Funding Code 13N14685

Milestone Component

„4.3 Development Gas Detection"

GTE contribution / as of 17th February, 2020

(out of sub-project description)

Within WP 4.3, sensorial (1), electronical (2) and software components are linked, qualified and tested mainly in the laboratory. For this purpose, components of existing infrared detection systems, existing fire gas sensors and optical scattered light detectors will be used. Special consideration is given to aspects of the ship's environment such as the salinity of the air, the large geometric dimensions of the ferry decks (3) and possible disturbance variables such as cleaning agents, solvents or exhaust gases (4).

1 Sensor Selection

2 „Sensoric Platform" – Electronics

3 Sensitivity / Aspects of the Arrangement

4 Disturbance Variables

1 Sensor Selection

→ Determination of the detection target

<u>Experiments on fires of rechargeable batteries</u>

Preparation and execution of fire tests with Li-Ion bicycle batteries

A) <u>Experiments on "Detection before thermal runaway“</u>

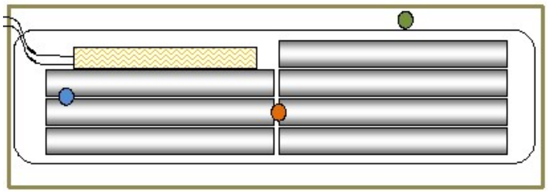


Figure 1: Sketch of the prepared bicycle battery including heating resistor

Figure 2: Prepared bicycle battery at the moment of ignition during thermal runaway

4 tests were carried out with one bicycle battery each, state of charge more than approx. 70%.

Within an additional surrounding steel sheet enclosure, the cells were brought into thermal runaway using heating resistors and extinguished immediately afterwards. Results are described in the next section. The use of an additional surrounding steel sheet enclosure is intended to reconstruct the enclosure of the battery modules found in practice. The cell temperature as well as emitted gases thus reach the outside with a delay.

<u>B Experiments on "Detection during/after thermal runaway“</u>

Further tests on the fire behavior of Li-Ion batteries were carried out (4x) with 4 bicycle batteries each within a larger aluminum box. The focus was on fire behavior and extinguishing technology. It is important to note that the enclosure of the batteries plays a role; extinguishing water cannot penetrate and any oxygen required to ignite a flame inside is also access-limited. This makes extinguishing more difficult and increases the amount of toxic smoke released.

Figure 3: Setup: 4 batteries in a box, hotplate as ignition source

Figure 4: Before ignition Figure 5: After ignition

The evaluation of this part of the tests was carried out by ISV.

<u>Results for Thermal Runaway</u>

Attempt	**T cells**	**ΔT outside**	**H_2 in 1m³**	**Lead Time** (first H_2-detection)
Prismatic Cells 1	>150°C	7 K	45 ppm	25 min
Round Cells 2	>60°C	10 K	2 ppm	< 2min; not significantly
Pouch Cells 3	>120°C	6 K	40 ppm	8 min
Pouch Cells 4	>120°C	5 K	20 ppm	3 min

Table 2: Results - measured values at the time of test termination (ignition, strong sudden release of smoke)

The cell temperature was delineated using a thermocouple on the outside of the cell.

The thermal runaway announces itself with emission of hydrogen. The gas release with a few ppm in a cubic meter of still air is very small, but still detectable. Since corrosion (metal + seawater) or combustion processes also release H_2, i.e. are expected on the ship, pure H_2 detection is not sufficient for reliable hazard detection.

