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Toxicity of materials used in the manufacture of lithium batteries

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Abstract

The growing interest in battery systems has led to major advances in high-energy and/or high-power density lithium batteries. Potential applications for lithium batteries include radio transceivers, portable electronic instrumentation, emergency locator transmitters, night vision devices, human implantable devices, as well as uses in the aerospace and defense programs. With this new technology comes the use of new solvent and electrolyte systems in the research, development, and production of lithium batteries. The goal is to enhance lithium battery technology with the use of non-hazardous materials. Therefore, the toxicity and health hazards associated with exposure to the solvents and electrolytes used in current lithium battery research and development is evaluated and described.

Keywords: Lithium batteries; Safety; Toxicity

1. Introduction

The resolution of the safety and reliability issues have been a major concern to individuals involved in the research and development of lithium batteries [1,2]. The goal has been to produce a lithium battery that not only provides a wide margin of safety during use or abuse but one that also retains excellent performance and a good shelf life. In general, lithium batteries contain a significant amount of energy and can cause injury through both chemical and physical means if abused. Early studies examining the safety issues associated with lithium batteries have therefore focused on the release of toxic materials following venting of cells due to an overdischarge, exposure to high temperatures, recharging, crushing, or puncturing [3,4]. However, this paper examines the toxicity and health hazards associated with the potential exposure to individual components of the newer non-aqueous lithium batteries.

There is no fixed composition generally employed in non-aqueous lithium batteries. Different compositions impart various advantages, and a diversity of electrolyte compositions are used depending on the intended application. The purpose of this paper is to describe and characterize the toxicity of some of the more popular solvents and electrolytes used in current lithium battery research, development and manufacturing processes. The current permissible airborne exposure limits [5,6] are also described when this information is available.

2. Discussion

2.1. Solvents

Early solvents used in lithium battery manufacturing included very toxic and hazardous solvents such as thionyl chloride, acetonitrile, or sulfur dioxide. Thionyl chloride is an extremely irritating and caustic material that effects the eyes, lungs, skin, and mucous membranes. Furthermore, it decomposes upon reaction with moisture to hydrogen chloride and sulfur dioxide, both of which are extremely irritating gases [7,8]. Acetonitrile exposure by any route (oral, dermal or inhalation) can produce cyanide poisoning from metabolic cyanide release after absorption. Exposure to slight concentrations may cause nausea, vomiting, headache, and lassitude. Serious acute exposure can result in respiratory depression, shock, coma and seizures [9]. The current preference in lithium battery technology is the use of nontoxic solvents.

In general the new solvents in lithium battery research and development include aprotic organic and inorganic solvent systems that are thermodynamically and/or kinetically stable toward lithium metal [10]. The solvents

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have a wide liquid state range, low viscosity, a fairly high dielectric constant, and a fairly high solvating power to dissolve the lithium salts. Examples of the types of solvents currently used in lithium battery research and development are the carbonates, glymes, lactones, and furans.

The family of carbonates which include propylene carbonate, ethylene carbonate, and diethyl carbonate are generally colorless liquids with slight or pleasant odors. Exposure to these solvents generally results in respiratory tract, skin and eye irritation. Acute inhalation exposure can cause sore throat, coughing, shortness of breath and headaches [7]. Acute toxicity studies on this family of compounds has indicated that the LD_{50}, dose which leads to death in 50% of the animal test population studied, is quite high relative to toxic substances in general [11]. Carbonate solvents are presented in Table 1 which summarizes the available toxicity information on the common solvents used in lithium battery manufacturing. Comparing this, data to common toxic materials as listed in Table 2 or to the toxicity of earlier solvents used in the battery manufacturing industry, Table 3, indicates that the toxicity of the carbonate family of solvents is comparable with that of ethyl alcohol.

A second class of solvents or co-solvents currently being used in lithium battery manufacturing are the glymes. This family of compounds includes three specific glymes that are used as solvents or co-solvents: (i) dimethoxyethane (DME), (ii) diethoxyethane (DEE), and (iii) triglyme [13]. These solvents are generally clear colorless liquids with a mild ethereal odor. They are low in oral toxicity, appreciably irritating to the eyes and mucous membranes but not to the skin, and considered are potential reproductive toxins. Acute inhalation exposure to the family of glymes can also cause central nervous system depression, nausea, vomiting, diarrhea, and headache. As described in Table 1, the range of acute toxicity for this family of compounds appears to be in the range of moderately toxic materials for DME (TDLo, range from 300 to 16 000 mg/kg) to practically non-toxic DEE and triglyme with an TDLo range from 5000 to 28 000 mg/kg [9].

Another solvent, described in Table 1, that has shown promise in the battery manufacturing industry is γ-butyrolactone. This material is a hygroscopic, colorless to pale yellow oily liquid with a mild odor. It is considered to be slightly toxic by ingestion as evidenced by a mouse and rat oral LD_{50} of 1720 mg/kg and 1540 mg/kg, respectively [11]. It is primarily an eye, skin, and mucous membrane irritant [5].

