(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
24 March 2022 (24.03.2022)

WIPO | PCT

(10) **International Publication Number**
WO 2022/060845 A1

(51) **International Patent Classification:**
H01M 10/48 (2006.01) *G01R 31/382* (2019.01)
H02J 7/00 (2006.01) *H02J 7/02* (2016.01)
H02J 7/04 (2006.01)

(21) **International Application Number:**
PCT/US2021/050471

(22) **International Filing Date:**
15 September 2021 (15.09.2021)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
17/021,711 15 September 2020 (15.09.2020) US
63/202,962 01 July 2021 (01.07.2021) US

(71) **Applicant: AMPHENOL THERMOMETRICS, INC.** [US/US]; 967 Windfall Road, Saint Marys, Pennsylvania 15857 (US).

(72) **Inventors: ENGLE, Brian Allen**; 12446 Crestridge Loop, New Port Richey, Florida 32655 (US). **ROBERTS, Neil**; 58 Gainsborough Drive, Ascot SL5 8TB (GB).

(74) **Agent: MITCHELL, Jonathan P.**; Blank Rome LLP, 1825 Eye Street N.W., Washington, District of Columbia 20006 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,

(54) Title: THERMAL RUNAWAY DETECTION SYSTEMS FOR BATTERIES WITHIN ENCLOSURES AND METHODS OF USE THEREOF

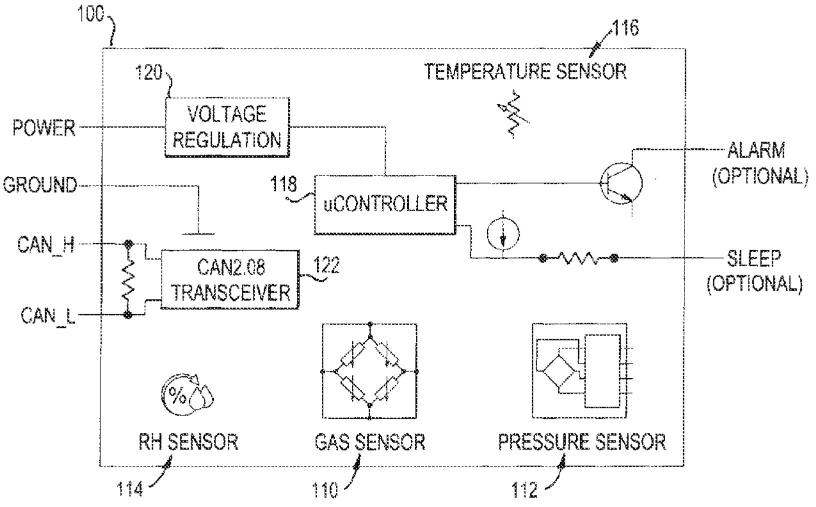

FIG. 9

(57) **Abstract:** A battery thermal runaway detection sensor system for use within a battery enclosure housing one or more batteries. The system has at least one gas sensor for detecting a venting condition of a battery cell and providing a sensed output in real time. A microcontroller determines power management and signal conditioned output on the concentration of specific battery venting gases based on the sensed output from said at least one gas sensor. Methods of using such sensor systems are also described.

[Continued on next page]

UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

THERMAL RUNAWAY DETECTION SYSTEMS FOR BATTERIES WITHIN ENCLOSURES AND METHODS OF USE THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. Application No. 17/021,711, filed on September 15, 2020, and claims the benefit of U.S. Provisional Application No. 63/202,962, filed on July 1, 2021, the entire contents of each of which are hereby incorporated by reference.

FIELD OF THE DISCLOSURE

[0002] The disclosure relates generally to a detection system for detecting battery failure and more particularly to a detection system for detecting thermal runaway of batteries within enclosures, for example, batteries used with electric vehicles, FIG. 2(a), or stationary battery energy storage systems, FIG. 2(b). The disclosure also relates to methods of detecting thermal runaway in a battery using such systems.

BACKGROUND OF THE DISCLOSURE

[0003] As Li-ion battery technology improves, battery energy density has continued to increase and this in turn increases the risk of battery failures. Li-ion battery thermal runaway is a critical safety issue for electric vehicles. For example, the proposed global technology regulation No. 20 by the United Nations on Electric Vehicle Safety (EVS) requires an advanced warning 5 minutes prior to the evolution of hazardous conditions caused by thermal runaway.

[0004] Referring to FIGS. 1(a), 1(b), thermal runaway in lithium ion based batteries is a process under which an exothermic reaction occurs within a failed cell that increases the internal temperature, which in turn releases energy that sustains the internal degradation reactions and increases the temperature until ultimate failure of the cell, often accompanied by sudden release of the electrolyte and gas products of decomposition, which may result in fire. In modern lithium batteries, the risk of explosion can be reduced by design to incorporate a controlled venting location in the cell (see FIG. 4), but risk of fire and explosion due to thermal runaway has not been eliminated in most liquid electrolyte lithium-based batteries.

[0005] Turning back to FIGS. 1(a), 1(b), certain triggers and abuse conditions can lead batteries, e.g., lithium-ion cells, to breakdown or failure, which in turn can result in a thermal runaway. Thermal runaway can be caused, for example, by external short circuit, internal short circuit (particle, dendrites, separate failure, impact/puncture), overcharge, over-discharge, external heating, or over-heating (self-heating). With elevated temperatures is the generation of gas. If heat dissipation occurs faster than heat generation, there can be a safe outcome.

[0006] However, if left unhindered, or if the heat cannot be dissipated faster than it is being generated, this can result in a rapid increase in temperature, release of flammable and hazardous gases during venting, flames, and possibly explosion. This can especially be problematic for vehicles having large format battery systems, as shown in FIG. 3, and in particular battery electric vehicles and stationary storage, where the thermal runaway of a single cell (FIG. 4) can lead to a cascade of thermal runaway events that can engulf the entire pack, resulting in catastrophic fire and release of hazardous gases. Although battery packs can be constructed to passively contain several failed cells and satisfy the EVS regulation, thermal runaway propagation can still happen. Therefore, detecting a cell undergoing thermal runaway inside a pack is important.

[0007] Sensors have been developed to detect thermal runaway. However, simple gas sensors, such as a hydrocarbon sensor, can only detect electrolyte gas concentration, and also suffer from cross sensitivity to other gases as well as substantial drift and so make poor long-life thermal runaway detection sensors.

[0008] There is therefore a need for a robust early detection system for detecting thermal runaway in mobile and stationary applications that is fast and reliable.

[0009] No admission is made that any reference cited herein constitutes prior art. Applicant expressly reserves the right to challenge the accuracy and pertinence of any cited documents and information.

SUMMARY OF THE DISCLOSURE

[0010] A detection system is disclosed that addresses the challenges of fast, robust thermal runaway detection within a battery enclosure that is generally agnostic to electrochemistry, cell packaging (cylindrical, prismatic, or pouch), cell size, as well as battery configuration (series/parallel) by identifying attributes of initial cell venting that are shared between numerous design types and responding to venting gases of a failing cell.

[0011] During thermal runaway decomposition reactions, the cell converts substantial cathode and electrolyte material into gas and vents the pressurized gas mixture in time spans of seconds when the faulted cell is at a high State of Charge, FIG. 1(b). Of the typical cell chemistries such as lithium-manganese-cobalt-oxide (NMC) batteries, Lithium Cobalt Oxide (LCO), and Lithium Iron Phosphate (LFP) batteries, thermal runaway testing has shown the release of several gases, including large quantities of carbon dioxide and hydrogen, see FIG. 5. Carbon dioxide is generally evolved during the oxidation reaction of carbonate solvents and hydrogen is generally released as a product of the reduction of water deriving from combustion reactions by carbon monoxide and/or free lithium, with methane and ethane compounds also present from reduction reactions of the electrolyte and ethylene carbonate at the lithiated anode.

[0012] Also disclosed in the use of such systems for the detection (e.g., early detection) of thermal runaway, thereby, for example, helping to prevent cell-to-cell propagation of thermal runaway originating from a single cell. In one embodiment, a cell venting is detected. In one embodiment, thermal runaway is detected. In one embodiment, thermal runaway decomposition products are detected.

