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An experimental study of a lithium ion cell operation at low temperature conditions

Asma Mohamad Aris*, Bahman Shabani

School of Engineering, RMIT University, Melbourne 3000, Australia

Abstract

Lithium-ion (Li-ion) batteries are widely used for various applications such as telecommunication, automotive, and stationary applications. With their wide range of safe operating temperatures (i.e. -10 °C to 50 °C), the Li-ion is preferred over other types of matured battery technologies such as lead acid and nickel-cadmium (NiCd). Nevertheless, operating the Li-ion batteries at cold climate conditions can potentially harm the batteries and lead to issues such as degradation and reduction in their capacity and power density. This paper aims to experimentally investigate the behavior of a Li-ion cell operating at low temperatures (i.e. -15 °C to 25 °C) with respect to its charging and discharging behavior. It was observed that at sub-zero temperatures (i.e. -5 °C, -10 °C and -15 °C) the Li-ion cell's capacity is reduced due to the impedance effect which then increases the cell's internal resistance. Moreover, at such low temperatures the best state of charge (SOC) of the cell (i.e. during charging mode) has reduced to about 7-23% of its maximum initial SOC (i.e. 100%). To complement the experimental finding, an existing simplified adaptive thermal model was used to obtain the discharge curves at various current rates based on the function of extracted charge (Q_{out}). The discharge curve of equilibrium potential (E_{eq}) is then extrapolated towards zero current in order to obtained the overpotential heat generation curve based on the discharge current of the cell. The result showed a good agreement to the discharge curves that were obtained experimentally. Likewise, with the finding of cell voltage (E), current (I) and temperature (T) that were obtained experimentally, the thermal behavior of the cell in respect of its internal temperature is predicted and represented by comparing both the simulated and experimental cell internal temperatures.

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Keywords: Lithium ion; batteries; cold climatre condition; charging; discharging; heat transfer; theoretical modelling

* Corresponding author. Tel.: +6-139-925-6138; fax: +6-139-925-8099.
E-mail address: asmamohamadaris@gmail.com

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1. Introduction

Advanced lithium ion (Li-ion) battery technology is now broadly used in a range of applications such as telecommunication, personal transportation (e.g. e-bikes and scooters), automotive, aerospace, grid, and stationary applications [1-7]. With its wide range of safe operating temperatures (i.e. -10 °C to 50 °C), the Li-ion batteries have gained distinction that is comparable to other types of matured battery technologies such as lead acid and nickel-cadmium (NiCd) batteries [8]. Nevertheless, unlike the simplicity of deploying lead acid battery, the Li-ion batteries require electronic control circuitry to maximize their performances and reinforce their safety that are very important in applications such as telecommunication and electric vehicles (EVs) [2].

In recent years, the thermal management of Li-ion batteries has been the focus of a number of studies as it is a crucial consideration to get them operated at optimum conditions. While both cooling and heating are equally critical, the emphasis of recent studies were mainly towards high temperature applications (e.g. for EV operation in hot climate condition or for remote area power supply (RAPS) system at desert area) with noticeably less attention to their operation in low temperature climate conditions (i.e. particularly for stationary applications). This calls into question on issues relating to the effect of low temperature operation on the performance of Li-ion batteries: for instance reduced energy and power densities of the batteries [9]. It is noteworthy that the Li-ion batteries operate at the same temperature range of human's tolerable range; however, both the high and low temperatures can greatly reduce their performances while overheating can lead to safety issues such as thermal runaway and explosions [10].

As reported by Gering [11], the limitations of the Li-ion batteries can be put into two categories of intrinsic and operational limitations. The intrinsic limitations are due to unavoidable materials-related constraints that are irrespective to the battery usage condition. Examples of the intrinsic limitations include transport characteristics of the electrolyte, charge transfer rates within the electrode materials, and others. Meanwhile, the operational limitations are related to how actively a cell is being cycled under specified state of charge (SOC) and temperature [11]. Hence, it is known that the challenges faced by the Li-ion batteries at low temperature conditions are clearly related to the operational limitations.

