Hazardous Chemicals in Lithium Ion Batteries

Source 1

Multidisciplinary Digital Publishing Institute

http://www.mdpi.com/2313-0105/2/1/5/pdf

Table 1. Eleven crucial gas mixture constituents and their hazards. EMC: ethyl methyl carbonate; DEC: diethyl carbonate; EC: ethylene carbonate; CO: carbon monoxide; and COS: carbonyl sulfide.

Substance	Hazards According to EU Regulation (EG) Act 1272/2008
EMC	Eye irritation; flammable liquid; H226; H315; H319; H335; Skin irritation, specific target organ toxicity-single exposure.
DEC	Eye irritation; flammable liquid; H226; H315; H319; H335; skin irritation; specific target organ toxicity-single exposure.
EC	Eye irritation; H315; H319; H335; skin irritation; specific target organ toxicity-single exposure.
Benzene	Aspiration hazard; carcinogenicity; eye irritation; H225; H304; H315; H319; H340; H350; H372; germ cell mutagenicity.
Toluene	Aspiration hazard; flammable liquid; H225; H304; H315; H336; H361d; H373; reproductive toxicity; skin irritation; specific target organ toxicity-repeated exposure.
Styrene	Acute toxicity; eye irritation; flammable liquid.; H226; H315; H319; H332; H361d; H372; Skin irritation; Specific target organ toxicity-repeated exposure.
Biphenyl	Aquatic acute toxicity; aquatic chronic toxicity; eye irritation; H315; H319; H335; H400; H410.
Acrolein	Acute toxicity; aquatic acute toxicity; aquatic chronic toxicity; carcinogenicity; corrosive to the respiratory tract; eye damage; flammable liquid; H225; H300; H300 + H330; H302;H311;H314;H317;H318;H330;H341; H351; H400; H410; germ cell mutagenicity; skin corrosion; skin sensitization.
CO	Acute toxicity; flammable gases; H220; H280; H331; H360DM H372M gases under pressure; reproductive toxicity; specific target organ toxicity-repeated exposure.
COS	Acute toxicity; eye irritation; flammable gases; H220; H280; H315; H319; H331; H335; Gases under pressure.
Hydrogen fluoride	Acute toxicity; corrosive to the respiratory tract; H300; H310; H314; H330; skin corrosion.

Source 2

Research for life safety - http://www.brandforsk.se/

http://www.brandforsk.se/MediaBinaryLoader.axd?MediaArchive_FileID=8605faf9-52ed-4d4e-89d6-0147c894f91f&FileName=BF_402_111_Rapport.pdf&MediaArchive_ForceDownload=true

Investigation of fire emissions from Li-ion batteries

*Shows hydrogen fluoride and POF3 (also fluorinated compound)

Source 3

Journal of Electrochemical Society

http://jes.ecsdl.org/content/163/6/A821.full.pdf

pose a high risk due to their high toxicity combined with (very) high volatility. Other highly toxic compounds such as propylene carbonate (PC), ethylene carbonate (EC), γ-butyrolactone (γ-BL) and tetramethylene sulfone (TMSO) are significantly less volatile and therefore present lower risk at room temperature.

Such risk analysis was unfortunately not possible for a number of substances such as, for example, ethyl methyl carbonate (EMC), γ-valerolactone (γ-VL) and 1,2-diethoxyethane (DEE) due to the fact that no acute exposure reference values are defined for these substances. At the same time the latter compound is identified by the European Chemicals Agency as a substance of a very high concern due to its carcinogenic, mutagenic or toxic for reproduction properties.[38] This emphasizes the need for determination of the acute exposure reference values for a broader spectrum of chemical substances expected to enter our everyday life in the near future.

An additional aspect that may need to be considered is the operating temperature of a battery which may be higher than room temperature,[39] and hence warm electrolyte is likely to be released from a battery cell. Hence, data on vapor pressure of the solvents at elevated temperature needs to be analyzed; for some carbonate compounds this data is not available and needs to be generated.