[0013] In other examples of the disclosure, at least one additional sensor is provided for detecting a secondary condition of the battery and providing information on a rate of progression of the cell venting and thermal runaway in real time including pressure or temperature, wherein said microcontroller provides a rate of progression of the thermal runaway based on the provided information from said secondary sensor. The at least one additional sensor can detect a pressure or temperature in the battery compartment housing to determine rate of progression of the venting/thermal runaway. A sensor housing can be provided to enclose the at least one sensor and the at least one secondary sensor. Output from the primary gas sensor and the secondary gas sensor allows for differentiation between electrolyte leakage and venting/thermal runaway. The system software can be embedded within the sensor microcontroller to determine if threshold levels for thermal runaway have been exceeded and to send an alarm to the battery management microcontroller or charging system controller.

[0014] In yet other example embodiments, the threshold levels for thermal runaway are selected from: (i) a carbon dioxide level of greater than about 10,000 ppm; (ii) a hydrogen level of greater than about 40,000 ppm; (iii) a carbon dioxide level above its lower explosive limit; (iv) a hydrogen level above its lower explosive limit; and (v) any combination of thereof. A multichip printed circuit board can be provided to be mounted on battery management controller printed circuit board. A power management system can be provided that allows for fast data acquisition mode during active battery system charging/discharging, and reduced acquisition rate/lower power mode when the battery system is neither charging nor discharging. The detection system can send a wake-up command to the main battery system controller upon detection of venting/thermal runaway. The sensor system can include multiple gas sensors selected from more than one hydrogen sensor, more than one carbon monoxide sensor, more than one carbon dioxide sensor, and any combination of any of the foregoing, for redundancy in safety critical applications. The detection system can also include a humidity sensor, a pressure sensor, a temperature sensor, or any combination thereof.

[0015] In another example embodiment, a method is provided for detecting a thermal runaway condition of a battery within a battery enclosure. The method includes providing a detection system as described above, measuring and/or analyzing one or more gases venting from the battery, and determining if the analyzed gas levels are at or above a predetermined threshold level that indicates thermal runaway of the battery. The gases analyzed can include hydrogen, carbon monoxide, carbon dioxide, or any combination thereof.

[0016] This summary is not intended to identify essential features of the claimed subject matter, nor is it intended for use in determining the scope of the claimed subject matter. It is to be understood that both the foregoing general description and the following detailed description are exemplary and are intended to provide an overview or framework to understand the nature and character of the disclosure.

BRIEF DESCRIPTION OF THE FIGURES

[0017] The accompanying drawings are incorporated in and constitute a part of this specification. It is to be understood that the drawings illustrate only some examples of the disclosure and other examples or combinations of various examples that are not specifically illustrated in the figures may still fall within the scope of this disclosure. Examples will now be described with additional detail through the use of the drawings, in which:

[0018] FIG. 1(a) is a flow diagram showing the progression of thermal runaway;

[0019] FIG. 1(b) is a chart of thermal runaway and temperature;

[0020] FIG. 2(a) is a typical battery pack in an electric vehicle;

[0021] FIG. 2(b) is a drawing of a typical battery pack in an energy stationary storage enclosure;

[0022] FIG. 3 shows a battery thermal runaway detector;

[0023] FIG. 4 shows a typical battery cell before and after thermal runaway;

[0024] FIG. 5 is a diagram of gas released from thermal runaway events in cells with different electro-chemistries: LCO/NMC, NMC, and LFP;

[0025] FIG. 6 is a plot of cascading thermal runaway propagating through pack enclosure wherein initial cell triggered thermal runaway in several adjacent cells;

[0026] FIG. 7 is a plot of hydrogen concentration rise immediately after initial vent followed by slight pressure rise within the enclosure over one minute later as gas expansion exceeds pack level venting capability;

[0027] FIG. 8 is a plot of thermal runaway initiation showing rapid carbon dioxide concentration rise within the enclosure; and

[0028] FIG. 9 is a schematic of thermal runaway management system.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0029] In describing the illustrative, non-limiting embodiments illustrated in the drawings, specific terminology will be resorted to for the sake of clarity. However, the disclosure is not intended to be limited to the specific terms so selected, and it is to be understood that each specific term includes all technical equivalents that operate in similar manner to accomplish a similar purpose. Several embodiments are described for illustrative purposes, it being understood that the description and claims are not limited to the illustrated embodiments and other embodiments not specifically shown in the drawings may also be within the scope of this disclosure.

[0030] The Battery Thermal Runaway Detector is predisposed within the void airspace of a typical battery enclosure, for example as shown in FIG. 3. The enclosure completely surrounds one or more battery modules, each battery module having one or more battery cells aligned in parallel or series with one another. The battery cells of each module are in electrical communication with the adjacent cells, and the battery modules are in electrical communication with each adjacent module. A battery controller is in communication with each battery module and/or battery cell. The battery controller can operate each battery cell either directly or via the module, such as to turn the cell on/off or control the voltage output of each cell.

[0031] The enclosure protects the battery cells and modules from water, debris, and to protect users and occupants from the electrical hazards within the enclosure. Enclosure void space volumes (the volume of air space within the enclosure) can vary from as little as a few liters to as much as 200 or more liters, typically containing air. The battery enclosure is generally provided with air venting features inclusive of a single or multiple small openings that allow for pressure equilibrium inside and outside the enclosure to prevent strain and damage to the pack. These openings are generally protected with hydrophobic membranes that allow for air exchange but prevent the direct flow of liquid water into the enclosure. The enclosure may also include valves or similar devices to allow over pressure from a thermal runaway to safely vent from the enclosure, reducing risk of explosion and harmful shrapnel.

[0032] Turning to FIG. 9, a thermal runaway detector or detection system 100 is shown in accordance with one non-limiting exemplary embodiment of the present disclosure. The detection system 100 resides within the battery enclosure void space as in FIG. 3 and includes a primary detector, here a gas detector 110. The detection system 100 also includes a pressure sensor 112, relative humidity (RH) sensor 114, and/or temperature sensor 116.

[0033] In one embodiment of any of the detection systems described herein, the primary gas detector 100 comprises one or more sensors for the detection of decomposition products formed during thermal runaway.

[0034] For example, in one embodiment of any of the detection systems described herein, the primary gas detector 110 comprises one or more sensors, and in one embodiment comprises one or more of: a CO_2 sensor, a carbon monoxide (CO) sensor, a HF sensor, a H_2 gas sensor and/or a water vapor sensor.

[0035] In one embodiment of any of the detection systems described herein, the primary gas detector 110 comprises a CO_2 sensor, a CO sensor, a HF sensor, a H_2 gas sensor and a water vapor sensor.

[0036] In one embodiment of any of the detection systems described herein, the primary gas detector 110 comprises a CO_2 sensor, a CO sensor, a HF sensor, and a H_2 gas sensor.

[0037] In another embodiment of any of the detection systems described herein, the primary gas detector 110 comprises a CO_2 sensor, a CO sensor, a H_2 gas sensor and a water vapor sensor.

[0038] In another embodiment of any of the detection systems described herein, the primary gas detector 110 comprises a CO_2 sensor, a CO sensor, and a H_2 gas sensor.

[0039] In another embodiment of any of the detection systems described herein, the primary gas sensor 110 examines the unique physical properties of the sensed gas without chemically interacting with it, thereby providing for a reliable and robust primary sensor.

[0040] In another embodiment of any of the detection systems described herein, the primary gas detector 110 further comprises one or more secondary gas sensors for the detection of one or more gases that are vented from a cell prior to thermal runaway (e.g., during initial cell venting of gas products of SEI decomposition and electrolyte).

[0041] For example, in one embodiment of any of the detection systems described herein, the primary gas detector 110 further comprises one or more secondary gas sensors for the detection of one or more of: methane, ethane, oxygen, nitrogen oxides, volatile organic compounds, esters, hydrogen sulfide, sulfur oxides, ammonia, chlorine, propane, ozone, ethanol, hydrocarbons, hydrogen cyanide, combustible gases, flammable gases, toxic gases, corrosive gases, oxidizing gases, and/or reducing gases.

[0042] In another embodiment of any of the detection systems described herein, the primary gas detector 110 further comprises one or more secondary gas sensors for the detection of one or more of: CH_4, C_2H_2, C_2H_4, C_2H_6, diethyl carbonate (DEC), dimethyl carbonate (DMC), ethylene carbonate (EC), ethyl methyl carbonate (EMC), C_4H_{10}, C_3H_6, C_3H_8 and/or POF_3.

