Beyond consumer batteries: Challenges of cell venting physics in lithium ion battery e-Aero applications

As lithium ion battery technology grows beyond cell phones, tablets, and other consumer products into electrification of aerospace systems such as drones, e-aircraft and electronic subsystems in larger aircraft, failure modes such as battery thermal runaway must be considered in design. With a push for high energy density and larger format systems, the phenomenon of cell venting and thermal runaway must be considered in design.

REDTR: Pragmatic approach to cell venting detection

Battery Failure Leads to Fire at [redacted] Technologies

By DEREK BROUWER

Published August 29, 2022 at 9:03 p.m.

The damaged container | COURTESY OF THE SOUTH BURLINGTON FIRE DEPARTMENT

[redacted] fire involved lithium-ion batteries which ignited after hours of powerplant tests

By Jon Hemmerdinger | 20 November 2020

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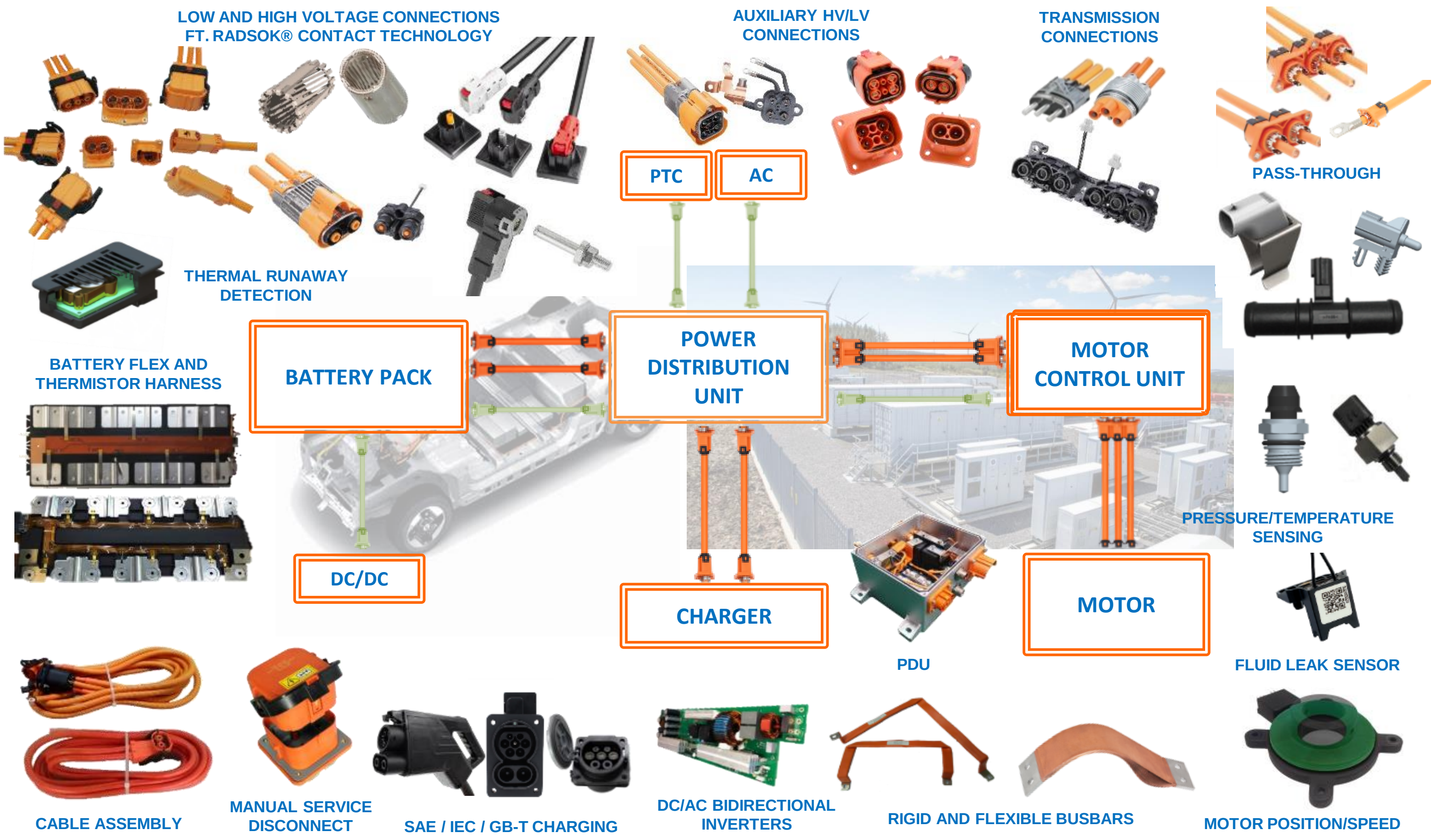
Supporting Mobile and Stationary Sensing & Electrification Solutions



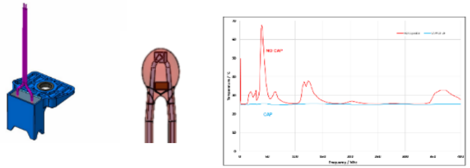
Combining skills and expertise to solve critical issues

Sensing:

- *Temperature*
- *Pressure*
- *Gas concentration*
- *Current*
- *Fluid Level*
- *Concentration*
- *Speed*
- *Rotary/Linear Position*
- *Accoustic /ultrasonics*
- *Vibration / Acceleration*
- *Force*
- *Air Quality*
- *Particulates / Dust*
- *Moisture / Humidity*
- *Process Controls*
- *Validation Instruments*

Amphenol Battery Sensor Portfolio

- **Robust Early Detection of Thermal Runaway (REDTR)**
  - Mobile and Stationary applications
  - Surface mount sensors & standalone monitors



- **Cell & Pack Diagnostics**
  - Coolant breach/water intrusion sensor
  - EMC immune Temperature sensors
  - Current Sensing

1	Sensor type	Assemby method	Main parameters	Sensor view
2	Water temp sensor	Thread M12	R25C=10K/100K/2.08K -40°C to 125°C	
3	Water temp sensor	Quick lock	R25C=10K/100K -40°C to 125°C	
4	Water temp sensor	Pipe surface 12/15 to18	R25C=10K/100K -40°C to 125°C	
5	Coolant medium temp s	Thread M12	R25C=10K/2.828K -40°C to 130/150°C	
6	PT sensor	Tread M14&M12	50-300KPa GE-2098 -1..10bar to - 1...100bar -40°C to 125°C/130°C	

- **Battery / xEV Heat Pump / HX Sensors**
  - Full suite of thermal management sensors
  - Pressure and Temperature

- **Cell Connection Systems**
  - World’s largest supplier of Cell Connection Systems

Working Together to Improve Battery Safety, Diagnostics, & Robustness

Facts from surface vehicle field experience:

- Beijing Inst. Of Technology: ~7-8 EV TR events/day in China (30% while charging, 40% while parked)
- Automotive cells are the highest grade of lithium ion cells in the sorting process
- Typical cells have over 300 separate quality checks and defect rate < 0.1ppm (1 ppb needed)
- Automotive cells have sophisticated BMS and thermal management with constrained SOC/SOH control
- xEV's have ~***90% LOWER probability*** of experiencing a fire incident than ICE vehicles
- While incident level is low, severity of TR is very high

2022 Hurricane Ian flood vehicle

Challenges with xEV's / Lithium-ion Battery fires:

- Pack location is difficult to access
- Thermal Runaway temps >600 – 1000 C; solid state >1800C
- Hazardous and flammable gas release; explosive risk
- High Voltage (400 to 1.2kV) systems external shorts if relays fail
- Gases, particulates and water vapor increase risk of arc discharge
- Lithium-ion batteries provide their own oxygen to support combustion
- Damaged cells/stranded energy can cause re-ignition
- Difficult to assess state of cell, pack and determine "end of event"
  - Events require hours of engagement and 1,000's of liters of water to extinguish
- ***New technology requires training, new processes, new tools***

Why are lithium ion battery fires so pernicious?

