Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Power Sources 119–121 (2003) 821–825
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

AC-impedance measurements during thermal runaway process in several lithium/polymer batteries

I. Uchida*, H. Ishikawa, M. Mohamedi, M. Umeda

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 07 Aramaki Aoba, Aoba-Ku, Sendai 980-8579, Japan

Abstract

In this work, we present a set of thermal characterization experiments of charged prismatic polymer lithium-ion battery (PLB) comparatively with those of a lithium-ion battery (LIB). These cells at different state of charge (SOC) were tested inside an accelerated rate calorimeter (ARC) to determine the onset-of-thermal runaway (OTR) temperatures. In addition, the thermally activated components of these cells were followed by monitoring the impedance (at 1 kHz) and the open-circuit voltage (OCV) as a function of temperature. An increase in the impedance was observed at around 133 °C corresponding to the polyethylene separator shutdown. Above 140 °C, the OCV dropped to zero indicating an internal short-circuit due the separator meltdown suggesting that the pinholes created in the separator at meltdown are large enough to create an internal short-circuit.

Keywords: Lithium-ion batteries; Polymer lithium-ion; Safety; Thermal characteristics; Impedance

1. Introduction

Safety is a general challenge for Li-ion batteries, and an increasing amount of research now focuses on this. During battery charge/discharge, various chemical and electrochemical reactions as well as transport processes take place. At elevated temperatures, reactions involving the active electrode material, electrode binder, and the non-aqueous electrolyte lead to self-heating of the cell thereby causing the cell temperature to rise without further external heating. This condition, usually referred to as the thermal runaway condition, could potentially lead to catastrophic disassembly of the cell [1–3]. Therefore, quantitative measurements of the heat generation rate inside the battery during normal and abuse conditions are important to design and develop a suitable thermal management system for scaled-up battery systems. Such measurements can be obtained using the accelerated rate calorimeter (ARC). Safety features provided by the thermally activated components in several-discharged Li-ion cells can be studied by monitoring the impedance (internal resistance) and the open-circuit voltage (OCV) of these cells as a function of temperature [3,4]. The present paper reports on characterization of thermal cut-off of charged prismatic polymer lithium-ion batteries (PLBs) comparatively with a lithium-ion battery (LIB).

2. Experimental

Experiments were carried out inside an accelerated rate calorimeter (ARC) 2000^{TM} (Columbia Scientific Industries) in combination with a battery cycler (TOSCAT-5000U, Toyo System Co.) shown in Fig. 1. The cell was placed inside the ARC cavity was first charged to the desired state of charge (SOC), and was left at OCV condition for at least 12 h. Then, the cell was heated stepwise to thermal runaway conditions. The cell temperature was measured with a thermocouple attached to the cell surface. The experimental sequence is based on the ARC heat-wait search (HWS) mode, where the cell temperature is increased 10 °C min^{-1} in each step followed by 30 min wait time. During wait time, if the self-heating rate of the cell is larger than 0.05 °C min^{-1}, this is considered an indication of the onset of an exothermic reaction. The ARC then shuts down the heating and records the cell temperature till the end of the thermal runaway process. The total impedance of the cells was measured at 1 kHz using a Hewlett-Packard 4338B Milliohmmeter and OCV was measured using a Keithley 610C. Furthermore, impedance measurements were carried out using a Solartron 1286/1260 system that covered the frequency range from 10 kHz to 100 mHz in each state of charge.

The cells used in this study were of the prismatic Li-ion type. Three kinds of cell supplied by three different manufacturers were tested. Two cells were polymer lithium-ion batteries (PLBs), and one cell was a lithium-ion battery

* Corresponding author.
E-mail address: uchida@est.che.tohoku.ac.jp (I. Uchida).

