Toxicity Study of Gases from Li-ion Batteries

CATL

Previous Achievements

I. Statement of technical rationale and justification

01. Definitions of terms related to REESS requirements and its applicability:

The following terms are used for setting the pass-fail criteria of REESS requirements;

- "**Electrolyte leakage**" (3.38)
- "**Venting**"(3.41)
- "Rupture" (3.31.)
- "Fire" (3.18.)
- "Explosion" (3.15.)

- take from Final GTR-EVS text proposal from TF3

Previous meetings have discussed the potential hazard of electrolyte leakage. However, the hazard (toxicity) of gases from lithium ion battery is not receiving due attention.

Fire Accidents of EVs Are Not Fresh News

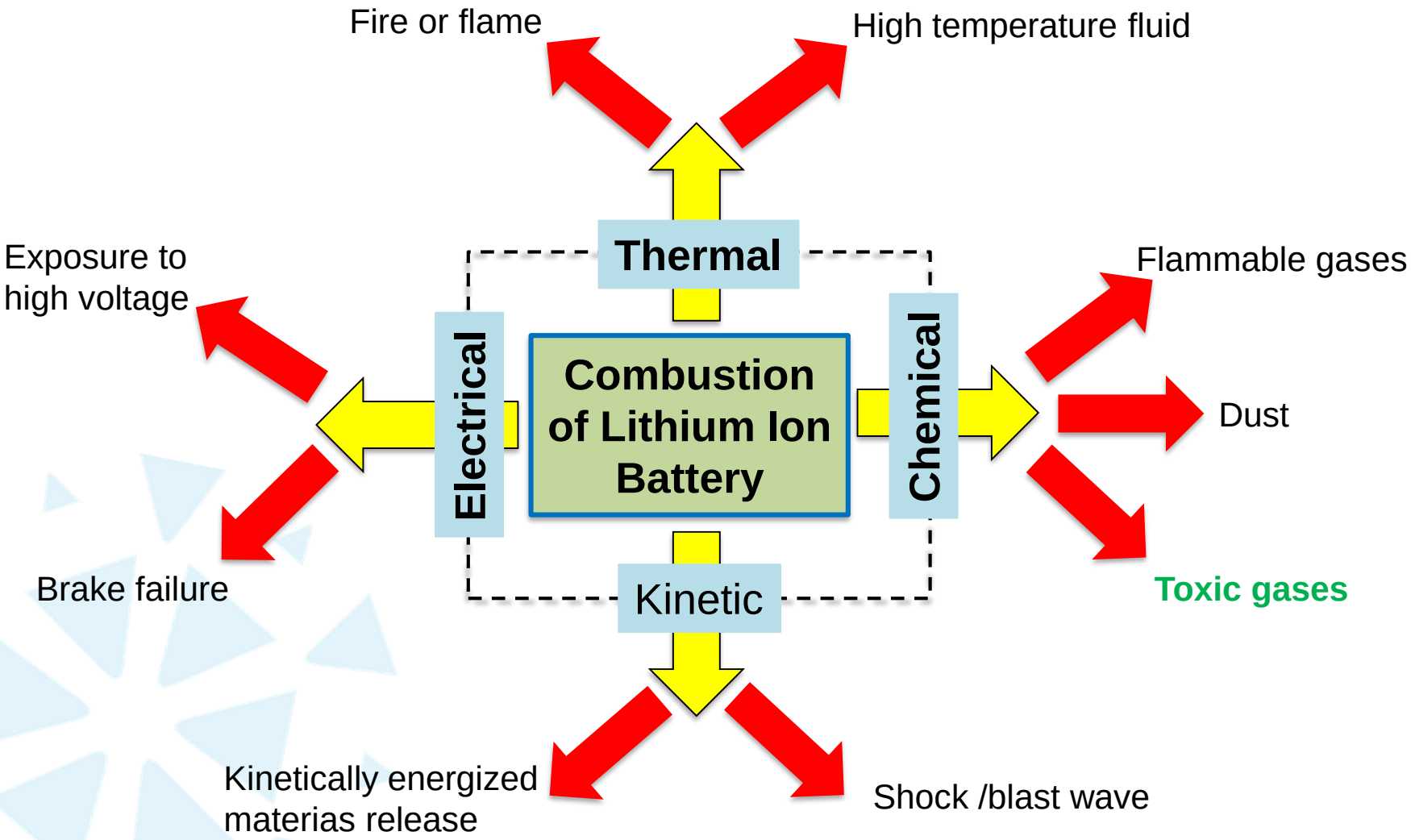
Although tremendous efforts have been made to ensure the safety of electrical vehicles (EVs), the fire accidents of EVs are not fresh news.