Previous research studies have shown that rapid charging of the Li-ion batteries at subzero temperatures can potentially harm the batteries and lead to their degradation [12]. For example the capacity of the Li-ion batteries is greatly reduced as much as 95% when operated at -10 °C rather than at 20 °C [13]. This drop in the capacity is unacceptable in many applications when the Li-ion battery storage system fails to meet the load demand due to aging behavior associated with their operation at extreme cold conditions. It was suggested that such occurrence of performance loss at cold conditions is caused by a significant rise of internal resistance that tends to increase the cell's internal temperature (warming the cell) and potentially degrade the Li-ion in the long run [14, 15]. Hence, among the efforts suggested to improve the Li-ion's performance are advanced thermal behavior study, upgraded electrode materials, improved charging/discharging arrangement and comprehensive battery's thermal management [16-20].

In this paper, the behavior of Li-ion cells is studied based on charging and discharging of the cell at various low operating temperatures. The results of this experimental study will then be used to establish the reliability of an existing simplified thermal model used to predict the performance of Li-ion batteries operated under various temperatures. A small-scale experimental study was carried out on a Li-ion cell at operating temperature ranging between -15 °C to 25 °C. The manufacturer's recommendation of current rate (C-rate) values (i.e. 20C for charging and 5C for discharging) are used to identify the effect of the battery's temperature on its performance.

Nomenclature

m	Mass of cell (g)
C_p	Specific heat capacity ($J.g^{-1}.K^{-1}$)
Q_t^{in}	All processes that generate heat (W)
Q_t^{out}	All processes that dissipate heat (W)
Q_n	Overpotential heat generation (W)
Q_s	Entropic heat generation (W)
Q_c	Heat convection (W)
Q_R	Heat radiation (W)

η_t	Total overpotential (V)
η^{Ω}	Ohmic losses in cell (V)
η^{m}	Diffusion and migration of Li-ion through the electrolytes (V)
η^{d}	Diffusion of Li-ion cell inside the electrodes (V)
η^{ct}	Charge transfer reactions at the electrode (V)
E	Cell voltage (V)
E_{eq}	Equilibrium potential (V)
I	Current (A)
Q_{out}	Extracted charge from the cell (Ah)
t	Time (s)
t_{end}	Time at end of discharge (s)
h	Convective heat transfer coefficient ($W.m^{-2}.K^{-1}$)
A	External surface area of the cell (m^2)
T	Surface temperature of cell (K)
T_a	Ambient temperature (K)
σ	Stefan-Boltzmann constant ($W.m^{-2}.K^{-4}$)
ε	Emissivity

2. Experimental Study

2.1. An Overview

An experimental investigation was conducted to test the performance of three 3.7 V 1500 mAh rechargeable Li-ion polymer cells based on a specified temperature range of -15 °C to 25 °C. A climatic chamber was used to recreate the cold climate conditions where the tested cells were placed in the chamber for capacity measurement during charging and discharging. A recommended C-rate value (i.e. 5C for discharge and 20C for charge) by the Li-ion cell's manufacturer was selected as the charging and discharging rate in order to minimize the risk of cell's damage and explosion. Table 1 shows the specifications of the Li-ion batteries used in the experiment. To observe the cell behavior when operating at low temperature, a series of procedure is applied to the experimental setup with the objective of investigating the effect of low temperature operation to the Li-ion cell's performance. The details of this setup are shown in Fig. 1.

Table 1. The specifications of the Li-ion batteries used in the experiment.