While rare, Lithium ion battery fire pose unique challenges to suppression

Peugot 208 EV fire 10/2022
50 kW-h pack

1. Lithium ion cells undergoing thermal runaway can provide their own oxygen as a reactant

SEI Decomposition: $(CH_2OCO_2Li)_2 \xrightarrow{\Delta H} Li_2CO_3 + C_2H_4 + CO_2 + \frac{1}{2}O_2$

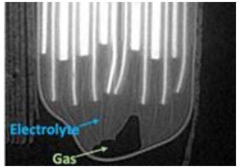
Carbonate combustion & Lithium rx with binder and electrolyte :

$$\frac{5}{2}O_2 + C_3H_4O_3(EC) \xrightarrow{\Delta H} 3CO_2 + 2H_2O$$

$$\text{-}CH_2\text{-}CF_2\text{-} + Li \xrightarrow{\Delta H} LiF + \text{-}CH{=}CF\text{-} + \frac{1}{2}H_2 \qquad CMC\text{-}OH + Li \xrightarrow{\Delta H} CMC\text{-}OLi + \frac{1}{2}H_2$$

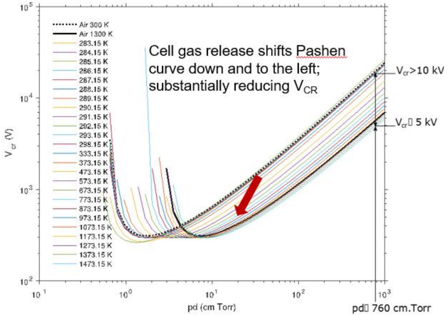
2. Battery TR releases hazardous and flammable gases and electrolyte

- Cells can achieve temperatures of >600C, transferring heat to adjacent cells
- Electrolyte can cause external fires on other cells
- ***Gas /particulate release increases potential for HV discharge***
- Once external oxygen is consumed, flammable gases can reignite with reintroduction of O2
- H_2O hydrolysis inside/outside cell



3. Battery packs can be difficult to access

- It is often difficult to remotely assess the state of a battery cell
- No clear path to identify "End of Event"
- Stranded energy /damaged cells can generate reignition events



Courtesy Jeremy Riousset, FIT

Hazards proximate to pack include: fire/explosion, hazardous gas/asphyxiation, HV discharge

Typical clearance standards – IEC 60664-1:2020

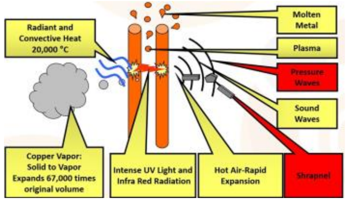
…and why they do not apply when lithium ion battery cells vent…

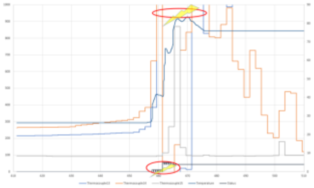
Lithium ion battery system design engineers generally use standards such as IEC 60664.

IEC 60664-1:2020 deals with insulation coordination for equipment having a rated voltage up to AC 1 000 V or DC 1 500 V connected to low-voltage supply systems. This document applies to frequencies up to 30 kHz. It applies to equipment for use up to 2 000 m above sea level and provides guidance for use at higher altitudes. It provides requirements for technical committees to determine clearances, creepage distances and criteria for solid insulation. It includes methods of electrical testing with respect to insulation coordination. The minimum clearances specified in this document do not apply where ionized gases are present. Special requirements for such situations can be specified at the discretion of the relevant technical committee. This document does not deal with distances:

- – through liquid insulation;
- – through gases other than air;
- – through compressed air.

- During cell venting, the cell ejects a highly conductive mixture containing hydrogen, carbon dioxide, hydrogen fluoride, VOC's, water vapor, and conductive particulates. At ejecta temperatures of 1000 degrees C, this may even be considered a plasma.
- At least 4 major EV OEM's have experienced HV discharge and arc damage (vaporized busbar materials and electromagnetic events)
- Scientific literature on the phenomenon is lacking

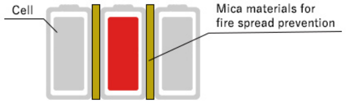




Good News: State of the Industry for Thermal Propagation countermeasures

- **On vehicle:**
  - Control – Charge balancing, impedance spectroscopy, etc
  - Thermal isolation (Mica, aerogels)
  - Phase change materials that absorb heat - Aerogels
  - Aggressive HX
    - Coolant
    - refrigerant
  - On board extinguishing agents (busses)
  - Dielectric coolant
  - Load dump from affected modules (as with MegaPack)
  - Disable regen braking contribution to pack charging
  - Disable charging
  - Access port
  - "Livestream" data to secure server

Lithium-ion batteries with mica materials for fire spread prevention



Mica materials for fire spread prevention prevent an ignited cell from affecting adjacent cells.

Explosion Hazard: Hyundai Kona

Hyundai Kona Electric Blast: High Voltage Battery Area Had The Most Damage

That indicates where the issue began. Anyway, Transport Canada reinforces the cause is still under investigation.

Jul 28, 2019 at 2:16pm ET

Lithium has offered us the most efficient battery until now, but it is also very flammable. This is why any fire situation with a huge lithium-ion battery may be very difficult to extinguish. The newest such case comes from Canada. More specifically from Île-Bizard, Montreal. And it involves a vehicle that had not presented any similar problem until now, the Hyundai Kona Electric.

Piero Cosentino bought his last March. On July 26, he was about to have lunch when he heard ***an explosion and the fire alarm went off. Thick black smoke was coming from the door that leads to his garage.***
"As soon as I saw that, I immediately turned off the breaker," he told CBC. "My first instinct was to go out and run outside so I did not have to open doors and feed the fire." Cosentino then started to fight the fire with the help of a garden hose while he waited for the firefighters.

It was only there Cosentino could see the extent of the damage. The explosion ***set his garage door to the other side of the street. Part of the roof of the garage went down.***

Around 30 men managed to put out the fire. Louise Desrosiers, a Division Chief from the Montreal Fire Department, said they found no other possible cause to the fire apart from the Hyundai Kona.

"It was a fully electric vehicle, and there was nothing around that could have caused the explosion. We will be following up [...] closely with the owner to understand the problem in anticipation of other cases," she told Radio Canada, which also took the pictures in this article.

The story gets even weirder. Cosentino claims his Kona was not charging. And that is was not even connected to a socket.

Latency: Sacramento Tesla Incident

Jun 13, 2022 at 10:46am ET
By: **Steven Loveday**

According to reports issued by *Metro Fire of Sacramento*, firefighters from the unit recently experienced their first Tesla fire. Interestingly, it wasn't at the scene of an accident, but rather, at a wrecking yard.
As the story goes, the Tesla Model S was totaled in an accident, and it had been sitting at the Sacramento yard for about three weeks. Based on reports, despite the accident, the electric car had never caught fire prior to the incident at the yard, which makes this an interesting case.
As you can see from the brief video, the Tesla electric car is certainly not just sparking up or smoldering. This is a full-on fire engulfing the car, with clouds of thick black smoke clouding the air around the area.
The fire department shared that the firefighters were able to put out the flames, though the car kept re-igniting thanks to thermal runaway from the Tesla's battery pack. After turning the car over and learning that the battery pack was continuously re-igniting, the team went to great lengths in order to get the fire to go out and stay out. They dug a pit, placed the car inside, and filled the pit with water.
One Twitter user responded to the initial tweets saying that the firefighters should have finished putting the car out in the first place. It seems the person thought that perhaps the Model S had already been on fire after it recently crashed. However, Metro Fire of Sacramento responded that this was the car's first and only fire.
As far as the fire department was concerned, the car never caught fire at the scene of the crash, or for the three weeks prior to this incident unfolding.

"This was the 1st and only. The vehicle sat parked in a wrecking yard for 3 wks after a vehicle accident (not involving fire), and then caught fire in the yard. Our crews were dispatched and ensured the vehicle was extinguished after well over an hour of firefighting operations."

Fortunately, no one was injured at the wrecking yard. While Tesla has recently shared that fires are becoming less common among its vehicles, there have been a few other recent incidents that are concerning.

As we previously reported, a Tesla Model 3 caught fire in late May while parked (and not running or charging) in California City. Meanwhile, right around the same time, a Model Y started on fire while its owner was driving it in Canada, and NHTSA already requested information from Tesla. Check out the related stories below, and then leave us a comment.

https://insideevs.com/news/591794/tesla-fire-wreckage-yard-three-weeks-after-crash/

Tesla Goes Up In Flames Weeks After Crash That Didn't Involve Fire

The Tesla Model S was sitting in a wrecking yard in Sacramento for three weeks before it was suddenly ablaze.

Metro Fire of Sacramento
@metrofirepio

Photos of the pit the crews created...

5:57 AM · Jun 12, 2022

Solid State cells: “BlueBus” fleet in Paris

Paris Suspends 149 Bolloré Electric Buses After Two Fires

Two Bluebus 5SE electric buses were completely destroyed by fires in two separate incidents on April 4 and April 29.

