The use of Sensors to Detect Lithium-Ion Cell Venting Events in EV Batteries to Allow Preventative Actions

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Lithium-ion and lithium-metal cells are known to undergo a process called thermal runaway during failure conditions. Thermal runaway results in a rapid increase of battery cell temperature and pressure, accompanied by the release of flammable gas. These flammable gases will often be ignited by the battery’s high temperature, resulting in a fire. In addition to the combustion of these gases as they vent, another concern is the accumulation and potential explosion of the gases.

USA Federal Aviation Administration
The use of Sensors to detect Lithium Ion Cell venting events in EV Batteries to allow preventative actions

Neil Roberts
Agenda

- Company overview
- Causes of thermal runaway (TR)
- The breakdown timeline
- Vented chemicals
- Solutions
Amphenol Corporation

Amphenol
Connecting People and Technology

>120 Companies in 8 Groups • > 80,000 Employees • > 8.2 Billion US$ Sales 2018
Causes of Failure

- Overcharge (electrolyte decomposition, dendrite formation, phase stability of materials)
  - Example: charger failure, wrong charger

- Crush (crash, drop test) (multi layer strike between electrodes, electrodes and construction elements)
  - Example: Crash, damage from road

- Thermal exposition (multi layer strike mainly via separator failing, activation self heating process, balance heat generation/heat injection and heat dissipation)
  - Example: Production quality issues, vibration

- High voltage/current exposition (local overheating, high voltage breaking through)
  - Example: Charge or discharge fail, faulty monitoring

- External short circuit
  - Example: crash, maintenance, detritus in pack
Heat rate grows exponentially, and becomes very difficult to extinguish in later stages

# Stages of Thermal Runaway

<table>
<thead>
<tr>
<th>Stages of TR</th>
<th>Hazard</th>
<th>Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage 1: Offgas</td>
<td>Flammable offgas</td>
<td>80-120 °C</td>
</tr>
<tr>
<td>Stage 2: Burning Packaging</td>
<td>Combustion heat</td>
<td>120-200 °C</td>
</tr>
<tr>
<td>Stage 3: Total</td>
<td>Thermal runaway, high heat</td>
<td>&gt;200 °C</td>
</tr>
</tbody>
</table>

Smoke, fire, and even explosion, are the most common features of thermal runaway.
Regulatory Status

CHINA EV Safety & EV Battery Safety Regulation (GB DRAFTS)
• Latest draft, 2019, Jan
• Expect effective date July, 2020

AUTOMOTIVE THERMAL INCIDENT WARNING
China Lead Advocate
• Lead efforts at UN to adopt testing protocol in GTR
• First cc 5.2.7.2 Battery pack or system shall have occupants’ protection analysis and validation under thermal propagation per 5.2.7.2. The battery pack or system shall provide an alarm of thermal event 5 min prior to the hazard occurrence in passenger compartment. The hazard is caused by thermal propagation triggered by single cell thermal runaway.

5 Minute Warning
• Detect and alert occupants
• Allow occupants to safely exit vehicle within 5 minutes
• * Insufficient time for safe extraction if occupant incapacitated (based on US 1st responder 8.5 minute “first on scene”
• Draft does not consider first/second responder TR events

ADDITIONAL DRAFT REGULATIONS / SAE:
• UN GTR 20 (EV Safety) cites requirement to protect occupants; does not contain pass/fail requirements
• Amphenol chairs SAE battery sensors subcommittee, member of G27/AE7D, Battery Safety committees
Readings of the sensors in test V1. The dashed line labeled with “visible venting” indicates the time when a venting was visible outside of the battery housing. All sensors detect the thermal runaway effects of the cell within a time window of about 20 s.

Extract from: Fast Thermal Runaway Detection for Lithium-Ion Cells in Large Scale Traction Batteries Batteries 2018,4,16 By Sascha Koch
Sensor readings during test V2. The dashed line indicates when the trigger cell is fully penetrated. The detection time window is about \( t_{\text{detectWin}} \) 44 s wide, mainly stretched by the late drop in the cell voltage.

