The effect of temperature on the electrochemistry in Lithium-ion batteries

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Abstract

Temperature is known to have significant impacts on the performance, safety and cycle lifetime of Lithium-ion battery (LiB). However, the detail effect of temperature on LiB is not known. In this work, we present the temperature effect of each component in LiB using the electrochemistry based model developed recently. The findings allow us to have a better understanding of the effect of temperature and it also reveals phase transformation of the anode when LiB is operating beyond 45 ^{o}C.

Keywords: Electrochemistry based electrical model, electrodes, electrolyte, Warburg element

1. Introduction

LiB is one of the key elements in global green energy initiative due to its high energy and power density, long lifetime, safe operation and reasonable cost [1]. For example, LiB enables the possibility of electric vehicles (EVs), hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs). Extensive research on LiB can be found recently [2].

However, operating ambient temperature of LiB must be well controlled as its performance, health and safety depends critically on the temperature. High temperature can lead to shortened lifetimes or catastrophic failure of the battery via thermal runaway that result in fire hazard and possible explosion in extremes cases [3].

While one can design a cooling system for the LiB system, a detail understanding of the temperature effect on each component inside LiB will be useful to improve its design and could extend its usability if its allowable operation temperature range can be extended. Unfortunately, such understanding is lacking.

With the recent development of electrochemistry based electrical model [4] where the performance of each components inside LiB can be determined through its discharging curve (i.e. terminal voltage vs time during discharging), we employ this model to examine how the performance of each component will be affected if LiB is operating at different temperature. The findings will help us to be one step forward in our understanding of the temperature effect on LiB. Fig. 1 shows the electrochemistry based electrical model where R_e is the ohmic resistance of electrodes and electrolyte, C_{dl} is the double layer capacitance, R_{ct} is the total charge transfer resistances at the electrodes, K is the charge transfer rate constant at the electrode embedded in the Butler-Volmer impedance (Z_{BV}), and R_n and C_w are the Warburg element in the electrolyte.

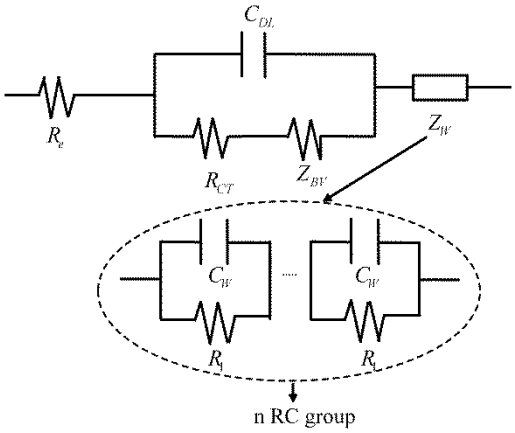

Fig. 1 electrochemistry based electrical model [4]

2. Experimentation

The LiB studied in this work is the prismatic cell from Sony. Its specification is shown in Table I. Fig. 2 shows the photo of the cells used in this work.

The charge and discharge cycles were performed in CALCE. A standard constant current/constant voltage charging profile with a fixed current rate of 0.5C until the voltage reach 4.2V, followed by maintaining 4.2V until charging current dropped to below 0.05A, was used for all the cells under study. For the discharging experiments, all the cells were discharged at a constant current of 0.5C to cut-off voltage of 2.7V at the ambient temperature of 25 ^{o}C, 35 ^{o}C, 45 ^{o}C and 55 ^{o}C respectively. Fig. 3 shows a typical example of the discharging curve of a cell. The red curve is computed by the battery model used in this work, and one can see good agreement between the computed and experimental discharge curve. Note here that the model is valid up to 50% SoC, and the initial fast discharging

portion is excluded in the model.

Table I Sony Prismatic LiB specification [5]

Battery	Characteristics
Series	Prismatic cell
Chemical System	LCO
Nominal voltage	3.6V
Capacity	1,350mAh Typical
Charging Condition	CVCC 4.2V max.0.5 C-rate (675mA), 50mA cut-off 25 °C
Discharging Condition	CONSTANT CURRENT, 2.7V cut-off 25 °C
Dimensions (mm)	6.6 x 33.8 x 50
Approx.Weight	28(g)

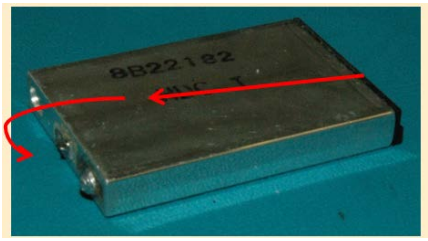

Fig. 2 The prismatic cell used in this work.

