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Effects of overdischarge on performance and thermal stability of a Li-ion cell

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Abstract

Overdischarge effects on cycle-life and thermal stability of a commercially available Li-ion cell (rated at 780 mA h) were investigated. Cells were overdischarged and kept at 2.0, 1.5, 1.0, 0.5 or 0.0 V for 72 h (3 days) and then cycled five times (discharge to 3.0 V at 0.4 A and charged to 4.2 V at 0.8 A). This process was repeated five times. The cells overdischarged between 2.0 and 0.5 V experienced irreversible capacity losses of 2–16%. The same cells lost between 8 and 26% more capacity after they were cycled 100 times between 4.2 and 3.0 V at 0.8 A. Behavior of the cells overdischarged to 0.0 V was unpredictable. Some cells lost nearly 65% of their initial capacities after 15 days of being kept at 0.0 V, and others failed in different stages of overdischarging to 0.0 V. Overdischarging to 0.5 V had minimal effects on thermal stability, overcharge performance and a.c. impedance, but led to considerable swelling of the cells. Overdischarge to 0.0 V caused cell thickness and a.c. impedance to increase by ∼70 and 250% of their initial values, respectively. This article addresses concerns that overdischarging of Li-ion cells below 1.5 V may cause capacity losses and/or thermal stability changes which could impact tolerance to abuse conditions.

Keywords: Lithium-ion cells; Overdischarge; Overcharge; Thermal stability and impedance

1. Introduction

Portable electronic products such as cell phones, notebook computers, MP3s and DVD players are more popular than ever. The popularity of these products has led to increasing demands for higher functionality and smaller sizes. Today's cell phones, for example, may include digital cameras, high resolution LCDs, large memory space for video and audio storage, wireless connectivity, and remote information sensing capabilities. Combinations of such functionalities and small form factors have led to increased systems complexity, power consumption, and heat generation. Video games, for example, require high power to operate the system's RF, base-band, video/audio processors, and display. Rechargeable batteries used for powering these products self-heat while operating because of their inherent electrical, thermodynamic and electrochemical impedances.

Li-ion cell technology has been adopted as the primary source of energy for batteries used in most portable electronic products because of its high energy density (450–550 W h L^{-1}, depending on the cell design) and long cycle-life (>400). Application challenges of the Li-ion cells, however, include the vulnerability of their thermo-chemical stability against operation under abnormal conditions. To date, many groups have published articles on the effects of elevated temperatures, short circuits and overcharge on cycle-life and thermal stability of Li-ion cells [1–9]. These publications and our internal data show:

1. Operation of Li-ion cells at temperatures above 60 °C could lead to different levels of swelling, impedance growth and cycle-life degradation depending on charge/discharge voltage and current applications.
2. External short circuit of Li-ion cells at room temperature causes their surface temperature to approach 120 °C with a remote possibility of thermal runaway. Shorting cells at temperatures greater than 60 °C could cause thermal runaway, especially if the cells use a polyethylene separator that melts near 135 °C.
3. Overcharge to voltages greater than 4.2 V degrades both capacity and thermal stability of Li-ion cells using a $LiCoO_2$

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cathode, and thermal runaway could occur if the overcharged voltages are greater than 4.5 V with charge currents greater than 2 C.

From an application standpoint, however, understanding the effects of overdischarge on cycle-life and thermal stability of Li-ion cells is also important, though published findings are scarce. A Li-ion battery may self-discharge in several ways (leakage currents in the circuitry, the cell's own internal shorts, or self-discharge during long-term storage) that could lower its stability against abusive conditions or even normal operation.

It has been noted that discharging Li-ion cells to voltages less than 1.5 V could lead to anodic dissolution of the copper (Cu) current collector which causes oxidization of Cu atoms to Cu^{2+} ions [10–12]. Some believe that because of the voltage difference between the anode and cathode in Li-ion cells, the Cu^{2+} ions could penetrate through the separator and cause copper shunts. The same occurs if the cell is driven into negative polarity and kept in that state temporarily. Others discuss the possibility that Cu^{2+} ions disperse among the anode's carbon particles where they create alloying-sites for Li-metal dendrites to grow. Continuation of such processes during cycling could lead to the formation of Li-metal bridges that internally short the cell or weaken its thermal stability against abusive conditions such as high temperature and/or overcharge.

