries, nickel metal hydride batteries
25   and redox-gel batteries with each system having its benefits and specific target applications.

The power control system may also be used to improve the standby

performance of remote area power system, load levelling and emergency back-up battery systems. Stationary battery systems used in remote area power systems and emergency back-up applications may be left fully charged for extended periods. As cells self-discharge at different rates the power control system can be programmed to scan the individual cell conditions periodically and use cell-balancing techniques to balance the cells internally. Alternatively, the charging system may be left on standby and be controlled by the power control system as required.

CLAIMS

1.   A redox gel battery comprising at least one cell consisting of a positive redox gel electrolyte, a negative redox gel electrolyte, a membrane between the positive and negative redox gel electrolytes, a positive electrode electrically connected to the positive redox gel and a negative electrode electrically connected to the negative redox gel electrolyte.

2.   A redox gel battery according to claim 1 wherein the negative and positive electrodes are inert non-metallic electrodes.

3.   A redox gel battery according to claim 1 wherein the gel electrolytes contain reactive metallic ions to store energy.

4.   A redox gel battery according to claim 1 wherein the gel electrolytes contain non-metallic reactive ions to store energy.

5.   A redox gel battery according to claim 1 wherein the gel electrolytes do not involve solid phase transfer reactions.

6.   A redox gel battery according to claim 1 wherein the gel electrolytes involve solid phase transfer reactions.

7.   A redox gel battery according to claim 1 and further including metallic additives which enhance the performance of the gel electrolytes.

8.   A redox gel battery according to claim 1 and further including non-metallic additives which enhance the performance of the gel electrolytes.

9.   A redox gel battery wherein the gel electrolytes are formed with an inert conductive matrix.

10.   A redox gel battery according to claim 1 wherein the positive gel electrolyte comprising a half cell containing a reactive species and a negative half cell containing a different reactive species.

11.   A redox gel battery according to claim 1 wherein the negative gel electrolyte comprising a half cell containing a reactive species and a negative half cell containing a different reactive species.

12.   A redox gel battery according to claim 1 wherein the electrodes are spiral wound.

13.   A redox gel battery wherein the electrodes are compressed plate electrodes.

14.   A redox gel battery in combination with a battery management system for a battery having at least one cell that has at least a pair of electrodes and which is susceptible to polarisation, said battery management system comprising:-

     (i)   means for monitoring a predetermined parameter of the or each cell that is indicative of the level of polarisation,

     (ii)   means for storing a predetermined amount of the power being transferred into or out of the battery, and

     (iii)   means for inducing a reverse charge or pulse to the electrodes so as to reduce the polarisation.