An EVs catched fire after the collision with another car and caused three dead in ShenZhen, China, May, 2012.

Eleven EVs catched fire and caused one dead in Xiamen, China, July, 2015.

An Tesla Model S catched fire after the collision a tree and caused three dead in Indianapolis, America, November, 2016.

Combustion of Lithium Ion Battery is the Major Reason for the Fire Accidents of EVs.



The Combustion of Lithium Ion Batteries Generates Many Kinds of Toxic gases, Threatening the Health of Passengers and Pedestrians.

Fire of Tesla Model S, America

Burning of EV, Hebei, China

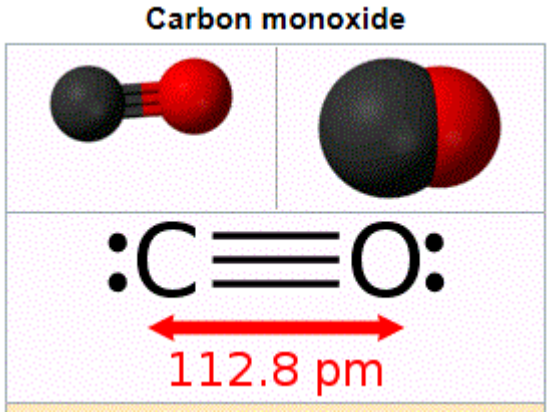
Released gases	Damage
Type1 : Oxide of carbon, sulphur and nitrogen: CO, CO_2, SO_2, NO_x …	Asphyxia & Corrosion
Type2 : hydrogen halide：HF, HBr, HCl	Strong corrosion & Strong irritation
Type3 : Organics: aldehydes, hydrocarbons…	Carcinogenicity & Cancer promotion
Type4 ：Dust	Explosion & Asphyxia

Toxic Gases From the Combustion of Lithium Ion Batteries

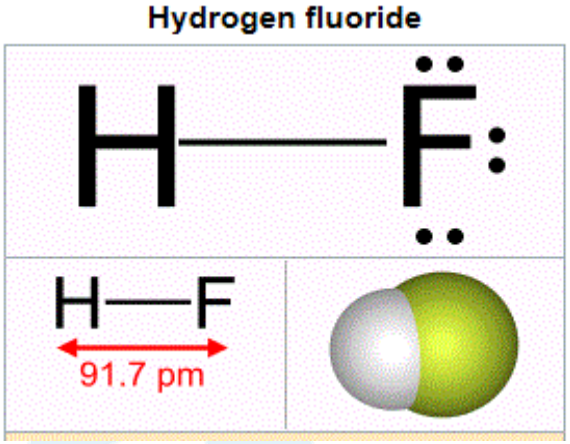
Part of Lithium Ion Battery	Material	Toxic Gases May Be Generated
Anode	Carbon material	CO, CO_2
Cathode	$LiCoO_2$	Co_3O_4
	$LiMn_2O_4$	Mn compound
	$LiNiO_2$	NiO, Li_2O
Electrolyte	$LiPF_6$	PF_5, HF, P_2O_5
	$LiBF_4$	HF, Li_2O, B_2O_3
	$LiClO_4$	$LiCl$, , Cl_2
	$LiAsF_6$	HF, arsenide
Solvent	EC，PC，DMC，EMC	CO, CO_2, aldehyde
Diaphragm	PP, PE	CO, CO_2, aldehyde

Every part of the lithium ion battery may generate toxic gases during the combustion.