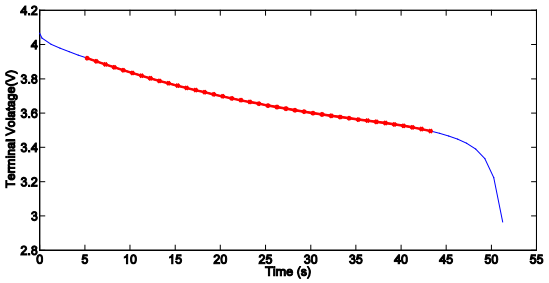

Fig. 3 Comparison of Experimental and computed discharge curve of the Sony prismatic cell.

3. Results and Analysis

3.1 Temperature effect on maximum initial capacity

Fig. 4 shows that the maximum initial capacity increases with temperature. This increase is expected from enhanced electrochemical reduction-oxidation (redox) at anode and cathode as shown by [6, 7]. The increase is significant after 35 °C, and it slows down after 45 °C. The slowing down is due to the reduced activity of the anode as represented by the reduced value of m_1 as can be seen in Fig. 5.This m_1 can be viewed as efficiency of anode in providing its stored Li ion for discharging. Similarity parameter for graphite electrode is m_2 [4]. The performance of the graphite electrode is stable against the temperature as seen in Fig. 6. The detail mechanism of the reduced activity of the anode at high operating temperature remains to be explored, and it could possibly link to the phase transformation of anode material at high temperature [8].

The significant increase within 35-45 °C in the maximum charge implies one can extract more current if the LiB is to be operated within the temperature range. It also indicates that if the Qm is computed at lower temperature (below 35 °C), the coulomb couting method to compute the SoC will be underestimated, and this will always happen as the temperature of cell will increase during its operation.

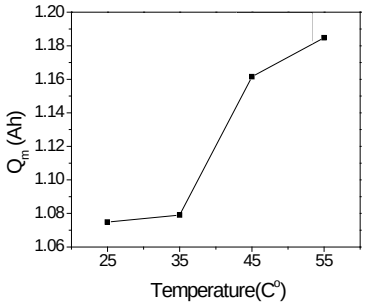

Fig. 4 Maximum initial capacity vs. temperature.

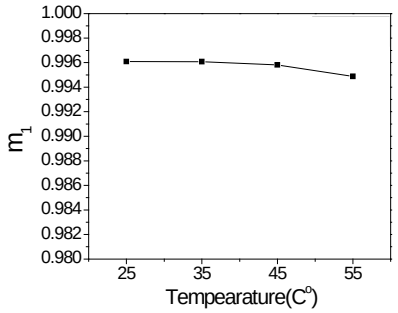

Fig. 5 m_1 of cobalt-oxide electrode vs. temperature.

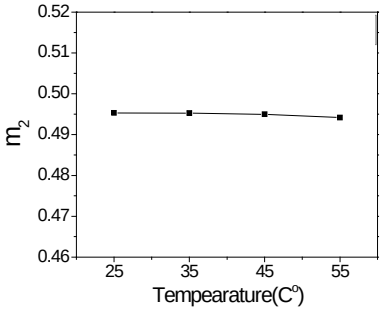

Fig. 6 m_2 of graphite electrode vs. temperature.

3.2 Temperature effect on electrolyte

The diffusivity of active Li ion in the electrolyte increases with temperature [8], and this together the with increased Li ion concentration that flow through the electrolyte due to the increase in Qm will render a decrease in the apparent resistance of the electrolyte as shown in Fig. 7. The effect of the larger increase in Qm within 35-45 °C on the electrolyte resistance can be seen vividly in Fig. 7.

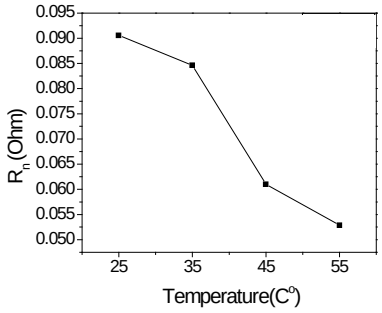

Fig. 7 Warburg element resistance vs. temperature.

The increase in Warburg element capacitance with temperature can be seen in Fig. 8, and it can be explained by the increasing number of ionic charge stored at the double layer near electrode due to the increase in Qm. One can again see the correlation between the larger increase in Qm within 35-45 °C and larger increase in the capacitance in the same temperature range.

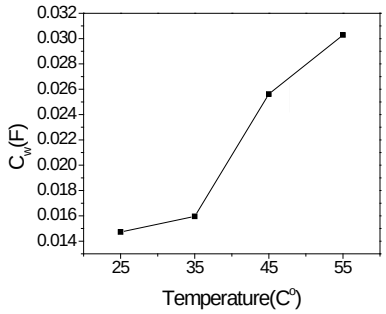

Fig. 8 Warburg element capacitance vs. temperature.