[0043] In one embodiment of any of the detection systems described herein, the gas detector 100 comprises one or more primary sensors for the detection of decomposition products formed during thermal runaway and one or more secondary gas sensors for the detection of one or more gases than are vented from a cell prior to thermal runaway (e.g., during initial cell venting of gas products of decomposition and electrolyte).

[0044] The detectors/sensors 110-116 are positioned about the enclosure, and any suitable combination of detectors and/or sensors 110-116 can be utilized.

[0045] The thermal runaway detection system 100 also contains a voltage regulator 120 that provides and regulates sufficient power to operate the sensors 110-116, microcontroller or microprocessor 118, and communications transceiver 122. The sensor elements 110-116 are electrically connected to the microcontroller 118 within the detection system 100. The microcontroller 118 interprets the sensor output from each of the sensors 110-116 and provides necessary signal conditioning to convert the raw sensor signals to engineering values for each component. The values are then transmitted to the communications transceiver 122, which provides a data stream of sensor information to the battery management system master controller or other electronic monitoring system.

[0046] When a CO_2 gas sensor 110 is used as one of the primary gas sensors 110, it detects carbon dioxide levels in the enclosure (FIG. 3) and has long term reliability and a fast response time (under 6 seconds to record an event). Carbon dioxide background concentration levels are generally less than 1,000 ppm, during a battery cell venting conditions, these concentrations can easily exceed 60,000ppm within the enclosure, providing very robust gas signal for detection, as shown in FIG. 8. With ejecta speeds during venting often exceeding 200 m/s, diffusion of carbon dioxide within the enclosure void space happens very rapidly, reaching the gas sensor 110 within 2 seconds or less regardless of the sensor proximity to the venting cell.

[0047] In one embodiment of any of the detection systems described herein, the primary gas sensor 110 for the detection of CO_2 is an infrared (e.g., near-dispersive infrared) spectroscopy sensor.

[0048] For example, in one embodiment of any of the detection systems described herein, the gas sensor 110 provides the output to the processing device 118, which can determine if the sensed condition exceeds a predetermined threshold or if there is a rapid change in the sensed condition.

[0049] In one embodiment of any of the detection systems described herein, the predetermined threshold for the detection of carbon dioxide concentration signaling the triggering of a thermal runaway event is greater than about 1,000 ppm, such as greater than about 10,000 ppm, greater than about 20,000 ppm, greater than about 30,000 ppm, greater than about 40,000 ppm, greater than about 50,000 ppm, greater than about 60,000 ppm or greater than about 75,000 ppm. In one embodiment of any of the detection systems described herein, the predetermined threshold for the detection of carbon dioxide concentration signaling the triggering of a thermal runaway event is greater than about 10,000 ppm.

[0050] Thus, in one embodiment of any of the detection systems described herein, the system indicates that a thermal runaway event has occurred when the concentration of carbon dioxide detected by the sensor is greater than about 1,000 ppm, such as greater than about 10,000 ppm, greater than about 20,000 ppm, greater than about 30,000 ppm, greater than about 40,000 ppm, greater than about 50,000 ppm, greater than about 60,000 ppm or greater than about 75,000 ppm. In one embodiment of any of the detection systems described herein, the system indicates that a thermal runaway event has occurred when the concentration of carbon dioxide detected by the sensor is greater than about 10,000 ppm.

[0051] In a similar fashion, background concentrations of hydrogen in atmospheric air are generally around 200 to 300 ppb. Under battery cell venting conditions, hydrogen concentrations inside the battery enclosure can easily exceed 140,000 ppm, also providing a robust signal to noise ratio for gas detection, as shown in FIG. 7

[0052] In one embodiment of any of the detection systems described herein, the primary gas sensor 110 for the detection of H_2 is a thermal conductivity sensor.

[0053] In one embodiment of any of the detection systems described herein, the predetermined threshold for the detection of hydrogen concentration signaling the triggering of a thermal runaway event is about greater than about 200 ppb, such as greater than about 300 ppb, greater than about 1 ppm, greater than about 100 ppm, greater than about 1,000 ppm, greater than about 10,000 ppm, greater than about 40,000 ppm greater than about 50,000 ppm, greater than about 100,000 ppm or greater than about 150,000 ppm. In one embodiment of any of the detection systems described herein, the predetermined threshold for the detection of hydrogen concentration signaling the triggering of a thermal runaway event is greater than about 40,000 ppm.

[0054] Thus, in one embodiment of any of the detection systems described herein, the system indicates that a thermal runaway event has occurred when the concentration of hydrogen detected by the sensor is greater than 200 ppb, such as greater than about 300 ppb, greater than about 1 ppm, greater than about 100 ppm, greater than about 1,000 ppm, greater than about 10,000 ppm, greater than about 50,000 ppm, greater than about 100,000 ppm or greater than about 150,000 ppm. In one embodiment of any of the detection systems described herein, the system indicates that a thermal runaway event has occurred when the concentration of hydrogen detected by the sensor is greater than 40,000 ppm.

[0055] In one embodiment of any of the detection systems described herein, the system indicates that a thermal runaway event has occurred when the concentration of hydrogen detected by the sensor is above its lower explosive limit (4 %).

[0056] In one embodiment of any of the detection systems described herein, the system indicates that a thermal runaway event has occurred when the concentration of CO detected by the sensor is above its hazardous limit and/or its lower explosive limit (12.5 %).

[0057] The use of the principle of thermal conductivity for hydrogen and non-dispersive Infrared measurement of CO_2 primary sensors are robust, absolute measurement devices that have limited cross sensitivity to other gases, making them ideal for this application where there is little or no opportunity to recalibrate or service the devices in the field. This is generally due to the selection of measurement principles based on physical behaviors unique to these gas molecules, while not chemically interacting with the target gases or other gases in the environment.

[0058] In one embodiment of any of the detection systems described herein, the secondary gas sensor is a MO_x or Pellistor based sensor (e.g., for the detection of hydrocarbons).

[0059] The pressure sensor 112 detects the gas pressure levels in the void space of the battery enclosure. Nominal air pressure within the enclosure approximates atmospheric pressure. During thermal runaway venting, the pressure may rise abruptly if the venting phase is highly energetic, as in the case of a cell that is at 100 percent state of charge as shown in FIG. 6. But the initial accompanying pressure rise may also be very low, especially in the case of smaller cells or cells whose state of charge is much lower, as shown in FIG. 8. While there is dependence on the enclosure venting system, an increase in gas pressure or temperature can provide information on the rate of thermal runaway. The pressure sensor 112 is small and low cost, has a fast time response with low power consumption, but has been shown to provide poor data during slow venting phenomenon where the battery enclosure venting system allows release of the trapped gas at a rate that offsets gas generation. When used to supplement the gas sensor 110, however, the pressure sensor 112 can provide valuable insight as to the progression of the thermal runaway as it cascades from the initiation cell to adjacent cells within the enclosure, as shown in FIG. 6, where the consecutive increases in hydrogen gas concentration and accompanying pressure spikes indicate that the thermal runaway has progressed to additional cells, leading to cascade failure of the pack.

[0060] The temperature sensor 116 detects the temperature within the enclosure void space, and like the pressure sensor 112, can be used in conjunction with the gas sensor 110 to estimate the rate of progression of the thermal runaway (FIG. 6). Progressive increases in temperature that accompany each successive cell thermal runaway provide critical data in determining if the reaction has stopped or is progressing at such a rate as to require immediate safety measures, such as providing protective countermeasures including, but not limited to, introduction of water or extinguishing agents, aggressive cooling, introduction of dilution air or nitrogen, and the electrical isolation or discharge of suspect cells.

[0061] In one embodiment, the temperature sensor 116 detects temperatures in the range of from about 100° C to about 1200° C, such as from about 600° C to about 1000° C.

[0062] The relative humidity sensor 114 monitors the humidity within the void space of the enclosure and can also be used in conjunction with the gas sensor 110 to observe substantial changes in water vapor within the enclosure indicative of the formation of water vapor due to the decomposition reaction products.

[0063] The detection system 100 can be utilized for a variety of suitable applications. In the embodiment shown in FIGS. 2(a), 3, the detection system 100 is implemented in a vehicle having a battery enclosure, a power distribution unit, and a battery controller and/or Motor Control Unit (MCU). The battery enclosure can be made up of a plurality of battery cells and housed inside a battery enclosure.