Extract from: Fast Thermal Runaway Detection for Lithium-Ion Cells in Large Scale Traction Batteries Batteries 2018,4,16 By Sascha Koch
Timing of gas release during thermal runaway

CO₂ is detectable before the process becomes violent. (~ 40 seconds)

Data from: RSC Adv., 2014, 4, 3633
Total gas released during thermal runaway for 100% SOC cells

Majority of total gas released during thermal runaway is CO, CO₂, and H₂ depending on chemistry — Higher concentration — easier to detect

25% of cell weight is converted to gas during thermal runaway

The majority of 1st ventilating gas is CO₂, and is produced by solid-electrolyte interphase (SEI) decomposition.

Figure adapted from: Journal of Power Sources 307 (2016): 56-62.
Detection Considerations

Constraints:
- size/cost
- response time
- power consumption
- temperature operating range
- false alarm (α and β types)
- diagnostics
- data transmission
- ASIL (ISO26262) compliance
- Lifetime

Considerations:
- Construction of the battery pack
- Location of the sensor
- Efficiency to detect all failure modes (slow, fast)
Detection Solutions

<table>
<thead>
<tr>
<th>Measure</th>
<th>Sensor</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss of cell voltage</td>
<td>Voltage</td>
<td>too slow / not effective for high cell configurations</td>
</tr>
<tr>
<td>Heat generation</td>
<td>Temperature</td>
<td>too slow / not enough sensing points</td>
</tr>
<tr>
<td>Gas generation</td>
<td>Gas sensor</td>
<td>consider cross sensitivity / long term drift</td>
</tr>
<tr>
<td>Build up internal pressure</td>
<td>Pressure</td>
<td>cell v air volume/venting; pack shell breach</td>
</tr>
<tr>
<td>Swelling of cell</td>
<td>Force</td>
<td>distinguish thermal effect; signal/noise</td>
</tr>
<tr>
<td>Smoke generation</td>
<td>Particulate or Smoke</td>
<td>need particulate products / long term stability</td>
</tr>
<tr>
<td>Volatile Organic Compound</td>
<td>VOC</td>
<td>Fast / long term stability</td>
</tr>
</tbody>
</table>
Improved GAS SENSOR DETECTION – Thermal conductivity sensor (H₂ target gas)

Hydrogen gas has the highest thermal conductivity of all known gases. Thermal conductivity sensors exploit this property for detection and monitoring of hydrogen.

Thermal conductivity sensors consist of two identical elements.

Any hydrogen concentration change in the target gas causes a change in the sensor temperature which changes the resistance of the element. Then, the concentration is indicated by the resistance change.

- Do not require the presence of air/oxygen to operate
- Tested/proven intrinsically safe
- Used as safety hazardous gas sensor in field today
- Suffer less from long term drifts and not prone to contamination like catalytic and MOX sensors.

\[
\lambda_m = \sum_{i=0}^{n} \frac{y_i\lambda_i}{\sum_{j=1}^{n} y_j A_{ij}}
\]

- \(\lambda_m\) = thermal conductivity of the gas mixture
- \(\lambda_i\) = thermal conductivity of component gas i
- \(y_i, y_j\) = mole fraction of components i and j
- \(A_{ij}\) = a function, defined in equation 2
Carbon Dioxide Sensing

• Originally developed for in cabin detection, fully Automotive qualified
• Single digital output only
• 12V supply
• Firmware
  • Has operating modes (Park, Drive etc)
  • CO₂ output

• Benefits
  • Developed
  • Long term reliability known
  • Batteries emit a lot of CO₂ in failure

• Issues
  • response time: <10 sec to record event
  • event may take seconds to reach sensor
  • relative free volume in pack
Pressure Sensor

Benefits:
• small and low cost
• very fast (msec) time response
• low power consumption

Issues:
• Dependent upon air restriction level/venting
• Sensitivity based on air volume capacitance
• Cell size, SOC