0378-7753/03/$ – see front matter
doi:10.1016/S0378-7753(03)00248-9

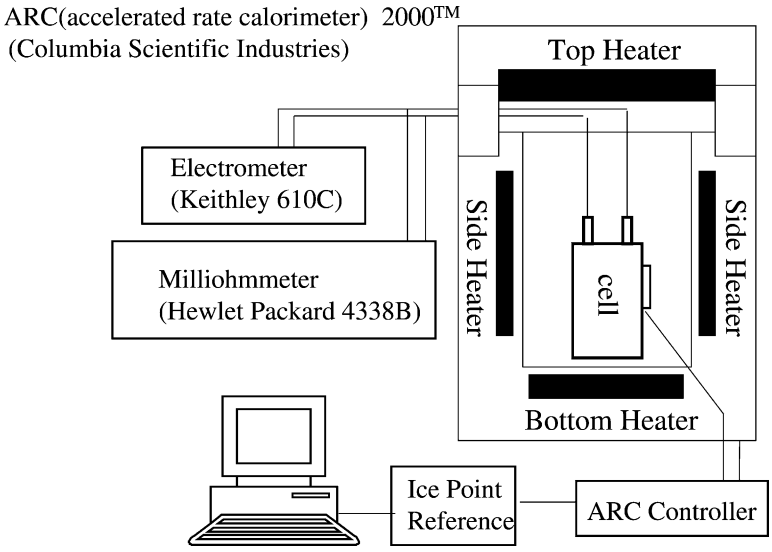

Fig. 1. Experimental accelerated rate calorimeter (ARC) for studying thermal cut-off characteristics of Li-ion cells.

(LIB). Table 1 lists the specifications and main components materials for each cell, classified as A, B, and C. $LiCoO_2$-based materials were used in their cathodes. According to manufacturers, the three cells used a polyethylene separator.

3. Results and discussion

3.1. Thermal cut-off characteristics

Fig. 2 illustrates thermal runaway tests for cells A, B, and C as function of two state of charge (SOC) of 25 and 75%. The onset-of-thermal runaway temperature (OTRT) was observed within 147 and 168 °C temperature range. The OTRT was found to depend on the state of charge for cells A and C, i.e. it decreased by at least 10 °C when the cells were charged from 25 to 75% SOC. On the other hand, the OTRT was SOC-independent for cell B. One also notices that cells A and C at 25% took more time to reach the OTRT.

Figs. 3–5 show the plot of impedance (at 1 kHz) and open-circuit voltage (OCV) as a function of cell temperature for cells A, B, and C charged to 25 and 75% SOC. At 25% SOC, increasing cell temperature from ambient to about 130 °C resulted in 157, 38, and 24 mW increase in the impedance value for cells A, B, and C, respectively. This behavior has been explained due to the positive-temperature coefficient (PTC) that is responsible for the impedance jump that takes place at around 110 °C in the impedance–temperature curve [4]. However, cells used in this work did not have any internal or external PTC. We believe that the first increase we witness is due to the solid electrolyte interphase (SEI) formed at the anode. At around 100 °C, the metastable components of the SEI at the anode decompose very rapidly. This provides a small temperature boost to the remaining reactants in the cell as proposed by Dahn and co-workers [5].

At around 133 °C, the impedance increased by about two orders for the PLBs, and four orders of magnitude for cell C. Polyethylene separators have shutdown temperatures between 130 and 140 °C, which corresponds to the melting point of the PE separator [6–8]. Thus, the increase in the impedance at around 133 °C is due to a separator shutdown mechanism in the microporous separator membrane present in the Li-ion cells. An increase in the impedance by two orders of magnitude may not be large enough for complete shutdown, i.e. cells may continue to overcharge although at lower rates and this will continue to be a safety hazard. The

Table 1
Samples of prismatic lithium-ion cell for thermal runaway test

	Cell A	Cell B	Cell C
Type	Polymer Li-ion	Polymer Li-ion	Li-ion
Dimensions (mm) (thickness × width × length)	4 × 30 × 52	3 × 33 × 48	3 × 34 × 56
Capacity (mAh) as rated by cell manufacturer	560	500	680
Weight (g)	13.2	11.2	15.1
Cathode material	$LiCoO_2$	$LiCoO_2$	$LiCoO_2$
Anode material	MCMB-based	MCMB-based	B-doped MCF
Electrolyte	EC–DEC–$LiPF_6$–PVDF	PC–EC–$LiPF_6$–PVDF	$LiBF_4$–EC–GBL
Separator	Polyethylene (PE)	Polyethylene (PE)	Polyethylene (PE)
OCV (SOC = 25%; SOC = 75%)	(3.77 V; 3.96 V)	(3.76 V; 3.97 V)	(3.77 V; 3.99 V)