[0064] The sensors 110-116 each output a sensed signal to a processing device, such as the microcontroller 118. The microcontroller 118 converts the analog sensor signal to engineering values and transmits that data, such as in the form of an alarm signal or output signal, to the Battery Management System via a wired or wireless transceiver 122. The microcontroller 118 can also determine if the values from the sensors 110-116 exceed a critical threshold value for that sensor to indicate cell venting as well as provide algorithms to determine if the sensors 110-116 are operating normally and within specifications. The detection system 100 may utilize redundant sensors 110-116 to meet Safety Index Levels.

[0065] One or more of the sensors 110-116 are located in a free space within the battery enclosure (FIG. 3) of the vehicle, so that the sensors 110-116 are in communication (e.g., gas or pressure communication) with the air space proximate to the batteries and/or battery compartment and receive and detect the conditions resulting from a battery cell venting. The sensors 110-116 provide the output to the processing device 118, which can determine if the sensed condition exceeds a predetermined threshold (i.e., the threshold which, if exceeded, signals that a thermal runaway based cell venting has initiated) or if there is a rapid change in the sensed condition. The entire system 100, including the sensors 110-116, microcontroller 118, regulator 120, and transceiver 122, can all be housed in a single sensor housing and positioned at one location in the battery compartment. In another embodiment, the system 100 can be separate devices each with their own housing and each housing positioned at separate locations in the battery compartment, including surface mounted on the battery management system electronics.

[0066] As shown and described, the detection system addresses the problem of robust detection of thermal runaway in lithium ion batteries, where the outgassing precursor to thermal runaway can occur in timespans of seconds or hours. The detection system measures multiple physical parameters of the outgassing event that can allow detection of rapid thermal runaway as well as slower events. The multiple detection technology reduces the risk of false positive and missed detection errors and provides sufficient redundancy to meet market safety requirements. The system measures, at a minimum, hydrogen and/or carbon dioxide concentration, and may be supplemented with air pressure and or temperature and humidity in the enclosure.

[0067] In other variants, the detection system could also include hydrocarbon detection of the electrolyte, including methane, esters, and ethane gases. During the initial cell venting that precedes thermal runaway, vented gases include H_2, CO, CO_2, and hydrocarbons in sufficient concentration to be detected by the individual sensors. By combining them into a single sensor platform with signal conditioning and analysis, it is possible to determine with relative certainty that the event is a single cell undergoing thermal runaway, and by monitoring the gases simultaneously, determine the difference between less urgent electrolyte leakage and more urgent thermal runaway condition. The use of the principle of thermal conductivity for hydrogen and non-dispersive Infrared measurement of CO_2 sensor are robust, absolute measurement devices that have limited cross sensitivity to other gases, making them ideal for this application where there is little or no opportunity to recalibrate or service the devices in the field.

[0068] Referring more specifically to FIG 6, an example runaway is shown. In this illustrative example, the thermal runaway cascades from one cell to adjacent cells. Starting at T=0, the battery system is operating under normal conditions, and the hydrogen level 150, temperature 160, and pressure 170 are all normal. At a first time period, T=1, a first single battery cell of a first battery module experiences thermal runaway. As a result, it releases a gas, here Hydrogen. The hydrogen sensor of the gas detector 110 measures the hydrogen level, and has a sensed gas level output. It transmits the sensed gas level output to the microcontroller 118. In addition, the pressure sensor 112, detects the pressure, and has a sensed pressure output. It then transmits the sensed pressure output to the microcontroller 118. Further, the temperature sensor 116 measures the temperature in the enclosure, and provides a sensed temperature output. It transmits the sensed temperature output to the microcontroller 118.

[0069] The sensors 110-116 immediately send the sensed outputs to the microcontroller 118 in real time without delay or manual intervention. The sensors 110-116 can send sensed outputs to the microcontroller 118 continuously or at intermittent random or predetermined periods (such as several times a second).

[0070] In the example embodiment of FIG. 6, a cascading thermal runaway event is shown propagating through pack enclosures where initial cell triggers thermal runaway in adjacent cells. The microcontroller 118 receives a sensed gas, pressure and temperature outputs from the gas, pressure and temperature sensors 110, 112, 116, respectively. At T=1, the hydrogen gas level 150 and pressure 170 both exhibit a spike. However, the temperature 160 only increases slightly. The venting in the battery enclosure enables the pressure 170 to quickly dissipate back to normal levels, though the Hydrogen vents more slowly and stays at an elevated level. Based on these conditions and receipt of the sensed outputs, the microcontroller 118 determines that at least a first battery cell has experienced a thermal runaway event, and generates an alarm signal that it sends to the battery controller. The battery controller, in response, might for example take a first response, such as to indicate to the operator that service is needed, to reduce the voltage requirements for the battery module, or to control the battery so that it does not get as hot.

[0071] At T=2 in the example embodiment of FIG. 6, another cell experiences a thermal runaway. Here, the microprocessor 118 determines, based on sensed outputs from the gas sensor 150 and pressure sensor 160, that there is another spike in gas and pressure, respectively, and that the temperature has again increased slightly. The pressure again returns to normal rather quickly due to venting conditions, but the temperature and hydrogen level continue a rising pattern. Accordingly, the microprocessor 118 determines that another thermal runaway event has occurred, and sends another alarm signal to the battery controller. The battery controller can continue to take the same response or can escalate the response such as by shortening the alert response time, for example by indicating that immediate service is needed, or by turning off one or more of the battery modules. The microcontroller 118 determines that there are further spikes at T=3, 4. The various levels of gas, temperature and pressure may vary based on venting conditions and the specific thermal runaway event. For example, following T=4, the pressure may decrease as the enclosure hydrophobic vents fail, though spikes occur with each successive cell thermal runaway event as additional cells fail within the enclosure. The microcontroller 118 or battery controller can further determine that there is a cascading pattern to the event and take additional responsive actions. The responsive actions can be sent from the battery controller to the microcontroller 118 via the transceiver 122, which then controls operation of the cells and modules.

[0072] Turning to FIG. 7, another example thermal runaway event is shown. Here, the system 100 has a gas sensor 110, here a Hydrogen sensor, and a pressure sensor 112. At T=1, the hydrogen concentration 150 rises immediately after initial vent, followed by a slight pressure 170 increase at T=2 (one minute after T=1) within the enclosure as gas expansion exceeds pack level venting capability. Thus, at T=1, the microprocessor 118 generates an alert that thermal runaway has initiated. The pressure rise at T2 in FIG. 7 demonstrates the delayed response of pressure signal in this instance, wherein there exists hydrogen gas above the Lower Exposure Limit at T1, yet the pressure does not substantially increase for over one minute.

[0073] Turning to FIG. 8, yet another example embodiment is shown. Here, the gas detector 110 is a carbon dioxide sensor. The plot shows rapid carbon dioxide concentration 150 rise within the enclosure, while pressure 170 remains the same and the temperature 160 exhibits a slight increase. At T=2, the microcontroller 118 determines that a thermal runaway has occurred, and generates an alarm that it sends to the battery controller.

[0074] Thus, the microcontroller 118 uses the sensed outputs from the gas, pressure, RH, and/or temperature sensors 110, 112, 114, 116, respectively, to determine if there is a thermal runaway event or other condition within the battery enclosure. The microcontroller 118 can base that determination on a single sensed output, or on a combination of sensed outputs. For example, the microcontroller 118 can determine based on the presence of a gas spike alone, that a thermal runaway might be occurring and then refer to the sensed pressure output and/or the sensed temperature output to determine if the thermal runaway event is cascading to additional cells throughout the pack by utilizing a combination of gas measurement to determine initial thermal runaway event and monitoring for increases in pressure or temperature to assess the magnitude of the event. Increasing temperature or pressure within the pack coincident with high gas concentration levels are indicative that countermeasures have not isolated the event to a single cell, and generate an alert escalating a response. For example, the initial alert could be to notify the vehicle owner to take the vehicle in for service as soon as possible, and the escalating alert could be to notify the vehicle occupants to bring the vehicle to the side of the road, exit the vehicle and the BMS would shut the vehicle down except for the heat exchanger system to try to slow the process down. However, if the temperature and pressure do not increase, the microcontroller 118 can determine that the thermal event has ceased and has been isolated to a single cell or group of cells, and not generate an alert escalating the response. Thus, in the example given, the alert would continue to notify the vehicle owner to have the vehicle serviced.

