Journal of Power Sources 316 (2016) 197–206

Contents lists available at ScienceDirect

Journal of Power Sources

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

Scenario-based prediction of Li-ion batteries fire-induced toxicity

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HIGHLIGHTS

- Combustion tests of 1.3 Ah based LiFSI and $LiPF_6$ cells using *Tewarson* apparatus.
- Data processing of 'source terms' for thermal and toxicity impact assessment.
- Analysis of a 100 cells – 6.5 Ah module fire scenario in a 30 m^3 ventilated enclosure.
- Comparative fire induced toxicity as differentiated from the salt viewpoint.

ARTICLE INFO

Article history:
Received 4 December 2015
Received in revised form
19 February 2016
Accepted 29 February 2016
Available online 4 April 2016

Keywords:
Li-ion battery
Combustion
LiFSI
Fire gases toxicity
Tewarson apparatus

ABSTRACT

The development of high energy Li-ion batteries with improved durability and increased safety mostly relies on the use of newly developed electrolytes. A detailed appraisal of fire-induced thermal and chemical threats on $LiPF_6$- and LiFSI-based electrolytes by means of the so-called "fire propagation apparatus" had highlighted that the salt anion was responsible for the emission of a non negligible content of irritant gas as HF (PF_6^-) or HF and SO_2 (FSI^-). A more thorough comparative investigation of the toxicity threat in the case of larger-size 0.4 kWh Li-ion modules was thus undertaken.

A modeling approach that consists in extrapolating the experimental data obtained from 1.3Ah $LiFePO_4$/graphite pouch cells under fire conditions and in using the state-of-the-art fire safety international standards for the evaluation of fire toxicity was applied under two different real-scale simulating scenarios. The obtained results reveal that critical thresholds are highly dependent on the nature of the salt, $LiPF_6$ or LiFSI, and on the cells state of charge. Hence, this approach can help define appropriate fire safety engineering measures for a given technology (different chemistry) or application (fully charged backup batteries or batteries subjected to deep discharge).

1. Introduction

Electrification of ground and even partially air transportation is seen as an important aspect of cutting emissions and reducing global warming, and nowadays Li-ion batteries are considered as the most appropriate technology in terms of energy and power capacities. However, safety is still regarded as a thorny issue as a Li-ion battery failure can lead to fire and smoke generation, which has, for instance, made airline companies ground flights, causing significant economic damages.

Many research efforts are devoted to finding more stable battery active materials [1], electrolyte [2] and separator chemistry [3]. For that purpose, the prediction of toxic combustion products and the comparative assessment of the effect on humans following acute exposure to these chemicals may yield valuable results.

Owing to its relative narrow potential stability window and its flammable constituents, the electrolyte is viewed as the weak link of the Li-ion battery (LIB). However, the development of optimized lower-potential lithium-iron phosphate as positive electrode material [4] offers opportunities to use safer electrolytes. For instance, ionic liquids [5], glyme ethers [6,7], gels and polymers [8] are all subject to intensive research with the aim to replace carbonates solvents. Other lithium salts can also be envisioned as substitutes

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http://dx.doi.org/10.1016/j.jpowsour.2016.02.090
0378-7753/© 2016 Published by Elsevier B.V.

for the $LiPF_6$ which is used in the ~4 V functioning LIBs because of aluminum collector corrosion [9,10] though prone to promote deleterious PF_5 Lewis acid formation at elevated temperature. Hence, nowadays Lithium bis(fluorosulfonyl)imide $LiN(SO_2F)_2$ (called LiFSI) [11,12] is a serious candidate for entering the composition of liquid electrolytes in the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ [13] or $LiFePO_4$-based batteries, with the aim to provide higher conductivity and the best low temperature performances.

From our previous studies devoted to the combustion behaviour of $LiPF_6$- or LiFSI-based carbonate electrolytes [14], the fire-induced pollutant emission was found, in well ventilated conditions, to be mainly dictated by the nature of the salt as a source of HF or SO_2, with very limited concerns emanating from the organic solvents. As a continuing part of this detailed stepwise investigation, we undertook a comparative fire-induced chemical threats examination of 1.3 Ah $LiFePO_4$/graphite cells containing previously tested electrolytes, through *Tewarson* calorimetry experiments. Afterwards, experimental data obtained on tested cells were used to predict the fire-induced toxicity of a fictive 0.4 kWh module (obtained by a series/parallel assembly of 100 such cells) under different real-scale simulating fire scenarios. For both testing the cells on the *Tewarson* apparatus as well as in the relating modeling exercise, well ventilated conditions were maintained experimentally for reasons of consistency with previous experimental work performed [14] and similarly, same conditions were assumed prevailing in the modeling exercise. It must be noticed that fuel rich conditions which would result from under-ventilated fire conditions that might occur in enclosure fires (low O_2 environment) might significantly change results: in terms of toxicity, conventional toxics like CO_x would likely dominate the chemical threat as in most conventional such fires. Although of less important impact, air moisture may also affect HF concentrations in fire smoke achieving remote locations, due to hydrophilic nature of HF gas.

