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Accelerating-Rate-Calorimetry Study on the Thermal Stability of Laminated Lithium-Ion Polymer Cells

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Laminated lithium-ion polymer cells exhibit the attractive characteristics of high energy density, high working voltage, and great flexibility in configuration. Previous work demonstrated the impressive cycle life and endurance performance of this type of cell in a simulated space environment (vacuum, radiation, and vibration). To verify the potential for space application of these laminated lithium-ion polymer cells, this work further investigates the thermal stability of 0.60 Ah-class laminated lithium-ion polymer cells using accelerated-rate-calorimetry (ARC) measurement. Because these cells are expected to operate at a taper voltage of 3.95 V for space applications, two lithium-ion polymer cells were fully charged to 3.8 and 4.0 V, and then applied for ARC measurement. The examined cells exhibited a high onset of thermal runaway temperature (OTRT) of 148°C. In contrast to common lithium-ion cells with liquid-state electrolytes, OTRT of the examined cells was almost independent of the state of charge in the examined taper-voltage range. Furthermore, cell internal shorting did not occur until at a high temperature of 183°C, indicating good thermal stability of this type of cell.

I. Introduction

MOST recently, development emphasis for power sources in spacecraft applications has shifted to lithium-ion cells.[1–5] Compared with conventional alkaline technologies, lithium-ion cells exhibit attractive performance characteristics, such as a high energy density above 100 Wh/kg and a high working voltage up to 4 V. In particular, laminated lithium-ion polymer cells, which use aluminum laminate film as packaging material and polymer support material to form gel electrolytes by incorporating organic electrolytes, provide great flexibility in configuration and hence enable effective utilization of the satellite volume.

To verify the potential for space applications of laminated lithium-ion polymer cells, the cycle life and endurance testing of laminated lithium-ion polymer cells were conducted in a simulated space environment (vacuum, radiation, and vibration).[6–9] The satisfactory results suggest that this type of cell can reasonably be expected to work normally for storing power on a space mission.

One possible problem inherent in practical space applications of lithium-ion cells is safety, which is especially true for manned spacecraft. Lithium-ion cells consist of a high-reductive carbon-based anode, a high-oxidative lithium transition metal oxide cathode, and a flammable organic electrolyte, and can steeply accelerate the net accumulation of thermal energy when damaged by events such as short circuiting and overcharging. Ultimately, these cells can undergo self-heating and rigorous temperature rise, which is usually referred to as thermal runaway, and can even ignite and explode.[10] Therefore, further experimental investigations are necessary to understand the thermal stability of laminated lithium-ion polymer cells. One powerful approach to investigate cell thermal stability is accelerating-rate-calorimeter (ARC) measurement, where cell safety features can be evaluated by monitoring cell internal impedance and open-circuit voltage (OCV) as a function of temperature. Actually, a few groups have reported satisfactory ARC results in determining the thermal properties of lithium-ion cells or single-electrode materials with a common liquid-state electrolyte.[11–18] Nevertheless, there are very little available data on lithium-ion polymer cells with a gel electrolyte.

The primary objective of this work is to characterize the thermal stability of laminated lithium-ion polymer cells for space applications. ARC determined the onset temperature of exothermic chemical reactions that would force the cell into thermal runaway. The effect of cell state of charge (SOC) on internal impedance and OCV were evaluated as a function of temperature. Because these cells are expected to operate at a taper voltage of 3.95 V for space applications,[1] two lithium-ion polymer cells were fully charged to 3.8 and 4.0 V and then applied for ARC measurement.

II. Experimental

The typical specifications of the lithium-ion polymer cells used in this work are listed as follows, with the cells consisting of a $LiCoO_2$ cathode, a graphite anode, a gel electrolyte supported by polymer material, and an aluminum laminate package: nominal capacity is 0.60 Ah; nominal voltage is 3.7 V; cell weight is 14.47 g; and dimensions are 60, 35, and 3.5 mm. [Discharge is in constant-current (CC) mode with a current of 0.12 A and a cutoff voltage of 2.75 V after charging in CC-constant-voltage (CV) mode with a current of 0.6 A, taper voltage of 4.2 V, and total charge time of 3 h.]

ARC measurement was conducted inside an ARC (2000™, Columbia Scientific Industries) in combination with a battery tester (TOSCAT-5000U, Toyo System), as shown in Fig. 1. Before it was placed inside the ARC cavity, the cell was first charged in CC-CV mode with a taper voltage of 4.0 or 3.8 V, a current of 0.2 C, and a

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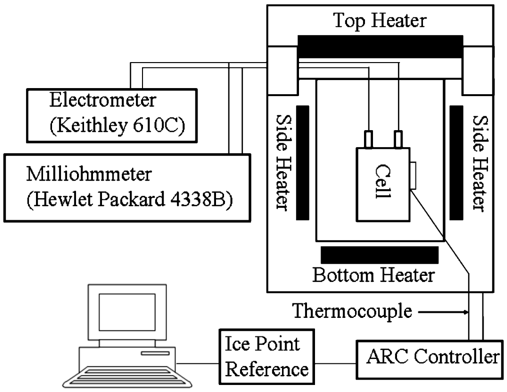

Fig. 1 Illustration of ARC measurement.