[0075] It is noted that a microcontroller 118 is provided to receive the sensed outputs, determine spikes and send an alarm to the battery controller via the transceiver 122. However, the microcontroller operation can instead be performed by the battery controller itself, and sensed outputs can be transmitted, via the transceiver, to the battery controller. And responsive action signals can be sent directly from the battery controller to the cells, via the transceiver 122.

[0076] Advantages of the detection system 100 include, for example, the use of known, validated and field proven sensor technology, leveraging a specific combination of sensors to allow for layering of the detection mechanisms related to chemical and thermal physics of phenomena associated with the thermal runaway event. The system requires little, if any customization to be suited for various xEV enclosure size/cell configuration/electrochemistry. The system also has very fast time response (generally 3 to 5 seconds) in an environment where positive detection of thermal runaway requires fast response with minimal risk of missed/false detection. The system is compact and can be operated in multiple modes for reduced parasitic power consumption when the battery enclosure is neither actively charging nor discharging. These modes can be controlled within the sensor assembly 100 utilizing information received from the battery Management system on active mode (either driving or charging, where fast detection is critical and power consumption less important, or in passive mode, where power consumption is critical and sampling rate can be reduced to reduce device power consumption.

[0077] The system and methods of the present invention include operation by one or more processing devices, including the microprocessor 118. It is noted that the processing device can be any suitable device, such as a processor, microprocessor, controller, application specific integrated circuit (ASIC), or the like. The processing devices can be used in combination with other suitable components, such as a display device, memory or storage device, input device (touchscreen), wireless module (for RF, Bluetooth, infrared, WiFi, etc.). The information may be stored on a computer medium such as a computer hard drive, or on any other appropriate data storage device, which can be located at or in communication with the processing device. The entire process is conducted automatically by the processing device, and without any manual interaction. Accordingly, unless indicated otherwise the process can occur substantially in real-time without any delays or manual action.

[0078] In another aspect, the present disclosure relates to a method of detecting thermal runaway of a battery (e.g., detecting thermal runaway of one or more battery cells) within an enclosure.

[0079] In one embodiment, the method comprises:

(i) providing a detection system according to any of the embodiments described herein within the battery enclosure;

(ii) measuring and/or analyzing one or more gases venting from the battery;

(iii) determining if the analyzed gas levels are at or above a predetermined threshold level that indicates thermal runaway of the battery.

[0080] In one embodiment, the gases analyzed comprise hydrogen, carbon monoxide, carbon dioxide, or any combination thereof.

[0081] In one embodiment, any of the detection systems and/or methods described herein do not i) receive a sensor signal, ii) evaluate the sensor signal relative to a threshold, or iii) generate an alert based on a result of the evaluation, or any combination of the foregoing.

[0082] In another embodiment, any of the detection systems and/or methods described herein do not monitor an ambient gas in an ambient gas environment.

[0083] It will be apparent to those skilled in the art having the benefit of the teachings presented in the foregoing descriptions and the associated drawings that modifications, combinations, sub-combinations, and variations can be made without departing from the spirit or scope of this disclosure. Likewise, the various examples described may be used individually or in combination with other examples. Those skilled in the art will appreciate various combinations of examples not specifically described or illustrated herein that are still within the scope of this disclosure. In this respect, it is to be understood that the disclosure is not limited to the specific examples set forth and the examples of the disclosure are intended to be illustrative, not limiting.

[0084] As used in this specification and the appended claims, the singular forms “a”, “an” and “the” include plural referents, unless the context clearly dictates otherwise. Similarly, the adjective “another,” when used to introduce an element, is intended to mean one or more elements. The terms “comprising,” “including,” “having” and similar terms are intended to be inclusive such that there may be additional elements other than the listed elements.

[0085] Additionally, where a method described above or a method claim below does not explicitly require an order to be followed by its steps or an order is otherwise not required based on the description or claim language, it is not intended that any particular order be inferred. Likewise, where a method claim below does not explicitly recite a step mentioned in the description above, it should not be assumed that the step is required by the claim.

WHAT IS CLAIMED IS:

1. A battery thermal runaway detection sensor system for use within a battery enclosure housing one or more batteries, the sensor system comprising:

(i) at least one primary gas sensor for detecting a thermal runaway condition of a battery cell and providing a sensed output in real time; and

(ii) a microcontroller determining power management and signal conditioned output on the concentration of specific battery thermal runaway gases based on the sensed output from said at least one primary gas sensor and providing a sensed output in real time.

2. The detection system of claim 1, wherein the system further comprises a secondary gas sensor for detecting an electrolyte leakage condition.

3. The detection system of claim 1 or claim 2, wherein the primary gas sensor comprises one or more of: a CO_2 sensor, a CO sensor, a HF sensor, a H_2 sensor and/or a water vapor sensor.

4. The detection system of any one of claims 1-3, wherein the primary gas sensor comprises one or more of: a CO_2 sensor, a CO sensor, and/or a H_2 sensor.

5. The detection system of any one of claims 2-4, wherein the secondary gas sensor comprises one or more sensors for the detection of methane, ethane, oxygen, nitrogen oxides, volatile organic compounds, esters, hydrogen sulfide, sulfur oxides, ammonia, chlorine, propane, ozone, ethanol, hydrocarbons, hydrogen cyanide, combustible gases, flammable gases, toxic gases, corrosive gases, oxidizing gases, reducing gases, or any combination of any of the foregoing.

6. The detection system of any one of claims 2-5, wherein the secondary gas sensor comprises one or more sensors for the detection CH_4, C_2H_2, C_2H_4, C_2H_6, diethyl carbonate (DEC), dimethyl carbonate (DMC), ethylene carbonate (EC), ethyl methyl carbonate (EMC), C_4H_{10}, C_3H_6, C_3H_8, POF_3 or any combination of any of the foregoing.

7. The detection system of any one of claims 2-6, wherein the at least one primary gas sensor detects a level of hydrogen gas, carbon monoxide gas and/or carbon dioxide gas in the battery compartment housing.

8. The detection system of any one of claims 1-7, further comprising at least one additional sensor for detecting a secondary condition of the battery and providing information on a rate of progression of the cell venting and thermal runaway in real time including pressure or temperature, wherein said microcontroller provides a rate of progression of the thermal runaway based on the provided information from said secondary sensor.

9. The detection system of claim 8, wherein said at least one additional sensor detects a pressure or temperature in the battery compartment housing to determine rate of progression of the venting/thermal runaway.

10. The detection system of any one of claims 1-9, further comprising a sensor housing enclosing said at least one sensor and said at least one secondary sensor.

11. The detection system of any one of claims 1-10, wherein output from the primary gas sensor and the secondary gas sensor allows for differentiation between electrolyte leakage and venting/thermal runaway.

12. The detection system of any one of claims 1-11, wherein the system software embedded within the sensor microcontroller to determine if threshold levels for thermal runaway have been exceeded and to send an alarm to the battery management microcontroller or charging system controller.

13. The detection system of claim 12, wherein the threshold levels for thermal runaway are selected from:

(i) a carbon dioxide level of greater than about 10,000 ppm;

(ii) a hydrogen level of greater than about 40,000 ppm;

(iii) a carbon dioxide level above its lower explosive limit;

(iv) a hydrogen level above its lower explosive limit; and

(v) any combination of thereof.

14. The detection system of any claims of 1-13, that is composed of a multichip printed circuit board to be mounted on battery management controller printed circuit board.

15. The detection system of any claims of 1-14, that includes power management system that allows for fast data acquisition mode during active battery system charging/discharging, and reduced acquisition rate/lower power mode when the battery system is neither charging nor discharging.

16. The detection system of any one of claims 1-15, wherein the system can send a wake-up command to the main battery system controller upon detection of venting/thermal runaway.

17. The detection system of any one of claims 1-16, wherein said sensor system includes multiple gas sensors selected from more than one hydrogen sensor, more than one carbon monoxide sensor, more than one carbon dioxide sensor, and any combination of any of the foregoing, for redundancy in safety critical applications.

18. The detection system of any one of claims 1-17, wherein the system further comprises a humidity sensor, a pressure sensor, a temperature sensor, or any combination thereof.

19. A method of detecting a thermal runaway condition of a battery within a battery enclosure, the method comprising

(i) providing a detection system according to any one of claims 1-18 within the battery enclosure;

(ii) measuring and/or analyzing one or more gases venting from the battery;

(iii) determining if the analyzed gas levels are at or above a predetermined threshold level that indicates thermal runaway of the battery.