15.   A redox gel battery according to claim 14 wherein the predetermined parameter is the internal resistance of the or each cell.
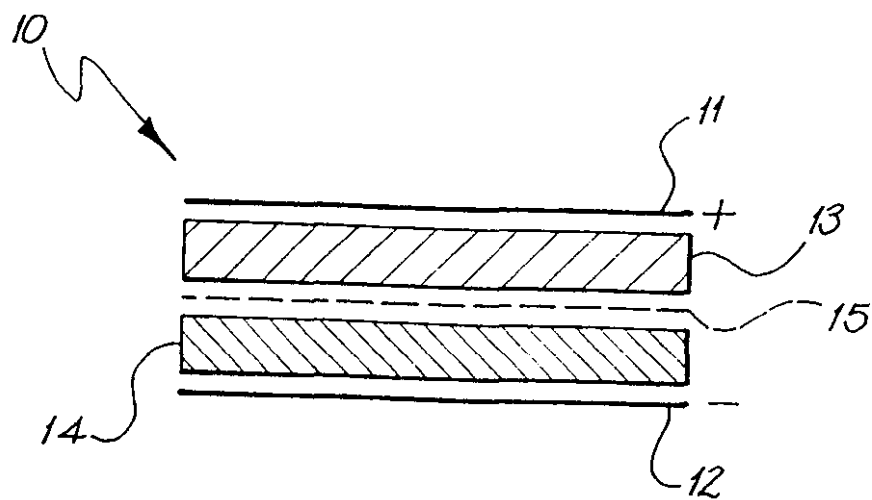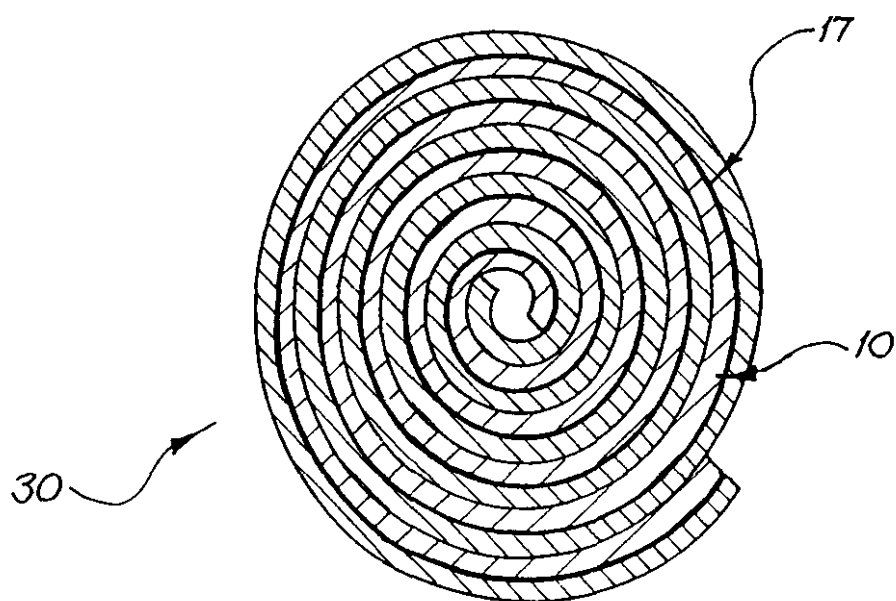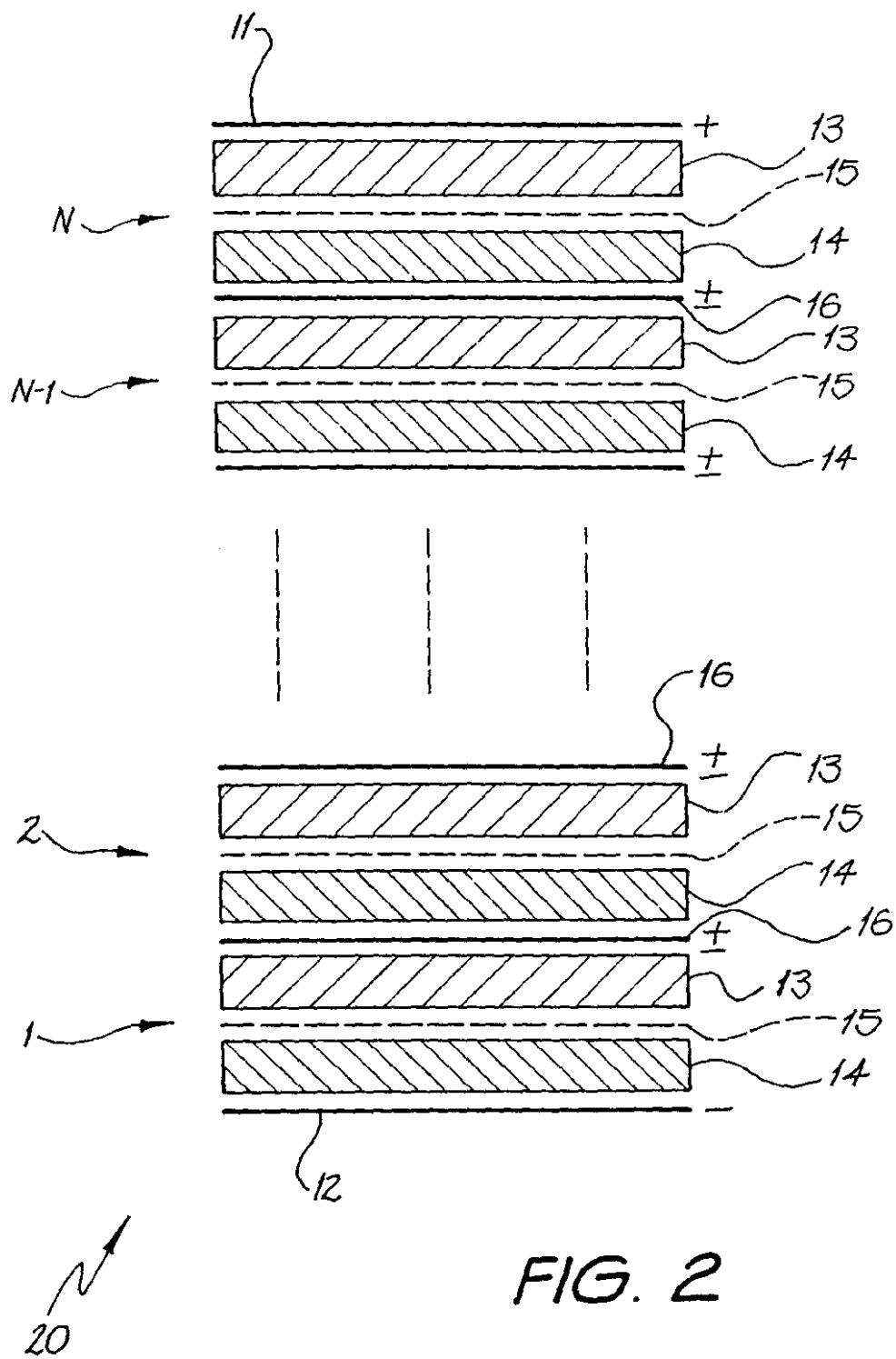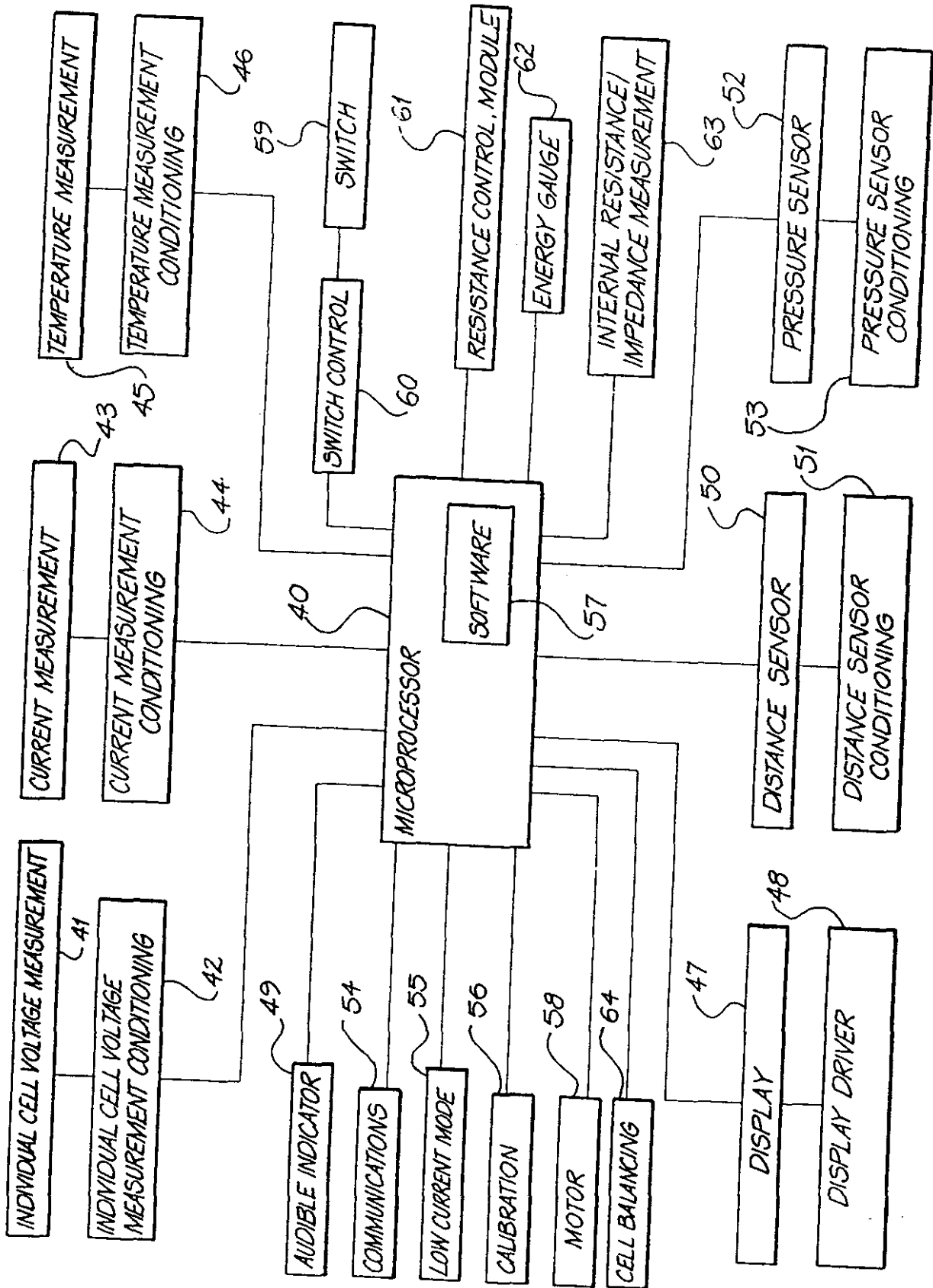
FIG. 1