Type	Nominal Capacity (Ah)	Nominal Voltage (V)	Upper cut-off voltage (V)	Lower cut-off voltage (V)	Operating temperature
Li-ion polymer cell	1.5	3.7	4.2	3.2	-30 °C ~ 60 °C

The procedures undertaken for conducting this experimental study are as follows:

- Step 1: The temperature of climatic chamber temperature (T_{amb}) was set to a designated testing temperature (T_{test}).
- Step 2: The Li-ion cells were placed in the climatic chamber until it reaches thermal equilibrium that was when the temperature of the cell (T_{cell}) was measured to be the same as the T_{test}.
- Step 3: The Li-ion cells were discharged from maximum state of charge (SOC) to their cut-off voltage of 3.2V. Throughout this phase, the increase in the internal temperature of the cell indicated a heat generation due to the electrochemical reaction within the cell. The T_{cell} was recorded during the test.
- Step 4: Once the discharge cycle was completed, the cells were rested until they reached 25 °C (i.e. the assumed T_{amb}). To ensure identical SOC in different tests of the Li-ion cells they were left rested overnight. Before the start of the experiment
- Step 5: The charge cycle was continued until the cell's voltage reached its maximum value of 4.2 V.

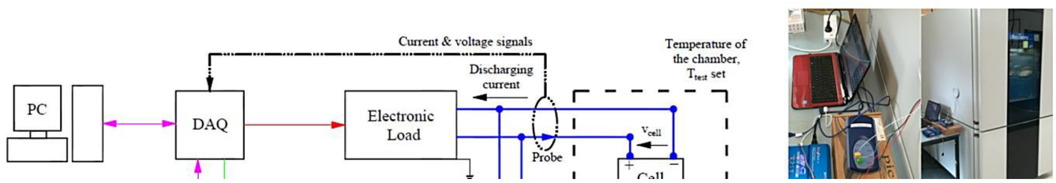


Fig. 1. (a) Schematic diagram of experimental setup; (b) Climatic chamber used for testing; (c) Type of rechargeable Li-ion polymer cell used in testing

2.2. Effects of Li-ion Cell Performance

To understand the behavior of the Li-ion cell used for this study, the experimental data has been analyzed as a series of plotted curves. The effects of temperature on charging/discharging characteristics of the Li-ion cell are presented in Fig. 2. In Fig. 2 (a), the charge voltage profiles of a Li-ion cell at various testing temperatures (i.e. $T_{test.}$ = -15 °C to 25 °C) and at a constant charging current of 1 A are shown respectively while Fig. 2 (b) shows the discharging characteristics at a constant current of 0.25 A in different temperatures. From the curves, the cell delivers substantially less capacity at subzero temperatures during both charging and discharging modes as compared to that at ambient temperatures of 15 °C and 25 °C.

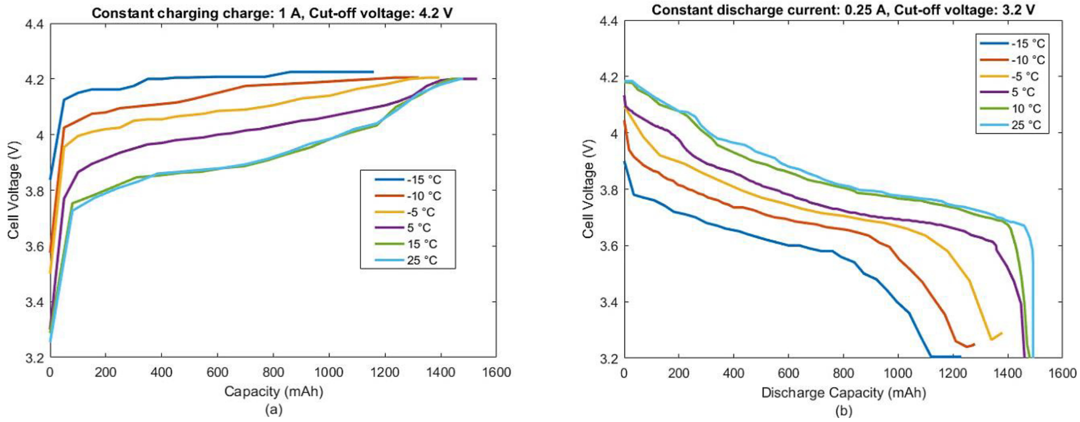


Fig. 2. (a) Charge-temperature characteristics of a Li-ion cell at 20C rate; (b) Discharge-temperature characteristics of a Li-ion cell at a 5C rate