Toxicity of CO, HF



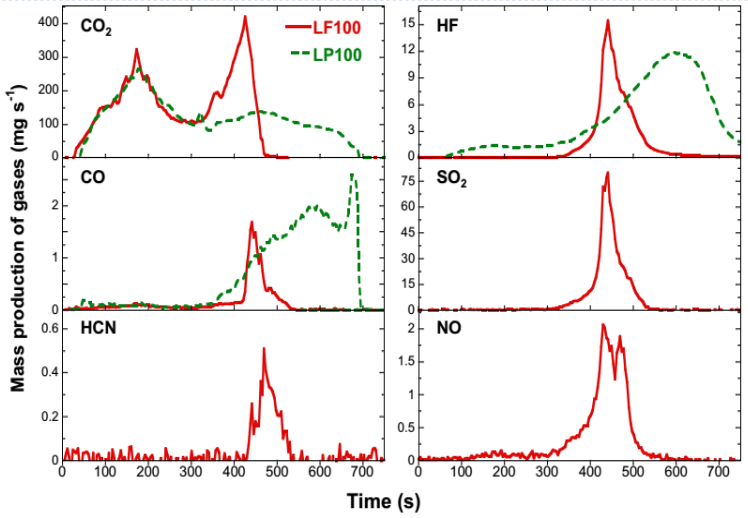
CO combines with hemoglobin to produce carboxyhemoglobin, which usurps the space in hemoglobin that normally carries oxygen, but is ineffective for delivering oxygen to bodily tissues. Concentrations as low as 667 ppm may cause up to 50% of the body's hemoglobin to convert to carboxyhemoglobin. A level of 50% carboxyhemoglobin may result in seizure, coma, and fatality.




HF burns, not evident until a day after

Upon contact with moisture, including tissue, hydrogen fluoride immediately converts to hydrofluoric acid, which is highly corrosive and toxic, and requires immediate medical attention upon exposure. Breathing in hydrogen fluoride at high levels or in combination with skin contact can cause death from an irregular heartbeat or from fluid buildup in the lungs

Research Status



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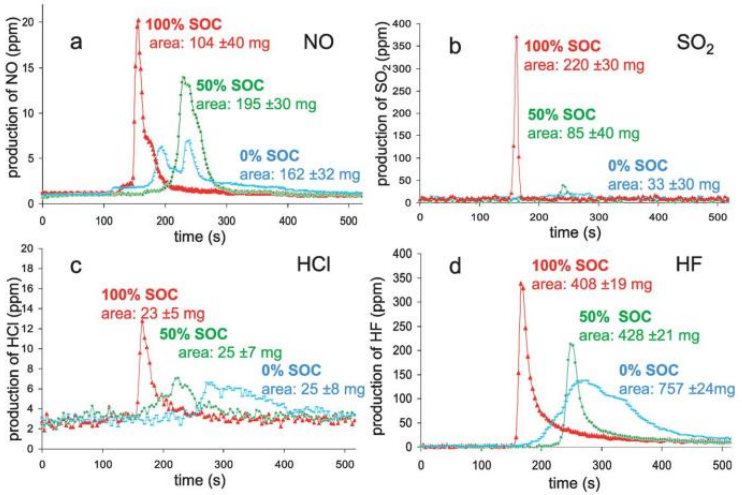

Enerav Environ. Sci.. 2012. 5. 5271

Table 3
Organic highly hazardous and extremely hazardous gaseous product from 18,650 LIBs cell (with 4 SOCs 0%, 50%, 100% and 150%) combustion analyzed by GC-Mass.