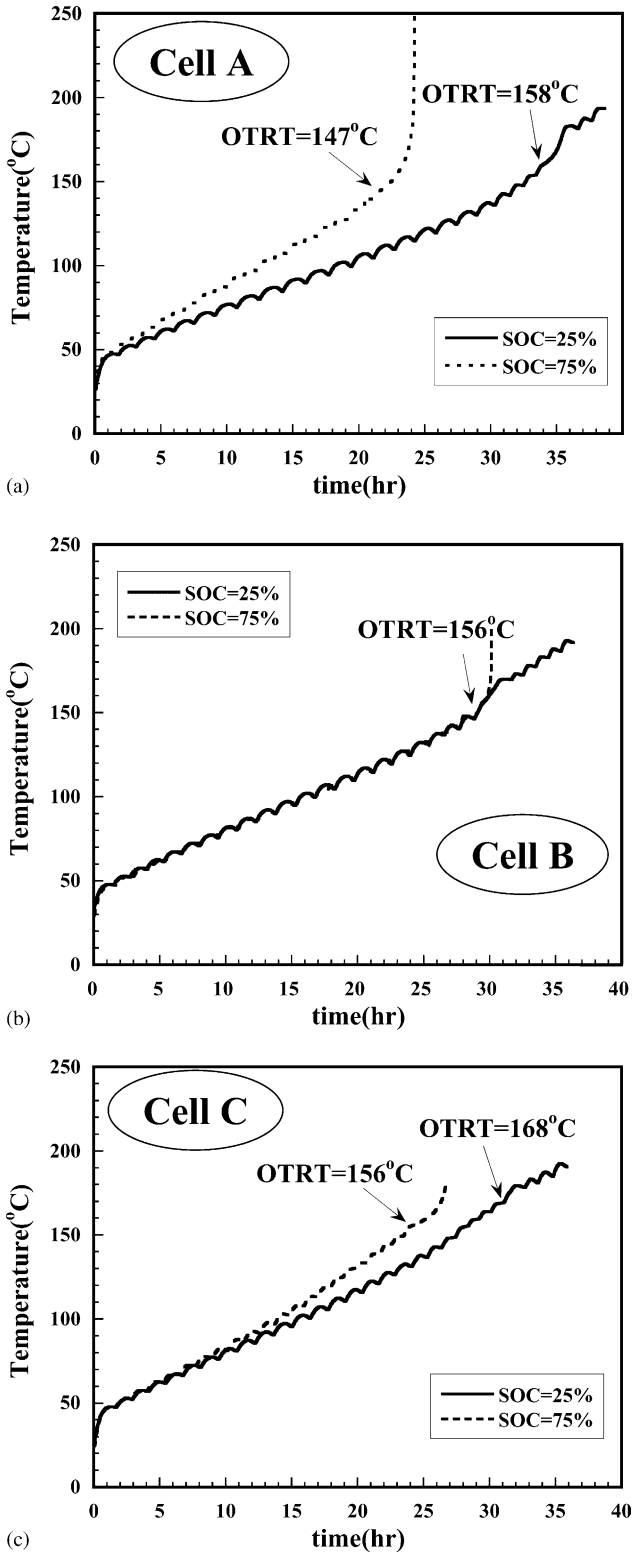

Fig. 2. Thermal runaway experiments for (a) cell A (PLB), (b) cell B (PLB), and (c) cell C (LIB) vs. time and at 25 and 75% of state of charge (SOC).

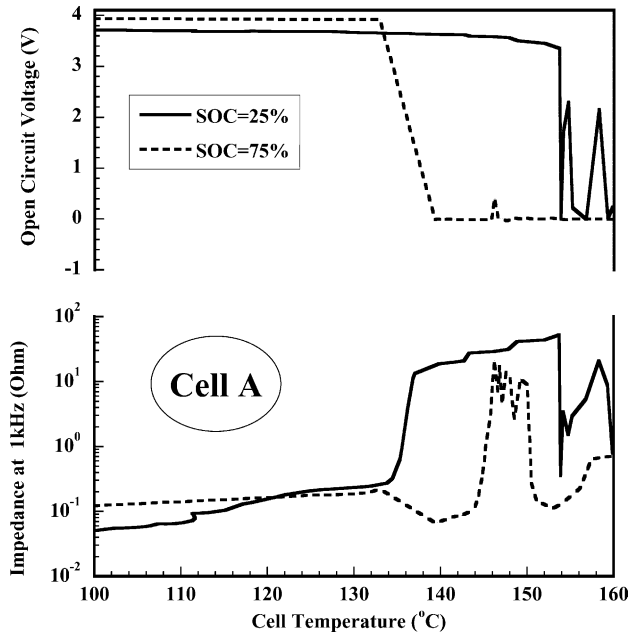

Fig. 3. Impedance at 1 kHz and open-circuit voltage (OCV) of cell A (PLB) as function of temperature.