The furans are another potential solvent family in lithium battery manufacturing. These solvents are colorless liquids with a mild odor. They are considered moderately toxic by inhalation exposure and only slightly toxic by the dermal route of exposure. Irritation of the eyes, skin, and mucous membranes are the predominant effect of exposure to the these solvents [7,9]. However, high acute inhalation exposures (i.e., 25 000 ppm) have been shown to produce anesthesia with delayed induction and recovery periods, accompanied by a fall in blood pressure and strong respiratory stimulation. The margin of safety between anesthesia and death is small and, therefore, may result in an immediate death in high exposure concentrations [7]. In addition, these solvents are extremely explosive and present a hazard due to their potential to flash [5].

2.2. Positive electrodes

Some of the most widely studied positive electrode materials for lithium batteries include the transition metal oxides such as vanadium pentoxide (V_2O_5), man-

Table 1
Acute toxicity of solvents and co-solvents used in non-aqueous lithium batteries

Solvent	Rat oral–LD_{50}	Mouse oral–LD_{50}	Rabbit skin–LD_{50}
Propylene carbonate (mg/kg)	NA [a]	20700	>20000
Ethyl carbonate (mg/kg)	10000	NA	>3000
Diethyl carbonate (mg/kg)	15000 (LDLo) [b]	500 [c]	NA
Dimethoxyethane (mg/kg)	660 (TDLo) [c]	360–16000 [c]	NA
Diethoxyethane (mg/kg)	4390	5000–23640 [c]	NA
Triglyme (mg/kg)	NA	7500–28000 [c]	NA
γ-Butyrolactone (mg/kg)	1540	1720	>5000
	10000–68000 [d]	68000–200000 [d]	
Tetrahydrofuran (mg/kg)	1650	4550 [d]	NA
2-Methyltetrahydrofuran (mg/kg)	NA	NA	4500

[a] Not available.
[b] LDLo: Lethal dose low = the lowest dose required to produce lethality in the study population.
[c] TDLo: Toxic dose low = the lowest dose required to produce a toxic effect in the study population. Toxic effects endpoints included effects on fertility, reproduction, and development.
[d] TDLo: Toxic dose low = the lowest dose required to produce a toxic effect in the study population. Toxic effects endpoints included weight loss or decreased weight gain in the adult animal.

Table 2
Approximate LD_{50}s of some common chemical substances and their toxicity rating [12]

Agent	LD_{50} [a]	Toxic range	Descriptive term
Ethyl alcohol (mg/kg)	10000	5000–15000	Practically non-toxic
Sodium chloride (mg/kg)	4000	500–5000	Slightly toxic
DDT (mg/kg)	100	50–500	Moderately toxic
Strychnine sulfate (mg/kg)	2	1–50	Very toxic
Tetrodoxin (mg/kg)	0.10	<1	Extremely toxic

[a] Rat oral–LD_{50}.

Table 3
Acute toxicity [a] of solvents and co-solvents used in non-aqueous lithium batteries [11]

Solvent	Rat oral–LD_{50}	Mouse oral–LD_{50}	Rabbit skin–LD_{50}
Acetonitrile (mg/kg)	2730	269	1250
Thionyl chloride (ppm/1 h)	500 [a]	NA	NA
Sulfur dioxide	2520 (ppm/1 h) [a]	3000 (ppm/30 min) [a]	NA

[a] LC_{50}: Lethal concentration 50 = Lethal concentration which leads to death in 50% of the test population studied by inhalation exposure.

ganese dioxide (MnO_2), copper oxide (CuO), and cobalt oxide (Co_2O_3) or the transition metal sulfides such as molybdenum disulfide (MoS_2), copper sulfide (CuS), or titanium disulfide (TiS_2). Table 4 summarizes the airborne permissible exposure limits, as determined by the Occupational Safety and Health Administration (OSHA) and the American Conference for Governmental Industrial Hygienists (ACGIH), for a few of the popular current electrolyte solutions [5,6].

Of these materials the sulfides are the least toxic. Upon exposure, the sulfides commonly exhibit effects of mild irritation to the eyes, skin, and respiratory tract which can be exacerbated upon reaction with water. However, dermatitis, following long-term or repeated exposure, has not been reported in exposed workers [7]. In general, the toxicity of these materials is related to the toxicity of the free metal and occupational exposure limits have been determined as such.