No.	Compound	CAS	Toxicity classification	LCO	LMO	NMC	LFP
1	2-Propenal (C_3H_4O)	107-02-8	I	0%, 150%	50%	0%, 50%	50%
2	Propanedinitrile ($C_3H_2N_2$)	109-77-3	I			100%	
3	Propanenitrile (C_3H_5N)	107-12-0	I	100%			
4	Naphthalene ($C_{10}H_8$)	91-20-3	II	50%, 100%, 150%		0%, 100%, 150%	
5	Carbonyl sulfide (COS)	463-58-1	II		0%		
6	Butane, 1-isocyanato- (C_5H_9NO)	111-36-4	II		50%, 100%	100%	
7	Oxirane, ethyl-(C_4H_8O)	106-88-7	II	50%, 100%	50%, 100%		
8	1,3-Pentadiene (C_5H_8)	504-60-9	II	50%, 100%		100%	
9	1-Butanamine ($C_4H_{11}N$)	109-73-9	II				0%
10	1,3-Cyclopentadiene (C_5H_6)	542-92-7	II	100%, 50%	100%	100%, 150%	
11	2-methyl-2-Propanamine ($C_4H_{11}N$)	75-64-9	II	0%, 150%	100%		100%
12	Propyleneoxide (C_3H_6O)	75-56-9	II	0%, 150%			
13	Sulfur dioxide (SO_2)	7446/9/5	III	150%			

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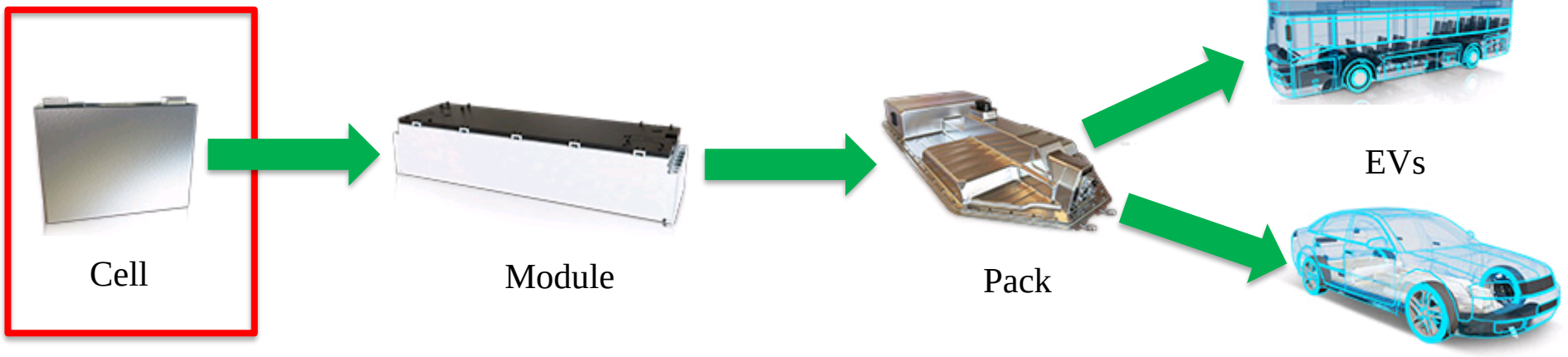
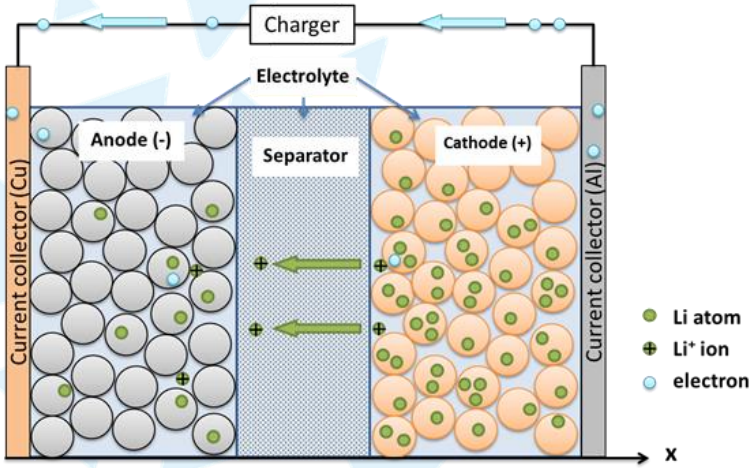
It is a pity that few studies have been conducted to study the toxicity of gases due to the combustion of lithium ion batteries.