May 02, 2022 at 3:16pm ET

By: Dan Mihalascu
RATP, the public transport operator in Paris, has temporarily withdrawn 149 electric buses made by Bolloré Group’s Bluebus brand from operation after two separate bus fires.

On April 29, a fire broke out on a Bluebus 5SE electric bus on line 71 in the 13th arrondissement of Paris, close to the French capital's national library. The driver immediately evacuated the passengers and no injuries were reported.

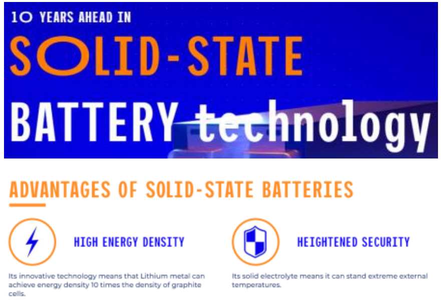
Fortunately, the fire department responded very quickly, with around 30 firefighters managing to put out the blaze. The François Mitterrand Library station, located nearby, was closed from 9 a.m. to 11 a.m. as a safety measure. The electric bus released thick clouds of black smoke and a strong smell of burning plastic, according to eyewitnesses interviewed by BFMTV.

The incident was caught on camera and shows the violent fire engulfing the roof of the electric bus where the battery packs are located. It certainly looks scary as burning debris were ejected from the roof, falling onto the sidewalk and the road like a rain of fire.
This was the second fire involving a Bolloré Bluebus in less than a month. On April 4, another Bluebus 5SE caught fire in central Paris on the Saint-Germain boulevard. That vehicle was also completely destroyed but no one was hurt. As a safety precaution, RATP has decided to temporarily suspend 149 electric buses belonging to the same Bluebus 5SE series as the two vehicles affected by fires.
Bolloré said that its Bluebus subsidiary was actively cooperating with the RATP and relevant authorities to determine the causes of the fires.

The state-owned public transport operator in Paris has 500 electric buses in its fleet of 4,700 vehicles. The electric buses are supplied by Bolloré, Alstom, and CNH's Heuliez Bus.

Bolloré's 12-meter (39-foot) long electric buses can transport up to 109 passengers and offers an estimated driving range of up to 320 kilometers (199 miles) from ***Lithium Metal Polymer (LMP) battery packs totaling 441 kWh*** of stored energy. On its website, Bluebus describes the batteries as "completely solid, with no liquid components, no nickel and no cobalt."

Since the Bluebus 5SE is a low-floor bus, the batteries are spread around the roof and rear of the vehicle.



e-Aerospace Challenges with Li- batteries

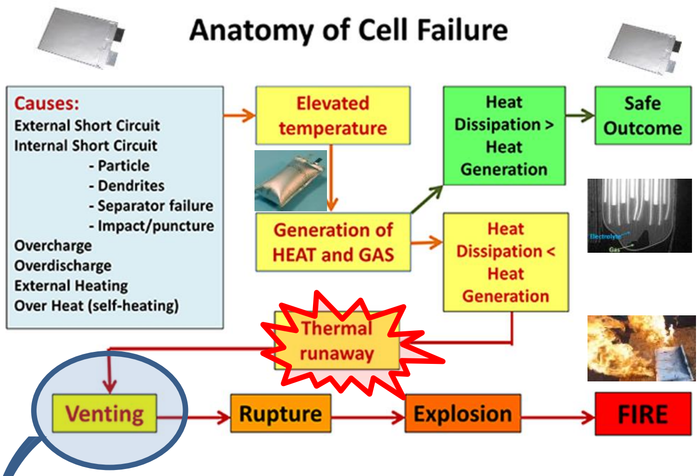
Unique Aircraft needs:

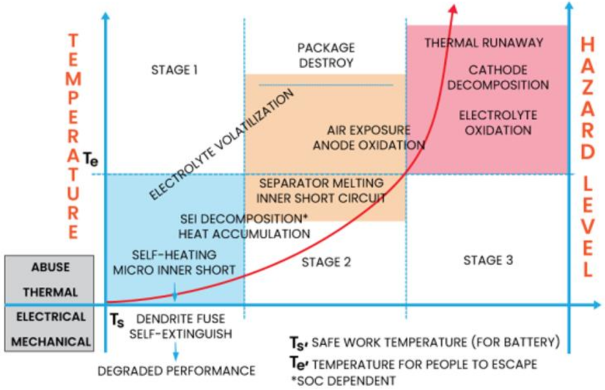
- ❑Must maintain operation much longer than surface vehicles in presence of a failure
- ❑Must maintain lift – may need to draw energy from damaged cells/modules
- ❑Most research on cell failure at sea level (altitude effects on creepage/clearance, arc, moisture/condensation/freezing

Designing to deal with cell venting:

- ❑Cell vent gases must be isolated from cabin
- ❑Cell vent temperatures must not compromise aircraft structure
- ❑Vented plasma must not damage other critical components
- ❑Anti propagation features must endure aggressive attack (mica, aerogels, metals)

Anatomy of Cell Failure and available detection technology:





Reference from Sinovoltaics

Indicator:

- **Voltage/Current** drop
- **Heat** generation
- **Gas** generation
- **Pressure** in pack airspace
- **Swelling** of cell
- **Smoke** generation

Detection Technologies:

- **Voltage** monitoring (slow / not effective for parallel strings)
- **Temperature** sensing (slow / not enough sense points)
- **Gas** sensing (need to prevent cross sensitivity / drift)
- **Pressure** sensing (cell v air volume/venting; pack shell breach)
- **Force** sensing (deconfound thermal/intercalation; signal/noise)
- **Particulate / Smoke** sensing (need particulate products)

Each sensor technology has strengths & weaknesses

Requirements for Detection:

Challenges:

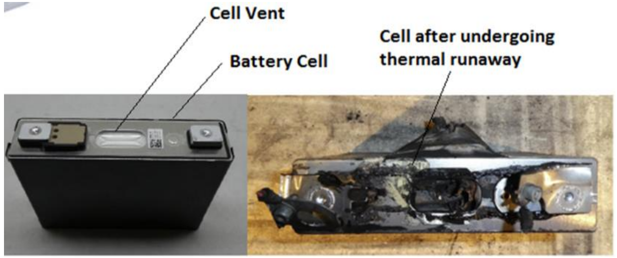
- Defining the threshold for failure generating a hazard: Electrolyte leakage, initial/soft venting, thermal runaway, fire

  Once a cell vents flammable gas, the hazard is present

- Do lab tests accurately represent real world Thermal Runaway? (soft vents, electrolyte leakage)

System Level Requirements:

- Stable Detection capability over entire pack service life (>20 years?)
- Continuous Lifetime operation, two operational states:
  - In flight/charging (fast response)
  - Parked ; neither flying no charging (low power consumption; < 5 mA @ 3V)
- TR venting can happen in seconds, requiring fast sampling
- Robust solution must be agnostic to:
  - Cell / module/ pack configuration
  - Electrochemistry
  - Cell size
- Must not exhibit Type 1 (Missed Detection) or Type 2 (False Positive) faults
- Meet SIL (Safety Integrity Level) Requirements
- Value/Cost sensitive



Venting Explosive Gases

Energy sufficient to generate fire/explosion

Cell venting :

- Venting products include 4 combustible gases above their Lower Explosion Limit (LEL)*
- Electrolyte leakage can release Ethyl/Methyl based compounds with low vaporization temperatures