In Fig. 3 (a), the effect of temperature on the Li-ion cell when charging at subzero temperatures (i.e. -5 °C, -10 °C and -15 °C) is plotted with respect to the SOC of the cell. From the curves, lower temperatures affect the cell's capacity significantly by dropping its SOC from 100% (initial testing) down to about 93%, 88% and 77% at -5 °C, -10 °C and -15 °C respectively. Moreover, the same trend can be also presented during discharging of the cell at subzero temperatures, where the cell capacity reduces to 92%, 85% and 82% of the cell's depth of discharge (DOD) at -5 °C, -10 °C and -15 °C respectively (Fig. 3 (b)). This loss of capacity is mainly due to the increase of internal resistance that causes some warming effect to the cell during charging and discharging [20].

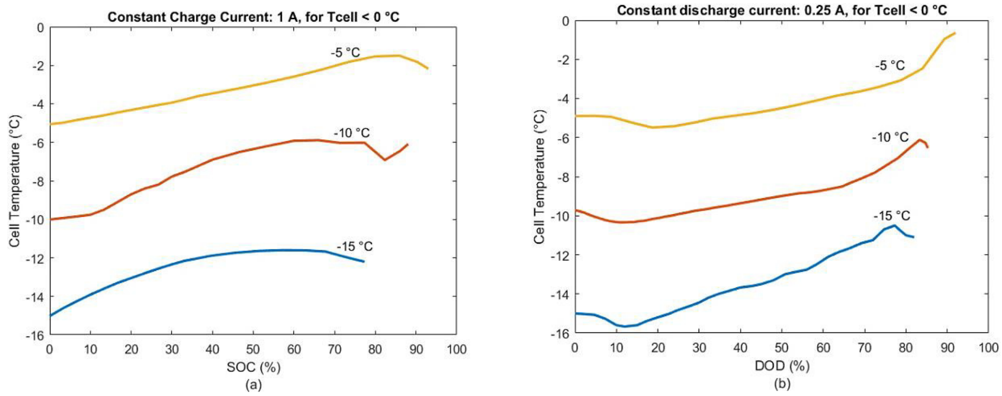


Fig. 3. The effect of temperature on a Li-ion cell SOC and DOD when: (a) charging at sub-zero temperature (i.e. -5 °C, -10 °C and -15 °C) based on Li-ion cell SOC; (b) discharging at sub-zero temperature (i.e. -5 °C, -10 °C and -15 °C) based on Li-ion cell DOD

Table 2 presents the temperature difference between the maximum and minimum cell internal temperature when operating at 25 °C, -5 °C, -10 °C and -15 °C. It can be observed that the experimental finding has a good agreement with the effect of low temperature operation increases the cell internal temperature. Prolong of the low temperature operations can potentially lead to reduced lifetime of the cell; in which the temperature difference (ΔT) is recommended to be below 5 °C [5, 21].

Table 2. Temperature difference between the battery and its surrounding ambient for charge and discharge of a Li-ion cell operated at sub-zero temperatures.

	Charge				Discharge			
Testing Temperature (T_{test})	Min. Temperature	Max. Temperature	Temperature Difference (ΔT)	SOC	Min. Temperature	Max. Temperature	Temperature Difference (ΔT)	DOD
25 °C	23.6 °C	25.9 °C	2.3 °C	100%	24.9 °C	27.7 °C	2.8 °C	100%
-5 °C	-5.0 °C	-1.7 °C	3.3 °C	93%	-5.1 °C	-0.5 °C	4.4 °C	92%
-10 °C	-10.0 °C	-6.0 °C	4.0 °C	88%	-10.1 °C	-6.0 °C	4.1 °C	85%
-15 °C	-15.8 °C	-10.4 °C	5.4 °C	77%	-15.8 °C	-10.3 °C	5.3 °C	82%

