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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.
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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/Potentiostat (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

• All-charge steps terminated while cell voltage kept at 4.2V and current dropped below 40 mA.
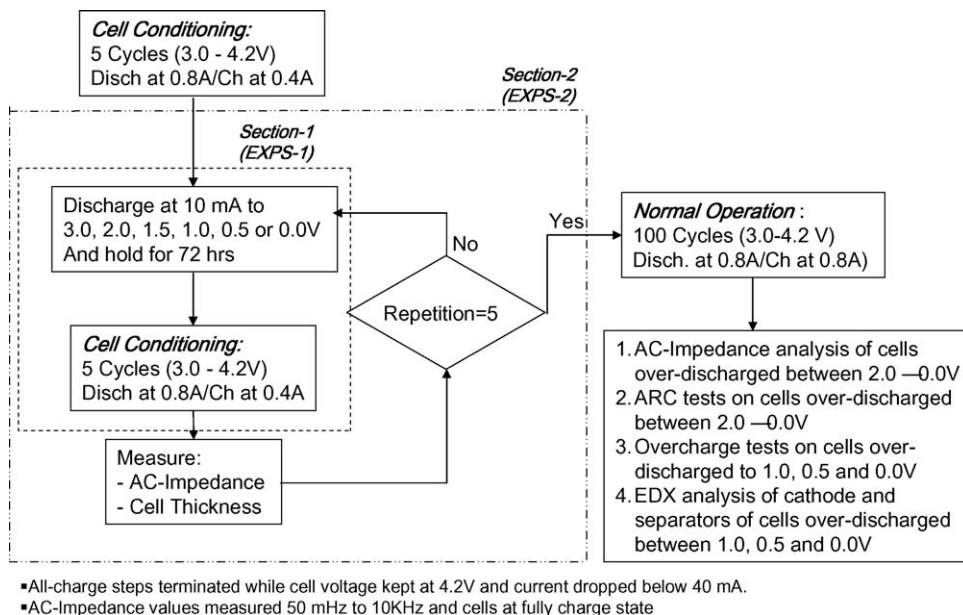• AC-Impedance values measured 50 mHz to 10KHz and cells at fully charge state
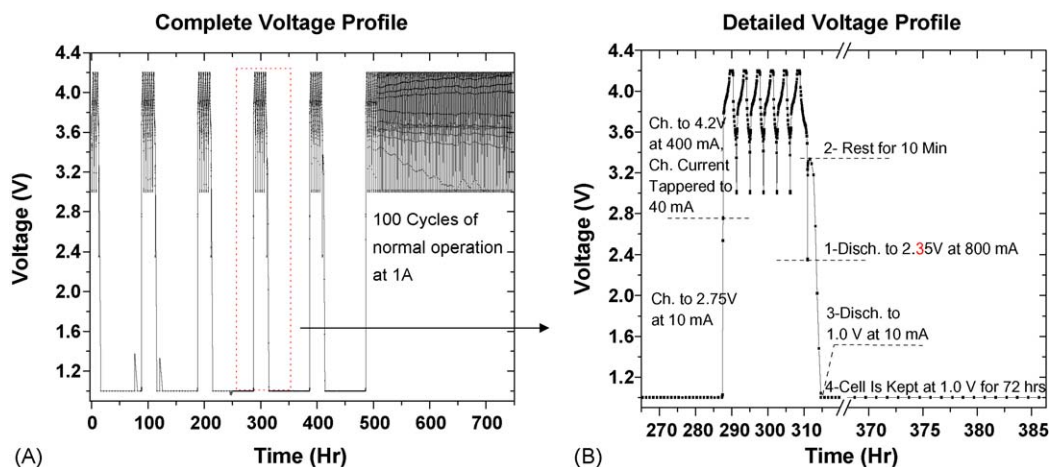
Fig. 1. Experiment flowchart.

Fig. 2. (A) Voltage profile of a cell that was cycled five times (conditioning), and undercharged to 1.0 V for 72 h (3 days) (5×), and then cycled 100 times under normal operating condition; (B) charge/discharge steps details: five cycles of cell conditioning followed by overdischarge to 1.0 V and 72 h.

details of step EXPS-1 for a 1.0 V overdischarged cell, obtained using a Maccor Battery Tester.

2.2. Thermal stability and materials analysis

After completion of the experiment above, the same Li-ion cells were used for overcharge (4.6 V/3.0 A) and accelerating rate calorimetry (ARC-2000, Columbia Scientific) tests. Also, energy dispersive X-ray (EDX, Hitachi-S4100) was used to determine the presence of copper particles on the separators and cathodes recovered from the cells.