No.	Cell	SOC (%)	θ_R (°C)	θ_m (°C)	Δm (g)	n_{exam}^{ideal} (mmol)	H_2 (%)	CO_2 (%)	CO (%)	CH_4 (%)	C_2H_4 (%)	C_2H_6 (%)
1	NCA	0	—	302	—	65	1.7	94.6	1.6	1.6	0.3	—
2	NCA	0	160	316	4.4	52	1.8	94.7	1.9	1.2	0.4	—
3	NCA	0	160	315	4.5	55	1.2	96	1.5	1.1	0.2	—
4	NCA	0	161	214	4.4	39	0.9	96.2	1.1	1.4	0.3	—
5	NCA	0	150	243	4.4	59	0.8	96.6	1	1.3	0.3	—
6	NCA	25	150	739	5.9	67	15.5	62.7	5.5	8.7	7.5	—
7	NCA	50	140	970	8.5	157	17.5	33.8	39.9	5.2	3.2	0.4
8	NCA	75	140	955	—	217	24.2	20.8	43.7	7.5	3.3	0.5
9	NCA	100	144	904	—	273	22.6	19.7	48.9	6.6	2.4	—
10	NCA	100	138	896	20.5	314	26.1	17.5	44	8.9	2.7	0.9
11	NCA	100	136	933	20.9	244	28.5	22.7	41.5	5.9	1.3	0.3
12	NCA	112	144	—	19.2	252	25.1	18.8	48.1	5.9	2.1	—
13	NCA	120	80	929	—	281	23.5	20.8	48.7	5.4	1.6	—
14	NCA	127	80	983	—	317	28.8	16.2	46.6	6.4	1.3	0.3
15	NCA	132	80	943	17	262	25.8	18.9	49.2	4.7	1.4	—
16	NCA	143	65	1075	20.1	303	26.2	22	43.4	6.9	1.5	—
17	LFP	0	—	251	6.1	55	2.7	93.5	1.8	0.7	0.7	0.7
18	LFP	25	195	231	6.1	31	7.1	85.3	3.1	1.2	3.1	0.2
19	LFP	50	130	283	6.1	32	20.8	66.2	4.8	1.6	6.6	—
20	LFP	75	149	362	6.3	41	21.8	62.6	6.4	1.9	6.3	1
21	LFP	100	140	440	7.1	32	29.4	48.3	9.1	5.4	7.2	0.5
22	LFP	115	155	395	6.2	61	34	52.2	6.4	2.6	4.7	0.1
23	LFP	130	80	448	—	58	30.1	55.8	7.7	6.4	—	—

RSC Advances (2015) 5, 57171; Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge.

Combustible gases concentrations are far above the Lower Explosive Limit (LEL) (4% for H2, 4.4% for CH4, 12.5% for CO, 2.7% for Ethylene (C2H4), 3% for Ethane (C2H6)

- Typical pack dilution volumes from ~1l to 400L
- Testing has shown H_2 in pack > 4x LEL (~160 000ppm) from single cell
- CO_2 in high concentration has dilutive effect, displacing available O_2 in the enclosure

Cell Venting, even without fire, releases flammable gases into pack vapor space, where any ignition source can initiate fire/explosion

Thermal energy available for gas ignition

Cascading TR within enclosures:

Flash point - the lowest temperature at which vapor of a volatile material can be ignited with an ignition source present

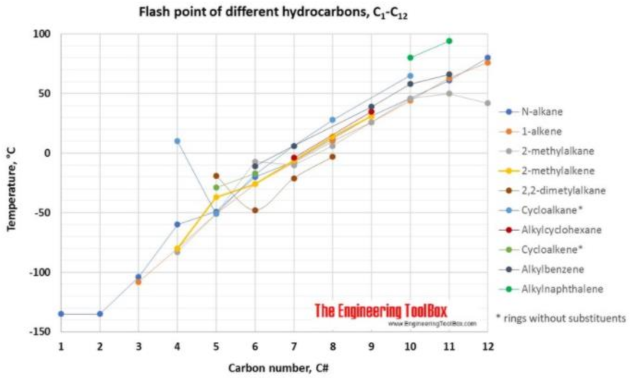
- H_2 flash point: -253°C
- Ethylene flash point: −136 °C
- Methane flash point: −188 °C
- Ethane flash point: −135 °C

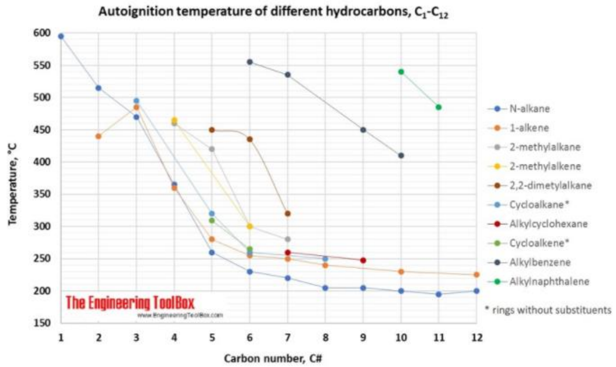
Autoignition temperature = kindling point
- is the temperature at which a material spontaneously ignites in a normal atmosphere without an external source of ignition.
- is the temperature required to supply the activation energy for combustion
- is usually applied to combustible fuel mixture

  - H_2 autoignition temp: 585°C
  - Ethylene autoignition temp : 450°C
  - Methane autoignition temp: 580°C
  - Ethane autoignition temp: 472°C

- Aluminum melts at 660C, Copper melts at ~1085C

- **Cell temps during venting/TR can approach 1000°C, providing ample thermal energy for gas autoignition provided sufficient reactants and oxygen are present between LEL and UFL**





Hazardous Gas Release (Lebedeva, Prenmath, et al)

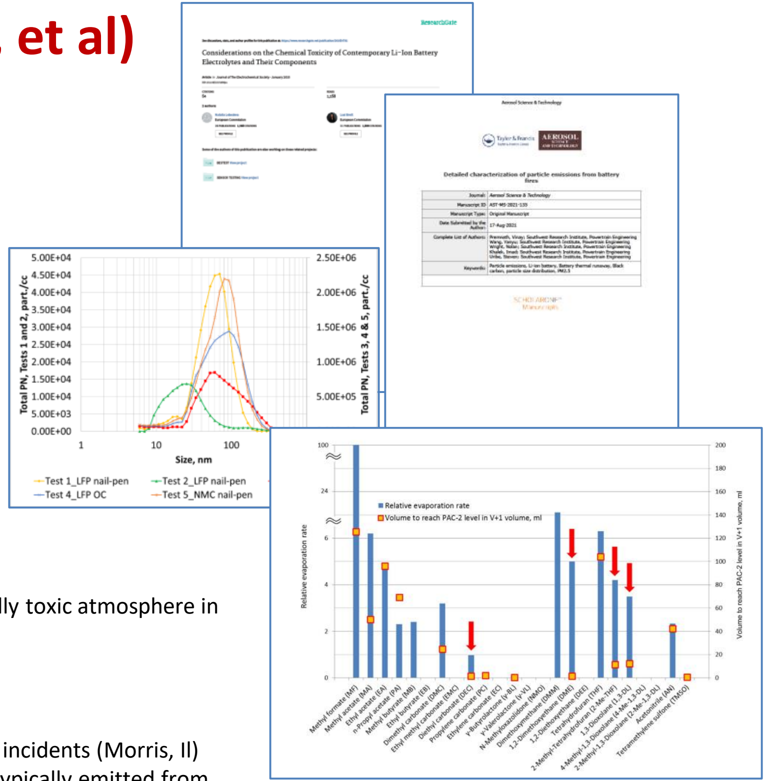
Solvent	Volume of evaporated solvent*, ml	
	PAC-2 level	PAC-3 level
Dimethyl carbonate (DMC), CAS # 616-38-6	25	149
Acetonitrile (AN), CAS # 75-05-8	6.6	19.2
	Volume of evaporated electrolyte*, ml	
	PAC-2 level	PAC-3 level
Hydrogen fluoride (HF), CAS # 7664-39-3	12.3 (20.5)**	22.1 (36.9)**

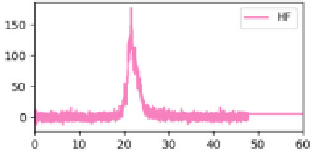
Can be achieved from **1 cell only**

* *Volume, solvent/electrolyte evaporates into, is defined as vehicle + 1-m clearance; 61.5 m³ in this study*
** *Dependent on the stoichiometry of $LiPF_6$ hydrolysis – 1:5 (1:3)*

N.P. Lebedeva, L. Boon-Brett, Considerations on the Chemical Toxicity of Contemporary Li-Ion Battery Electrolytes and Their Components, Journal of the Electrochemical Society 163 (2016) A821

European Commission



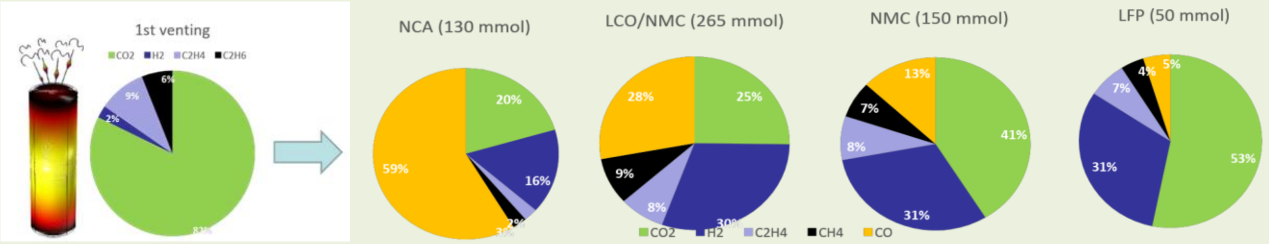


Summary Conclusions:

- (JRC) Li-ion cells contain enough free electrolyte in amounts sufficient for the formation of potentially toxic atmosphere in enclosed spaces from the electrolyte from a single cell
- Thermal Runaway vaporizes the electrolyte and creates hazardous decomposition products
    - A single EV pack can contain 100's of cells
    - Substantial amounts of HF gas have been found in independent studies as well as real world incidents (Morris, Il) (SWRi) Venting emission particulate rates are 5 to 6 orders of magnitude higher than those typically emitted from the exhaust of a modern heavy-duty diesel engine.
    - (SWRi) LFP overcharge tests yielded *HF that exceeded IDLH limits (30ppm) while the NMC nail penetration test yielded formaldehyde beyond IDLH limits (20 ppm).*

Li-ion cell TR gas release across electrochemistries

Total gas released during thermal runaway for 100% SOC cells



Data adapted from: RSC Advances 7.39 (2017): 24425-24429.
RSC Advances 4.7 (2014): 3633-3642.