Here, the effects of overdischarge on performance and thermal stability of a commercially available Li-ion cell (size, 4.3 mm × 34 mm × 50 mm) rated at 780 mA h were investigated. This cell consisted of a graphite anode, polyethylene (PE) separator, and a $LiCoO_2$ cathode. Its electrolyte was a mixture of $LiPF_6$ with organic solvents ethylene-carbonate (EC) and diethyl-carbonate (DEC).

2. Experiments

2.1. Effects of overdischarge on cycle-life

1. Discharged and charged cells five times between 4.2 and 3.0 V at 0.8 and 0.4 A, respectively. This is identified as "*cell conditioning step*".
2. After cell conditioning, the cells were discharged to 2.3 V at 0.8 A; rest 10 min and discharged further to either of 2.0, 1.5, 1.0, 0.5 or 0.0 V at 10 mA.
3. All cells were kept at their pre-fixed discharged voltage for 72 h (3 days); then charged to 2.75 V at 10 mA and further to 4.2 V at 0.4 A and finally discharged and charged five times using the same current and voltage as in step 1. Steps 2 and 3 are identified as "*EXPS-1*".
4. Measured a.c. impedance of fully charged cells using impedance analyzer (Solatron-1260) and Galvano/Potentio stat (EG&G 273A) between 10 kHz and 50 MHz.
5. Measured thicknesses of fully charged cells using a micrometer.
6. Repeated steps 2–6 five times (i.e. cells were kept 15 days at each of the prescribed low voltages and cycled 25 times). The five repetitions of EXPS-1 are identified as "*EXPS-2*".
7. Finally, all cells were cycled 100 times between 4.2 and 3.0 V at 0.8 A (*normal operation step*) and then their a.c. impedance and thickness were measured again using the procedure in steps 4 and 5.

In all cases above, charge steps terminated while cell voltage was kept at 4.2 V and current dropped below 40 mA and a.c. impedance values measured while cells were fully charged. For clarity, Fig. 1 is a flowchart of the experimental procedure. Fig. 2A shows voltage versus time profiles for a cell that was overdischarged to 1.0 V per the steps listed above. Fig. 2B shows

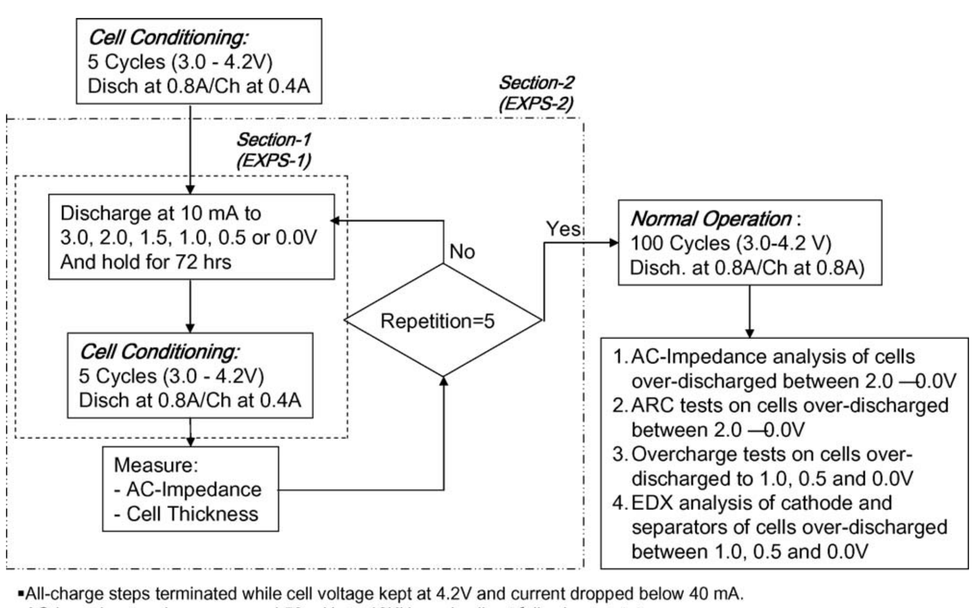

Fig. 1. Experiment flowchart.