20. The method of claim 19, wherein the gases analyzed comprise hydrogen, carbon monoxide, carbon dioxide, or any combination thereof.

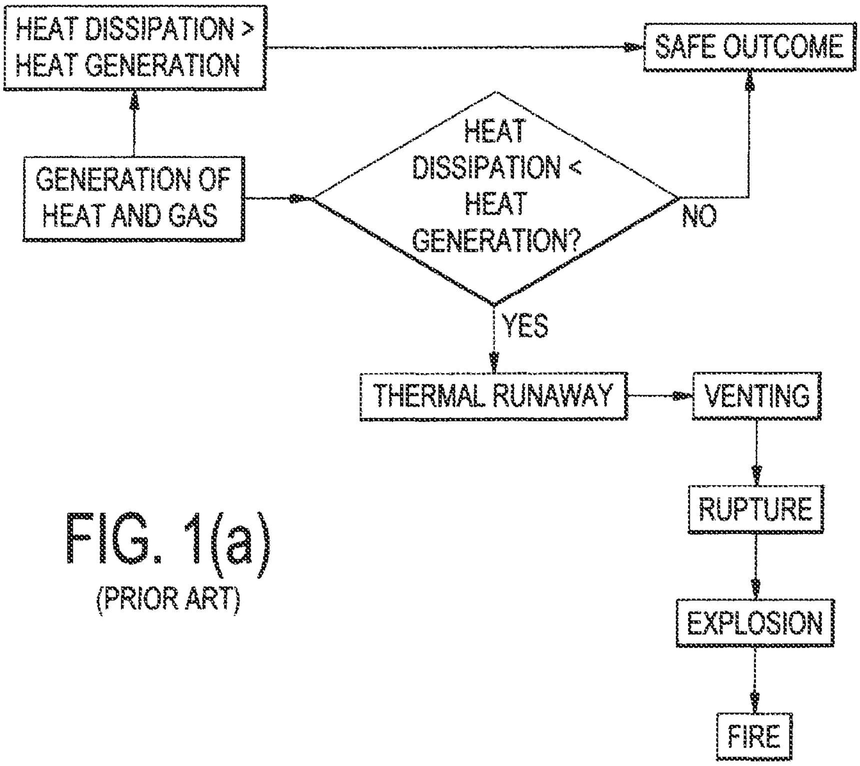

FIG. 1(a)
(PRIOR ART)

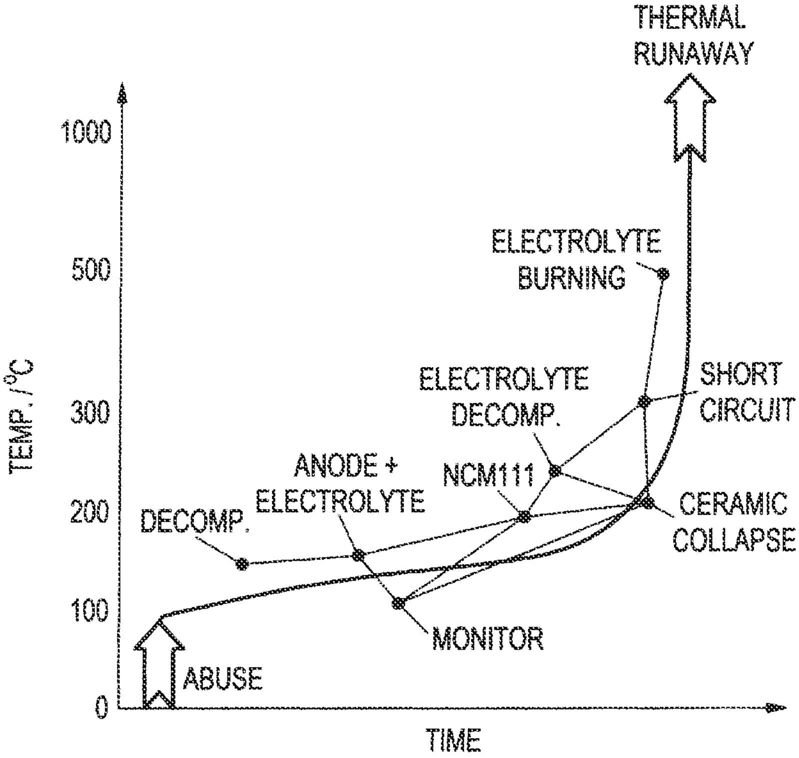

FIG. 1(b)
(PRIOR ART)

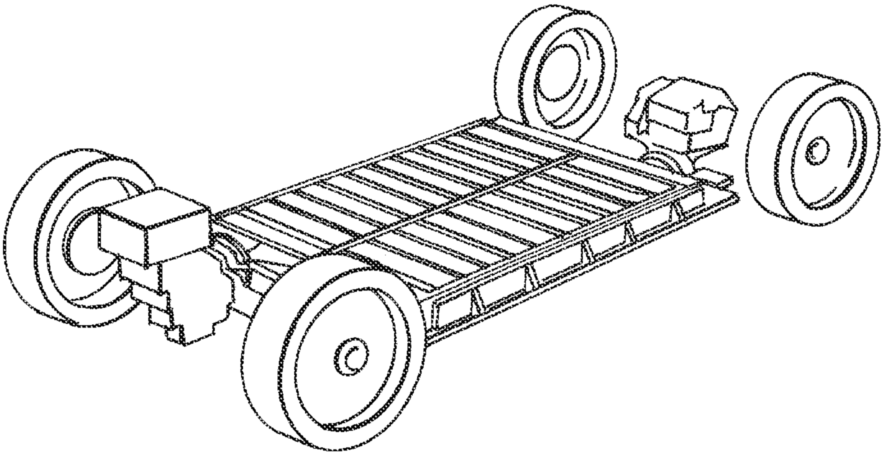

FIG. 2(a)
(PRIOR ART)

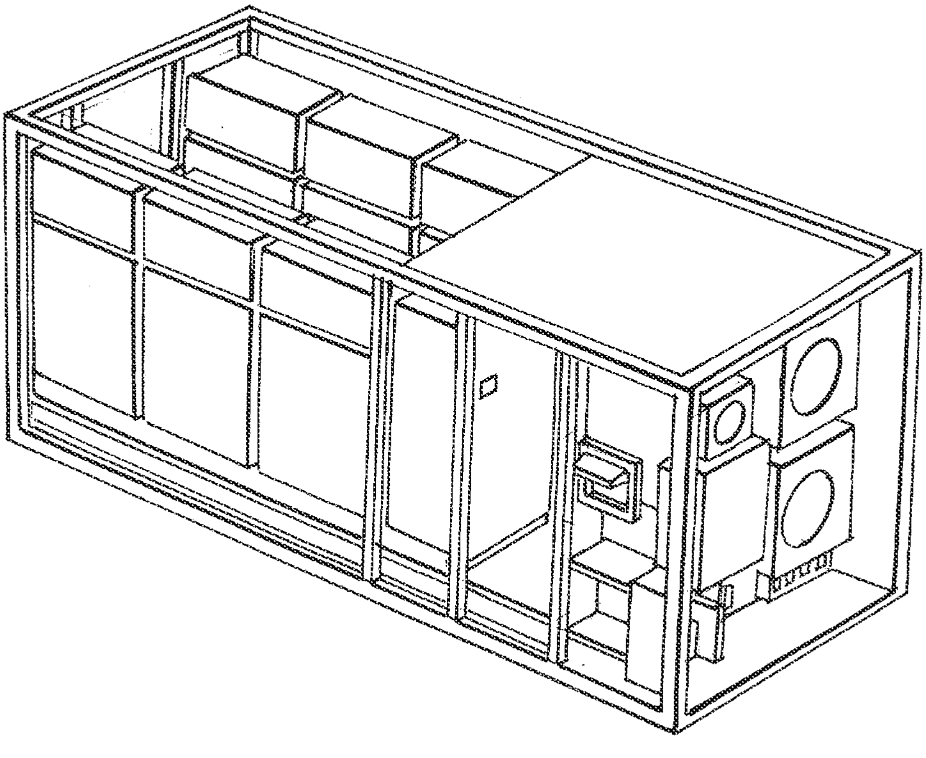

FIG. 2(b)
(PRIOR ART)