- Majority of total gas released during thermal runaway are CO_2, H_2
- Hydrogen release much higher than background concentration
- Gas concentration is 100 times background level; very strong signal:noise for detection
- Data has shown overall similar ratios of gas concentrations in testing

Gas sensor Selection Process

Electrolyte

Hydrogen

CO_2

Sensor Technology	Principle	Gases	Accuracy	Selectivity	Temperature	Life Expectancy (> 10 years)	Comments
Photoionization Detector (PID)	Photons break molecules into positive ions, bombarded with UV photons; ionized and form electrical current	non selective VOC's	Good	Good	Good	Poor	high current required
Metal Oxide Semiconductor (CMOS)	Heated catalyst interacts with gas, creating a voltage	VOC's	Good	Poor	Good	Poor	can suffer from drift and poisoning of the catalyst
Electrochemical (EC)	Oxidation or reduction reaction generates electrochemical reaction	Selective VOC's	Good	Good	Good	Poor	Catalyst can be poisoned
Pellistor	small "pellets" of catalyst loaded ceramic whose resistance changes in the presence of gas	Semi selective VOC's	Goods	Poor	Good	Poor	Catalyst can be poisoned
Photoacoustic	the measurement of the effect of absorbed electromagnetic energy (particularly of light) on matter by means of acoustic detection.	CO2 , VOC's	Poor	Very Good	Very Good	Good	particulate and humidity sensitive
Thermal conductivity	electrically heated filament in a temperature-controlled cell. Under normal conditions there is a stable heat flow from the filament to the detector body. When an analyte elutes and the thermal conductivity of the column effluent is reduced, the filament heats up and changes resistance. This resistance change is often sensed by a Wheatstone bridge circuit which produces a measurable voltage.	H2, He, VOC's	Very good	Good	Very Good	Very good	cross sensitive to helium
Tunable diode laser spectroscopy	technique for measuring the concentration of certain species such as methane, water vapor and many more, in a gaseous mixture using tunable diode lasers and laser absorption spectrometry.	CO2, CO, VOC's	Very Good	Very Good	Good	Very Good	substantial current draw when light source active
Non dispersive infrared spectroscopy	White light or narrow band light source projected down an optical chamber at a n IR sensor with selective band filter tuned to absorption frequency of gas. Intensity of receieved light is inversely proportional to gas concentration	CO2, VOC's	Very Good	Very Good	Good	Very Good	substantial current draw when light source active

Cross sensitivity/drift/aging effects

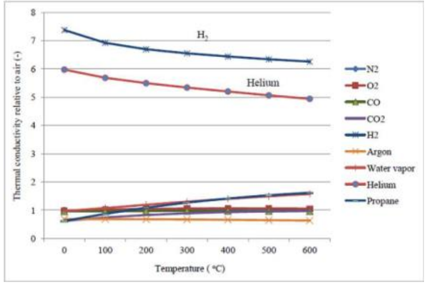
From the available technologies, it is critical to understand sensor response to analyte, cross sensitivity, signal to noise ratio as well as aging properties.

TC and Spectroscopy measure physics behavior, not chemical behavior

H2 Sensor: Principle of operation

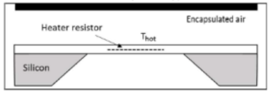
OPERATING PRINCIPLE

The elements operate on the thermal conductivity principle. The sensing element is open to the atmosphere under test and the reference element is supplied sealed in reference air in a second similar package. The response of the devices is dependent upon the difference between the thermal conductivity of the atmosphere under test and the reference air. When the atmosphere under test has a thermal conductivity higher than the reference air, the sensing element loses more heat to the surroundings than the reference element. This increased heat loss causes a cooling of the sensing element and a subsequent reduction in the resistance of the sensing element compared to the reference element. Two identical MEMS devices are glued on separated ceramic headers and wire bonded.

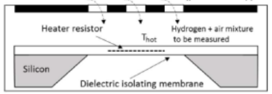


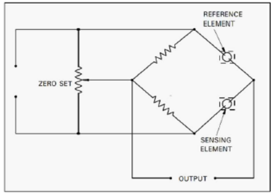
- Gas detection operates on the principal of thermal conductivity
- The sensing elements are made up of a micro machined diaphragm with intrinsically safe embedded planar heater resistor meander
- The typical maximum operating temperature of the heater is 450°C at 3Vdc
- A Wheatstone bridge circuit is used for monitoring the sensing elements
- The bridge circuit is supplied with 3Vdc and is pulsed on and off through an N-Channel MOSFET
- A microcontroller is used to control the MOSFET and subsequently the power consumption of the bridge
- Power consumption of the bridge circuit is approximately 150mW in continuous operation, but is cycled for 35msec “on time”/350 msec “off time”
- The bridge circuit provides a difference voltage between the reference leg and sensing leg reducing the affect of bridge supply voltage variation
- In the current configuration, gas detection uses an active and reference sensing element
- Using active and reference elements built on the same technology in a bridge circuit allows for temperature compensation
- In operation as the thermal conductivity of the atmosphere varies, the effective resistance of the heater varies causing a bridge output voltage differential change

The reference element TC-1326-AS is covered with a sealed metal cap and encapsulated in reference air.



The sensing element TC-1326-A is covered with a perforated metal cap allowing air/gas mixture access (here below).

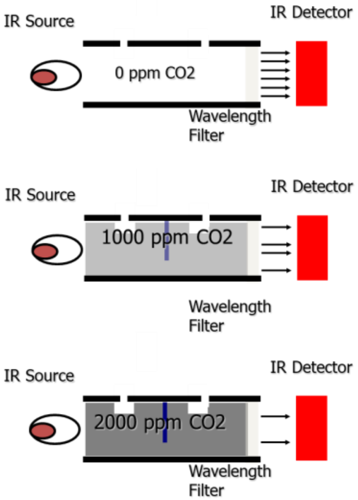


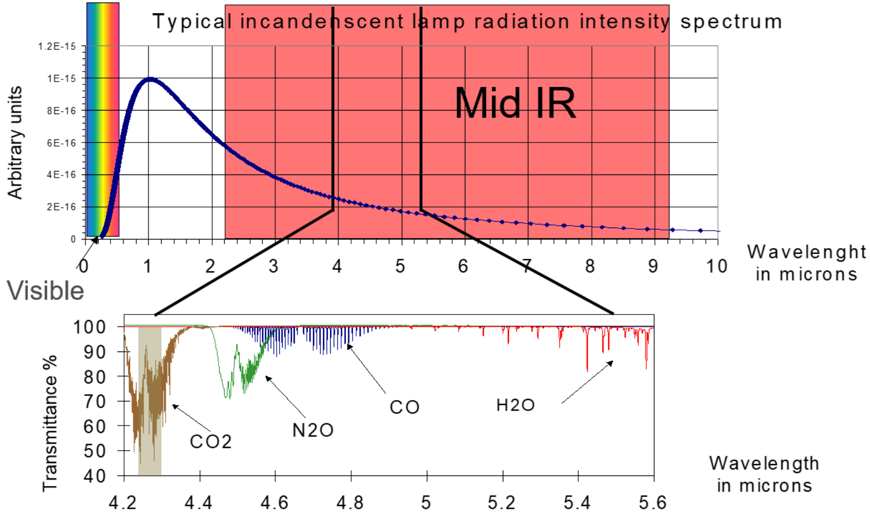


CO2 Sensor: Principle of Operation

Gas molecules have a number of vibration-rotation resonant frequencies. These frequencies are fundamental characteristics of the molecule. For most of gases these frequencies are located in IR spectral band of EM radiation in 2-10 micron wavelength. Absorption of infrared radiation leaves gas molecules in an excited state, which de-excites by colliding with other molecules, raising gas temperature and/or pressure.