Salt-related hazards.—Many Li salts have been researched for use in Li-ion batteries,[25,26] but $LiPF_6$ was the first one to be commercialized and remains till now the most used salt for Li-ion batteries.[25] As explained in the review work of Xu,[25] ". . . the success of $LiPF_6$ was not achieved by any single outstanding property, but rather by a combination of well-balanced properties with concomitant compromises and restrictions". Two well-known properties of $LiPF_6$ salt are its poor stability and reactivity with water.[25,26]

Even at room temperature, both solid $LiPF_6$ salt and $LiPF_6$ dissolved in aprotic solvents to form electrolyte, exist in equilibrium with its decomposition products:[25,40]

$$LiPF_6 \text{ (solid or in solution)} \rightleftarrows LiF \text{ (solid)} + PF_5 \text{ (gas or in solution)} \quad [4]$$

Upon contact with either atmospheric moisture or traces of water in the electrolyte, $LiPF_6$ undergoes hydrolysis forming HF among other products:[25]

$$LiPF_6 + H_2O \rightarrow LiF + 2HF + POF_3 \quad [5]$$

Phosphoryl fluoride (POF_3) is a reactive compound that easily undergoes further hydrolysis according to the following equation:[41]

$$POF_3 + H_2O \rightarrow HF + POF_2(OH) \quad [6]$$

This results in the generation of additional HF and difluorophosphoric acid, which reacts further with water only very slowly:[29]

$$POF_2(OH) + 2H_2O \rightarrow 2HF + H_3PO_4 \quad [7]$$

Depending on the time scale considered, one may thus expect different apparent reaction stoichiometries of the $LiPF_6$ hydrolysis.

For the evaluation of the hazards associated with the formation of HF in the hydrolysis of the $LiPF_6$ salt, it is important to consider the properties of this compound. HF is known to be very poisonous and corrosive compound both in gaseous and aqueous solution forms.[42,43] The toxicity of HF is such that acute inhalation toxicity thresholds are reached at levels of just a few ppms (see Table IV).

Properties of anhydrous hydrogen fluoride, as well as aqueous solutions of HF, are well understood and described in detail.[40,41] HF gas is hygroscopic and readily soluble in water.[40,44] In aqueous solutions HF acts as a weak acid (pKa = 3.19 in dilute solutions) and the majority of HF molecules remain undissociated at HF concentration above ca 0.1 M.[42] Similar to water, HF has a pronounced tendency to exhibit strong hydrogen bonding.[40] Distribution of HF between the aqueous solution and the gas phase above it is well understood and quantified

Chemicals Involved Besides Fluorinated Compounds

Ethyl methyl carbonate Methylating agent

Diethyl carbonate Methlyating agent

Ethylene carbonate Methylating agent

Carbonyl sulfide

http://nj.gov/health/eoh/rtkweb/documents/fs/0349.pdf

EMERGENCY RESPONDERS >>>> SEE LAST PAGE

Hazard Summary

Hazard Rating	NJDOH	NFPA
HEALTH	-	3
FLAMMABILITY	-	4
REACTIVITY	-	1
FLAMMABLE POISONOUS GASES ARE PRODUCED IN FIRE CONTAINERS MAY EXPLODE IN FIRE		

Hazard Rating Key: 0=minimal; 1=slight; 2=moderate; 3=serious; 4=severe

- **Carbonyl Sulfide** can affect you when inhaled and by passing through the skin.
- **Carbonyl Sulfide** can irritate the skin and may cause pain and redness. Contact with the *liquefied gas* may cause frostbite.
- Eye contact can cause irritation with possible eye damage.
- Contact can irritate the nose and throat.
- Inhaling **Carbonyl Sulfide** can irritate the lungs. Higher exposures may cause a build-up of fluid in the lungs (pulmonary edema), a medical emergency.
- Exposure can cause nausea, vomiting, weakness and muscle cramps, and may cause an irregular heartbeat (arrhythmia)
- High or repeated exposure may affect the nervous system. Higher concentrations can cause convulsions, sudden collapse and even death.
- **Carbonyl Sulfide** may affect the brain.
- **Carbonyl Sulfide** is a FLAMMABLE GAS and a DANGEROUS FIRE HAZARD.

