Journal of Energy Storage 17 (2018) 409–416

Contents lists available at ScienceDirect

Journal of Energy Storage

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

Study on survivability of 18650 Lithium-ion cells at cryogenic temperatures

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ARTICLE INFO

Keywords:
Lithium-ion cells
Commercially-off-the-shelf 18650 cells
Cryogenic soak
X-ray computed tomography
Electrolyte freezing point

ABSTRACT

Passive survivability of Commercially-off-the-shelf 18650 lithium-ion cells is tested in a thermal scenario similar to lunar night. Survivability of cells in particular and battery pack in general is crucial for resumption of function of any lunar exploration rover after hibernation at every lunar night. The test is designed to include a batch of Commercial lithium-ion cells from different manufacturers, with different nameplate capacities and different States of Charge. The cell behaviour during the test is monitored in-situ using cell terminal voltage measurements. To comprehend the effect of exposure to extreme low temperatures some complementary tests like visual examination, dimensional measurements, Residual Gas Analysis to detect any leakage, electrical tests to appraise electrical performance and 3 dimensional x-ray computed tomography analysis to view cell internal features are carried out at ambient conditions on cells both prior-to and after soaking at low temperatures. Results indicate successful survivability of tested cells after extreme thermal soak without any significant physical or internal damage or electrical performance degradation. Variation in cell terminal voltage with temperature is a reversible change attributed to the reversible phenomenon of freezing of cell electrolyte which furthermore is confirmed through ex-situ measurement of freezing point of electrolyte extracted from tested cells.

1. Introduction

The Li-ion batteries have revolutionized the field of energy storage ever since the inception of their commercial production in early 1990s [1–5]. Today Li-ion (Lithium-ion) batteries stand-out as state-of-the-art energy storage devices. Having aptly met the massive demand for high performance portable batteries for consumer electronic goods the application of these batteries is expanding to new horizons like electric vehicles, defence and aerospace [6–8]. The application in space exploration missions pose a unique work environment for Li-ion batteries which is largely dictated by their ability to perform at lower temperatures. The low temperature operations undoubtedly depend on the ability of the cell electrolyte to support ionic conduction. The established Li-ion cell chemistry proves to be inferior for charge/discharge operations at temperatures below −20 °C [9–13]. A series of hindering factors are known to contribute towards decline in cell performance at low temperatures; mainly the increased electrolyte viscosity, low ionic conductivity, sluggish Li^+ ion desolvation and electrolyte phase transitions [10,12,16]. Recently lot of developments are brimming in where some task-centric formulations of electrolytes are being developed by fine tuning the electrolyte composition to suit tailor-made applications for operations in temperature range from −10 °C to −40 °C [14–19].

Every space exploration mission is unique in its design, approach and mission management and battery too as a subsystem in any of such space-craft has to cater to exceptional demands. A lunar rover mission for instance requires the battery to support the peak power load when the power generation through solar panels is in-sufficient. At all such operations during lunar day the battery pack temperature can be efficiently managed with-in the optimal window using rover's thermal management elements. The real challenge is to endure passively through the lunar night at prevailing temperatures as harsh as −180 °C for duration of 336 h [20], to be able to operate in the subsequent lunar day. From a battery point of view this challenge is only one of its kind where battery is required to operate (charge or discharge) at ambient temperatures and is required to survive passively (without any load) an exposure to extremely low temperatures preferably, without any permanent loss or damage. Even though the works cited in literature addresses the ways to tackle inferior charge/discharge characteristics of Li-ion batteries by altering electrolyte composition there is hardly any information available about the passive survivability of already existing chemistry of commercialized Li-ion cells at extreme low temperatures below −150 °C and the present work aims to throw some light at this ambiguity.

A Li-ion cell at open circuit conditions and at temperatures as low as

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https://doi.org/10.1016/j.est.2018.03.018
Received 7 January 2018; Received in revised form 18 February 2018; Accepted 28 March 2018

−150 °C or beyond, might experience irreversible damages more severe than electrolyte freezing. This includes probable events like, rupturing of cell's hermetic seal, permanent distortion of electrode jelly-roll or cell swelling beyond acceptable limits. Any of such unforeseen outcomes will result in degradation of cell's electrical performance or worst of all a case of cell failure. The problems stated above are just plausible events and the survivability of a cell is required to be proven against all such odds. This paper reports the ability of a bunch of randomly selected Commercially-off-the-shelf (COTS) 18650 Li-ion cells to passively withstand this challenging thermal circumstance posed by lunar night mission scenario, through a comprehensive set of in-situ and ex-situ measurements and characterizations. This comprehensive approach involves monitoring cell terminal voltage in-situ during the thermal soak. Furthermore verifying the overall health of the cells by conducting some complementary tests at NTP (normal temperature and pressure) both prior-to and after thermal soak. The complementary tests include visual examinations to see any physical damages, dimensional measurements to establish any swelling, Residual Gas Analysis (RGA) to detect any leakage, electrical tests to appraise the electrical performance and 3 dimensional x-ray computed tomography (3D x-ray CT) scan to view the cell internal features. To make the understanding more comprehensive the test is extended to include cells from different manufacturers with different nameplate capacities and each at two extremes of State of Charge (SOC) (very low < 1% and very high > 80%).