2. Methods

2.1. $LiFePO_4$/graphite Li-ion cells combustion tests (see Fig. 1)

The studied 1.3 Ah (4.2 Wh) $LiFePO_4$/Graphite flat pouch cells assembled at CEA (Grenoble) were activated with EC/PC/DMC (1/1/3, wt) 1 M LiFSI- or $LiPF_6$-based electrolyte (called LF100 resp. LP100). The LiFSI-based electrolyte was prepared inside a dried glove box (O_2 and H_2O < 0.1 ppm) with pure solvents (purity > 99.9%) purchased from Merck supplier and a high quality LiFSI salt obtained from Suzhou Fluolyte Co. Ltd. Both electrolytes contain 2 wt% of vinylene carbonate (VC) additive. Sodium carboxy methyl cellulose (Na-CMC) was used as binder at positive and negative electrodes. The active materials represent about 45%, the current collectors 17% and the remaining compounds as electrolyte, separator, binder and packaging materials 38% of the battery total mass (38 g).

The fire calorimetry tests were undertaken at three different states of charge (100, 50 and 0% SOC) and were reproduced two times. The electrochemical cycling was performed with a VMP system (Biologic, Claix, France) equipped with an amplifier. Initial formation of all cells was performed by galvanostatic charge/discharge cycle at C/10 between 2.5 and 3.6 V, then the cells were brought to the required state of charge in less than 12 h before conducting the fire tests.

Fire tests were carried out by means of the *Tewarson* apparatus also designated as the Fire Propagation Apparatus (FPA- ISO 12136) developed in the mid 70's up to standardization (NFPA, ASTM, and lately at ISO level) in the early 90's [15–17]. The thermal aggression of the cell placed in a combustion region physically delimited by a quartz tube was provided by a 25 kW/m^2 external heat flux using four infrared heaters (see working principle and picture of this fire calorimeter in Fig. 1). An air flow of 350 L min^{-1} was kept constant during the test in order to simulate well-ventilated conditions. As the preliminary fully charged cell fire test without ignition source resulted in a no burning event, a pilot flame placed at about 6 cm above the cell was set to induce piloted ignition.

Upon combustion, fire products were captured in the sampling duct, where the gas temperature and the product-air flow rate are measured. The in-situ on-line analysis of the diluted fire products includes the quantification of O_2 (using a paramagnetic analyzer), CO and CO_2 using a non-dispersive infra-red (NDIR) analyzer and a Fourier-transform infra-red (FTIR) spectrometer, soot through optical measurement and total hydrocarbons (THC) by means of a flame ionization detector (FID). An on-line FITR apparatus provides quantitative information regarding gas release such as CO, CH_2O, HCN, NOx, SO_2 or fluorinated species as HF according to calibration processes. CO_2, CO and O_2 quantification gives access to the effective heat of combustion and heat release rate thanks to fire calorimetry equations whose principles are expressed in Ref. [18]. The quantification of the asphyxiant and irritant pollutants will be used as input data for chemical threats assessment modelled for a 0.4 kWh module.

2.2. Scenario based analytical assessment of fire-induced toxicity

Section 1 explains how generic scalable data can be produced in terms of yields of toxic products issuing from a controlled combustion process, provided appropriate experiments are correctly implemented. However related toxic risk assessment must be scenario based to achieve relevance. This risk assessment constitutes the modeling part of the work. It was carried out considering other input data or assumptions in addition of previously presented experimental results, namely: i) a battery pack of capacity corresponding to actual potential applications was defined as an assembly of 100 cells having characteristics of those tested; ii) a fire propagation model was defined, allowing the discrimination of two scenarios and reflecting potential cascade failures of individual cells blocks according to localisation of first failed cell block; iii) emission of fire gases were assumed to perfectly and instantaneously mix within the defined enclosure which provides an analytic solution giving the concentration of each toxic species emitted during the fire scenarios studied versus time; iv) eventually, a fire toxicity model computing time to incapacitation was selected to translate toxic emission profiles into toxic impact to people. At least partial validation of the methodology has been performed. The toxicity incapacitation model is the best consensual model recognized by fire experts members of the ISO TC92 SC3 subcommittee (Fire Safety – Fire threat to people and the environment, standard 13471), the fire propagation model considers critical time defining “cascade failure” occurrence to nearby blocks of five cells according to real observations made by the authors in proprietary battery pack fire testing involving similar or larger pouch cells.

In practice, fire-induced toxicity assessment was exemplified by considering fires in an enclosure involving a reference module mocking-up a fictive battery pack obtained by an assembly of 100 pouch cells meeting characteristics of those tested at lab-scale, and arranged in a configuration 20s5p leading to a nominal voltage of 66 V, a nominal capacity of 6.5 Ah and a nominal energy content of 0.4 kWh. Indeed, one module with energy content limited to some 0.5 kWh is typically used for micro or micro-mild hybrid applications [19,20]. For simulation, the “fire” scenario is assumed to develop as such (fire propagation model): i) a block of 5 cells in parallel ignites simultaneously in all 5 cells first, ii) this first ignited block of cells consequently triggers a fire propagation process (wave propagation) to the other 19 blocks of 5 cells according to