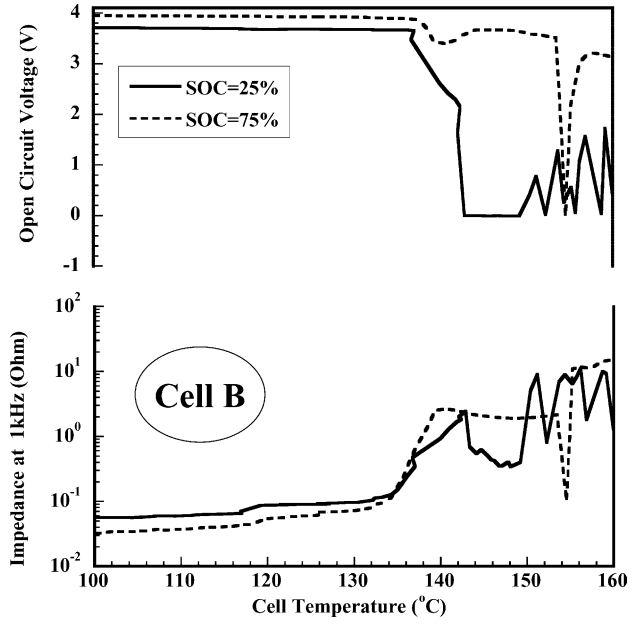

Fig. 4. Impedance at 1 kHz and open-circuit voltage (OCV) of cell B (PLB) as function of temperature.

impedance increase by four orders of magnitude at the shutdown temperature for cell C would make it safer. Our results confirm the use of PE separator since all the cells used whether PLB or LIB showed similar shutdown temperature that corresponds to the melting point of PE separator. Thus, it is expected that the impedance increase should be similar for all cells which is not the case as seen in Figs. 3–5. This indicates that separators in the three cells had important physical differences such as a different PE composition or a different structure of the PE separator. For the former, Liu et al. [9] have shown that the impedance (at 1 kHz) increase strongly depended on the PE content in gel

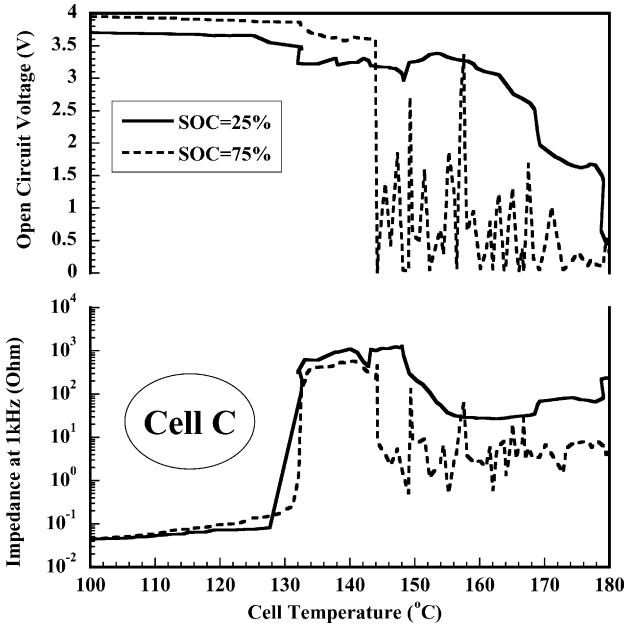

Fig. 5. Impedance at 1 kHz and open-circuit voltage (OCV) of cell C (LIB) as function of temperature.

electrolyte, i.e. a rise by three orders when the content was over 45 wt.%, two orders for 37 wt.%, and one order for 23 wt.%. With regard to the structure, the mechanical properties of the separator, for example a PE layer sandwiched between two porous polypropylene (PP) layers (PP/PE/PP) has demonstrated similar shutdown temperature as PE single layer but higher impedance value at the shutdown temperature [8].