Research Proposal: Research Gases from Single Cell First



From cells to EVs, the system is becoming more complex, and there are more substances contributing to the generation of toxic gases during the burning.

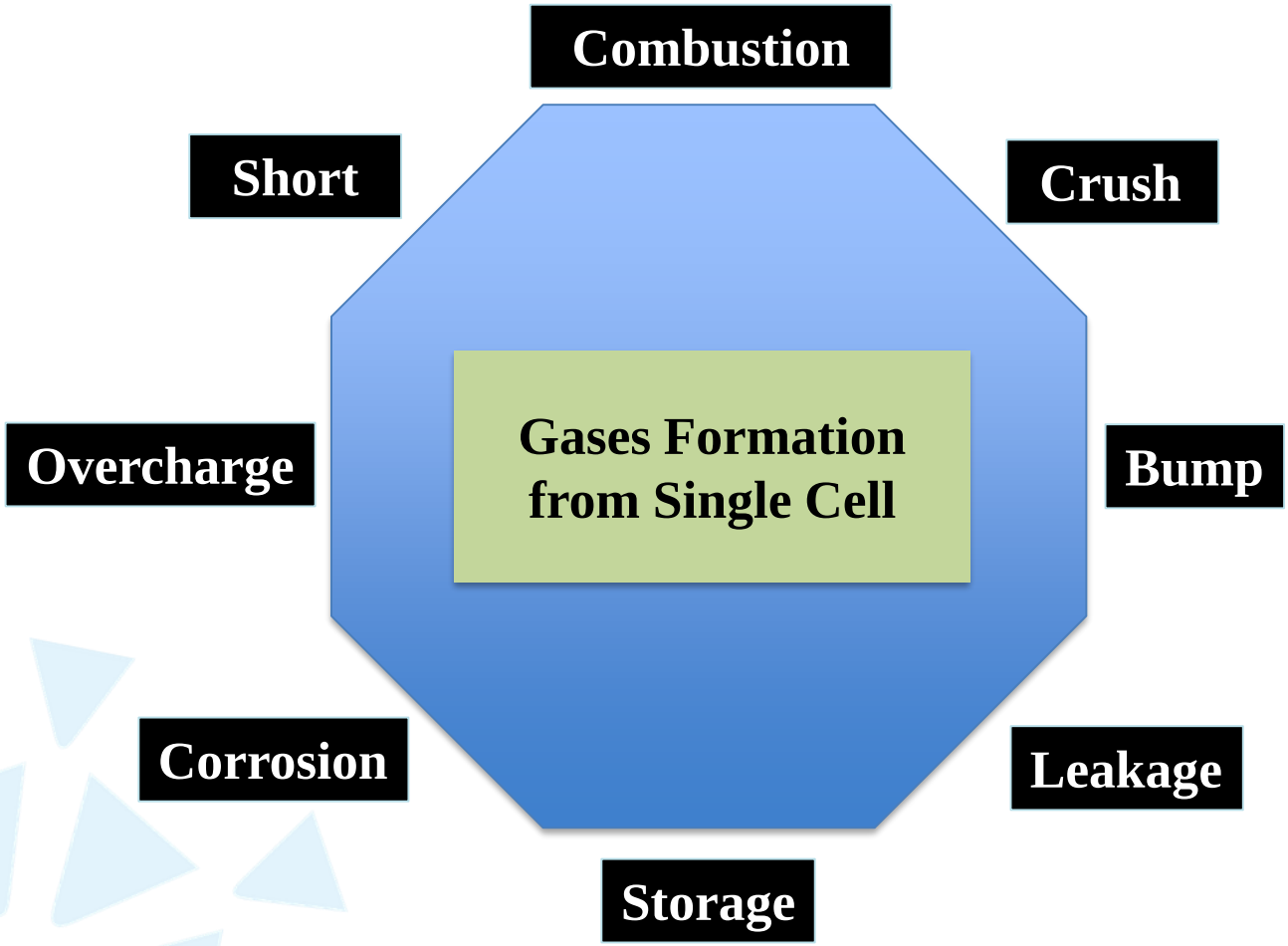


This figure is from http://epg.eng.ox.ac.uk/content/energy-storage

Suggestion：

only by figure out the toxicity of gases from the single cell can we understand the threaten of gases from lithium ion batteries in EVs during the burning.

Causes of Gases Generation from Single Cell



Except for the combustion, there are other factors contributing to the gases generation of lithium ion battery. Both the component, concentration, influence factor and toxicity of the gases should be studied.

The Final Goal is Studying the Toxicity of Gases Due to the Combustion of Lithium Ion Batteries in EVs

- The components of the toxic gases due to the combustion of Li ion batteries are complex (more than 100 kinds).