• Type I faults: (False positive)
  • Sticking poppet vent
  • Plugged hydrophobic vent
  • High humidity/battery under load

• Type II Faults: (Fails to detect)
  • Will not detect “slow” TR
  • Will not detect “slow” venting
  • Will not detect explosive gas
  • Will not detect hazardous gas

Pressure can work with gas sensors, but not alone to detect gas evolution
MOx / CMOS Sensor

Typical CMOS / MOx GAS SENSOR DETECTION

• **Benefits**
  • Fastest gas sensor to detect thermal runaway.
  • Broadband of gases at rather high concentration easily detected (H\textsubscript{2}, CO, CH\textsubscript{4}).
  • Several measurement technologies based on MEMS and other applicable (MOX for all reducing gases CO, H\textsubscript{2}, CH\textsubscript{4}, ... ; TCD for combustible gases H\textsubscript{2}, CH\textsubscript{4})

• **Issues**
  • Selectivity – may be confounded by pollution events present out of the battery pack, false alarm (Type I and Type II)
  • Stability – aging and temperature may generate a baseline change (compensated by SW)
  • Poisoning – contamination of metal-oxide sensitive layer leading to drop in sensitivity
  • Power consumption compared to thermal or pressure sensor
We recently observed by infrared spectroscopy that when a cell temperature rises, but before the start of TR, flammable organic compounds such as carbonate esters are ejected from the cell. This observation sheds new light on the thermal propagation processes in multi-cell Li-ion batteries.

•Rengaswamy Srinivasan Johns Hopkins University Applied Physics Laboratory
COMBINED SENSOR SOLUTION

- Uses multi gas detection principle (CO2 + H2 + pressure + (3 gas))
- Voting system: CO2/TC positive = TR; CO2 neg /TC pos = electrolyte leakage
- Pressure allows 3 vote system for layered response to different hazards
Beyond capturing initial venting

- Venting products include 4 combustible gases above their Lower Explosion Limit (LEL)*
- Electrolyte leakage on ageing cells (through seals and weakened joints) can provide Ethyl/Methyl based compounds with low boiling temperatures. Electrolyte leakage has also been shown to precede venting

According to the level of combustible gases concentrations by 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...), a solution to mitigate risks of explosion should also be investigated. The use of MEMS TC sensor with known intrinsically safe design is good option to use. CO2 measurement can be surrogate for available oxygen to support combustion (High CO2 means low O2). Diurnal pack breathing will influence the concentration over time through air exchange/diffusion.
Current Status / Activities

Sensor testing underway at multiple clients / Initial results analysis

• Amphenol kit of samples for development / R&D partners:
  • Automotive grade NPA 30 psia pressure sensors with ratiometric output on pcb with 1m wire leads for test
  • T6743 4K E Automotive CO2 sensor, AZ65A 3 gas sensor, H2, CH4 sensors
  • SGX CMOS gas sensor development kit available upon request for specialized gas detection
  • Amphenol Engineering support to setup hardware and analyze data

• University of Michigan (UofM) / Amphenol partnership to validate analytical model performance
  • Multiphysics models yielding good correlation to real world performance
  • Multiple customers have requested UofM to present work and technical papers on topic
  • Multiphysics models serve as tools to understand system and to set detection thresholds

• Data analysis / test results from multiple customers in analysis process
  • Data supports initial assumptions for calibration thresholds
  • AZ65A NO sensitivity may need to be increased; HC and CO signals high, signal derivative function can improve fault detection time
  • Need to adjust CO2 sensor Full Scale beyond 6.5 percent

• Next Steps / Actions:
  • Continue development of multi sensor platform (target CV level parts by Q3 2019)
  • Continue partner testing data analysis through July 2019
  • Continue input/support to SAE Battery Committee, SAE Battery Sensor subcommittee, and SAE Battery Safety Committees

ECS Meeting A03-0368 “Mechanical Measurements for Early Detection of Thermal Runaway Induced By an Internal Short Circuit” S. Pannala, M. Zhang, J. B. Siegel, G. B. Less, and A. G. Stefanopoulou