- Target gas absorbs radiation at signature wavelength
- Filter isolates wavelength that reaches detector
- More gas in chamber leads to lower signal to detector
- NDIR – non dispersive IR relates to the method of selecting the signature wavelength – with narrow bandwidth IR filter



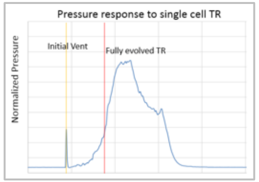


Tramsmittance spectra for N2O, CO , CO2 , and H20 vapor at 100 ppm-meters concentration

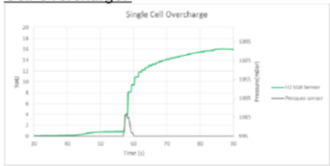
Auto OEM testing observations:

Air Pressure Sensor: Inconsistent performance

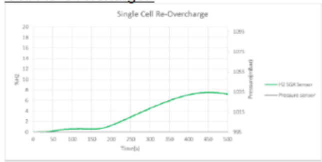
- ✓ Small, inexpensive, and ubiquitous
- ✓ Durable
- Too sensitive to Pack volume/venting effects
- Weak signal to noise ratio
- Must have fast ASIC to observe (<20 msec typ pressure rise)
- Cannot detect slow venting from lower SOH cells
- Cannot detect specific gases
- ***Type 1/Type 2 faults in the field***



Cell Overcharge:



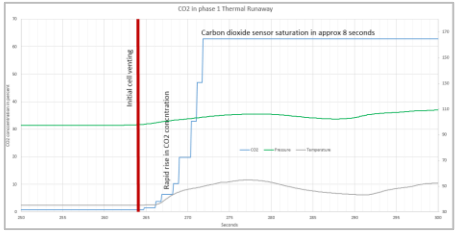
Cell Re-Overcharge:



Fails to detect slow venting

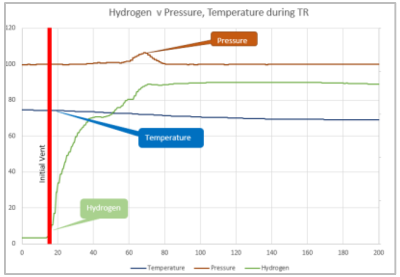
CO_2 IR Spectroscopy Sensor: consistent performance

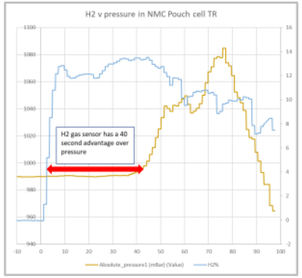
- ✓ 5 to 8 second response time
- ✓ Durable, stable in long term applications
- ✓ No cross sensitivity issues
- ✓ Strong signal to noise ratio
- ✓ Low risk of Type 1/Type 2 faults
- Higher power consumption
- Larger sensor footprint
- ➢ ***Useful for larger enclosure spaces for asphyxiation hazard***



H_2 Thermal Conductivity Sensor: consistent performance

- ✓ <1 to 3 second response time (faster than pressure)
- ✓ Durable, stable in long term applications
- ✓ Strong signal to noise ratio
- ✓ Only cross sensitive to He, not present in packs
- ✓ Low risk of Type 1/Type 2 faults
- ✓ Low power consumption
- ✓ Small sensor footprint
- ➢ ***Automotive/small pack applications for explosion hazard***





Gas sensors have substantial advantages in detecting even small cell TR venting

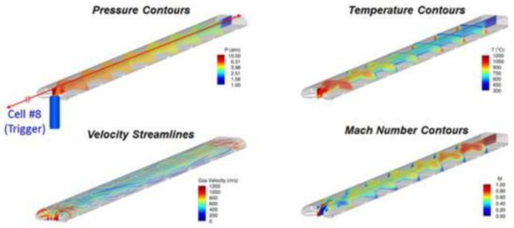
TR plasma plume velocity:

Ejecta plume velocities:

(Srinivasan, ECS 2020)

- LG HG2 18650 cells in pack arrangement
- Velocity profile modeled and verified with HS camera
- Ejecta plume velocity can exceed 200m/s and can even approach Mach
- Plume velocities and superheated gas substantially accelerate gas diffusion within the vapor space of a pack/enclosure

Velocity flow field within pack

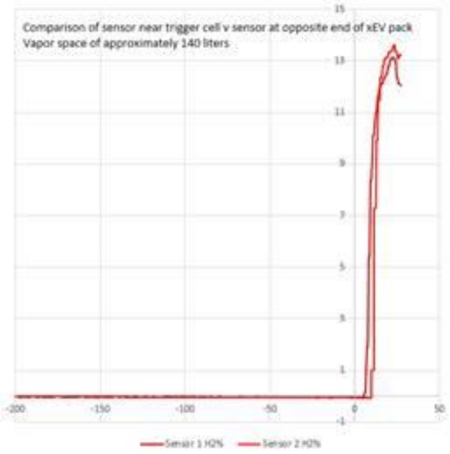


Supplementary Figure S5. Ejecta flow along the vent channels as predicted by CFD simulation.

Testing performed in large format traction battery pack:
Multiple tests performed with sensor proximate to trigger cell and at maximum distance from trigger cell (approximately 2m)

- Gas sensor response characteristics support conclusions of Srinivasan's study
- Sensor location within the enclosure space has little to no impact on response time
- Response data within measurement error

H2 sensor location not critical



Gas Sensors anywhere in "airspace" of pack can detect within seconds

Gas evolution and cascading TR

Relationship between signals and environment:

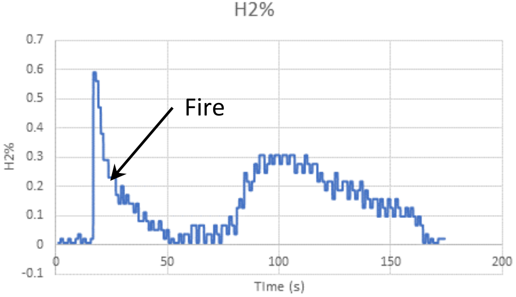
- Ratio of cell SOC/SOH(thermal capacity) to free air volume will drive sensor location, response characteristics (ie, smaller cells with lower SOC's venting will generate less gas to detect in large dilution volumes
- Current approach has been generally insensitive to dilution volumes
  - Superheated plume will initially drive gases to top of enclosure space, CO2 will cool and settle, hydrogen will try to escape via leaks/permeation
  - Gases can remain above LEL for hours inside enclosure

Cascading TR:

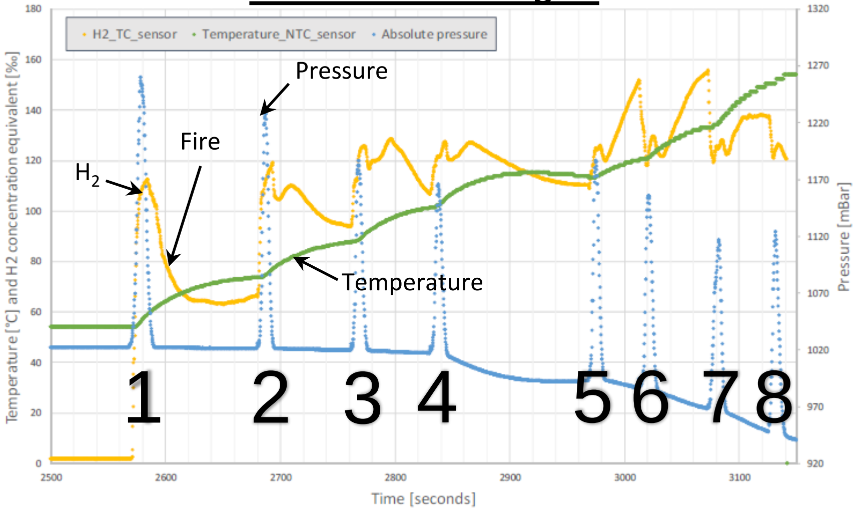
- Shown at right, prismatic cells in cascading TR in traction pack of ~150L dilution volume
- Concentration of H_2 (yellow) continues to rise after consuming available oxygen in the pack with each incremental cell venting
- Gas temperatures throughout the pack increase and sensor data limited by electronics overtemperature condition
- Gases can linger within enclosure for extended period
  - Once above LEL, diurnal temp changes can affect oxygen available for gas combustion

20 000l dilution volume (ISO container)