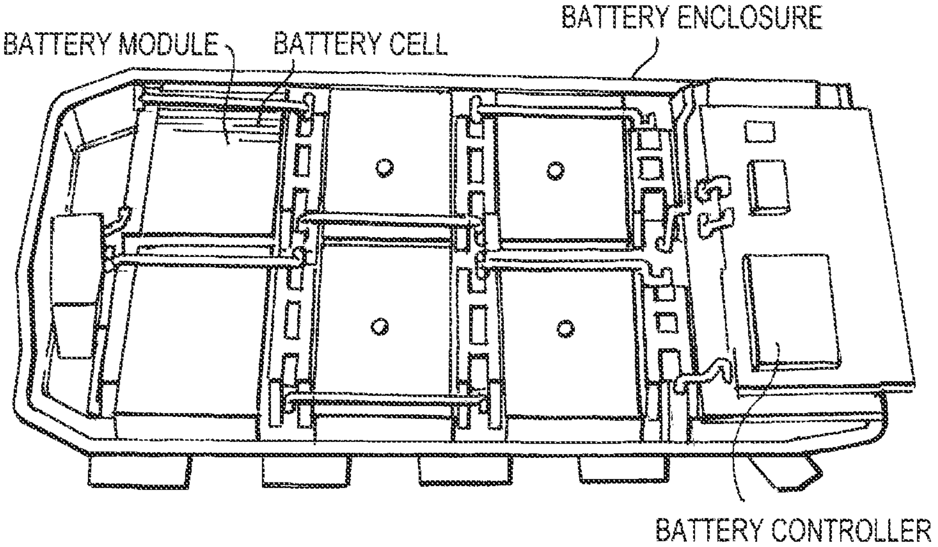

FIG. 3

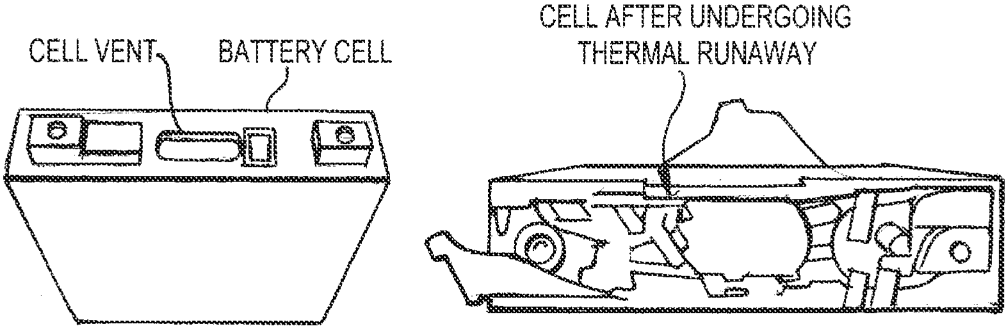

FIG. 4
(PRIOR ART)

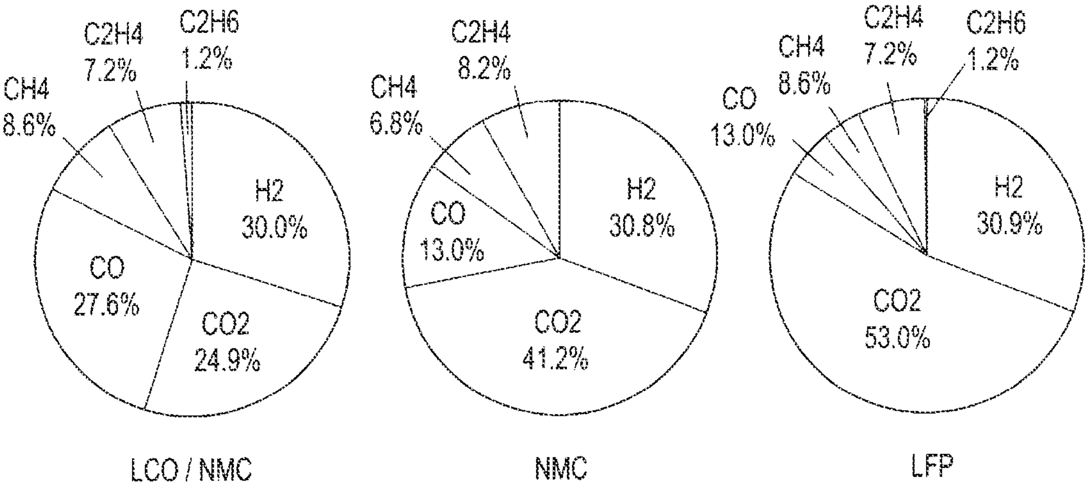

FIG. 5
(PRIOR ART)

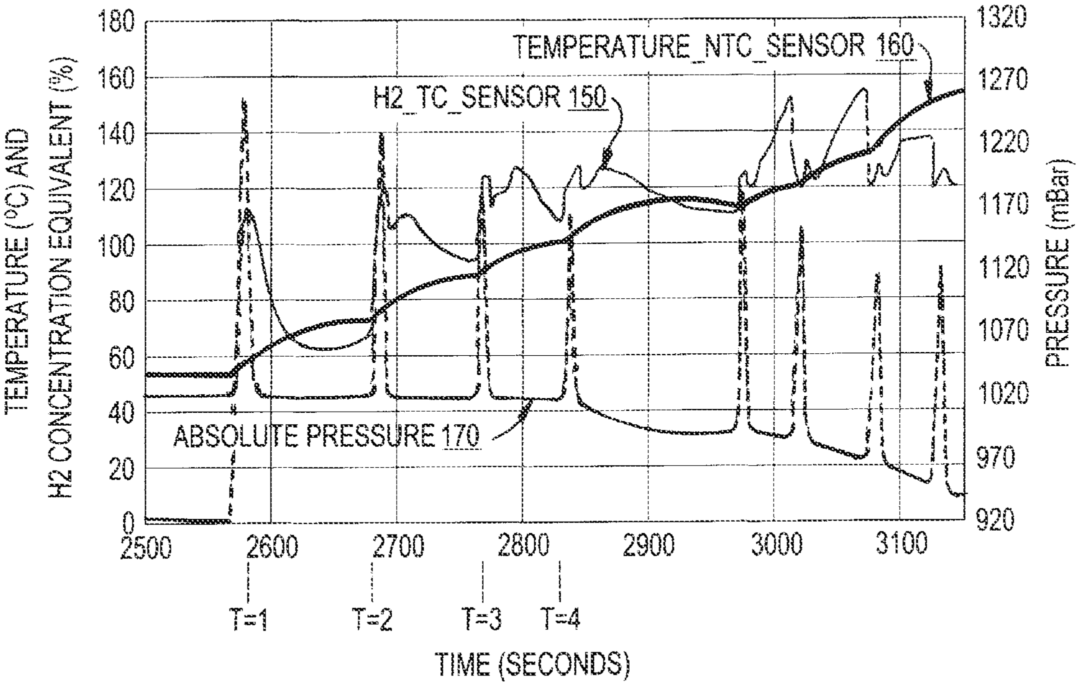

FIG. 6
CASCADING THERMAL RUNAWAY PROPAGATING THROUGH PACK ENCLOSURE WHEREIN INITIAL CELL TRIGGERED THERMAL RUNAWAY IN SEVERAL ADJACENT CELLS

