

LITHIUM BATTERIES SAFETY, WIDER PERSPECTIVE

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Abstract

Energy production and storage has become a pressing issue in recent decades and its solutions bring new problems. This paper reviews the literature on the human and environmental risks associated with the production, use, and disposal of increasingly common lithium-ion batteries. Popular electronic databases were used for this purpose focused on the period since 2000. Assessment of the toxicological and environmental impact of batteries should then have a holistic scope to precede and guide the introduction of appropriate safety measures. In this short review the authors will try to touch upon this complex subject and point out some important issues related to an unprecedented development of lithium ion batteries-powered world. Given the multi-billion dollar business with the risks associated with the development of new technologies requires careful consideration of whether the balance of profits and losses is beneficial to humans and the planet. *Int J Occup Med Environ Health.* 2023;36(1):3–20

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INTRODUCTION

Drive to mobility and dependency on technology, which accompanies people most of the time, result in a growing need for portable power sources. Lithium-ion batteries (LIBs) are currently the most common technology used in portable electronics, electric vehicles as well as aeronautical, military, and energy storage solutions. European Commission estimates the lithium batteries market to be worth ca. EUR 500 million a year in 2018 and reach EUR 3–14 billion a year in 2025. This rapid growth is, to a large extent, driven by the growing needs of plug-in

hybrid (PHEV) and electric vehicles (EVs), together with stationary storage industries [1]. In 2019 2.1 million electric cars were sold and this number is predicted to grow by a factor of 10 in 2040 [2].

Batteries produced in 2018 could store about 290 gigawatt-hours (GWh), while 2028 is anticipated to expand it to >2 terawatt-hour (TWh) [3]. Tesla predicts that a complete transition to electric-powered cars will require 10 TWh of battery capacity/year (ca. 100-fold growth from current status) and another 10 TWh/year (ca. 1600-fold growth) to fulfill the electricity consumption

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by other activities [4]. The dominating cell size/form factor is 18650 type, powering, e.g., Tesla S and X model EVs, which can store 10–13 watt-hour (Wh) of energy [5]. Coarse calculations then predict their production to rise up to 80 billion cells/year during the next 8 years. Concerning life span of 3–8 years batteries create new persistent waste stream, and earlier analyses predicted 25 billion units to become waste in 2020 in China only [6]. “The Global E-waste Monitor 2020” published by UNITAR reports 4.7 million metric tons (Mt) of small IT and telecommunication equipment waste produced globally in 2019 [7].

Taking into account that, e.g., 21.2% of mobile phone weight on averages is its battery [8] significant part of this waste stream consists of (often non-removable) batteries. If these devices 8.8% share in global e-waste production will not change, it will result in ca. 6.6 Mt of waste in 2030. Noteworthy is that rapport do not include cells from EVs or power storage solutions into any of mentioned e-waste types. It does state however that only 17.4% of e-waste in 2019 was collected and recycled in a documented way, which raises a question of the environmental fate of the remaining majority. These volumes illustrate a scale of mounting risks and challenges associated with a) sourcing raw materials, b) production, c) safety of use and d) recycling/repurposing of used batteries.

METHODS

Scoping literature review, used to identify the scope or coverage of a body of literature on a given topic is useful for examining emerging evidence when it is still unclear what other, more specific questions can be posed and valuably addressed by a more precise systematic review. Scoping literature review is conducted to explore more general research question. The following electronic databases were used for this purpose: Medline, Google Scholar, FreeFull PDF, MedNar, Science Research, World Wide Science, DOI. The literature review focused on the period

since 2000. In some aspects older publications, e.g., reports on toxicity, were also used. The review concerned papers published in English. In this review, the authors will try to address a number of issues related to the unprecedented development of energy storage technology i.e., a world powered by lithium-ion batteries.

RESULTS

Lithium battery components

Lithium-ion cell consists of 3 main parts: cathode, anode and a separator, all immersed in the electrolyte. Additional elements include current collectors, made of aluminum for the cathode and copper for the anode, as well as the casing made of Fe-Ni alloy, aluminum or plastic [9]. Container material does not affect battery properties and consists of readily recyclable and stable compounds. Anode, cathode, separator and electrolyte are, on the other hand, crucial for the cell cycling (charging/discharging) process. Their components, with an emphasis on metals building cathode, are also less indifferent to health and environment if not treated correctly.

Separator allows the flow of lithium ions between the cathode and anode, and prevent the flow of electrons (insulate against short circuiting) [10]. It is most commonly made of microporous polypropylene (PP), polyethylene (PE) or PE/PP membrane. Barrier made of these semi-crystalline polyolefins, or other materials (non-woven fabric mats, inorganic composites or their modifications) has to characterize with optimal permeability and mechanical strength to stop electrode particles and contain enough electrolyte [9]. Together with the separator, sandwiched between the 2 electrodes is lithium-containing electrolyte.

