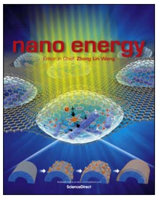
Nano Energy 27 (2016) 313–319

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen



Toxicity, a serious concern of thermal runaway from commercial Li-ion battery☆

Jie Sun [a,*], Jigang Li [a], Tian Zhou [a], Kai Yang [c], Shouping Wei [a], Na Tang [a], Nannan Dang [a], Hong Li [d,*], Xinping Qiu [b,*], Liquan Chen [d]

[a] Lab of Renewable Energy and Energy Safety, Institute of NBC Defence, P.O. Box 1048, Beijing 102205, China
[b] Department of Chemistry, Tsinghua University, Beijing 100084, China
[c] China Electric Power Research Institute, Beijing 100192, China
[d] National Laboratory for Condened Mater Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:
Received 11 March 2016
Received in revised form
16 June 2016
Accepted 17 June 2016
Available online 5 July 2016

Keywords:
Toxicity
Thermal runaway
Li-ion batteries
Combustion products
Identification
Emergency response

ABSTRACT

The toxicity analysis of combustion products from commercialized Li-ion batteries was performed in this work. More than 100 emitted gaseous products are identified, most of which are hazardous to the human beings and trigger negative impact on the environment. Moreover, the states of charge of battery was found to significantly affect the types of toxic combustion products, and the 100% state of charge even led to the most serious toxicity. The relationship between the concentration of toxic combustion products and battery capacity was also investigated. Interestingly, the concentration of carbon monoxide rose up rapidly up on the increase of the capacity instead of the toxic organic products. This investigation suggests that the efforts on effective battery emergency response could be potentially simplified to achieve cost down for manufacturers.

1. Introduction

Lithium ion battery (LIB) is one of the most attractive storage devices for new generation environmental friendly energy (hydrogen fuel, solar, wind, etc.) [1–3]. High energy density LIBs play the key roles for the development of electrical vehicles (EVs), portable electronics and stationary energy storages. Public has serious concern on the safety of lithium ion batteries for several years [4–6]. The origin and hazardness of the combustion and explosion of the batteries are understood gradually [7–9]. Abuse of LIBs, especially overcharging or high temperature operation (e.g. over ~130 °C for lithium cobalt oxide cathodes, ~250 °C for lithium manganese oxide cathodes or ~70 °C for graphite anodes), could susceptibly ignite the flammable substances in LIB and trigger thermal runaway [10–12]. The large amount of heat could lead to further exothermal reactions, which will propagate to adjacent cells and set fire to the surrounding combustible materials. Consequently, a pack of cells can easily be destroyed within a short time frame (in seconds) due to this chain reaction [13]. In this case, the fire starts unexpectedly due to the combustion of highly energetic active materials contacting flammable organic-solvent-based electrolytes, and eventually leads to a situation out of control [14–23]. The thermal runaway did cause safety concern for the LIB utilization, and consequently forced costly recalls of millions of batteries [16]. Even worse, the flammable and toxic gaseous mixture (H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, HF, POF_3, PF_5, ethyl fluoride, propylene etc. [14,15]) produced from these combustion reactions could be released into the air and cause environmental issues and incidents.

The safety of LIB has been improved significantly now through using of safer materials, better cell design, cooling system and enhancing the safety control of storage and transportation. However, the risk and accident of the LIB cannot be avoided 100%. The thermal runaway of LIBs was generally studied by external heating and fire test of various commercial available cylindrical and pouch batteries in a calorimetry, such as differential scanning calorimetry (DSC) or accelerating rate calorimetry (ARC) [19]. These instruments are equipped with controllable sensors for monitoring the heat and products release to stimulate the actual accidental scenarios. In some occasions, these instruments are constructed with

---

☆Electronic Supplementary Information (ESI) available: Video files of combustion, NMC-18,650 combustion, LMO-18,650 combustion, LCO-18,650 combustion, LFP-18,650 combustion, NMC-10 A h combustion, LMO-10 A h combustion. GC-Mass original spectrum and results of different LIBs and SOCs, NMC-18,650 0f 0%, 50%, 100%, 150% SOC; LMO-18,650 of 0%, 50%, 100%, 150% SOC; LCO-18,650 of 0%, 50%, 100%, 150% SOC; LFP-18,650 of 0%, 50%, 100%, 150% SOC; One GC-Mass test spectrum of 168 combustion production.

[*] Corresponding authors.

E-mail addresses: magnsun@mail.tsinghua.edu.cn (J. Sun), hli@iphy.ac.cn (H. Li), Qiuxp@mail.tsinghua.edu.cn (X. Qiu).

http://dx.doi.org/10.1016/j.nanoen.2016.06.031
2211-2855/

in-situ gas analysis equipment to classify the toxic exhausts and study the behaviors of hazardous gases. Large numbers of tests have confirmed that CO_2 and H_2 were generated by oxidation of the electrolyte at the surface of electrode associating with small amounts of CH_4, C_2H_4, C_2H_6, C_3H_8 etc. [20]. HF was considered as the most critical gas in F-containing cell components leading to the formation of fluoro-organic compounds (FOCs) [21–23]. Although these obtained results have confirmed that these vent gases are toxic and ignitable, the knowledge of toxicity is still very limited. Specific toxicity and flammability limits of different combustion mixtures are need to be estimated. In other words, more comprehensive data are highly desired to establish a full scale assessment of thermal database to prioritize the most important reactions and severe situations.