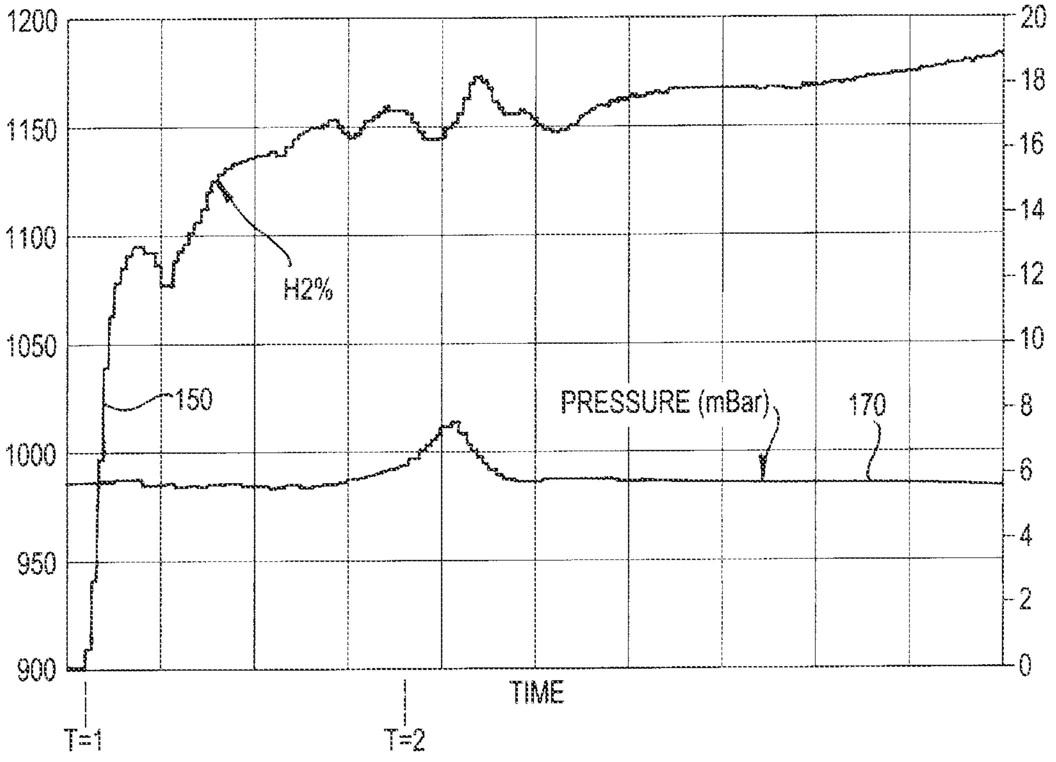

FIG. 7

PLOT OF HYDROGEN CONCENTRATION RISE IMMEDIATELY AFTER INITIAL VENT FOLLOWED BY SLIGHT PRESSURE RISE WITHIN THE ENCLOSURE OVER ONE MINUTE LATER AS GAS EXPANSION EXCEEDS PACK LEVEL VENTING CAPABILITY

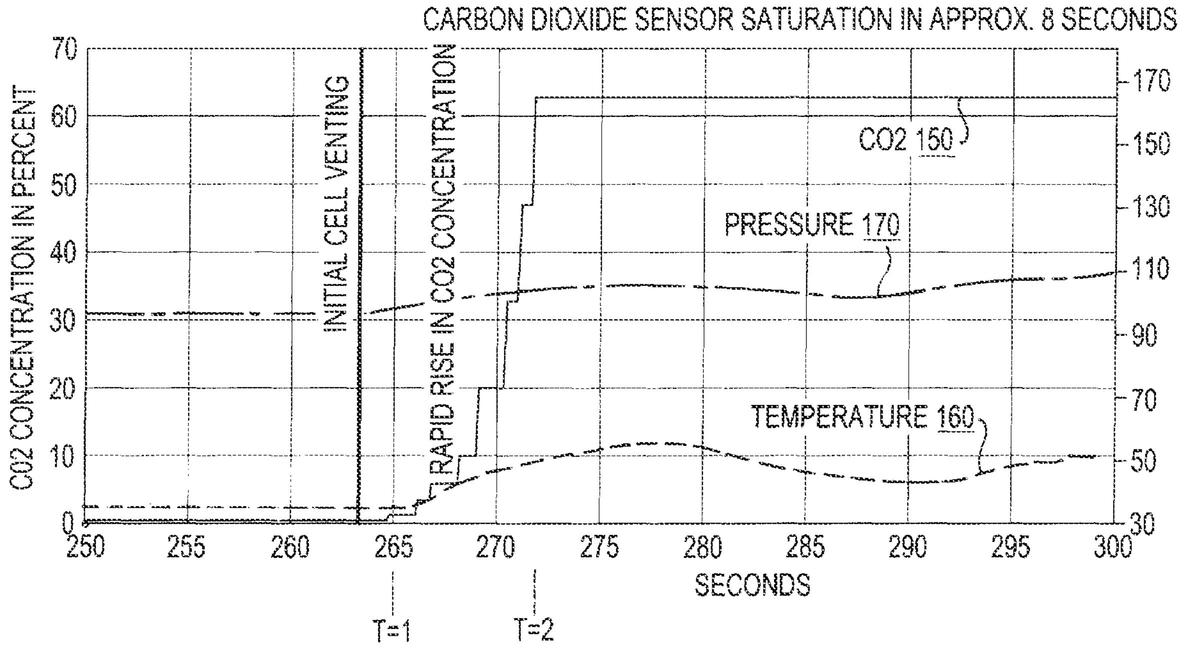

FIG. 8

CO2 IN PHASE 1 THERMAL RUNAWAY

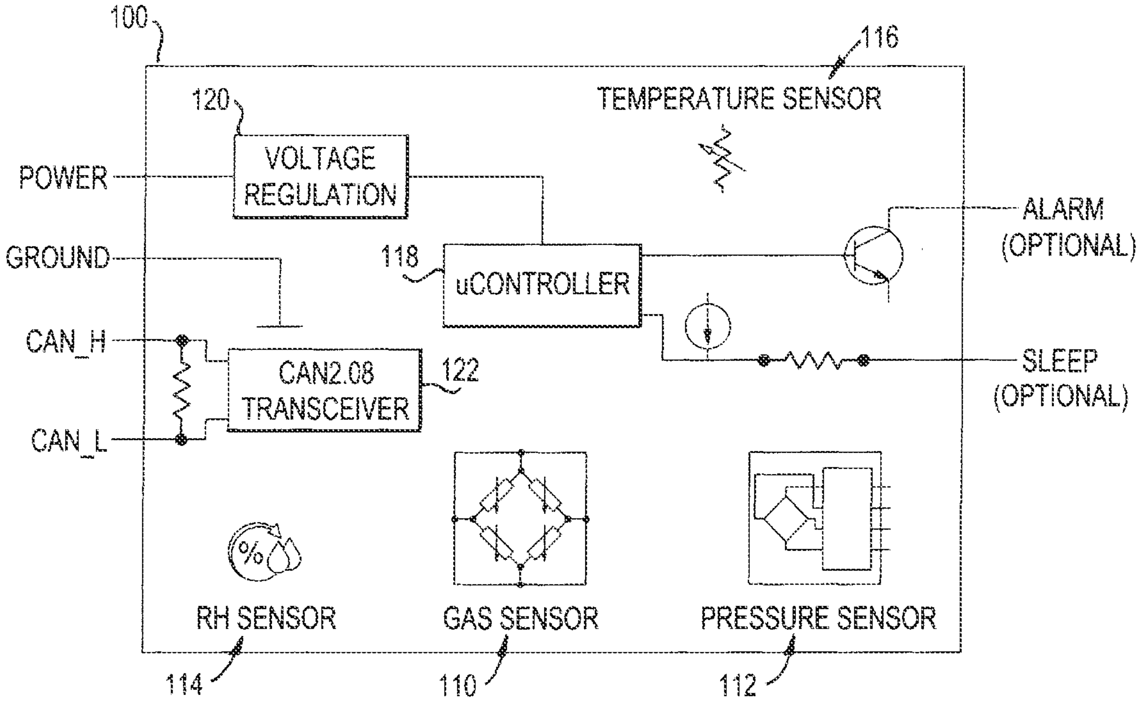

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2021/050471

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 10/48; H02J 7/00; H02J 7/04; G01R 31/382; H02J 7/02 (2021.01)

CPC - H01M 10/48; H02J 7/00; G01R 31/382; G01R 31/392; H02J 7/007 (2021.08)

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)

see Search History document

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

see Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

see Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/0303723 A1 (PALO ALTO RESEARCH CENTER INCORPORATED) 22 October 2015 (22.10.2015) entire document	1-3
A	US 2019/0319316 A1 (ASTRONICS ADVANCED ELECTRONIC SYSTEMS CORP. et al) 17 October 2019 (17.10.2019) entire document	1-3
A	US 2016/0116403 A1 (COLORADO STATE UNIVERSITY RESEARCH FOUNDATION) 28 April 2016 (28.04.2016) entire document	1-3
A	US 9,083,064 B2 (LEPORT) 14 July 2015 (14.07.2015) entire document	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"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 08 November 2021	Date of mailing of the international search report DEC 07 2021
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Harry Kim Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2021/050471

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.: 4-20
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:

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.