3. Theoretical Study

3.1. An Overview

A numerical modeling can be applied parallel to the experimental study as a hybrid approach in predicting the thermal behavior of Li-ion cell under different thermal conditions. In this study, an existing simplified adaptive thermal model that was developed by Rad, Danilov, Baghalha, Kazemeini and Notten [22] is used to establish the reliability of the experimental finding. The assumptions made when deploying the model is that the internal temperature and heat generation of the cell are uniform. Based on the general energy balance equation represented as equation (1), the processes that contribute to the heat evolution comprise of heat generation, Q_t^{in} (i.e. Ohmic heat, irreversible heat and reversible heat) and heat transfer, Q_t^{out} (i.e. heat convection and heat radiation from the outer surface of the cell) [5, 23]. However for simplification of this study, only Q_n is taken into consideration when quantifying the heat generation of the cell due to its substantial source of heat generation inside the cell.

$$mC_p \frac{dT}{dt} = (Q_n + Q_s) - (Q_c + Q_R) \quad (1)$$

Based on the experimental findings, the cell voltage (E), current (I) and temperature (T) can be derived and represented as equilibrium potential (E_{eq}) at each SOC and temperature. The difference from E and E_{eq} indicate the overpotential (η_t) in which the overpotential heat generation (Q_n) can be calculated by multiplying with applied current [5]. Equation (2) defined the various heat generations inside the cell. The total overpotential heat generation (Q_n) can be calculated using equation (3).

$$\eta_t = E - E_{eq} = \eta^{\Omega} + \eta^{m} + \eta^{d} + \eta^{ct} \tag{2}$$

$$Q_n = n_t I \tag{3}$$

Fig. 4 (a) illustrates the discharge curves at various current rates based on the function of extracted charge (Q_{out}). The E_{eq} is determined by generating the discharge curves and extrapolating it towards zero current as suggested in [5, 22], in which the curve is represented as the Electromotive Force ("EMF") line. By using the "EMF" curve and by incorporating it into equation (3), the overpotential heat generation curves at various discharge currents are plotted for every DOD (Fig. 4 (b)).

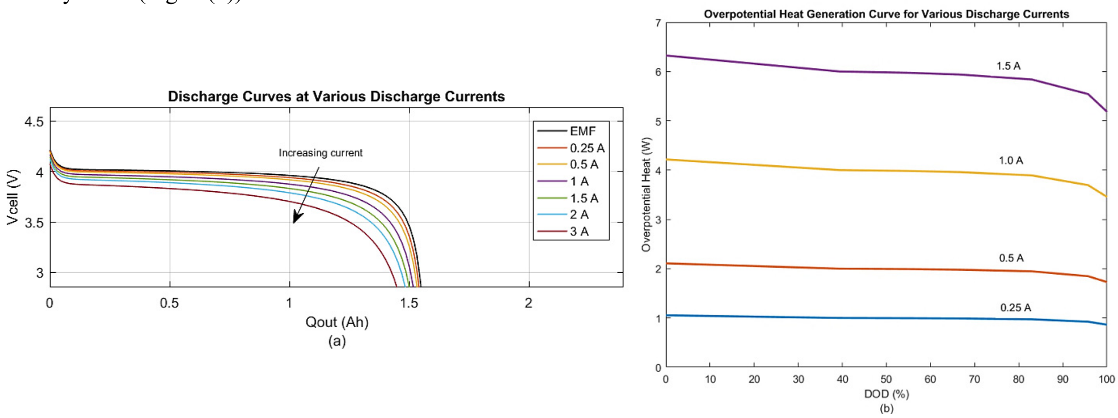
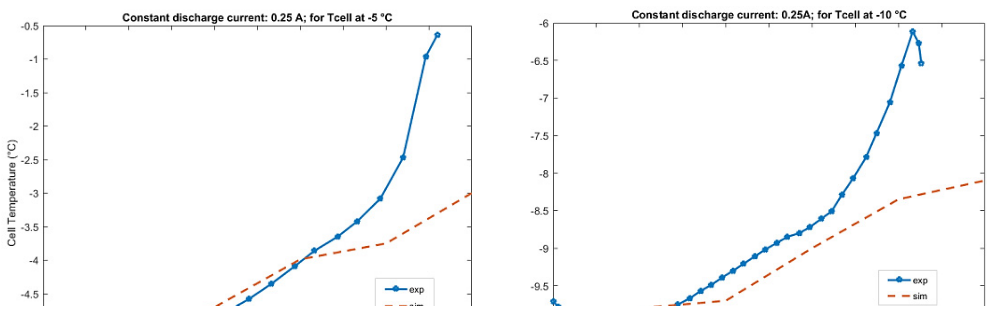