21700 cell



Prismatic cascading TR

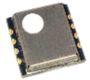


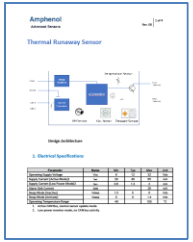
Multiphysics sensors with high concentration calibrations can track performance of TR countermeasures

Amphenol
www.amphenol.com

Surface Mount REDTR MiniModules for BMS mounting:


TELAIRE
Internal CO_2 Sensor for Automotive Applications
NDIR CO_2 Single Channel, Diffusion Sampling Method
Amphenol
Advanced Sensors




Amphenol
Advanced Sensors
Thermal Runaway Sensor


Thermal Runaway Sensor
Amphenol
Advanced Sensors

Components for BMS or assembly:

- H_2,CO_2 sensors for surface mount
- Auxiliary P, RH, T sensors
- Analog/CAN/I2C/SPI/LIN communications
- Power management on board
- Can operate independent of BMS with «wakeup»
- Small package size
- >20 year design life
- Can detect single v cascade TR
- AEC Q
- In production with multiple OEM's

Components to surface Mount on BMS, or as "sentinel" standalone device with CAN BMS wakeup

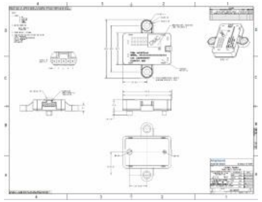
RedCAN: Plug and Play fully compensated detection capabilities

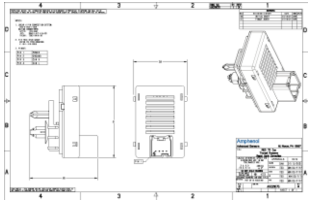
Content and Features:

- H2/Rh/T/P Sensor
- CAN communications
- Fully compensated gas sensor assembly
- >20 year design life
- Can detect single v cascade TR
- Plastic enclosure with integrated mounting features
- Designed to meet ASIL requirements

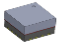
Ideal for:

- ***Applications with remote or “off shelf” BMS***
- ***Aerospace eVTOL, eAero, applications***
- ***Mobile energy storage***





Amphenol TR family

System/ Configuration	Amphenol Development Tool AX220054 Engineering Tool	Amphenol TRDU5 Production	Amphenol RedCAN Fully packaged H2/RhT assembly w/ CAN AX221075 Production	Amphenol CO2 Detection select solder or module assembly AX221087 Production	Amphenol Gen 2.0 H2 miniPCB Surface AX221058 Production	Amphenol T8200 AX221042 In Development	Amphenol NPB surface mount pressure sensor In validation	Amphenol BLD1 Fully packaged H2 w/ CAN Production	Amphenol BLD2 Fully packaged H2 & CO w/ CAN Production
Pressure Range	260 to 1260 mBar	20mbar to 2500mbar	50 to 200 kPa	260 to 1260 mBar	Optional	260 to 1260 mBar	260 to 1260 mBar or 50 to 300 kPa (other pressure ranges available)	N/A	N/A
Pressure accuracy	± 1%FSO	± 0.1mBar	± 1.5%FSO	± 0.1mBar			± 0.1mBar	N/A	N/A
Gas	**H2 / CO2 / P/ RhT**	**H2/P/CO/NH3 with RhT compensation**	**H2/P/Rh/T**	**CO2**	**H2 w/ RhT compensation**	**Co2 / H2/ Rh/T**	**Press only**	**H2 with RhT compensation**	**H2/CO with RhT compensation**
Temperature (-40 to 150C ; <±2 ℃)	Y	-40℃ to 85℃	-55 to 105C	Y	Y	Y	Optional	-40 to 85C	-40 to 85C
Relative Humidity (0 to 100% <±4%)	Y	5%- 95%± 3%RH	Y	N/A	Optional	Y	N/A	0 to 95%RH	0 to 95%RH
Power Supply	10 to 32V DC max	9-18V	12V / 24V	6 to 12V, 32V DC max	3V to 5V	6 to 12V, 32V DC max	1.7V~3.6V	9 V to 18V	9V to 18V
Power mode	single	single	variable	variable	single	single mode/ relay	single	single	single
Q Current (µA)	30mA	<80mA	10 mA / < 25uA* *sensor not active	10 mA / < 25uA* *sensor not active	12mA / <0.1mA *	18-30 VAC RMS, 50/60 Hz, or 10.8 to 42 VDC, polarity protected 0.50 A at 125 VAC, 1A 24 VDC	35uA	<25mA / <100uA sleep mode	<25mA / <100uA sleep mode *sensor not active
Interfaces	CAN 2.0A ISO 11898 SAE J2284	LIN 2.1	CAN 2.0A ISO 11898 SAE J2284	LIN 2.1	Ratiometric	MS/TP RS485 TCP IP	18 bit DSP I2C & SPI	HS CAN	HS CAN
Wake up BECM	Yes	No* *BMS continuous powered	Optional	Yes	No	Relays on H2 nd Co2 sensors	N/A* *(capable if CANFD xceiver chip is used)	No	No
Physical Dimension (module)	66 x 42x 12mm	35 x 39 x 37mm	38 x 51 x 48mm	47 x 2 x 10mm	25 x 20 x 1.5 mm surface mount	116 x 81 x 27mm	4 x 4mm QFN surface mount	35 x 39 x 37mm	35 x 39 x 37mm
Automotive	UL94 Planned	AEC Q104	N/A	AEC Q100	AEC Q104	N/A	AEC Q100	AECQ-104	AECQ-104
Additional features	IP5K0, w/ hsg; optional coolant breach/water intrusion detection	IP6K7 w/ hsg	IP6K7	IP6K7	IP6K4K	UL94 5VA; CE and RoHS, REACH, and WEEE compliant	IP5K0	IP6K7	IP6K7
Samples	4 wks ARO	4 wks ARO	4 wks ARO	4 wks ARO	4 wks ARO	4 wks ARO	4 wks ARO	4 wks ARO	4 wks ARO
Available	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

**** Note: Any Amphenol variant can be installed in custom plastic housing as needed**

Background

OEM / Amphenol Dialog on Battery Cell Venting October 2021 Countermeasures and Field Experiences

NTSB Report – Jan 2021 (T. Barth)

<u>Safety Issues:</u>

• Inadequacy of emergency response guides for minimizing risks to first and secondary responders from Li-ion battery fires

• Gaps in safety standards for high-speed, high-severity crashes involving Li-ion battery vehicles

<u>Recommendations:</u>

NHTSA:

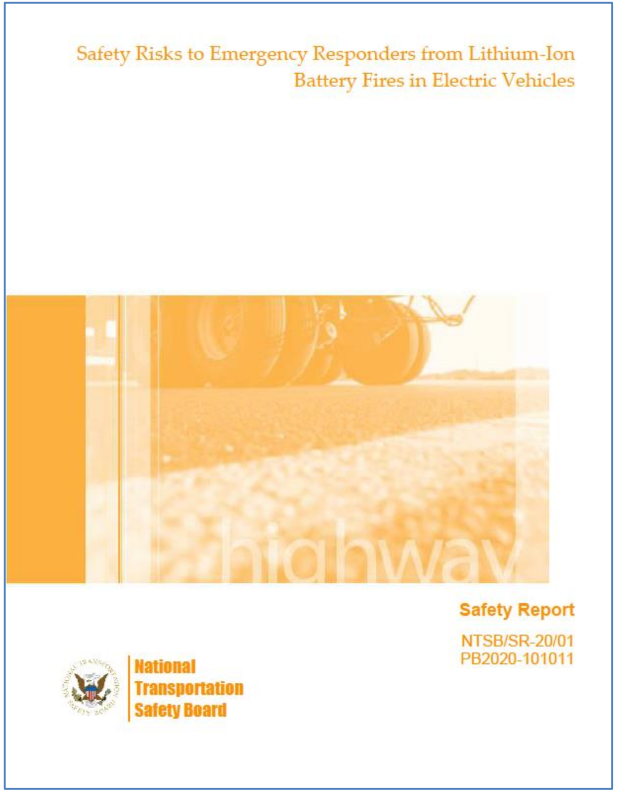
• Incorporate Emergency Response Guides (ERGs) into NCAP
• Continue research on mitigating or de-energizing stranded Energy

EV Manufacturers (cars, trucks, buses in USA)

• Model ERGs on ISO 17840 and SAE J2990
• Vehicle specific information on fire fighting, stranded energy, safe storage