- It may be easy to obtain the toxicity information of the single component such as CO, HF, et . al., but it is challenge to acquire the total toxicity of the whole gases.
- To our best knowledge, few systematic study of the toxic gases from the combustion of lithium-ion batteries has been conducted.

Chemical

Components
Concentrations
…

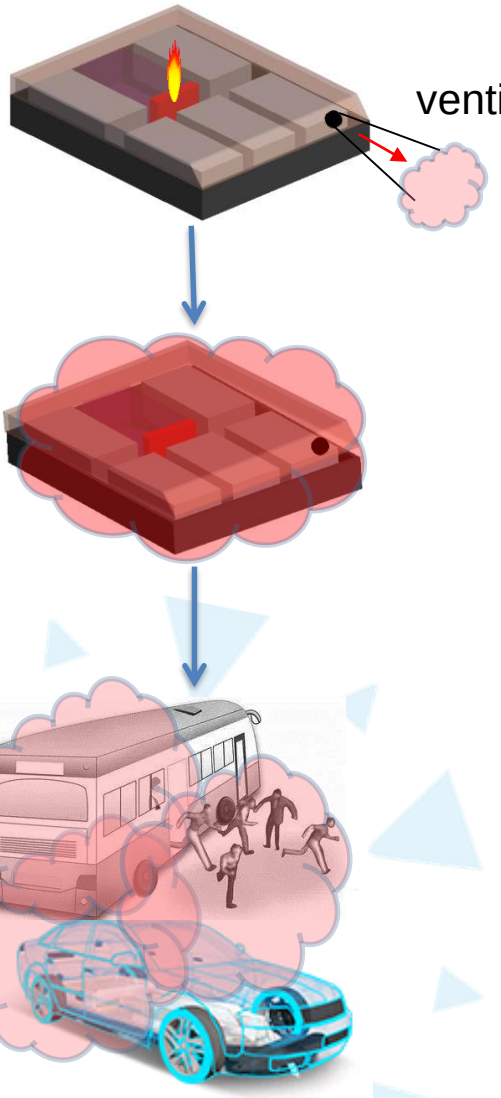
Physical

Temperature
Pressure
Volume
…

Biological

Selection of tested organisms (white mouse, rabbit)
Selection of the test mode
How to relate the test results from organisms to humans?
……

Target and Scope



Component of smoke

- The SOC of the battery
- The material of the battery
- Typical electrolyte additive
- The amount and concentration of the gas

Toxic of smoke

- Sensor testing
- Diffusion properties
- Concentration at different site
- **Toxic testing . Acute toxicity (CO, et. al.) or chronic toxicity (HF, et .al.)**

感谢聆听

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