Inhalation of the dust or fume is the most common form of poisoning from the metal oxides. Metal fume fever, an influenza-like illness that may occur due to the inhalation of freshly formed metal oxides, is not

Table 4
Summary of exposure limits for positive electrode materials contained in non-aqueous lithium batteries

Compound	Permissible exposure limits	Target effects
Vanadium pentoxide (mg/m^3)	0.05 [a,b] (as V_2O_5, respirable dust and fume)	Severe respiratory irritant Liver and kidney toxin Developmental and reproductive toxin
Manganese dioxide (mg/m^3)	5 [a] (dust) 1 [a,b] (fume)	Severe respiratory irritant Neurotoxin
Copper oxide (mg/m^3)	1.0 (copper dusts and mists as Cu)	Severe respiratory irritant Gastrointestinal irritant
Cobalt oxide (mg/m^3)	0.05 [a] (cobalt metal, dust, and fume as Co)	Respiratory irritant Liver and kidney toxin Sensitizer – respiratory and dermal
Molybdenum disulfide (mg/m^3)	5 (soluble compounds) 10 [a,b] (insoluble compounds as Mo)	Irritant upper respiratory tract
Titanium disulfide	No occupational exposure limits established	Irritant upper respiratory tract
Copper sulfide	No occupational exposure limits established	Irritant upper respiratory tract

[a] OSHA, 8 h = Time-weighted average (TWA).
[b] ACGIH, 8 h = TWA.

Table 5
Summary of exposure limits for electrolyte salts contained in non-aqueous lithium batteries

Compound	Permissible exposure limits	Target effects
Lithium trifluoromethanesulfonate	No occupational exposure limits established	Nervous system Thyroid and kidney toxin
Lithium tetrafluoroborate (mg/m^3)	2.5 [a,b]	Irritant upper respiratory tract
Lithium hexafluoroarsenate (mg/m^3)	0.01 [a,b] (arsenic, inorganic and soluble compounds)	Neurotoxin Carcinogen (IARC-1, NTP-1, ACGIH-A1)
Lithium perchlorate	No occupational exposure limits established	Nervous system Thyroid and kidney toxin
Lithium hexafluorophosphate	No occupational exposure limits established	Irritant upper respiratory tract

[a] OSHA, 8 h = time-weighted average (TWA).
[b] ACGIH, 8 h = TWA.

expected with inhalation of the oxides used in the lithium battery manufacturing industry [14]. Symptoms may be similar however, and may include upper respiratory tract irritation accompanied by coughing and dryness of the mucous membranes, lassitude and generalized malaise. Acute poisoning by the metal oxides may affect the liver and kidneys. In addition, chronic exposure to manganese oxide may result in a systemic poisoning known as 'manganese', a Parkinsonian-like syndrome characterized initially by anorexia, asthenia, headache, insomnia, irritability, restlessness, and spasm pain in the muscles followed by the onset of neurological effects [15]. Repeated or prolonged exposure to cobalt compounds may lead to sensitization or photocontact dermatitis and there is limited evidence in humans to suspect these metals and their inorganic compounds as carcinogens [14].

2.3. Lithium salts

Various lithium salts are used as the electrolyte in lithium battery technology. These lithium salts include lithium triflate, lithium trifluoromethanesulfonate ($LiCF_3SO_3$), lithium tetrafluoroborate ($LiBF_4$), lithium hexafluoroarsenate ($LiAsF_6$), lithium perchlorate ($LiClO_4$), lithium hexafluorophosphate ($LiPF_6$), lithium imide, or lithium bis(trifluoromethane sulfonimide) ($LiN(CF_3SO_2)_2$. The lithium salts are discussed and listed in Table 5 along with their current permissible exposure limits and potential target effects [5,6].

The lithium salts are generally white to off-white hygroscopic powders. In general, acute exposures to lithium salts may result in severe gastroenteritis and effects on the central nervous system, renal function and fluid and electrolyte balance. Symptoms, which are usually delayed include nausea, vomiting, thirst, anorexia, diarrhea, blurred vision, drowsiness, weakness, tremor, staggering, bradycardia, and coma. In severe cases, death may occur due to renal failure or cardiac or pulmonary complications [7].

Of these lithium salts, only lithium hexafluoroarsenate may be considered a human carcinogen by the Occupational Safety and Health Administration (OSHA), National Toxicology Program (NTP), and the International Agency for Research on Cancer (IARC) [5,6]. In addition, inorganic arsenic compounds such as lithium hexafluoroarsenate are considered immediately dangerous to life or health at airborne concentrations of 100 mg/m^3 [5]. Death within 1 to 48 h is usually due to circulatory failure but coma and convulsions may occur terminally. Death delayed 3 to 14 days is usually due to dehydration, electrolyte imbalance and gradual hypotention [7]. In addition, in the presence of moisture, lithium hexafluoroarsenate has the potential to form hydrogen fluoride, a highly corrosive material [5].

Summary

Research on the safety and reliability of non-aqueous lithium batteries has focused on the safe use, abuse, shipment, and disposal of these batteries. The focus of this paper is the toxic properties of the specific materials involved in the research, development and manufacture of high energy, high-energy-density lithium batteries.

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