Styrene

https://www.atsdr.cdc.gov/toxprofiles/tp53-c2.pdf

2.2 SUMMARY OF HEALTH EFFECTS

Styrene-induced neurotoxicity has been reported in workers since the 1970s. Studies over the last 15 years have firmly established the central nervous system as the critical target of toxicity. Both short- and long-term exposures to styrene can result in neurological effects. Acute exposure data are limited to the finding of impaired performance on tests of vestibular function in test subjects exposed to 87–376 ppm for 1–3 hours and studies finding no alterations in performance of neurobehavioral tests

Diphenyl

https://www.cdc.gov/niosh/idlh/92524.html

Immediately Dangerous to Life or Health Concentrations (IDLH) May 1994

CAS number: 92-52-4

NIOSH REL: 1 mg/m^3 (0.2 ppm) TWA

Current OSHA PEL: 1 mg/m^3 (0.2 ppm) TWA

1989 OSHA PEL: Same as current PEL

1993-1994 ACGIH TLV: 1.3 mg/m^3 (0.2 ppm) TWA

Description of Substance: Colorless to pale-yellow solid with a pleasant, characteristic odor.

LEL(@232 F): 0.6% (10% LEL(@232 F), 5,000 mg/m^3)

Original (SCP) IDLH: 300 mg/m^3

Basis for original (SCP) IDLH: The chosen IDLH is based on the following statements by Hakkinen et al. [1973]: "one fatal case of liver necrosis with some areas of cirrhosis occurred in a worker who had been regularly exposed to concentrations of vapor of approximately 100 mg/m^3. Other workers with repeated exposure to concentrations greater than 5 mg/m^3 had gastrointestinal symptoms as well as polyneuritic complaints, with abnormalities of both the electroencephalogram and electromyogram. Some showed hepatic damage detected by liver function tests and biopsy."

Short-term exposure guidelines: None developed

ACUTE TOXICITY DATA

Lethal dose data:

Acrolein

https://www.atsdr.cdc.gov/toxprofiles/tp124.pdf

Respiratory Effects. Acrolein may affect the entire respiratory tract, from the nasal epithelium to the alveolar spaces. The variety and severity of effects and depth of the respiratory tract to which effects extend increases as exposure level increases. Nasal irritation appears to be the most sensitive respiratory effect, based on reported irritation in humans and animals and cellular changes observed in animals. Rapid onset of nose and throat irritation and a reduction in breathing rate (believed to be a protective measure triggered by nose irritation) was reported by volunteers acutely exposed to low levels (0.3 ppm); mild nasal epithelial dysplasia, necrosis, and focal basal cell metaplasia have been reported in rats at similar concentrations (0.25 ppm). Respiratory irritation was observed in animals as evidenced by decreased respiratory rates in mice and rats exposed to 1–3 ppm. Higher acute inhalation exposure levels (2–5 ppm) have resulted in more severe effects in animals, including epithelial hyperplasia, inflammation, and moderate to severe histological alterations of the nasal, tracheal, and bronchial epithelium, bronchial

epithelial destruction, pulmonary edema, and lung hemorrhage have been seen in mice, rats, and guinea pigs. Four human case reports of massive acute acrolein inhalation exposures, either occupationally or from heated cooking fats, list similar effects, including high fever, dyspnea, coughing, foamy expectoration, cyanosis, pulmonary edema, and death (concentrations unknown). Fatal pulmonary edema may develop many hours after a high, acute exposure. Observed effects following intermediate- and chronic-duration exposures to acrolein (1–3 ppm) include histological alterations and inflammation across the entire respiratory tract of rats, monkeys, guinea pigs, dogs, rabbits, and hamsters. Respiratory effects seem to be similar in type of effect and severity across species and exposure duration.