Lithium salts dissolved in the electrolyte are the primary source of positive lithium ions (Li^+). Their movement between anode and cathode (through the electrolyte and separator) allows electron flow between positive and negative current collectors and so battery charging and discharging. Lithium, in the form of conductive LiPF_6 ,

$\text{Li}[\text{N}(\text{CF}_3\text{SO}_2)_2]$, LiBF_4 , $\text{Li}(\text{CF}_3\text{SO}_3)$, LiClO_4 or LiAsF_6 salts makes up for 1.2–2.0% of battery mass [9,11]. These solid/crystalline substances are dissolved in low viscosity, high conductivity cyclic or linear carbonate, e.g., dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate or γ -butyrolactone, in case of liquid electrolytes. This type of electrolyte usually contains numerous additives, including Li deposition improvers (fluoroethylene carbonate), shutdown additives (cyclohexylbenzene or biphenyl), fire-retardants, overcharge protectors (anisole derivatives), surface-film-forming additives (vinylene or vinyl ethylene carbonates), cathode protection agents (dimethyl acetamide, silicones or tributylamine) or stabilizers protecting Li salt decomposition [7,9]. Additives also help to prevent decreasing of solvent liquidity (e.g., in low temperatures), which lowers Li-ion cell performance. Solid inorganic (lithium lanthanum zirconate, amorphous lithium phosphorous oxynitride sulfidic glasses) or polymer (solvent-free polyethylene oxide) electrolyte technologies, aided by different additives, start to penetrate the market, although the most popular still include liquid ones.

Anode (negative) and cathode (positive electrode) temporarily bind/release Li ions and their chemical characteristics strongly affects lithium-ion cell properties (energy density, capacity etc.). During discharge Li^+ released from metallic lithium, stored between graphite layers of anode, travel to cathode and forms metal oxides. To fuse electrode material to respective collector, inert binder, like polyvinylidene fluoride (PVDF) is used. Most popular types of cathode and anode chemistries, together with some of their properties are listed in Table 1.

Graphite or other carbon forms (e.g., amorphous) are the most prevalent anode material. Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO), lithium alloys and lithium metal as well as lithium metal nitrides, transitional metal vanadates and nanocomposites (e.g., silicone nanowires) make their way into new designs and promise to improve their perfor-

mance [9,12]. Binders allowing electrode layer formation may include carboxymethyl cellulose and styrene-butadiene rubber [13]. Anode accounts for a 15–30% of a battery weight, which includes a copper collector [14].

Most widespread cathode materials include transition metals' oxides and lithium iron phosphate [9]. Depending on cathode chemistry, during discharge lithium iron phosphate (LFP), lithium cobalt (LCO), lithium manganese (LMO), lithium nickel manganese cobalt (NMC) or lithium nickel cobalt aluminum (NCA) oxide are the end products of reduction half-reaction. Electrons (through external circuit) and lithium ions (through separator) are released from anode in oxidation half-reaction and combine in the cathode. Charging is a reverse of this process, where electrons are delivered via external circuitry. Active material, as in anode formation, is mixed with binder(s), e.g., PVDF [13]. Transition metals building cathodes account for up to 14% of battery mass (cathode type depending) [11] and strongly affect battery production cost (51%) and recycling cost-effectiveness [12].

They are, in parallel, the main source of (eco)toxicological biohazards, especially accounting for projected market growth, energy-hungry supply chains and waste management.

Sourcing raw materials

Aluminum (Al), iron/steel (Fe), copper (Cu), manganese (Mn), cobalt (Co), lithium (Li), nickel (Ni) and graphite are the raw materials crucial for electrodes (and electrolyte) production (Figure 1). With exception of iron and copper they were listed among 50 critical minerals by the US Geological Survey [15] indicating high economic and political importance. They are also classified as energy transition metals (ETMs), which status and demand for is rapidly growing due to their use in green energy technologies (incl. acquiring solar and wind energy as well as its storage). Uneven distribution of some of their ores, though, locate mining operations in regions with fragile

Table 1. Li-ion batteries types according to cathode/anode material chemistry in 2020–2021 (based on [11,82,83])

Active compound	Short name	Chemical formula	Commercialization year	Cycle life*	Application	Comment
Cathode						
lithium cobalt oxide	LCO	LiCoO_2	1991	500–1000	mobile phones, tablets, laptops, cameras	very high specific energy; limited specific power; high cost due to Co use; currently less relevant
lithium iron phosphate	LFP	LiFePO_4	1996	>2000	portable and stationary equipment needing high load currents and endurance	very flat voltage discharge curve; low capacity; one of safest Li-ions; used for special markets (primarily energy storage); elevated self-discharge
lithium manganese oxide	LMO	LiMn_2O_4	1999	300–700	power tools, medical devices, electric powertrains (Nissan Leaf)	high power but less capacity; safer than LCO; commonly mixed with NMC to improve performance; currently less relevant
lithium nickel cobalt aluminum oxide	NCA	LiNiCoAlO_2	1999	500	medical devices, industrial, electric powertrain (Tesla model S)	shares similarities with Li-cobalt; serves as Energy Cell; good life span
lithium nickel manganese cobalt oxide	NMC	$\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ **	2008	1000–2000	e-bikes, medical devices, EVs, industrial, energy storage (Tesla Powerwall and Powerpack)	provides high capacity and high power; serves as Hybrid Cell; dominant cathode chemistry
Anode						
graphite			1991		dominant anode chemistry	low cost; high energy density
tin/cobalt alloy			2005		consumer electronics	better capacity than graphite
lithium titanate	LTO	$\text{Li}_4\text{Ti}_5\text{O}_{12}$	2008	3000–7000	UPS, electric powertrain (Mitsubishi i-MiEV, Honda Fit), solar-powered street lighting	long life, fast charge, wide temperature range; low specific energy; among safest Li-ion batteries; ability to ultra-fast charge; cost limiting to special applications
hard carbon			2013		home electronics	improved storage capacity
silicon/carbon			2013		smartphones	contains silicon nanowires

* Number of charge-discharge cycles is related to a number of conditions (e.g., depth of discharge or working temperature).