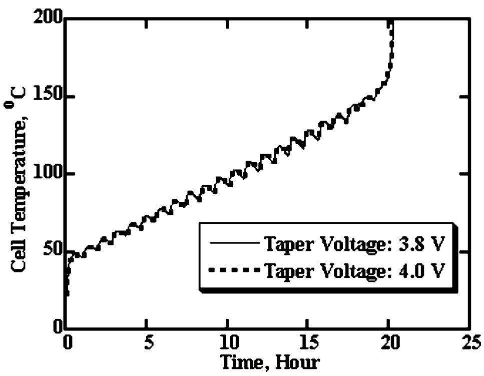

Fig. 2 Time vs temperature curves for thermal runaway experiment.

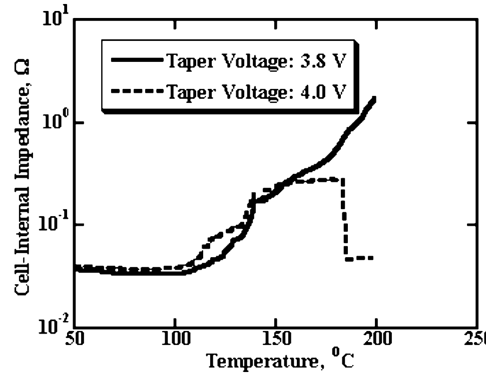

Fig. 3 Cell internal impedance at 1 kHz during ARC measurement.

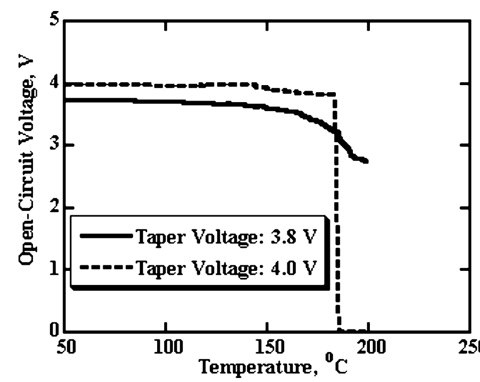

Fig. 4 OCV at different SOCs during ARC measurement.

total time of 8 h, and left at the open-circuit state for at least 12 h. The cell was then heated stepwise to thermal runaway. Cell temperature was measured with a thermocouple attached to the cell surface. The experimental sequence was based on the ARC heat-wait-search mode, where cell temperature was increased at 10°C/min in each step followed by 30 min wait time. During the wait time, a cell self-heating rate in excess of 0.05°C/min was considered an indication of the onset of an exothermic reaction. At that point, the ARC shut down the heating process and recorded the cell temperature until the end of the thermal runaway process. During the ARC measurement, cell internal impedance was measured at 1 kHz using a milliohmmeter (4338B, Hewlett-Packard), and OCV was recorded using an electrometer (610C, Keithley).

III. Results and Discussion

Lithium-ion cells cycle under various operating conditions and environments in space applications, such as ultrahigh vacuum states, radiation, long cycle-life requirements, and short charge and discharge intervals strictly limited by the spacecraft orbit.[19] Typically, the onboard rechargeable cells must operate without interruption for more than 30,000 cycles to meet the general low-Earth-orbit (LEO) mission life requirement of five years. For lithium-ion cells to be used in a spacecraft, they must be cycled under moderate conditions, such as with a low taper voltage of less than 4.0 V (Refs. 20 and 21). For this reason, the thermal stability of two laminated lithium-ion polymer cells was evaluated after fully charged at taper voltages of 4.0 and 3.8 V. Assuming the fully charged cell capacity (0.45 Ah) with a taper voltage of 4.0 V is 100% SOC, the SOC of a fully charged cell at the taper voltage of 3.8 V should be 33%.

