



External short circuit performance of Graphite-LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and Graphite-LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cells at different external resistances



Akos Kriston^{a,*}, Andreas Pfrang^a, Harry Döring^b, Benjamin Fritsch^b, Vanesa Ruiz^a, Ibtissam Adanouj^a, Theodora Kosmidou^a, Jürgen Ungeheuer^a, Lois Boon-Brett^a

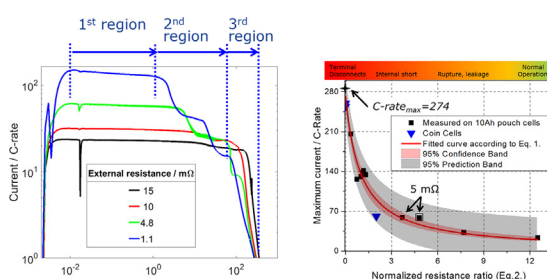
^a European Commission, Joint Research Centre (JRC), Directorate for Energy, Transport and Climate, Westerduinweg 3, 1755 LE Petten, The Netherlands

^b Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Lise-Meitner-Straße 24, 89081 Ulm, Germany

HIGHLIGHTS

- 10 Ah pouch, 4.5 mAh single coin cells and 3s 10 Ah Li-ion cells are compared.
- Double layer, mass transport and electromotive force limited regions are identified.
- The derived normalized external/internal resistance ratio influences the hazards.
- Soft short conditions up to resistance ratio ca. 10 can create hazardous situations.
- Implications on the relevance and fitness-for-purpose in standards are outlined.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aims at analyzing the response of Li-ion cells and at identifying the hazards and governing phenomena from hard to soft external short circuit conditions. 10 Ah pouch cells and 4.5 mAh coin cells were short circuited while synchronized current, potential and temperature signals, audio, IR and visual video recordings were registered. The anode, cathode and separator harvested from the cells were characterized by Scanning Electron Microscopy, micro X-ray Computed Tomography and 3D-profilometry.

The complex short circuit behavior obtained can be described by 3 regions: In the first region 274C-rate is observed which is mainly governed by the cell's double and diffusion layer discharge. In the second region, the current drops significantly to 50–60C-rate where mass transport becomes the current limiting factor. The maximum temperature (77–121 °C) is reached and cell rupture, venting and electrolyte leakage may occur. In the final, third region the current decline continues due to the decaying electromotive force. The normalized external/internal resistance ratio is found to be the main influential factor on current and hazards rather than the external resistance or the capacity of the cell. The implications on the relevance and fitness-for-purpose of external short circuit test in standards are outlined.

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* Corresponding author.

E-mail address: akos.kriston@ec.europa.eu (A. Kriston).

1. Introduction

Safety tests or abuse tests have been applied to Li-ion batteries since their first introduction to the market [1]. These tests were standardized for every specific application (e.g. portable applications IEC 62133:2012 [2]) to provide assurance that a product can be used safely in these applications (e.g. laptops, mobile phones). Despite the intensive testing, safety related events such as the Boeing Dreamliner incidents [3] or Samsung's Galaxy Note 7 battery overheating [4] show that safety standards and regulations still need to be improved.

One of the most widely applied electrical abuse tests is the external short circuit test, which simulates a situation when the battery terminals are inadvertently electrically connected. As a result, the stored electric energy rapidly converts to mainly heat, which may trigger safety related events such as venting, thermal runaway, fire and even explosion. As the external short circuit resistance may vary several orders of magnitude depending e.g. on the distance between the battery terminals and the fault location, the resulting short circuit current is also expected to vary considerably. As Table 1 illustrates, test parameters in standards and regulations typically require only one or two short circuit resistances (e.g. $\leq 5 \text{ m}\Omega$, $1/10$ of the minimum resistance of the cell). Different short circuit resistances (e.g. hard, soft short conditions) can create different hazardous situations and become dangerous for the users of the battery system. Hence the aims of this study are to analyze the response of Li-ion cells to external short circuit for a wide range of external resistances (ranging from sub $\text{m}\Omega$ to $15 \text{ m}\Omega$) and to identify the hazards and governing phenomena. The results can be used as further input for the development of evidence based standards and regulations.

Early studies of external short circuit test on lead acid batteries by Okazaki et al. [18,19] showed the importance of testing conditions (e.g. connection time of terminals) and predicted the initial short circuit current [19]. It was postulated that the maximum current in the beginning of the external short circuit is governed by only the internal ohmic resistance of the battery cell. Spotnitz et al. [20] compared different abuse scenarios by simulating the thermal behavior of Li-ion cells. For external short circuit, it was concluded that the Li-ion diffusion in the negative electrode is the rate limiting step for current and the heat generated by the electrolyte decomposition reaction in the positive electrode is responsible for the occurrence of thermal runaway. In experiments, Larsson et al. compared different lithium iron phosphate (LFP) batteries by applying sub $\text{m}\Omega$ external resistances. They found that during external short circuit tests, the cells reached temperatures slightly above 100°C , inflated and ruptured, emitting non-visible gases, but did not go into thermal runaway [21,22]. Systems with less robust terminals disconnected the circuit and consequently cells remained intact. Conte et al. [23] studied the impact of different cell capacities and showed that the external short circuit current increases with the cell's capacity. It was also highlighted that the response of batteries (e.g. module, pack) to external short circuit conditions can be different for different battery assemblies (serial or parallel connection).

Few numerical simulation studies of external short circuit can be found in the literature [24–26], but with several simplifications. In a multiphysics model, Zavalis et al. [27] compared internal, external and nail penetration caused shorts by solving a partial differential equation system for the behavior of porous electrodes. The results showed that the short circuit current, after a short initial transient region, is limited by the Li-ion diffusion in the electrolyte for all the considered scenarios.

Internal short circuit mechanisms [24,28–31] are more

Table 1
Comparison of external short circuit test conditions as set in standards and regulations. *ISO 12405-3; the test can be conducted at a lower resistance or higher temperature than specified in ISO 12405-1 (2).

Region of applicability	International	EU & Japan	USA	Korea	China
Standard or regulation	SAE J2464 [5]	UN 38.3 [6]	ISO 12405(1)(2)(3) [7–9]	USABC, Freedom CAR [14,15]	QC/T 743 [17]
Device under test (DUT)	Cell, module, pack	Cell, module, pack	Cell, module, pack	Cell, module, pack	Cell, pack
External resistance ($\text{m}\Omega$)	Hard short: ≤ 5 and « DUT DC impedance Soft short: ≥ 10 and resistance comparable to DUT DC resistance	Cell, module, pack 100	Cell, module, pack ≤ 5 (Cell) ≤ 20 (Pack)	Pack 50	Cell, pack < 5
SOC (% rated capacity)	95–100	100	100	≤ 5 ($1/10 R_{int}$ for test articles with $\leq 5 \text{ m}\Omega$)	100
Temperature	RT	57°C	Max. operating SOC RT	Max. operating SOC RT	Max. operating SOC RT

RT: Room temperature.

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