** x, y and z values indicate proportions between Ni, Mn and Co, which in most cases sum up to 1; e.g., $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ is shortened to NMC811.

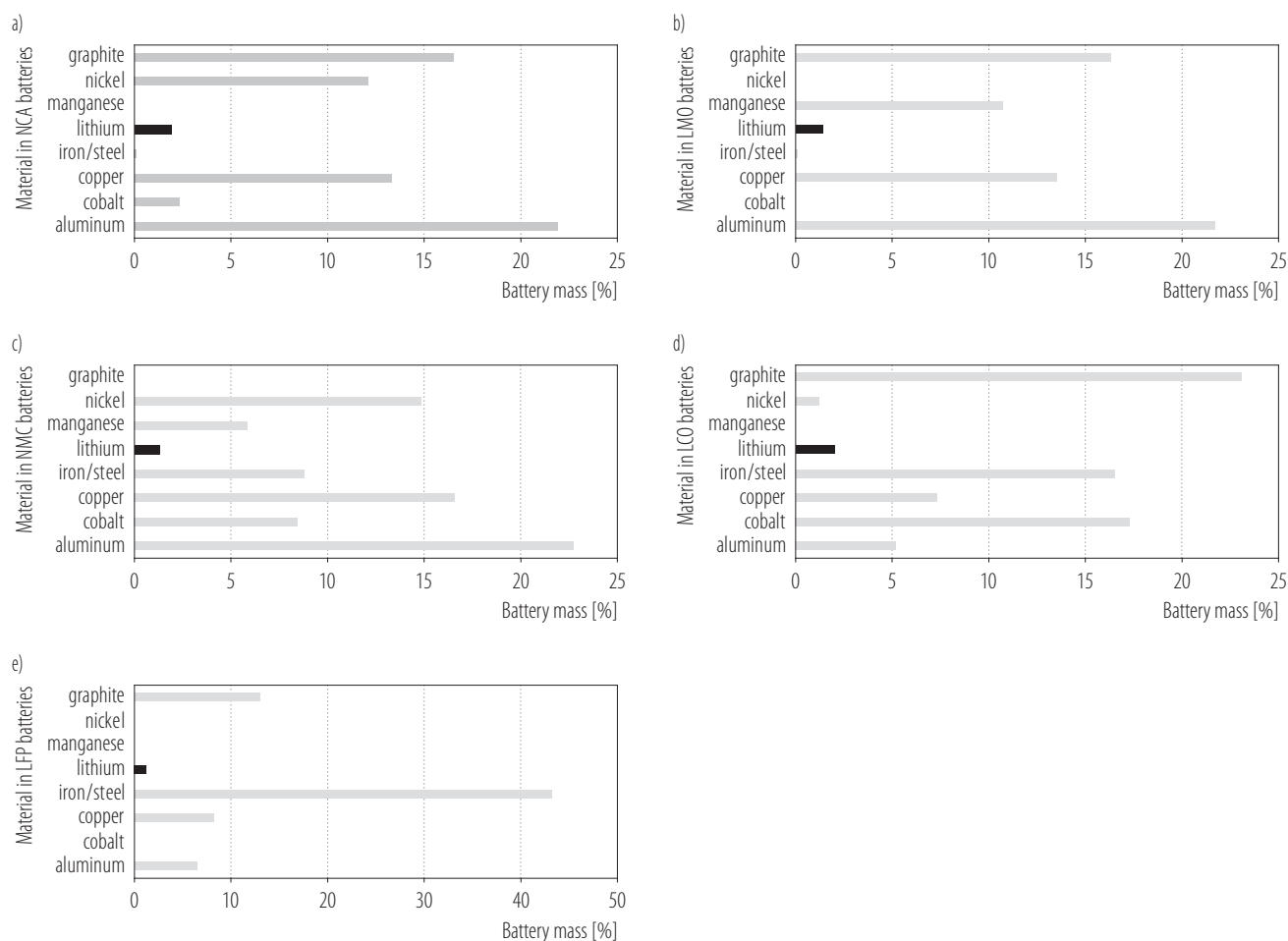


Figure 1. Content of selected materials in batteries of a) lithium nickel cobalt aluminium (NCA), b) lithium manganese (LMO), c) lithium nickel manganese cobalt (NMC), d) lithium cobalt (LCO), e) lithium iron phosphate (LFP) (based on [84–86])

economy and/or high corruption rates (Latin America and African countries, Russia, China) and accentuate environmental and social risks [16]. Concerning the severity of negative effects on environmental, social and governance dimensions Lèbre et al. [16] places mining of cobalt and manganese on second and third place. Copper scores eighth, nickel 10th, aluminum 12th while iron and lithium are 17th and 18th among 20 analysed commodities. Cobalt is a prime example of an ETM, which supply chain is considered not sustainable and harmful for environment and communities. It is present in only few LIBs types (LCO, NMC, NCA), which are however prevalent on the market. The main supplier of this rare (approx. 0.003%