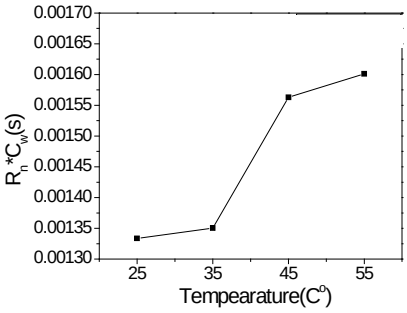

Fig. 9 Warburg RC time constant vs. temperature.

Fig. 9 shows the plot of the Warburg RC time constant, and one can see that increasing the temperature will increase the RC, and this implies that the response to the change in current deliver from LiB will become slower.

3.3 Temperature effect on electrode/electrolyte interface

Fig. 10 shows the decrease of the electrode cum electrode/electrolyte interface resistance with temperature. The decrease is not due to the increase in the Qm as the decrease is not significant in the temperature range of 35-45 °C. In fact, this decrease is due to the change in the charge transfer rate constant at the electrode as can be seen in Fig.11 which shows the rate constant K vs. temperature. As increase in Qm should be decrease in this series resistance within the temperature range of 35-45 °C (Fig. 10) does not show a significant trend as in Fig. 4, one can see that the resistance shown in Fig. 9 is mainly contributed by the interface resistance [8, 9].

The increase in K with temperature shown in Fig. 11 is expected as higher temperature will enhance the charge transfer process [8, 9].

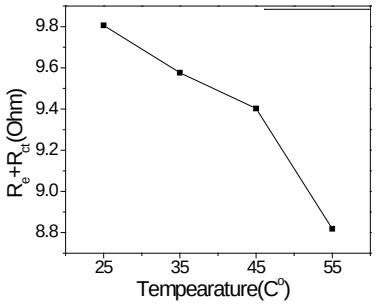

Fig. 10 The sum of ohmic resistance of electrode cum electrolyte and charge transfer resistance.

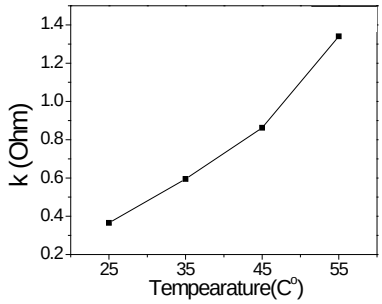

Fig. 11 Rate constant vs. temperature.

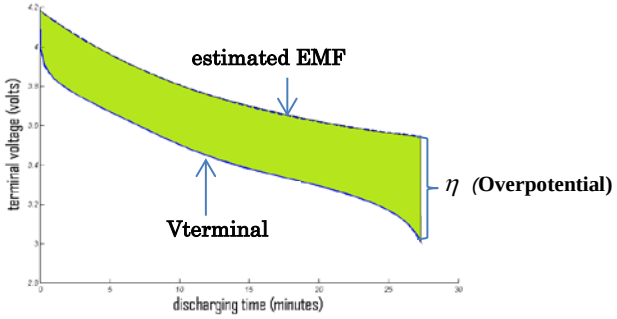

Fig. 12 Discharging curve of estimated EMF and terminal voltage

In examining Fig. 7 and 10, we can see that the toal series resistance of LiB is mainly due to the interface resistance. As

the over-potential of the cell increase with time as shown in Fig. 12, and the total series resistance decreases with temperature, one can expect a significant increase in power dissipation within the LiB as given by V^2/R where V is over-potential and R is the series resistance. As R decreases significantly if LiB is discharging beyond 90 ^oC as shown in [3], one can expect thermal runaway can happen beyond 45^oC, and much smaller value of R is expected if LiB is operated beyond 90 ^oC, one can expected the accumulated heat and the temperature inside the LiB will be much higher, and thus thermal runaway can happen beyond 90 ^oC as indeed observed [3]. Detail investigation on the mechanism of the decrease in the electrode/electrolyte resistance beyond 55 ^oC can help us to determine the on-set of thermal runaway, providing a good measure of the state of safety for LiB.

4. Conclusion

Temperature is important factors critically affect the health and safe operation of LiB. In this study, we develop a new approach to online detect and characterize the temperature effect on electrochemistry in LiB nondestructively. The performance of each component inside LiB has been determined at different temperature. It is shown that the phase transition after 45 ^oC was identified as the main course of changes for each component in the investigated battery cells. Through this approach, we also can study the possible root causes of thermal runaway from the performance of each component. It is possible provide early warning of the battery thermal runaway and hence enhance the safe operation of the cells.

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