2. Experimental details

2.1. Temperature profile for thermal soak experiment

A lunar night is equivalent to 336 h or 14 earth days. Just as the lunar night sets in, in the absence of any heat source the temperature of lunar rover components are estimated to drop sharply from an ambient value. The drop in temperature is steep during initial six hours of night and slows down as the night progresses. Temperature is estimated to stabilize after about 72 h to values below −200 °C [20]. Even though theoretically the lunar surface temperature drops below −200 °C, to simulate the same temperature conditions on ground is a practical difficulty. With liquid nitrogen (LN_2) cooled thermal cycling chambers the best achievable lower temperature is in the range of −150 °C to −170 °C. Hence the selected 18650 Li-ion cells were soaked at a best achievable lower temperature in the range −160 °C to −170 °C for duration of 336 h using a programmable LN_2 cooled thermal cycling chamber with the temperature profile stated above.

2.2. Sample selection

The experiment was designed to include a batch of three different types COTS 18650 Li-ion cells named as 'A', 'B' and 'C' with different nameplate capacities and each at two extremes of SOC. Cell 'C' is a high power cell capable of charge at 1C rate and discharge at C/2 rate. Sample cells were randomly selected from a lot. Tables 1A and 1B shows the details of the Li-ion cells selected for the study and some cell specific details.

Table 1A
COTS 18650 cells selected for low temperature soak test.

Sl No.	Cell label	Nameplate capacity (m Ah)	SOC (%)
1	Cell A1	2600	< 1
2	Cell A2	2600	> 80
3	Cell B1	2800	< 1
4	Cell B2	2800	> 80
5	Cell C1	1000	< 1
6	Cell C2	1000	> 80

Table 1B
Cell specific details giving comparison of selected cells.

Parameter	Cell A	Cell B	Cell C
Cathode active material	$LiNi_xMn_yCo_zO_2$	$LiNi_xMn_yCo_zO_2$	Li-Nickel Oxide
Anode active material	Li intercalated graphite	Li intercalated graphite	Li intercalated graphite
Electrolyte	$LiPF_6$ in EMC:DEC:EC	$LiPF_6$ in EMC:DEC:EC	$LiPF_6$ in DEC:EC
Separater	Single layer of PE	Single layer of PE with one side HRL coat (Alumina)	Single layer of PE

Abbrevations: $LiPF_6$- Lithiumhexafluorophosphate, EMC – Ethylmethyl Carbonate, DEC- Diethyl Carbonate, EC-Ethylene carbonate, PE-Polyethylene, HRL-Heat Resistant Layer.

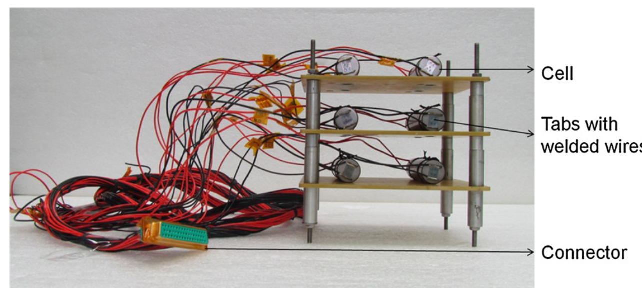

Fig. 1. The experimental setup.

2.3. Preparation of experimental setup

The cells chosen for the test were assembled together into a compact setup as shown in Fig. 1. For monitoring the cell voltages in-situ a provision was made by welding the nickel tabs with previously welded wires onto the cell terminals. The individual wires were connected to a suitable connector to interface with the electrical test system. After the completion of wiring the cells were anchored onto non-conductive base plates which later were stacked to form the test setup as shown in Fig. 1. To monitor the temperature during the progress of the soak, two thermo-couple leads were taped onto two cells in the setup. The test setup was placed inside the LN_2 cooled thermo-cycling chamber and subjected to low temperature soak with the profile close to lunar night mission scenario.

2.4. In-situ cell terminal voltage measurements

The cell terminal voltages were recorded before the start of the thermal soak test, at regular time intervals in-situ throughout the soak duration and finally after completion of the test using Data logger in auto mode with input impedance of > 1 GΩ.

2.5. Differential Scanning Calorimetry (DSC) for electrolyte freezing point determination

The electrolyte samples were extracted from tested COTS cells (at the end of all complementary tests) using an earlier developed procedure [21]. DSC measurements were carried out using instrument DSC Q100V9.6 Build 290, where the extracted electrolyte samples were first frozen by lowering the temperatures to −170 °C and later the frozen samples were gradually heated at a ramp of 5 °C/min till 25 °C. The sample heat flow was recorded as a function of temperature to distinguish the electrolyte phase transitions brought about by temperature changes. The electrolyte freezing point was determined as the temperature at which the sample showed a drastic change in heat flow.