FIG. 3

FIG. 2

TEMPERATURE MEASUREMENT

TEMPERATURE MEASUREMENT CONDITIONING — 46

45 — 43

SWITCH — 59

RESISTANCE CONTROL MODULE — 61

ENERGY GAUGE — 62

INTERNAL RESISTANCE/ IMPEDANCE MEASUREMENT — 63

PRESSURE SENSOR — 52

PRESSURE SENSOR CONDITIONING — 53

SWITCH CONTROL — 60

CURRENT MEASUREMENT

CURRENT MEASUREMENT CONDITIONING — 44

MICROPROCESSOR — 40

SOFTWARE — 57

DISTANCE SENSOR — 50

DISTANCE SENSOR CONDITIONING — 51

INDIVIDUAL CELL VOLTAGE MEASUREMENT — 41

INDIVIDUAL CELL VOLTAGE MEASUREMENT CONDITIONING — 42

AUDIBLE INDICATOR — 49

COMMUNICATIONS — 54

LOW CURRENT MODE — 55

CALIBRATION — 56

MOTOR — 58

CELL BALANCING — 64

DISPLAY — 47

DISPLAY DRIVER — 48

FIG. 4

FIG. 5
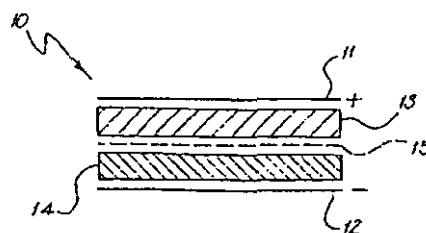
[54]发明名称 氧化还原胶体电池

[57]摘要

氧化还原胶体电池(10)由正氧化还原电解质(13)，负氧化 还原电解质(14)和位于两者之间的隔膜(15)构成。与正氧化还 原电解质(13)作电连接的正电极(11)；与负氧化还原电解质(14) 作电连接的负电极(12)。氧化还原胶体电池的运行能够通过电池 管理系统得以增强,电池管理系统将极化的影响最小化。

权 利 要 求 书

1. 一种氧化还原胶体电池，至少包括一个电池单元，组成包括正氧化还原胶体电解质，负氧化还原胶体电解质，位于正、负氧化还原胶体电解质之间的隔膜，与正氧化还原胶体电解质作电连接的正电极和与负氧化还原胶体电解质作电连接的负电极。

2. 根据权利要求1所述的氧化还原胶体电池，其特征在于正、负电极为惰性非金属电极。

3. 根据权利要求1所述的氧化还原胶体电池，其特征在于胶体电解质中包含活性金属离子来存储能量。

4. 根据权利要求1所述的氧化还原胶体电池，其特征在于胶体电解质中包含非金属活性离子来存储能量。

5. 根据权利要求1所述的氧化还原胶体电池，其特征在于胶体电解质不涉及固体相位转移反应。

6. 根据权利要求1所述的氧化还原胶体电池，其特征在于胶体电解质涉及固体相位传递反应。

7. 根据权利要求1所述的氧化还原胶体电池，其特征在于还包括提高胶体电解质性能的金属附加物。

8. 根据权利要求1所述的氧化还原胶体电池，其特征在于还包括提高胶体电解质性能的非金属附加物。

9. 一种氧化还原胶体电池，其特征在于胶体电解质由惰性导电基质形成。

10. 根据权利要求 1 所述的氧化还原胶体电池,其特征在于正胶体电解质包括一包含活性物质的半电池和一包含不同活性物质的负半电池。

11. 根据权利要求 1 所述的氧化还原胶体电池,其特征在于负胶体电解质包括一包含活性物质的半电池和一包含不同活性物质的负半电池。

12. 根据权利要求 1 所述的氧化还原胶体电池,其特征在于电极为螺旋盘绕型。

13. 根据权利要求 1 所述的氧化还原胶体电池,其特征在于电极为压缩平板电极。

14. 氧化还原胶体电池与用于一具有至少一个带有至少一对电极的电池单元的电池并对极化敏感的电池管理系统相结合,所述电池管理系统包括:

(1) 监控每个电池单元的指示极化程度的预定参数的装置;

(2) 存储预定量的被传送入电池或由其输出的电量的装置;

(3) 诱导反向电荷或对电极加以脉冲以减小极化的装置。

15. 根据权利要求 14 所述的氧化还原胶体电池,其特征在于所述预定参数为每个电池单元的内阻。

氧化还原胶体电池

发明所属领域

本发明涉及一种电池，尤其是提高了运行特性的电池。

背景技术

电池工业现在对电池管理技术的需求提高了。首先，由于消费者对电池供电的便携设备（如便携式电话、膝上型电脑等）的需求日益增长。其次，电池工业现在增长的趋向重点在于电动机驱动工具和零排放交通工具（电池为这新一代交通工具的主要动力来源）。这种趋向的原因是政府法令的迅速增加和消费者对空气及噪音污染的担忧。另外的要求高效电池的蓄能应用领域是，例如用于敏感电子元件的负荷均衡、应急/备用功率和功率质量系统。