Responder Associations (NFPA, IAFC, IAFF, AFTC, NVFC, TRAA

• Inform members of risks and available guidance



https://youtu.be/J6eS6JzBn0k

Surface vehicle standard practice to supress fire and relieve stranded energy

Response vehicles typically only have ~500 to 1500 gallons of water available on board

Current
"Water Immersion"
& "Large amounts of water"

New Development:
AVL Water "spike" into pack substantially reduced water usage

New field Tools for First Responders:
"Spike" systems from Murer, Rosenbauer

First
Application Example

- Renault Zoe Q210
  - Nominal power: 46 kW
  - Max. power: 65 kW
  - Battery capacity: 22kWh
  - Pouch Zellen
- Battery ignited by penetration
- Max temperature after penetration: >600°C
- Water consumption: approx. 300l
- Extinguishing time: 20min
  ->15l/min water
- Temperature after extinguishing: <90°C
- After extinguishing the vehicle was transferred in a container with water

Press release

rosenbauer

October 7, 2021

New extinguishing system for burning traction batteries in electric vehicles

- Safe deployment due to short deployment time on the burning vehicle and system activation with sufficient distance
- Efficient firefighting by cooling the modules and cells in the battery housing
- Lead users confirm the efficiency and ergonomics of the system

Rosenbauer launches a new extinguishing system for burning traction batteries in electric vehicles. The system can be used to safely and efficiently extinguish lithium-ion based high-voltage batteries. It enables direct cooling of the battery modules, or the cells within the modules, and thus a quick stop to the propagation of the thermal runaway of the cells.

The safety of the firefighter was the top priority during the development and is achieved by the fact that the firefighter only being in the vicinity of the burning vehicle for a very short time and the system is activated from a safe distance. The extinguishing system applies the water exactly where it is needed: to cool the cells and modules in the battery housing. Extinguishing thus takes place in a very resource-efficient way and reduces the spread of flue gases to a minimum.

5,000 to 30,000 gallons → **80 gallons**

- "Spike systems" need identified locations for piercing to avoid striking HV bussing & cables
- Pouch cells will self discharge when exposed to water, CID's in prismatic and cylindrical cells may prevent discharge

Stranded Energy and Second Responder safety need to be addressed

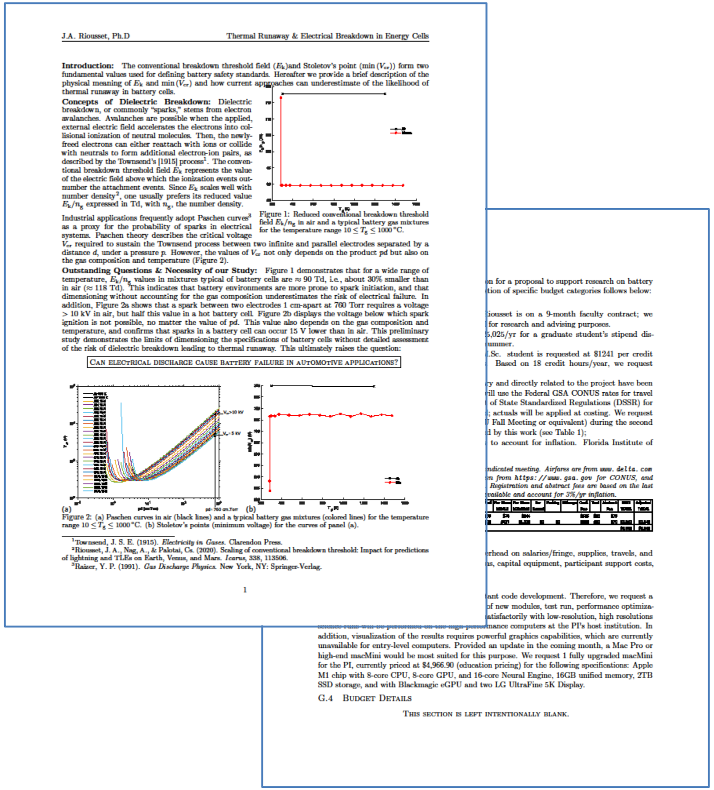
Venting Physics: Ad Hoc Group investigating HV Discharge w/ venting

B. Engle (Amphenol), Dr. Riousset, NASA/Florida Institute of Technology, T. Wilcox(VW), Dr. Harenbrock (M+H), Vinay Prenmath (SWRI), Dr. Essl (ViV), A Thaler (ViV), T. Bohn (ANL)

Background: Empirical evidence suggests vented gases create environment prone to HV discharge and EMI events. Damage inconsistent with flame temperatures and EM events have been witnessed

- Initial model shows 30% reduction in E_k required for electron avalanche w/ dry gas (in the 100's of volts)
- Paschen curves move down and left
- Need to add to model:
  - Relative humidity
  - Particulates
- Testing:
  - In situ battery cell testing with electrodes
  - Model verification with dry/wet gas samples

Need budget to further develop model and test


J.A. Riousset, Ph.D Thermal Runaway & Electrical Breakdown in Energy Cells

Introduction: The conventional breakdown threshold field (E_k)and Stoletov's point (min (V_{cr})) form two fundamental values used for defining battery safety standards. Hereafter we provide a brief description of the physical meaning of E_k and min (V_{cr}) and how current approaches can underestimate of the likelihood of thermal runaway in battery cells.

Concepts of Dielectric Breakdown: Dielectric breakdown, or commonly "sparks," stems from electron avalanches. Avalanches are possible when the applied, external electric field accelerates the electrons into collisional ionization of neutral molecules. Then, the newly-freed electrons can either reattach with ions or collide with neutrals to form additional electron-ion pairs, as described by the Townsend's [1915] process[1]. The conventional breakdown threshold field E_k represents the value of the electric field above which the ionization events outnumber the attachment events. Since E_k scales well with number density[2], one usually prefers its reduced value E_k/n_g expressed in Td, with n_g, the number density.

Figure 1: Reduced conventional breakdown threshold field E_k/n_g in air and a typical battery gas mixtures for the temperature range $10 \leq T_g \leq 1000\,°C$.

Industrial applications frequently adopt Paschen curves[3] as a proxy for the probability of sparks in electrical systems. Paschen theory describes the critical voltage V_{cr} required to sustain the Townsend process between two infinite and parallel electrodes separated by a distance d, under a pressure p. However, the values of V_{cr} not only depends on the product pd but also on the gas composition and temperature (Figure 2).

Outstanding Questions & Necessity of our Study: Figure 1 demonstrates that for a wide range of temperature, E_k/n_g values in mixtures typical of battery cells are ≈ 90 Td, i.e., about 30% smaller than in air (≈ 118 Td). This indicates that battery environments are more prone to spark initiation, and that dimensioning without accounting for the gas composition underestimates the risk of electrical failure. In addition, Figure 2a shows that a spark between two electrodes 1 cm-apart at 760 Torr requires a voltage > 10 kV in air, but half this value in a hot battery cell. Figure 2b displays the voltage below which spark ignition is not possible, no matter the value of pd. This value also depends on the gas composition and temperature, and confirms that sparks in a battery cell can occur 15 V lower than in air. This preliminary study demonstrates the limits of dimensioning the specifications of battery cells without detailed assessment of the risk of dielectric breakdown leading to thermal runaway. This ultimately raises the question:

CAN ELECTRICAL DISCHARGE CAUSE BATTERY FAILURE IN AUTOMOTIVE APPLICATIONS?

(a) (b)

Figure 2: (a) Paschen curves in air (black lines) and a typical battery gas mixtures (colored lines) for the temperature range $10 \leq T_g \leq 1000\,°C$. (b) Stoletov's points (minimum voltage) for the curves of panel (a).

[1] Townsend, J. S. E. (1915). *Electricity in Gases.* Clarendon Press.
[2] Riousset, J. A., Nag, A., & Palotai, Cs. (2020). Scaling of conventional breakdown threshold: Impact for predictions of lightning and TLEs on Earth, Venus, and Mars. *Icarus*, 338, 113506.
[3] Raizer, Y. P. (1991). *Gas Discharge Physics.* New York, NY: Springer-Verlag.

1

addition, visualization of the results requires powerful graphics capabilities, which are currently unavailable for entry-level computers. Provided an update in the coming month, a Mac Pro or high-end macMini would be most suited for this purpose. We request 1 fully upgraded macMini for the PI, currently priced at $4,966.90 (education pricing) for the following specifications: Apple M1 chip with 8-core CPU, 8-core GPU, and 16-core Neural Engine, 16GB unified memory, 2TB SSD storage, and with Blackmagic eGPU and two LG UltraFine 5K Display.

G.4 BUDGET DETAILS

THIS SECTION IS LEFT INTENTIONALLY BLANK.