Generally, the onset of thermal runaway temperature (OTRT) is an important parameter to evaluate cell thermal stability with ARC measurement: the higher the OTRT, the better the cell thermal stability. Figure 2 depicts cell temperature vs time curves as a function of SOC. Obviously, the examined lithium-ion polymer cell exhibited a high OTRT of 148°C, almost independent of cell SOC after fully charged at the examined taper-voltage range. This is very different from the thermal behavior of a lithium-ion cell with a liquid-state electrolyte, in which OTRT generally decreases with increasing SOC because of a highly oxidative cathode and a highly reductive anode at a high SOC.[22]

During the preceding testing, the internal impedance was measured at 1 kHz and OCV of each cell as a function of cell temperature and SOC, as shown in Figs. 3 and 4. Overall, the internal impedance curves exhibited the same tendency for these two cells, regardless of the SOC, at temperatures below 120°C. Below 104°C, the cell internal impedance decreased with increasing temperature. This can be attributed to the high mobility of lithium ions in electrolyte and electrode materials at a high temperature. Correspondingly, OCV was also stable in this temperature range. Above 104°C, cell internal impedance increased slightly with temperature. This behavior has been explained by the positive temperature coefficient (PTC) that is responsible for the impedance jump occurring at around 110°C in the impedance-temperature curve. However, the lithium-ion polymer cells examined here did not exhibit any PTC, as indicated by X-ray observation in the previous work.[9] This indicates that the slight impedance increase above 104°C was caused by the rapid thermal decomposition of solid electrolyte interphase at the anode, which provided a small impedance boost to the remaining reactants in the cell as proposed by Hatchard and coworkers[23] and Mohamedi et al.[18]

For lithium-ion cells with liquid-state electrolytes, a steep impedance increase is generally observed at about 140°C, together with a severe OCV fluctuation, regardless of SOC.[17] This has been attributed to the shutdown mechanism in the microporous polyethylene separator membrane, which is widely used in lithium-ion cells with liquid-state electrolytes, and has a melting point between 130 and 140°C. However, one cannot observe any obvious impedance increase and OCV fluctuation for the examined lithium-ion polymer cell above 120°C, indicating an important physical difference from the common lithium-ion cells with liquid-state electrolytes. One possible explanation for this phenomenon is that the cell uses a high-melting-point separator, rather than polyethylene. It is also possible that the cell does not use a conventional separator. The polymer electrolyte is a gelled solid and can serve as a separator for the cathode and anode in a lithium-ion polymer cell. Therefore, the lithium-ion polymer cell can be constructed without a conventional separator. Accordingly, the obvious OCV decline of the cell at a higher SOC only occurred at the relatively high temperature of 183°C and was caused by an internal short in the cell. At a low SOC, the cell exhibits a moderate change in internal impedance and OCV. This indicates that the lithium-ion polymer cells had good thermal stability.

In this work, we fully charged the cells at a taper voltage less than 4.0 V. This can be attributed to the special operating conditions and life requirement of lithium-ion cells for space applications. Indeed, lithium-ion cells for ground applications operate at a high taper voltage of up to 4.2 V with a required 500-cycle life. Lithium-ion cells for satellite applications have special life requirements and operating conditions. Typically, a spacecraft in LEO periodically experiences about 60 min of sunshine and 30 min of eclipse. This requires that the onboard rechargeable cells store power from the solar cells over a short interval of 60 min and generate enough power to meet the electrical demands of the bus and the mission over an even shorter interval of 30 min. LEO satellite applications additionally require lithium-ion cells to have a cycle life of more than 30,000 cycles. To meet these requirements, lithium-ion cells must operate under moderate conditions. For a lithium-ion cell with an $LiCoO_2$ cathode and a graphite anode, the taper voltage is generally limited to less than 4.0 V to suppress the decomposition of electrolyte components on the graphite surface and the destruction of the $LiCoO_2$ cathode. The lithium-ion polymer cells used in this work consist of an $LiCoO_2$ cathode and a graphite anode and are expected to operate at a taper voltage of 3.95 V (Ref. 1). In considering the possible cell-voltage dispersion of a lithium-ion battery with lithium-ion cells in series, we performed the ARC evaluation of lithium-ion polymer cells, fully charged, at a taper voltage of up to 4.0 V for this study.

We plan to do further ARC measurement of lithium-ion cells after fully charging them to a high taper voltage of up to 4.2 V. This could be beneficial for understanding the thermal behavior of these cells for use on the ground.

IV. Conclusions

The laminated lithium-ion polymer cells are expected to store power in a spacecraft. To understand the thermal properties of this type of cell, the ARC measurement was performed with 0.6 Ah-class laminated lithium-ion polymer cells consisting of an $LiCoO_2$ cathode, a graphite anode, and a gelled electrolyte supported by polymer material. Because these cells are expected to charge at a taper voltage below 4.0 V for space applications, the cells were fully charged at the taper voltages of 4.0 and 3.8 V before the ARC measurement.

The examined cells exhibited a high OTRT of 148°C. In contrast to common lithium-ion cells with liquid-state electrolytes, the OTRT of the examined cells was almost independent of the cell SOC after fully charged in the examined taper-voltage range. Furthermore, an internal cell short at the high taper voltage of 4.0 V was observed at a high temperature of 183°C, indicating good thermal stability of this type of cell. These promising results led us to conclude that laminated lithium-ion polymer cells can be expected to work normally in a satellite.

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