作为电池能源设备需求增长的结果，电池厂家需在竞争压力下生产出理想的电池。理想电池应该是超轻，超小，具有优秀的周期寿命和理想的充、放电性能，并在寿命结束后其自身不会产生环境污染。电池工业采用的最普遍的技术工艺是铅酸电池，它正在面对向更高能量密度、更小体积、更好的性能水准、更长周期寿命和保证回收等方面挑战。

传统的铅酸电池组，其容量利用率有限、放电深度低、周期寿命短、能量密度低、存在热管理问题并且需要不断提升充电来维持电池单元均衡。

铅酸电池组还要求充电时间长，高充电电流仅能在极低充电状态下使用几分钟。如果使用高电流，通常将导致电压高于允许值，从而导致电解质丧失和电池容量减小。如果遵从适当的充电形式，以提升充电进行铅酸电池的再充电时间最大可提高到 4 小时。

铅酸电池组的周期寿命在极大程度上取决于周期过程中所达到的放电深度（DOD）。电动交通工具应用中 90 - 100% 的放电深度并不罕见，在这样的放电深度水准下，传统深度周期铅酸电池组的周期寿命能达到接近 300 个周期。大多数控制器的运行是针对总的电池电压。通常个别电池单元会放电低于能接受的极限，因为整个电池电压技术所依靠的假定是所有电池单元处于同一充电状态，而这，通常不符合实际情况。在高负荷下，电池系统将严重失衡，个别电池单元在放电过程中可能实际上反置，甚至冒烟。这似乎有些极端，然而，当大型电池组在较高电压下提供电力时，可能会发生电池单元反向，而最初不会被检测到。

传统的镍氢电池（NiMH）采用先进的加工和高纯度的原料，导致电池系统的成本非常高。采用高纯度氢氧化镍化合物的扩展镍泡沫和经处理的金属合金原料都需要高度的质量控制以得到高性能电池。

NiMH 氢化物电池也存在自放电问题并且也易受到温度的影响。在某些系统用高电流萃取会破坏电池单元，而必须注意不要使电池组过充电。在这一方面，需要高档的电池充电器来确保完全充电。

氧化还原电池组经过多年研究，大体上是按照流体电池组的形式。氧化还原流体电池组将能量储存在液体电解质中，其电解质被分开地保存在电池槽中。在运行时，电解质通过系统再循环，能量在电解质中往复传递。在充电时，电量流入并存储在电解质中；在

放电时，电解质向负载释放出所存储的能量。氧化还原流体电池组的代表性缺点是低能量密度、因电解质通过系统再循环引起泵吸损失。在某些情况下，高自放电率可能取决于隔膜或存在有内泄漏以及旁路电流。

发明简述

本发明提供了一种氧化还原胶体电池，它至少包含一个电池单元，该单元包括正氧化还原胶体电解质，负氧化还原胶体电解质，位于正、负氧化还原电解质之间的隔膜，与正氧化还原胶体电解质连在一起的正电极，与负氧化还原电解质连在一起的负电极。

附图简要说明

图一是本发明的一个实施例的一个单氧化还原胶体电池的示意图；

图二是本发明另一实施例的一个多单元氧化还原胶体电池的示意图；

图三是本发明又一实施例的一个螺旋盘绕型单氧化还原胶体电池的示意图；
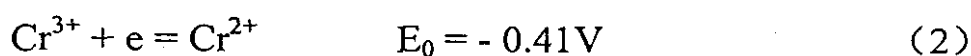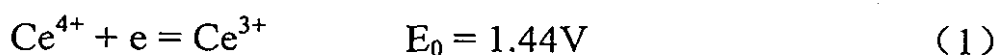
图四是本发明的氧化还原胶体电池的电池管理系统框图；

图五是图四中所示电池管理系统的阻抗控制模块的框图。

发明的详细描述

传统电池系统采用某种形式的固体金属电极，其包含有相位转移反应，导致重量增大和效率损失。本发明的氧化还原胶体电池采

用超浓缩胶体，它包含有各自胶体中的高浓缩正、负活性离子。所有活性元素或反应物质都包含在胶体中，并且无相位转移反应。由于损失最小，从而达到高的效率。

以铈/铬电池（典型的铈氯化物 CeCL3，和铬氯化物 CrCL3）为作为氧化还原胶体电池的实例，其典型的反应如方程 1 和 2 所示：

$$Ce^{4+} + e = Ce^{3+} \qquad E_0 = 1.44V \qquad （1）$$

$$Cr^{3+} + e = Cr^{2+} \qquad E_0 = -0.41V \qquad （2）$$

在充电状态，负极和正极胶体分别由 Ce^{4+} 和 Cr^{2+} 组成。当电池放电时，负极胶体电解质 Cr^{2+} 被氧化为 Cr^{3+}，正极胶体电解质 Ce^{4+} 被还原为 Ce^{3+}。

下面方程 3 给出了完整的放电反应，理论上电池电压基于方程 1 和方程 2 的标准电极电位，例如对于在 25 ℃ 时对 NHE 计算的水溶液，此电压为 1.85V。充电反应是方程 3 的逆反应。

$$Ce^{4+} + Cr^{2+} = Cr^{3+} + Cr^{3+} \qquad E_0 = 1.85V \qquad （3）$$

实际的电池电压将取决于氧化还原胶体介质中用于反应物的支持电解质。

如图 1 所示，一个单氧化还原胶体电池 10 包括一个惰性正电极 11，一个惰性负电极 12，正氧化还原胶体电解质 13，负氧化还原胶体电解质 14，以及位于 13 和 14 之间的隔膜 15。电极 11 和电极 12 最好选用非金属物质。