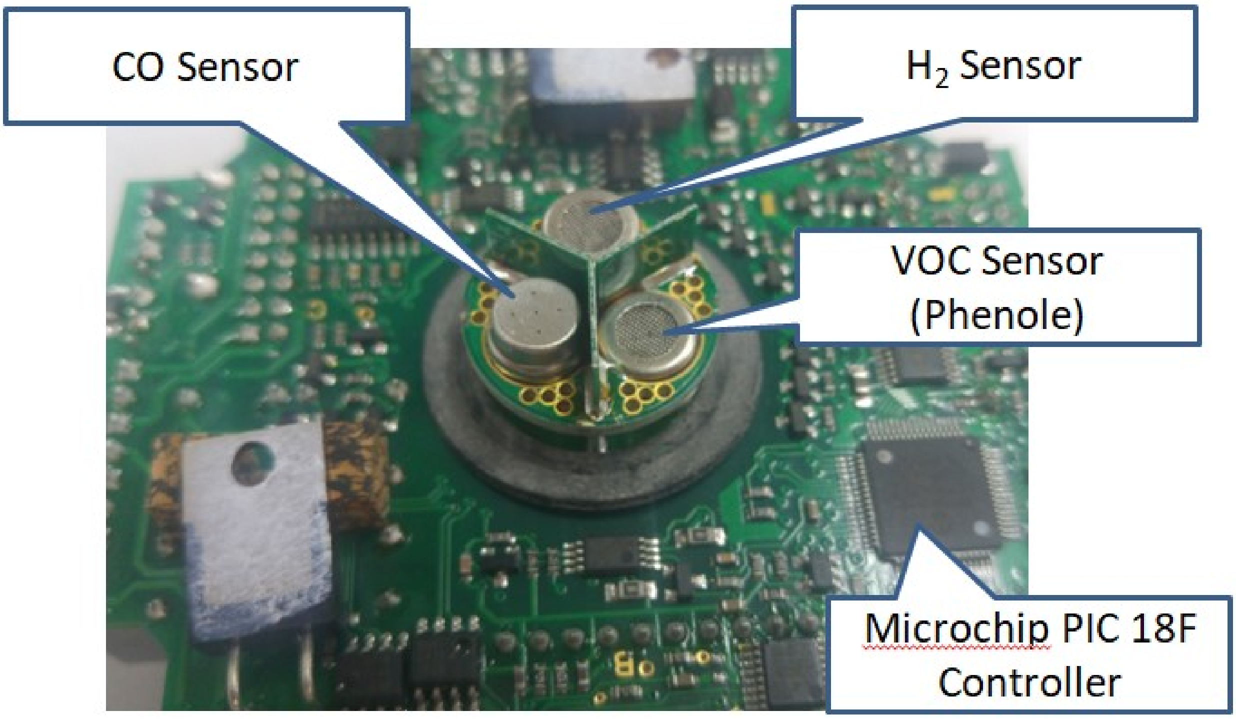
If the H_2 detection is coupled with the detection of the surface temperature, a sufficiently higher detectivity can be expected.

Therefore, the further development of sensor technology focuses on both H_2 sensor technology and IR thermographic sensors, which detect the surface temperature of the vehicles, also from below.

Measureand	**Suitability**	**Comment**
Gas H_2	yes	significantly, 5 to 50 ppm in test volume of 1 m^3
others Gases (Measurements HBRS)	limited	ethylene carbonate (depends on the cell type, not every battery uses this electrolyte) Benzene in traces (Attention: Benzene in the background as a gasoline component)
Surface Temperature	yes	significantly, 5 to 10 K increase
Aerosol (Smoke)	too late	released almost simultaneously with the ignition / explosion, after which the reaction cannot be stopped
Mid-IR (Flame-Light)	too late	flames appear in some tests released almost simultaneously with ignition / explosion, after which the reaction cannot be stopped

2 „Sensoric Platform" – Elektronics

For the gas sensors, the following existing platform is modified for sensitive detection of H_2.



Additional effort is required for heat detection of the battery surfaces:

A secondary requirement for sensors that can look down on the underside of vehicles from a low height is suitability for EX zone 1. For optical sensors, this means designing in an intrinsically safe version. Therefore, as a preliminary stage for use in a demonstrator, a sensor based on a thermopile array with 32 x 32 pixels was developed in intrinsically safe design.

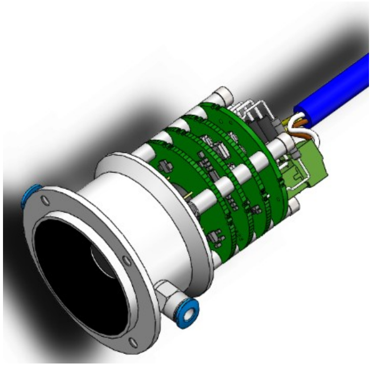


Figure 6: EX-capable IR thermal imaging sensor, development GTE

This sensor may be operated (after control via EX-approved barriers) in EX Zone 1.