of earth crust) and valuable metal's ore is Democratic Republic of Congo (DRC), which in 2021 provided over 70% of world mine production (120 000 t), mainly as a by-product of copper (and nickel) mining from sediment-hosted stratiform deposits [17]. The main cobalt refiner and consumer remains China, which allocates >80% of its production to rechargeable batteries industry. Growing demand, diminishing supplies and lack of substitutes in many technological processes places Co on the critical nonfuel minerals list [18]. In addition, it is considered as a “conflict resource” involving child labor and illicit export, which sponsor internal conflicts in already politically unstable DRC [19].

Lack of proper control over mines in this area and significant role of artisanal operations (15–20% of overall mining production) led to documented environmental pollution and health effects in surrounding communities. Studies from Congolese University of Lubumbashi have shown significantly elevated urinary levels of cobalt, as well as arsenic, cadmium, copper, lead and uranium in Katanga Copperbelt inhabitants living in the vicinity of mines or smelting plants. Measured urinary cobalt concentrations were 43-fold higher, in comparison to USA general population and the most affected group were children <14 years [20]. Following studies from the same group involved diggers working in the artisanal extraction areas and residents of the surrounding areas [21]. Significant raise of, correlated, Co levels in urine and blood were found in all studied groups. Stratification by age revealed 9.3-fold increase of urine and 7.5-fold of blood cobalt concentration in children, allied with 45 times elevated levels of oxidative stress marker – 8-hydroxydeoxyguanosine – in these children's blood samples. 8-Hydroxydeoxyguanosine is a product of guanine oxidation by reactive oxygen species, UV radiation or genotoxic agents. It is linked with aging, cancer development as well as memory formation, through 8-oxo-dG-dependent demethylation of CpG sites. Cobalt oxides absorbed from dust are distributed through the lymph and blood systems and primarily undergo uptake by liver and kidney as well as excretion in urine and feces. Following initial rapid removal, mainly renal, of metal ions (40% in the first 24 h and ca. 70% after a week) process decelerate, though, exposing tissues long term to remaining metal [22].

Physiologically cobalt is an important constituent of vitamin B₁₂, although in higher doses it is acutely toxic. Soluble cobalt salts characterize with LD₅₀ between 150–500 mg/kg [23] and are classified as possibly carcinogenic to humans (group 2B agents) by International Agency for Research on Cancer (IARC). Systemic effects of Co poisoning include hematological and endocrine

(at blood conc. >300 µg/l), as well as neurological (vision and hearing) and cardiovascular symptoms at concentration >700 µg/l [24]. Occupational, environmental, dietary or medical (e.g., from metal-on-metal hip prostheses) exposure to high concentration of cobalt particles leads to elevation of free Co²⁺ ions in serum. Those, in turn, are involved in ROS generation and oxidative damage to DNA, proteins and lipids, DNA repair impairment, alteration of erythropoiesis and mitochondrial functions, disturbance of iodine intake by thyroid and deregulation of iron and calcium homeostasis [25]. Carcinogenic potential of cobalt is also associated with its ability to activate hypoxia-inducible factor (HIF) and potentially inducing transcription of a number of genes promoting tumor growth [22]. Nickel constitutes ca. 80% of NCA and ca. 30% of NMC cathodes [26]. Accounting for a dominant market position of the latter and high energy density offered by the Ni-containing chemistries, their share in overall Li-ion batteries numbers is predicted to grow by 50% till year 2025. Despite battery production consume only ca. 5% of nickel production, this share will grow and increase process ecological costs. While Ni production constantly increases, its leading producers – Indonesia and Philippines – start to consider its environmental and human costs. In 2017 Philippines closed 23 (mostly nickel) mines to fight environmental degradation. Extracting Ni from low-grade ores (~1–2% nickel) renders it energy intensive process, which creates a conflict of interest between mining companies and diminishing tropical forest biodiversity in Indonesia and New Caledonia [27]. In comparison with other metals Ni is ranked 7th on a list of most damaging to human health and ecosystems and 9th for global warming potential [28]. Environmental contamination was documented also for nickel mines in Canada [29], Cuba [30], northwest Russia and Finland [31]. Emission of sulfur dioxide, leading to acid rain, as well as release of heavy metals and acidic mine drainage to soil and water were the main issues. Report

published in 2020 by World Resources Institute [32] focused on the effects of legal and illegal mining operations (including Ni extraction), which span over 20% of the indigenous Amazon region. Its outcomes confirm not only pollution found in at least 30 Amazonian rivers flowing through Guyana, Colombia, Ecuador, Peru, Bolivia and Brazil but also erodes local communities, which are proven to protect their local environment.