隔膜 15 的电阻抗极低，它以极低的电阻抗将氧化还原胶体电解质 13 和 14 隔离。氧化还原胶体电解质 13 和 14 可以由任何金属

离子、金属离子混合物、无机和有机化合物等构成，当电池在特征电压下接上负载后，能够使胶体导电并产生电流。胶体中还可以包含一些能提高性能的添加剂。

胶体电解质还包含某些凝胶剂，如二氧化硅，或者任何其他无活性成分沉淀有助于稳定胶体结构的物质。

氧化还原胶体电池与氧化还原流体电池的区别在于，其电解质为超浓缩胶体，包含在电池之中，无需进行再循环，如图1所示。

氧化还原胶体电池可以是如图1所示的单电池结构，图2所示的双极多单元电池组，或者是图3所示的螺旋盘绕式电池结构。

如图2所示，双极多单元电池组20由电池单元1，2…………N-1，N组成。从1到N，每个单元都包括一正氧化还原胶体电解质13和一负氧化还原胶体电解质14，以及位于13和14之间的隔膜15。公共电极16位于各单元之间。惰性负电极12位于单元1的外表面，惰性正电极11位于单元N的外表面。

如图3所示，单元螺旋盘绕型氧化还原胶体电池30包括一个如图1所示的电池单元结构以及隔离电池结构的盘绕段的绝缘膜17。

如图4所示，氧化还原胶体电池可以采用一个电池管理系统，它包含一个可以集成到电池组中的模块，以使极化的影响最小。因为电池管理系统的加速和监控，从而限制了极化现象并提供了一种高度的个别单元控制，氧化还原胶体电池的运行得以加强。

由于采用了超浓缩胶体，当电池系统应用在高负荷时，极化将趋向于增高，而电池管理系统能够减轻氧化还原胶体设计时的约束，特别适合于氧化还原胶体电池。

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专为氧化还原胶体电池设计的电池管理系统还可执行许多监控功能。例如监控个别电池电压和温度。可以监控密封电池组的内压和确定各种给定条件下系统容许负荷的极限。电池管理系统还具有一个附加能力，能够在任意充电状态采取积极行动来保持最佳的电池性能。这种高程度的系统控制下，本发明的氧化还原胶体电池，能够重复地在一非常长的周期寿命中利用它的全部容量。

优先选用的电池管理系统如图 4 框图所示，包括一个微处理器 40 和管理后述所有功能的相关软件 57。此例采用的是 8 位（bit）微处理器，运行速度为 8MHz，但也可采用 4、16、32 或 64 位处理器。处理器的速度可以是 4MHz～166MHz。也可根据个别电池需要选择数字信号处理芯片。微处理器包含电可擦除只读存储器（EEPROM）、只读存储器（ROM）和随机存取存储器（RAM），也可选用特定用途集成电路（ASIC）。

个别电池电压测量模块 41 采用一个单独导线连接每个电池的接点，这条导线单独用来测电压。每个电池单元电压以电池组接地为参考量起，可达到 24 伏特。也可根据精确度要求和需要，通过直接测量每个电池单元的电压实现。

单元电池电压测量调节由模块 42 实现。它包括一个电路，在该电路中，电池电压被电阻网络分压，并通过连接在分压器接地电阻两端的滤波电容器加以平滑。可采用应用运算放大器的有源滤波器或其他滤波设备。电压通过分压器和滤波器定标到适合作模数转换的电压。在此例中，4.95 伏特表示电池每个连接的预期的最大电压。一个 12 位的模数转换器用于测量每个电池单元的电压。模数转换器由微处理器串行控制，它通过定标各处电势，并从各电池单元的正极电势中减去其负极电势，将每一测量的电势转换为电池的电压。这种对每个电池单元的处理方法可应用于达到 24 伏特的电池电压。

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高于 24 伏特时，可通过光耦合串行通信（从而隔离电池单元电压）的设备传递连续的数字数据，将上述方法多级使用。另外，可采用跨接每个单元的电压频率转换器，直接测量电池单元电势并将此信息作为频率信号发送到微处理器。上述的电压频率转换器可以是电或光耦合到微处理器，用来测量频率信号并将其转换成电压值。

电流测量模块 43 是测量旁路电阻两端的电压，并用带有源滤波的电流读出放大器定标该值。也可选择利用霍耳效应器通过适当的信号波形调整来测定电流。

电流测量调节由电流模块 44 实现，此时，将测量的旁路电压转换成一个 0~5 伏特的信号，而不管随后被传送到被用于测量上述电压时的相同的 12 位模数转换器的入口的电流的方向。调节电路还向微处理器提供数字输入来指示电流方向。这可通过具有最少外部元件的集成电路实现。在这方面离散部件方案也可降低成本。

温度由电路模块 45 使用一个装在电路板上的集成温度传感器来测量。任何数量的这些可用来安置在不同的区域，如电池组，个别电池单元或者外部的环境温度。

温度测量调节由电路模块 46 实现。其中，温度值是一个电压的输出量，通过使用一个低补偿电压运算放大器将此值定标到 0~5 伏特的数值，以适合与同样的模数转换器接口的连接，该模数转换器用于测量电压和电流。

一个液晶显示器 47 用来显示诸如剩余容量、剩余千米数以及其他信息等。

显示驱动器 48 可通过根据存储在微处理器 40 内的查找表对存储单元写入适当的值来，由微处理器直接驱动。取决于微处理器的要求和液晶显示器的复杂性，可以采用一个单独的集成电路驱动器。也可使用发光二极管或气体等离子显示器，或者一个液晶显示模块。

声音指示器模块 49 包括一个压电蜂鸣器，能向用户提供声音讯号。声音指示器理想的由微处理器直接驱动，或在必要时也可采用晶体管驱动器。

距离传感器 50 装在使用本电池的运动车辆的轮子上。它采用电磁传感器的形式，其磁体位于轮子上，或霍耳效应传感装置装在车辆的固定部件或光传感器。

距离传感器调节由电路模块 51 实现。其中，距离传感器输出的频率值通过微处理器定标和测量，再将其转换成速度值或距离值。

压力传感器模块 52 位于电池中，包括一个能输出低电压（0～100mV）的压力传感器。

压力传感器调节模块 53 通过精密运算放大器将输出结果转化到 0～5 伏特之间并输出到模数转换器。

通信模块 54 确保所有控制和电池充电器发出的通讯信号能够通过串行总线直接由微处理器 40 传递。此串行总线为校准目的也可访问 PC。

为保证长的电池寿命，所有优化程序的组件都选择用于低电流消耗。通过微处理器向低电流模式模块 55 发出的信号，微处理器、模数转换器、以及其他所有电路都被设置在低电流消耗模式。