PE separators are used as secondary safety mechanisms, which help to limit cell temperatures by melting. The separator is microporous, and at the melting point, the pores collapse to the form of a relatively non-porous insulating film between the anode and the cathode [9]. Consequently, ions transport between the anode and cathode drastically decreases, thereby leading to an increase in cell impedance and passage of current through the cell is restricted [4,9]. This prevents further electrochemical activity in the cell thereby shutting the cell down before an explosion occurs. Increasing cell temperature resulted in an increase in the impedance value for all cells at around 130 °C (Figs. 3–5). Polyethylene separators have shutdown temperatures between 125 and 140 °C, which corresponds to the melting point of the PE separator. Thus, the increase in the impedance at around 130 °C is due to a separator shutdown mechanism in the microporous separator membrane present in the Li-ion cells.

At temperatures higher than 140 °C a drop in the OCV to zero indicating internal short-circuit was noticed. This behavior too is typical of polyethylene separators and is indicative of separator meltdown. The drop in the OCV to zero is likely due to the formation of pinholes in an otherwise non-porous polyethylene film, and suggests that the pinholes created in the separator at meltdown are large enough to create an internal short-circuit.

3.2. Post-mortem observation

A post-mortem examination of cells A, B, and C revealed that cells A and B ruptured and significantly expanded irrespective of the state of charge. These results indicate that the battery large amount of expansion is mainly due to the evolution of incondensable gases, followed by volumetric expansion of these gases at higher temperature, which in turn caused irreversible deformation of the metal cans. In addition, rupture and trace of fire were observed for cells A and B. On the other hand, cell C remained hermetic with no significant expansion. Cell C uses the $LiBF_4$/EC–GBL, which has a high boiling point of 216 °C, a high flame point of 129 °C, and a low vapor pressure of 24.6 mmHg at 80 °C [10]. The $LiBF_4$/EC–GBL electrolyte is electrochemically and thermally stable in the oxidation condition of the $LiCoO_2$, since the GBL solvent is not only thermally stable but also electrochemically stable under oxidation potential [11].

4. Conclusions

In this work, a comparative characterization of thermal cut-off of charged prismatic polymer lithium-ion battery (PLB) and a lithium-ion battery (LIB) was carried out. Since all cells rely on polyethylene separator, all of them almost showed similar shutdown characteristics. The shutdown temperature for all cells was at around 133 °C. A rise in impedance (at 1 kHz) was noticed at the shut down temperature. However, the increase in impedance was larger with LIB than with PLBs. This is likely due to the difference in construction of the polyethylene separator in each cell. Above 140 °C, the open-circuit voltage (OCV) dropped to zero indicating an internal short-circuit due the separator meltdown suggesting that the pinholes created in the separator at meltdown are large enough to create an internal short-circuit. This study also revealed no rupture, no swelling, and no trace of fire for the LIB. This is attributable to the thermal and electrochemical stability of $LiBF_4$/EC–GBL electrolyte against oxidation condition of the $LiCoO_2$ cathode material.

Acknowledgements

The present work was supported by Grant-in-Aids for Scientific Research (No. 10555297) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] J.-S. Hong, H. Maleki, S. Al Hallaj, L. Ready, J.R. Selman, J. Electrochem. Soc. 145 (1998) 1489.

[2] S. Al Hallaj, H. Maleki, J.S. Hong, J.R. Selman, J. Power Source 83 (1999) 1.
[3] J.R. Selman, S. Al Hallaj, I. Uchida, Y. Hirano, J. Power Sources 97–98 (2001) 726.
[4] G. Venugopal, J. Power Sources 101 (2001) 231.
[5] T.D. Hatchard, D.D. MacNeil, A. Basu, J.R. Dahn, J. Electrochem. Soc. 148 (2001) A755.
[6] F.C. Laman, M.A. Gee, J. Denovan, J. Electrochem. Soc. 140 (1993) L51.
[7] A.J. Bradley, R.E. White, J. Power Sources 70 (1998) 48.
[8] G. Venugopal, J. Moore, J. Howard, S. Pendalwar, J. Power Sources 77 (1999) 34.
[9] X. Liu, H. Kusawake, S. Kuwajima, J. Power Sources 97–98 (2001) 661.
[10] N. Takami, M. Sekino, T. Ohsaki, M. Kanda, M. Yamamoto, J. Power Sources 97–98 (2001) 677.
[11] S. Tobishima, T. Okada, Electrochim. Acta 30 (1985) 1715.