Nickel plays crucial role in plants growth and development and is considered an essential nutrient for some microorganisms and animals [33]. Enzymes and cofactors containing Ni were documented in archaea, bacteria, algae, primitive eukaryotes and plants [34], although it is physiological role in higher animals is not fully resolved. Nickel is considered the most important sensitizer among metals, often resulting with contact dermatitis [35]. Exposure to poorly soluble Ni sulfides and oxides was linked to immunotoxicity, cardiovascular and respiratory tract disorders (including asthma, lung fibrosis and cancer), observed at different doses and exposure lengths [30]. Despite its widespread commercial use, e.g., in coins, stainless steel cooking utensils or taps, nickel salts and oxides are classified as class 1 carcinogen, while metallic nickel and its alloys as possibly cancerogenic (group 2B) by IARC [36]. Toxic effects of Ni on immune and respiratory system are closely linked to occupational inhalation from fossil fuel combustion or nickel-related manufacturing. This route affects most often metal refineries or plating industry workers, although people inhabiting areas in proximity of nickel mining, processing and recycling sites are also endangered [37]. Molecular mechanisms of nickel toxicity, despite not fully understood, connect to oxidative stress and mitochondrial dysfunction, resembling mechanisms of cobalt toxicity (see above). Initial impairment of mitochondrial membrane potential leads to decrease in mitochondrial ATP levels and mtDNA damage [38]. More specifically, Ni promotes shift of energy metabolism towards anaerobic glycolysis by stabi-

lizing hypoxia-inducible factor-1 α (HIF-1 α) and inducing hypoxia-like response. Disturbed assembly of some iron-sulfur cluster proteins, like aconitase and mitochondrial complexes I, II and III, together with HIF-1 α -dependent activation of plasminogen activator inhibitor (PAI-1), vascular endothelia growth factor (VEGF), and the CXC chemokine genes are some of the involved mechanisms. Neurons exposed to Ni produced more ROS, which resulted with lipid peroxidation, disturbed membrane integrity and reduction of antioxidant mechanisms capacity. These cellular alterations are linked to nickel role in the etiology of numerous mental disorders [39] and align with findings of its accumulation in the central nervous system [38].

From 82 000 tons of lithium produced globally in 2020 >70% will be used by for battery manufacturing. Five mines in Australia, 2 brine operations in Chile and Argentina, each, and 2 producers (1 brine, 1 mineral) in China deliver >95% of this number. Overproduction and Li price drop prevent most of these companies to expand in 2020 and some to cease production, nevertheless projected market growth will result in securing and opening new sources if necessary. U.S. Geological Survey monography [40] concerning lithium states no ecological or human safety issues related to the element, adding though that with the rise in its production and consumption these will certainly appear. Alarming example of this happening are the effects of intense lithium recovery from underground brines in one of the driest areas in the world, namely Salar de Atacama in Chile. Expansion of lithium evaporation operations in this part of the “lithium triangle” already creates conflict with local communities and pressure to fragile ecosystems. Extraction of Tibetan resources, e.g., from lithium salts-rich Chabyer Tsaka salt lake, similarly lacks proper attention to indigenous ecosystem and inhabitants [41]. Both hard rock mining and extraction from underground reservoirs are burdened with high ecological costs, in-

cluding CO₂ production (15 tones/tonne of Li) for former or land (3124 m³/t of Li) and water (469 m³/t of Li) for the latter [42]. Development of efficient methods utilizing lithium-rich geothermal waters, though, opens new venues for “green lithium” extraction.

Lithium use is well established and effective therapy in bipolar disorder [43]. For that reason, data regarding its toxicity is widely available and its metanalysis indicates several side effects, associated with kidney, thyroid and parathyroid glands functioning, as well as possible teratogenicity [44]. Irreversible neuropathy, linked to cerebellar demyelination, was mentioned in few cases [45], although positive correlation was also suggested between lithium levels in drinking water and suicide risk reduction [46]. Lithium is predominantly absorbed in GI tract and excreted through kidneys [47] which may suggest lesser role of (occupational) inhalation as entry route. Even at therapeutic levels this metal can interfere with multiple enzymes, affecting also hematopoiesis, glycogen synthesis or embryonic development [48]. These and other actions of Li on the molecular level are attributed to its ability to interfere with phosphatidyl inositol (PI) second-messenger system, and related receptors activity, as well as to regulate protein kinase C (PKC) and arachidonic acid signaling cascades [49]. Toxicity towards human cardiomyocytes, in other studies, was connected with alteration in glycogen synthase kinase 3 beta signaling [50].

Risk associated with battery cell production

Depending on the level of production process automatization operators can be exposed to solvents, electrolytes or metal powders used in battery production process. Occupational safety regulations in many countries stipulate exposure limits for number of these substances (e.g., GESTIS – International limit values for chemical agents [51]). N-Methylpyrrolidone, used to dissolve the polyvinylidene fluoride (PVDF) binder

during cathode coating, is an example of toxic compound which emission has to be controlled in the process [52]. N-Methylpyrrolidone is most commonly absorbed through the skin and is irritating towards eyes, lungs, respiratory system. It also has teratogenic effects and prolonged exposure, as with many organic solvents, may harm kidneys, liver and nervous system. Permissible exposure limit (PEL), set by Occupational US Occupational Safety and Health Administration (OSHA) is 1 ppm during 8-hour work day [53].