The purpose of this paper is to report a comprehensive examination of LIB thermal runaway combustion products (CPs). In addition to gaseous products reported earlier, more than 100 organic molecules were identified after running the combustion testing of four kinds of commercial 18,650 LIBs. The CPs' toxicity dependence on batteries state of charge (SOC) and capacity, the response time for LIBs thermal runaway fire, and the possible reasons leading to the formation of the CPs were discussed.

2. Experimental section

2.1. Selection of LIB types

Two types of commercial LIBs (18,650 LIB and pouch LIB)were selected to do the thermal runaway combustion tests. The 18,650 LIBs was with four types of cathodes: spinel $LiMn_2O_4$, NMC material ($Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$), $LiCoO_2$ and $LiFePO_4$. The pouch LIBs were with two types of cathodes: NMC material ($Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$) and spinel $LiMn_2O_4$.

2.2. Combustion experiments

A combustion chamber was well designed for the LIBs combustion tests. The chamber was an 80 × 80 × 80 cm^3 stainless steel apparatus with a steel glass panel on side for in-situ video record. A hole on top of the apparatus was opened as the combustion gases outlet. The LIBs were ignited by a 2–3 cm high flame directly. A SiO_2 grid was placed in between the flame and the battery to evenly distribute heat. The flame was turn off right after the battery was ignited.

2.3. Methods description of combustion products detection

The volatile organic compounds (VOCs) of the combustion products were analyzed by GC-Mass (GC–MS HAPSite). A chemical identification system (INFICON® HAPSite ER) was used to separate and detect the VOCs. The emitted CO gas was detect by Multi-gas monitor (M40). The collected mix gas was diluted 2–100 times to test if CO concentration out of range. The CO_2, PO_x and HF gases were absorbed by saturated sodium hydrate water solution under negative pressure. The resulted solution contained $CO_3{}^{2-}$, $PO_4{}^{3-}$ and F^{-1} was diluted 20 times and examined by an ion chromatography (IC, Thermo Fisher™ ICS3000).

3. Results and discussion

3.1. Toxic volatile organic compounds from 18,650 LIBs combustion

The toxicity classification of the emitted VOCs is listed in Table 1. Six classification levels including I (very toxic), II (highly toxic), III (toxic), IV (harmful) and V (low toxic) and VI (Few Toxic) level are defined according to China National Standards including GB5044-1985 Classification of health hazard levels from occupational exposure to toxic substances and GBZ230-2010 Classification for hazards of occupational exposure to toxicant, and WHO/IPCS The User's Manual for the IPCS Health and Safety Guides.

Four kinds of 18,650 LIBs with $LiMn_2O_4$ (LMO), NMC, $LiCoO_2$(LCO) and $LiFePO_4$(LFP) cathodes, were chosen to be investigated right after assembled in this study. When the heat was applied to LMO cell, around 10–15 cm flame sputtered out from the sealed metal shell of the battery after about 2 min, then the battery exploded violently before the flame extinct. The NMC battery also had a 10–15 cm flame from the sealed metal shell after 1 min 20 s, accompanied with white smoke but no explosion occurs. Severe combustion was observed from LCO cell also. Only LFP showed a relatively milder combustion process, in which a weak flame with small amount of smog was observed after heat treated for 3 min 12 s, and then was extinct spontaneously. The combustion processes of four types of 18,650 LIBs of LMO, NMC, LCO and LFP are shown in **Video V1-V4(ESI†)**, respectively. These tests indicate that the LFP does show significantly enhanced safety in view of explosion.

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.nanoen.2016.06.031.

At various SOC of 0%, 50%, 100% and 150%, the batteries' volatile organic products from combustion (COPs) were examined from these four kinds of 18,650 LIBs. The GC-Mass spectrum original spectrum and analysis results are shown in Spectrum S1–S4 (ESI†) and Excel Table E1-E4 (ESI†), respectively. The identifications were based on the results by the INFICON® HAPSite ER identification system analysis of GC-Mass original spectrum, from which the possible COPs could be determined. The number of identifications (NIs) shown in Table 2 have been taken out the number of internal standard substances. Interestingly, the NIs of COPs from those four kinds of LIBs is dependent strongly on the batteries' SOC. Also, it is following the trend that the NIs increased with the SOC increasing

Table 1
Six levels toxicity classification for the volatile organic compounds form LIBs combustion.

Level	GB5044			GBZ230					WHO/IPCS		
	inhalation	via skin	via mouth	Inhalation			via skin	via mouth	via mouth	via skin	Inhalation
	LC50 mg/m^3	LD50 mg/kg	LD50 mg/kg	Gas cm^3/m^3	Vapor mg/m^3	Mog mg/m^3	mg/kg	mg/kg	mg/kg	mg/kg	mg/m^3, 4 h
I/Very toxic	< 200	< 100	< 25	< 100	< 500	< 50	< 5	< 50	< 25	< 50	< 500
II/Highly toxic	200–2000	100–500	25–500	100–500	500–2000	50–500	5–50	50–200			
III/Toxic	2000–20,000	500–2500	500–5000	500–2500	2000–10,000	500–1000	50–300	200–1000	25–200	50–400	500–2000
IV/Harmful									200–2000	400–2000	2000–20,000
V/Low toxic	> 20,000	> 2500	> 5000	2500–20,000	10,000–20,000	1000–5000	300–2000	1000–2000			
VI/Few toxic				> 20,000	> 20,000	> 5000	> 2000	> 2000			