为达到要求的精确度，微处理器的模拟输入通过校准模块 56 来校准，校准系数和残留偏差存储在电可擦除存储器中。

软件模块 57 最好是面向查询的以及用于时间紧急事件，例如能量利用积累的电流监控的中断。更可取的是，软件能确定个别单电池是否有故障，并通知电池充电器。

此软件包括一个电压电流算法的多项式，以打开开关防止电池过放电。此软件适用于以下方面：

（1）计算电池自放电并能启动电池均衡过程。

（2）记录循环次数，并将此信息发送给电池充电器。

（3）监控、传递和启动安全措施防止过电压或者电压不足。

（4）按规律的时间间隔采样电流，并相对时间将电流求积分，以提供已使用的安时和剩余量。

（5）根据电流循环期间的负荷校正已使用的安时和剩余量。

微处理器 40 可通过驱动 FETS 或 IGBT 来控制电动机 58 的电流。这能够向有刷电动机提供单个脉冲宽度调制控制。或者通过多输出，向无刷多类型电动机如磁阻电动机、无刷直流电动机等提供准正弦信号控制。

可采用一个 FET 或者 IGBT 开关 59 用来提供电池安全和保护。采用的是一个低阻值 FETS。

开关 59 由开关控制模块 60 控制。开关控制模块由微处理器 40 驱动，FETS 或 IGBTS 的驱动采用开关电源以提升高压来使能高侧驱动。

在阻抗控制模块 61 中，微处理器控制着一块 FET。该 FET 的功能是周期性向一个电容充电直到电压值超出电池电压，然后向电池中释放此电容电量，在此同时转换到另一电容器充电，以保持负载电流。

能量计 62 的输出显示在液晶显示器上，表示剩余容量，此值由电流对时间积分求得。电流按等时间间隔采样，并从累加器中减去此值，再转化成百分数给出剩余容量的输出值。

内阻/阻抗模块 63，采用测定电流改变前后电压的变化的方法来计算内阻和阻抗。在充电和放电的过程中都可以进行。交流电流或电压可能会注入电池，最后的电压或电流被测量来计算内阻和阻抗。

电池均衡模块 64 的运行，使得在当一个电池单元的自放电超过其他同组的其他电池单元时，将从整个电池组中提出电量，通过开关模式电源转换器被转化成适当的电压值，然后分配给最弱的电池单元，从而使电池达到平衡。

氧化还原胶体电池采用的电极的功能在于允许能量传入和传出胶体电解质。电极是惰性的，可以用专门开发的非金属导电物质制成，这些物质可以形成或铸塑成几乎任何特定形状。

电解质是用来存储所有包含在氧化还原胶体电池中的能量。胶体中所含的特定的离子可以根据应用和能量密度要求选择，并可利用单个的或多电子半电池单元反应。胶体电解质可制成带有或不带

有总合为胶体的电极矩阵。在此二种情形下,胶体存储电能这一主要功能保持不变。

因为胶体电解质的稳定性,氧化还原胶体电池具有很长的周期寿命。在胶体的基本形态下,电解质在存储能量时,无相位转移发生,电解后不产生降解,从而大大节省了整个系统的成本。由于轻便、稳定耐用的特性,氧化还原胶体电池非常适合用于 "租赁能量" 型车辆的电池更换过程,紧急备用和便携电源组。

参照图5,下面进一步描述控制极化和因而电池输出的方式。

如图 5 所示的控制系统 100 适用于提供从氧化还原电池系统 111 向终端或连接有负载如电动车等的输出装置 112 预定的能源输出。控制装置 114 位于输出终端 112 和氧化还原胶体电池系统 111 的终端 113 之间,来检测电池系统 111 的预定运行参数。在第一运行模式期间,控制装置 114 从电池系统 111 向输出终端 112 供电。

第一电容装置 115 连接在电池系统 111 和控制装置 114 之间,当控制装置 114 在第一运行模式下时,它存储电池系统 111 的预定电量;当控制装置 114 在第二运行模式下时,它响应控制装置 114 发出的指令信号,向电池系统 111 提供所存储的电量。

第二电容装置 116 连接在输出终端 112 和控制装置 114 之间,当控制装置 114 处于第一运行模式时,它存储由电池系统 111 提供的预定电量总量;当控制装置 114 处于第二运行模式时,它向输出终端 112 提供其所存储的电量,以响应控制装置 114 发出的指令信号。

因而,电源控制系统与两个电容网路相结合,当控制装置检测到异常时,例如在电池系统 111 中极化程度过高或自最初将电力加

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到负载开始过去了预置时间间隔，它将启动向电池系统 111 返回充电。在这放电周期中，控制装置 114 允许存储在第一电容网路 115 中的电能向电池系统 111 充电，与此同时，第二电容装置 116 向输出终端 112 以不间断电源供电。反此逆向周期即放电周期的时间间隔非常小，所以它可以有效的以定时间隔运行。

反向充电具有瓦解和最小化系统内的极化效应及相应的损失的能力。

电源控制系统还可以与充电器协同工作以在运行过程中提供最佳性能和随时电池维护。电源控制系统还适用于防止将未经许可的充电器连接到电池系统，由此防止了潜在的误用并确保车主在家里不会使用不正确的充电器来尝试为电池系统充电。

电源控制系统、充电器和车辆可以结合各个人的电子签名，从而能够高精度跟踪和监控整体系统。每当电池系统被装入充电装置，电源控制系统将自我识别，确认是否已从车辆中卸下以及用户在使用。

充电装置可用来监控电池的能量水平，再加上汇兑成本，电力和电池的月租费，并将这一数值通知用户。无论是使用支票还时信用卡，根据收到的这项支付金额，就可以发放新的电池并装入车辆。如果顾客违章使用或损害了电池，总而言之，都会在充电器中被鉴别出来。