Other example of occupational risks include contact with metal powders, either during their production or forming active cathode material. Finely divided lithium, cobalt, manganese or nickel can create combustible/explosive mixtures with air (combustible dust) [54] and pose serious health threat when inhaled, especially chronically. Assessment of these health risks led to establishing occupational exposure limits (by different regulatory bodies) for these 4 metals, which are summarized in Table 2. In addition, lithium (especially in the powder form), being an alkali metal, is as well very reactive in contact with moisture, while nickel and aluminum (used e.g., for current collectors) are a reactive metal pair, which must be kept separated. Environment where these materials are stored and used then need to be properly ventilated, and working with them organized towards minimizing effect on operators. This is achieved, among others, locating number of cell assembly steps, from electrodes constituents mixing to electrolyte filling, in controlled conditions of ISO 8 or ISO 7 class clean rooms [13]. Environment with defined upper limits of suspended particles and number of per-hour air changes (as per ISO 14644 standard) is required predominantly to achieve contaminant free electrodes, albeit creates work environment safer as well for the operators.

Another type of risk arising from battery manufacturing, although considered in a longer time perspective, is

Table 2. Occupational exposure limits for active metal cathode components (based on [87])

Organization	Exposure limit type	Active metal cathode component			
		lithium hydride	cobalt metal, dust and fume	manganese, compounds and fume	nickel, metal and insoluble compounds
OSHA	PEL-TWA (8-hour)	0.025 mg/m ³	0.1 mg/m ³		1 mg/m ³
	PEL-STEL				
	PEL-C			5 mg/m ³	
NIOSH	REL-TWA (up to 10-hour)	0.025 mg/m ³	0.05 mg/m ³	1 mg/m ³	0.015 mg/m ³
	REL-STEL			3 mg/m ³	
	REL-C				
ACGIH	TLV-TWA (8-hour)		0.02 mg/m ³ (inhalable particulate matter)	0.02 mg/m ³ (respirable particulate matter) 0.1 mg/m ³ (inhalable particulate matter)	elemental: 1.5 mg/m ³ (inhalable particulate matter) insoluble inorganic compounds (NOS): 0.2 mg/m ³ (inhalable particulate matter)
	TLV-STEL				
	TLV-C	0.05 mg/m ³ (inhalable particulate matter)			
Cal/OSHA (DOSH)	PEL-TWA (8-hour)		0.020 mg/m ³	0.2 mg/m ³	0.5 mg/m ³ (metal) 0.1 mg/m ³ (insoluble compounds)
	PEL-STEL			3 mg/m ³	
	PEL-C				

ACGIH – American Conference of Governmental Industrial Hygienists; Cal/OSHA – California Occupational Safety and Health Administration; DOSH – Division of Occupational Safety and Health; NIOSH – National Institute for Occupational Safety and Health.

C – ceiling (the concentration that should not be exceeded during any part of the working exposure); PEL – permissible exposure limit; REL – recommended exposure limits; STEL – short-term exposure (15-minute time-weighted average exposure that should not be exceeded at any time during a workday); TLV – threshold limit value; TWA – time-weighted average (over given period of time).

the CO₂ gas emission. According to MIT researchers, manufacturing LIBs holding 80 kWh (capacity of e.g., Tesla Model 3 battery) can produce 2400–16 000 kg CO₂ [55]. Lower estimates base on manufacturing located in Europe and U.S. while higher on locations in China and East Asia, and strongly correlate with energy mix involved. These values, however, include effects of raw materials mining and refining, electrode material production (e.g., coprecipitation and calcination of NMC powder) as well as cell production and battery assembly. Manufacturing is

responsible for ca. 30% of the overall energy used (and so CO₂ produced), predominantly for heating stages, and clean/dry environment preservation [56]. In respect to electric vehicles contribution to greenhouse gas (GHG) production during their lifecycle, EPA ascribe 18% of this value to batteries, assuming (among others) U.S. average grid emissions [57]. Interestingly, even with this component missing in gas cars, their overall GHGs emission is over 2 times greater than EVs with ~500 km (300 miles) range.

Risks during casual usage

Thermal runaway is one of the most recognized safety issues for lithium-ion batteries end users. It is a process of rapid self-heating, driven by internal exothermic reactions, which may end up in cell destruction, release of toxic gases and a high risk of fire or explosion [58]. This self-perpetuating process may be initiated by disruption of battery integrity (e.g., casing puncture), internal failure (e.g., short cutting) or its mistreatment (e.g., overheating or overcharging). Rise of cell temperature >70 – 90°C , state-of-charge depending, leads to protective SEI layer breakage. Exothermic decomposition of electrolyte and its reaction with intercalated lithium follows when temperature reaches $>120^{\circ}\text{C}$. Sealing separator pores at this stage aims to prevent anode and cathode shortcutting, although with further temperature growth most separators lose integrity. Between 150 – 350°C products of cathode decomposition react with electrolyte and deliver oxygen, which promotes further temperature increase and PVDF binder exothermic reaction with lithiated carbon ($>200^{\circ}\text{C}$). Temperatures during such events may exceed 600°C and melt aluminum current collectors and other casing elements. Regardless of cathode type during thermal runaway 18 650 cell releases around 1.2 l of gas per Ah of capacity [59]. This volume cannot be contained in standard enclosure and safety features, in a form of safety valves, aim to prevent uncontrolled pressure build up and explosion [60]. Physical injury and equipment damage are probable due to high temperature, corrosive nature of expelled materials as well as toxic nature of gases released. Garbage, recycle trucks and landfill fires ascribed to discarded batteries damage were documented. Fire accident involving cargo of batteries transported by UPS flight pushed U.S. Department of Transportation to establish regulations in this regard. While in 2006 some major laptop manufacturers had to recall a number of products after included batteries fires and explosions were reported [61].