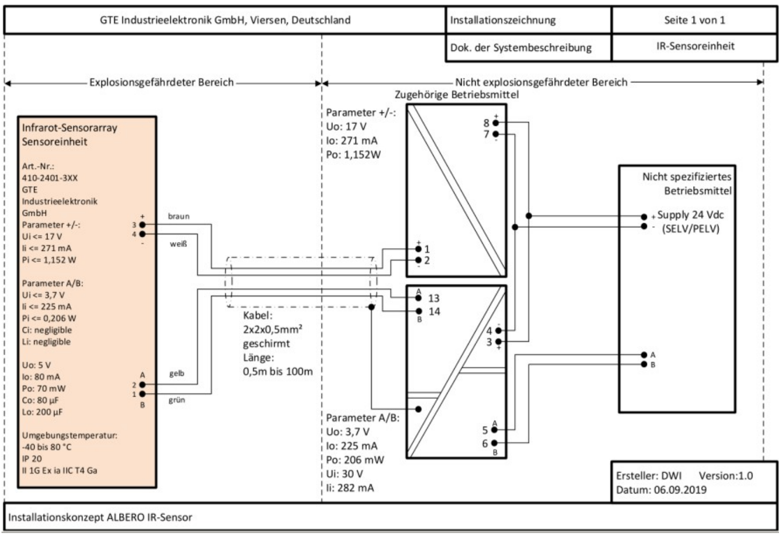


Figure 7: Electrical operating diagram of the EX-capable sensor incl. electrical barriers for intrinsically safe equipment

3 Sensitivity / Aspects of the Arrangement

The evaluation of the results of the fire tests provides:

Gas Release H_2:
Scale 10 ppm, in 1 m^3, for one cell block (ca. 40 Wh)

An estimation of the real situation shows:
Air Volume between 100 m^3 (ca. vehicle) and 10.000 m^3 (partly car deck)

The E-car battery has an energy content of up to approx. 100,000 Wh, a module approx. 10,000 Wh, 10% of which is 1000 Wh.

Therefore, we assume that the "burning" cell capacity is about a factor of 20 higher than for a bicycle battery as used in the fire tests.
(*20)
And the air volume that must be considered is at least about a factor of 100 higher.
(/100)

(20/100 = 1/5)
Hence the expected "to be detected" concentration is (approx.) 10 ppm / 5 = 2 ppm.
... if one detects "vehicle-exactly", i.e. directly at the vehicle

→ 2 ppm H2

→ vehicle-specific, i.e. detection "at" every vehicle

4 Disturbance Variables

Experiments on emission during normal charging of e-cars (BEV)

As a result of these tests with three purely electrically driven vehicles, it was concluded that H_2 is not expected to be released under normal circumstances during a charging process..

Furthermore, the typical heating of the underside of the vehicle in the area of the installed battery is only in the range below 10 K.

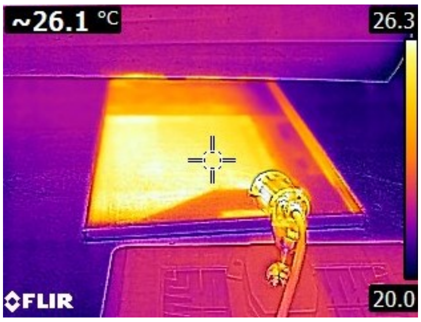


Figure 8: Thermal image of part of the underside of the vehicle

This thermal image shows one of the measurement setups for recording the underbody temperature during the charging process: in front, you can see the sensor that records the temperatures of the underbody via a reflective metallic surface.

Influence of the environmental conditions

Regarding Gas Sensor:

- Salt:

Tests of a detector with the same semiconductor sensor for H_2 in a salt mine from 2012 have shown:

No degradation of the operation of the semiconductor gas sensors used (target gases H_2 and CO) during operation for more than 1 year

- Water:

The design of a gas-sensing detector with sintered metal filter, as implemented in demonstrator 1.0, meets the requirement according to IPx4; i.e. protection against splash water from all sides..

Regarding IR Sensor:

The surface of the optics must be dry and free of dust or deposits. A sealing air device is provided for this purpose.

Our own tests have shown that a sealing air of 10 l/min sufficiently stops swirling dust (e.g. coal dust, flour).