控制系统不仅适用于鉴别电池的能量水平，还可以根据电流能量的使用程度来估计剩余的行程。因此，车辆司机可以得知靠剩余的电量还能够行驶多少公里路程。

每个充电装备都通过一个遥测系统连接到操作中心，该中心能够持续检测充电站网中所有位置的充电站。

电源控制系统还包含速度控制模块的功能和特征，这意味着车量管理者可以从车上去除速度控制装置，仅仅通过电源控制系统来控制输出，从而减少车辆成本，减少制造厂商的风险担保，而且还可通过遥控信息系统提供持续的性能检测监测。

电源控制系统可应用于很多电池系统，如阀调节铅酸电池组，镍氢电池组和氧化还原胶体电池组等，对每个系统都有特定的应用和益处。电源控制系统还可应用于改善边远程区电力系统，负荷均衡以及紧急后备电池系统的后备性能。应用在边远地区的电力系统和紧急后备应用中的稳定的电池系统，能维持在延长期间内满充电。由于电池单元自放电的速率不同，可将电源控制系统编程来定期扫描单个电池单元的状态，并使用电池平衡技术在内部平衡电池。充电系统还可以作为后备设备或者根据要求用电源控制系统来控制。
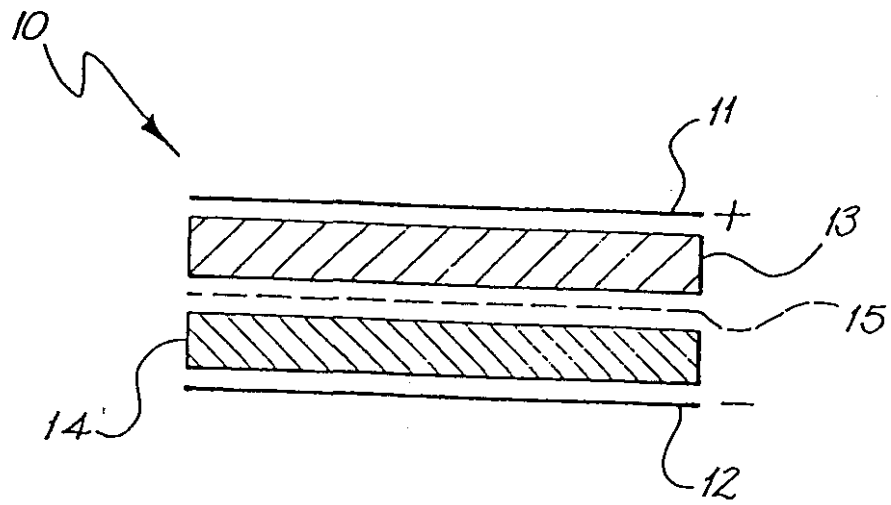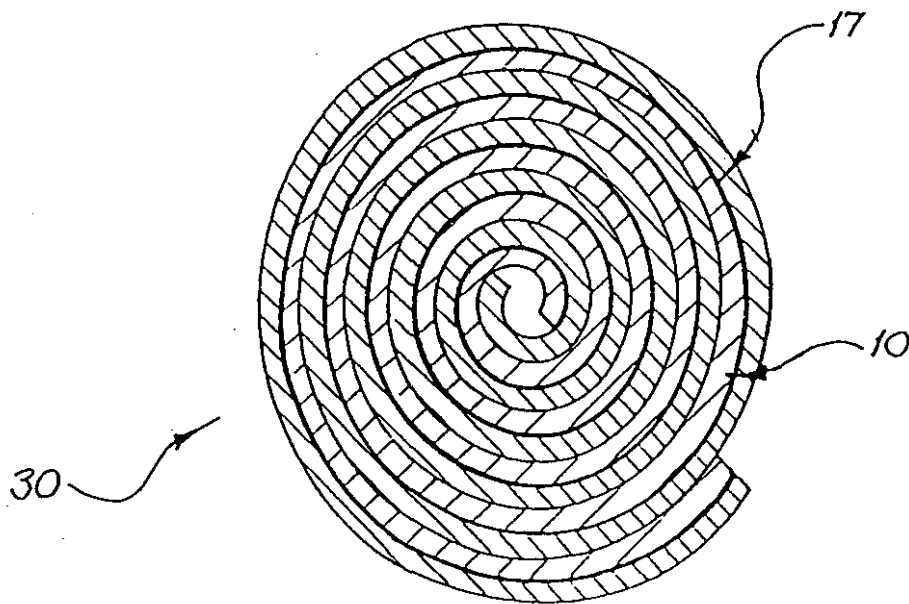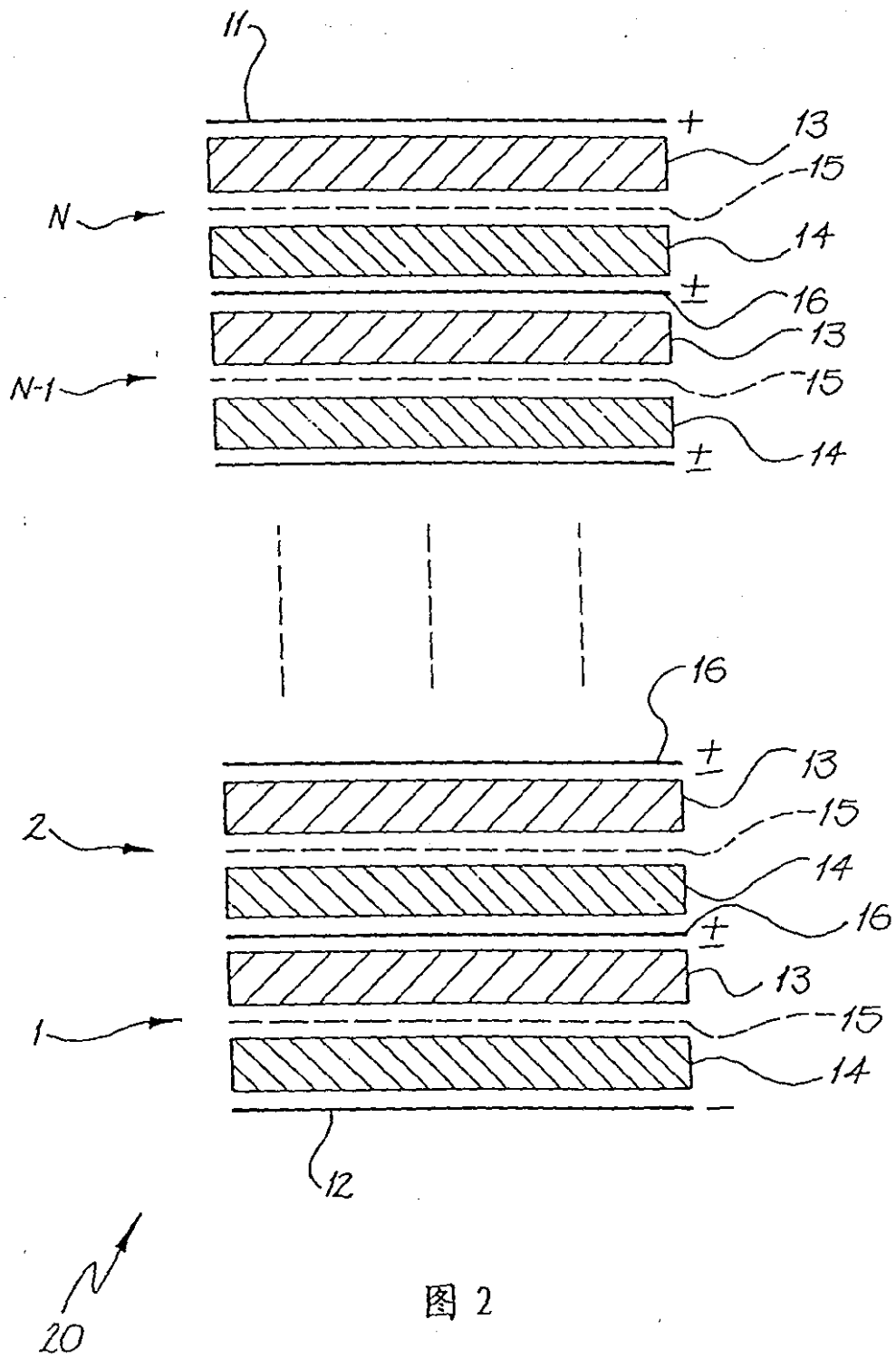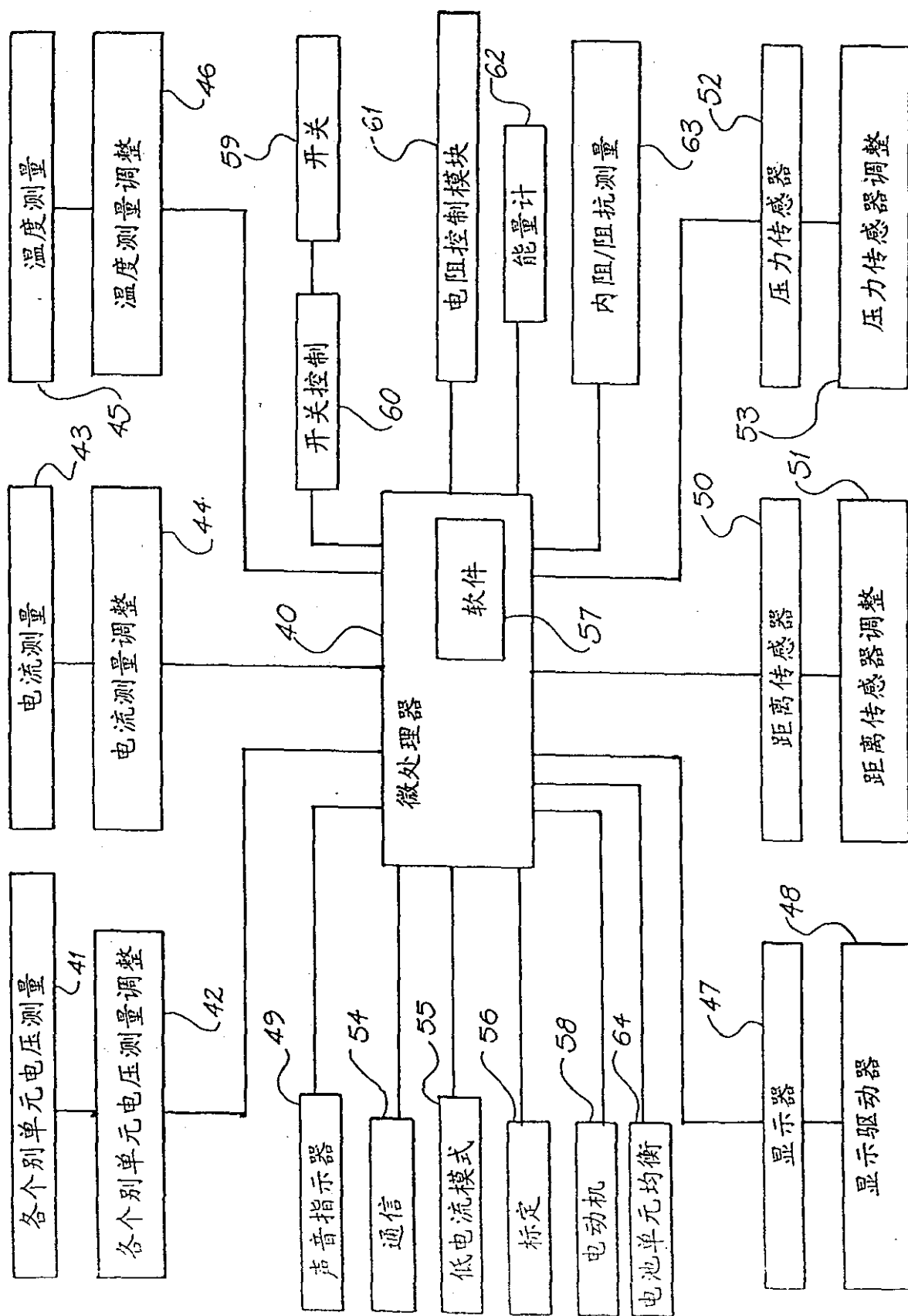
图 1

图 3

图 2

温度测量

温度测量调整 46

各个别单元电压测量 43

电流测量

电流测量调整 44

各个别单元电压测量 41

各个别单元电压测量调整 42

声音指示器 49

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压力传感器 52

压力传感器调整 53

距离传感器 50

距离传感器调整 51

图 4

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图 5