Released during thermal events is typically a mixture of flammable, toxic, and corrosive volatiles, including carbon di- and monoxide, hydrogen, oxygen, short chain hydrocarbons (e.g., ethane, methane) and compounds containing fluorine [62].

Another group of irritant, harmful, toxic and/or flammable LIB elements are solvents. According to U.S. Department of Energy Protective Action Criteria (PAC) classification [63] even 250 ml of most of commonly used solvents, released in a confined space, can be harmful. This amount invokes level 2 Acute Exposure Level Guidelines (AELGs) symptoms, i.e., irreversible or other serious, long-lasting, adverse health effects or an impaired ability to escape. For highly volatile electrolytes, e.g., diethyl carbonate, 1,2-dimethoxyethane, 1,3-dioxolane or 2-methyl-tetrahydrofuran this level of toxic effects may occur with volumes below 15 ml, evaporating into a 63 m^3 space [64]. Assuming that electrolyte accounts for 11–15% of a 46 g lithium battery weight (exception is NMC chemistry, where it is $<2\%$), three 18650 cells contain this volume. For reference, battery packs of Tesla's models S and X are built of >8000 of such cells, version dependent. Damage to battery casing in a closed space (storage facility, garage) then, may easily create life threatening conditions. In addition, evaporation of these volatile organic compounds in case of temperature rising is the primary risk factor for cell enclosure rupture.

Flame-retardant additives (e.g., fluorophosphates) present in solvents also contribute to vent gas toxicity.

The main source of hydrogen fluoride-containing compounds, however, are reactions including lithium salts and water. Residual water can be present in solvent itself or become available following cell damage. The effects include release of gaseous hydrogen fluoride (HF), phosphorus pentafluoride (PF_5) and phosphoryl fluoride (POF_3). Single publication suggests also pentafluoroarsenic and pentafluorophosphate presence in compromised batteries [65]. Considering PAC measures, 24 ppm (20 mg/m^3)

concentration of HF after 1 h exposure can lead to mentioned level 2 AEGLs health effects. This exposure level results from a release of ca. 20 ml of 1 mol LiPF₆ electrolyte in 62 m³ room [64].

Disposal and recycling

Spent batteries final destination is a municipal solid waste landfill, waste-to-energy facility (e.g., waste incinerator) or specialized recycling facility. The first option is still the most probable one, unless local regulations are introduced. It also bears the most significant risk of leaching metals from stored cell cathodes into underlying groundwater or places where biosolids (produced during landfill leachate treatment) are applied [66]. Potential to release toxic elements to water supplies is the reason for most of the countries to require dumpsites to introduce liner and leachate treatment systems.

Lithium-ion batteries have potential to release number of metals with varying levels of toxicity to humans. While copper, manganese and iron, for example, are considered essential to our health, cobalt, nickel and lithium are trace elements which have toxic effects if certain levels are exceeded [67]. All LIBs can potentially release lithium, cobalt is another metal of concern and nickel, copper, as well as iron have genotoxic effects and can lead to premature aging [68]. Thallium, occasionally found in LIBs, is absorbed through skin and has relatively high toxic potential when compared with other elements at similar concentrations [65]. Number of studies aimed assessing the risks associated with permanent storage of lithium batteries in landfills [11]. Using laboratory-scale leaching models, cobalt, copper and nickel, released from studied cells, significantly exceeded regulatory threshold concentrations (RTC). In regards to chromium, lead and thallium only some among studied samples have shown above-RTC levels [69]. Findings of Shen et al. [50] show, on the example of lithium, that lack of proper LIBs utilization/recycling together with their growing numbers

already poisons Yangtze and other Shanghai rivers. Elevated levels of this metal were also measured in Shanghai tap water. Higher amounts of Li are harmful for aquatic and terrestrial environments, while its concentration raising in food chains bring harm to humans and other animals.

Other cell elements are rarely treated as battery-specific risk factors, due to their stability and levels comparable to other waste streams. For example, carbon-based anode material in popular LIBs, including graphite, activated charcoal and some types of mesoporous carbon is inert and considered safe for the environment. Other types of mesoporous carbons however are IARC group 2B possible human carcinogens. Polypropylene and polyethylene separator materials are ubiquitous polymers, and dominating element of microplastic pollutants negatively affecting whole (predominantly marine) ecosystems. Polypropylene microparticles were also shown to stimulate immune response in human PBMC cells [70]. Toxicity of consumer plastic products lacks comprehensive assessment, despite number of concerns.