Fig. 4. (a) Discharge curves at various current; (b) Overpotential heat generation curves of a Li-ion cell at various discharge currents

Once the overpotential heat generation is known, the energy balance equation (equation (1)) can be solved. Moreover, to further predict the thermal behavior of the Li-ion cell with respect to its internal temperature, solving the energy balance equation can be done by assuming the entropy contribution to be negligible [22]. By calculating the total heat dissipation and rearrange the equations, the prediction of cell internal temperature can be computed in order to confirm the experimental data of Li-ion cell internal temperature. Fig. 5 shows the comparison between experimental and simulated Li-ion cell internal temperature for three subzero testing temperatures (i.e. -5 °C, -10 °C and -15 °C).

$$Q_c = hA(T - T_a) \tag{4}$$

$$Q_R = \sigma \varepsilon A(T^4 - T_a^4) \tag{5}$$



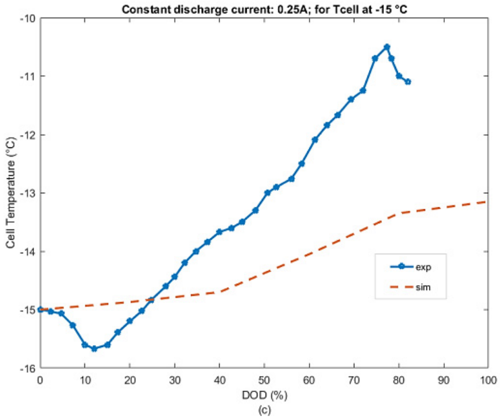


Fig. 5. Comparison of experimental and simulated internal temperature of Li-ion cell at constant discharge current for testing temperature of (a) -5 °C, (b) -10 °C, and (c) -15 °C

4. Conclusion

An experimental study relating to Li-ion batteries has been conducted based on their operations at cold climate conditions. Evidently, the relation between the cell's internal temperature in addition to electrochemical and thermal processes was established based on the temperature rise effect in the Li-ion cells. In order to confirm the experimental findings based on a certain degree of reliability, a simplified adaptive thermal model was used. The finding comes to a good agreement that reduced capacity of the cell is affected by low temperature and high current operations. Although in reality, the thermal analysis is more complex than what is presented here but for simplification purpose, the quantification of the overpotential heat generation is done as it is the most substantial heat generation yield by the Li-ion cell. Likewise, by using the energy balance equation, the thermal behavior of the Li-ion cell was predicted for discharging at subzero temperatures. The result showed that the simulated internal temperature of the cell was much lower than the experimental one when the model does not take into consideration the entropy effect. Thus, it is clear that the correlation between the experimental and theoretical findings lies on the operating temperature, current and voltage of the cell and that the cell chemistry have their effects on these parameters as well. For future works, a more complex thermal model will be developed further in order to comprehensively model the thermal behavior of the Li-ion cell with the aim of understanding the performance of the cell at low temperature operations.

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