In relation to the problem of heavy and transition metals (Hg, Pb, As, Cu, Ni and Cr) leaching and accumulation of in the environment it is worth to mention phytoremediation. This method harness plants for contaminated soil, water and air clean up. Some plants (hyperaccumulators), possibly through long-term exposure, gained abilities to bioaccumulate, degrade or render harmless pollutants in a solar-powered, although long lasting process. Nickel, cobalt, iron, platinum, palladium and other heavy metals accumulated in aerial parts of the plants may then be recovered through metal phytomining [71]. Example of *Alyssum bertolonii* Desv. (*Brassicaceae*) show that some nickel hyperaccumulators are able to reach its content of 1%, translating to 10% metal in the ash [72]. Nickel was also found to create complexes with citric and methylated aldaric acid in latex derived from other hyperaccumulator, endemic tree from New Caledonia – *Pycnanandra*

acuminata [73]. Other studies indicate that some bacteria and fungi can be used to bioremediation of various heavy metals pollution [34].

Report from research agency MarketsandMarkets [74] assesses that the global battery recycling market in 2020 was worth USD 17.2 billion and will grow to USD 23.2 billion in 2025. Concerning lithium-ion cells recycling specifically USD 1.5 billion in 2019 is believed to reach USD 12.2 billion in 2025 and USD 18.1 billion in 2030 [75]. Different factors however may be responsible for the development of spent LIBs recycling. Energy used during lithium-ion batteries raw materials extraction and transportation, often >20 000 nautical miles, exemplifies non-sustainable supply chain. These factors, in addition to a substantial CO₂ production led manufacturers to invest in recycling of used batteries and shift towards the use of recovered materials. The cost of cobalt, nickel as well and production technology are the main elements affecting final battery production cost [76]. Availability and price of metals composing cathode determine profitability of lithium batteries recycling. Anodes are recycled mainly for the copper collectors, although new chemistries may change that.

Eventuality of LIBs incineration with domestic waste stream produces incineration bottom ash (IBA), which contains recoverable metals. Specialized treatment trains are able to recover close to 90% of non-ferrous metals (from 4–50 mm particle size), which are the most valuable part of IBA. Interestingly, methods also exist for efficient metal extraction from IBA disposed of in landfills, which was practiced in the past. The scale of this approach is economically argued, and may become more significant in the future.

This approach aligns also with an idea to treat spent LIBs as “artificial minerals”, a source of metals which separation is much easier than from natural sources. Industrial scale extraction of these elements is currently based on 2-step process. Pretreatment, which includes deactiva-

tion, crushing and thermal/physical treatment result in separation of binder, plastics/aluminum (casing), electrolyte, steel, as well as smaller amounts of Co, Cu and Li₂CO₃. Subsequent are pyrometallurgical or hydrometallurgical processes, which in a step-wise manner delivers remaining metals. Drawbacks of the former include substantial energy required to render waste gases safe, as well as metal-rich slag byproduct not being cost effective for further processing [77]. Latter method involves the use of strong reductants and organic or inorganic acids as leaching agents. Number of proprietary processes involve both hydro- and pyrometallurgical elements [11] and depending on the (pre)treatment methodology, leaching and precipitation chemistry recovery rates of Li, Co, Mn, Ni (in pure or salt form) reach 100% in some cases, and >90% in most [78]. Growing size of this market and expected profitability propel studies in making recycling more efficient but also greener. Example are trials with bio-hydrometallurgical methods, which employ *Acidithiobacillus ferrooxidans* to produce sulfuric acid and ferric ions used for leaching [79]. Symptomatic for circular economy are also efforts to develop in-house recycling technologies and facilities by batteries manufacturers [80], leading to shortening supply chains, feeding-back/coupling know-how from production to recycling stage and vice versa.

CONCLUSIONS

The use of energy grows steadily for the last 65 years and will continue to do so, led strongly by the growth of Asian countries. Production and storage of this medium will have to follow demand, and use gradually more green and renewable resources. Batteries stand in the center of this process and adequate measures will have to accompany sourcing their substrates, developing better energy storage technologies and dealing with waste – destiny of each LIB after 3–10 years of usage. Efficiency of existing (and continuous search for improved) recycling methods allow

us to reduce the energy required for crucial energy transition metals extraction. On the other hand, recovering and repurposing of valuable batteries ingredients is not necessarily (yet) a profitable business model, especially in the absence of regional regulations.

In this review the authors focus on human and environmental costs of LIBs, recognizing that these are 2 “branches of the same tree.” Life-cycle environmental impact assessments (LCAs), published by manufacturers or independent organizations have the same aim, although demonstrate as well challenges of such comprehensive task. Recent review by Porzio and Scown [81] highlights that future LCAs should include, for instance, progression of shrinking resources obtainment costs, extraction and mining taking place outside controlled industry environment (e.g., artisanal cobalt mining), scale effects achieved in big manufacturing facilities or dropping kilograms of battery mass as a functional unit for its capacity. Existing and new LCAs, with the use of growing amount of data, will be needed to build energetically sustainable future. Strain exerted on the environment with scaling production, as well as LIBs manufacturing conditions have to be controlled. Mining and processing sites located in less developed countries and managed by Chinese, American or European companies not always seem to comply with their homeland regulations. Extraction and processing of transition metals creates a high-risk environment, where, in most cases limits of exposure to occupational risks are regulated. These thresholds however are also challenged due to lack of transparency, limited supporting data and heavy involvement of industry.

The authors hope that the above summary of selected issues related to the whole “ecosystem” of lithium-ion batteries life-cycle is another voice in the important discussion. Balancing multi-billion business offering us life-easing solutions on one and sustainable, green future on the other scale will never be easy, mainly for that latter side.

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