1. Overcharge test: A set of three samples from each set of cells that was overdischarged to 1.0, 0.5 or 0.0 V were fully discharged, wrapped in glass-mat and then overcharged to 4.6 V at 3.0 A for 8 h.
2. Accelerating rate calorimetry (ARC) test: One cell from each set of samples that was overdischarged to 2.0, 1.5, 1.0, 0.5 or 0.0 V was fully charged, placed in a lightweight aluminum-holder and mounted in the center of the ARC heater cavity. The cell and cell-holder assembly was heated from 35 to 350 °C in 5.0 °C steps with 20 min of wait-time between each step. The ARC was operated under heat–wait–search (HWS) mode while its sensitivity limit sat at 0.02 °C min^{-1}. In this case, the ARC went to adiabatic mode when the cell self-heat-rate (SHR) reached to $\geq$0.02 °C min^{-1}. After meeting this condition, the ARC generated just enough heat to follow only the cell's self-heating. This process was continued until the SHR of the sample fell below the ARC sensitivity limit of 0.02 °C min^{-1}. The ARC equipment and its functionality are covered elsewhere in detail [13,14].
3. Material analysis: EDX analysis was used to determine possible presence of copper on the separators (facing both anode and cathode) and cathodes recovered from cells that were overdischarged to 1.0, 0.5 or 0.0 V.

3. Results and discussion

Fig. 3 shows bar charts summary of the cells' initial discharge capacity values and their degradation after each EXPS-1 and the normal operation step. Data for cells cycled under a normal operating condition (charge to 4.2 V and discharged to 3.0 both at 0.8 A) are also included for comparison. Results showed overdischarge to 2.0 and 1.5 V had small effects on cycle-life, as revealed by the cells' total capacity losses of about 8% which is close to capacity losses (~10%) of the same cell-type cycled 100 times between 3.0 and 4.2 V. The small differences in capacity lost (2%), here, may be attributed to performance variability among cells. Discharge to 1.0 and 0.5 V led to total capacity losses of 29 and 38%, respectively, which is significantly higher than normally cycled cells. The 0.0 V cells showed two types of behavior. Of the seven cells that were tested, four cells were similar to the 0.5 V cells although with higher capacity losses.
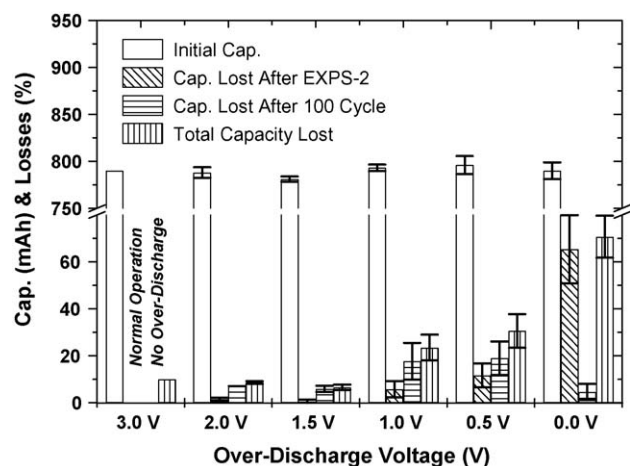

Fig. 3. Initial capacity values and losses after five consecutive overdischarging to voltages between 2.0 and 0.0 and five cycles of cell conditioning (EXPS-2), and after 100 cycles of normal operation. Cells cycled under normal operating condition (3.0–4.2 V) are also included for comparison.

However, three cells failed operation at various stages of overdischarge to 0.0 V. One cell lost a significant amount of its initial capacity after the first overdischarge to 0.0 V, and then shorted at the end of the EXPS-2 step. The other two cells continuously lost capacity throughout the five EXPS-1 repetitions until their capacities were completely depleted.

Kishiyama et al. [10] studied effects of 0.0 V overdischarge on Li-ion cells consisting of anodes with titanium and copper current collectors. They clearly demonstrated that copper dissolution is the main cause of capacity loss in a Li-ion cell. Also, the SEI-layer could break up if the anode voltage reaches above 3.5 V during overdischarge of a Li-ion cell to 0.0 V. Zhao et al. [12] studied oxidation and reduction of copper electrodes in three different electrolytes consisted of 1 M $LiPF_6$ with solutions of PC:EC:DMC (1:1:3 vol.), EC:DMC:DEC (2:2:1 vol.) or EC:DMC:MEC (1:1:1 vol.), normally used in Li-ion cells. They noted the presence of H_2O and/or HF enhances the extent of copper oxidation. The copper current collector of an anode oxidizes when a Li-ion cell, using $LiCoO_2$ as cathode material, is overdischarged to voltages less than 0.4 V. Mao [11] demonstrated that the anode potential can reach as high as 3.8 V when overdischarging a Li-ion cell to 0.0 V. Therefore, it is possible that both copper dissolution and SEI-layer breakdown are causing capacity loss when a Li-ion cell is repeatedly forced to and/or kept for an extended period of time at 0.0 V. However, it should be noted that the cathode and anode active material ratio, which may vary for different cell types and manufacturers, can play a role in the behavior of Li-ion cells overdischarged to 0.0 V.

Fig. 4A shows a.c. impedance profiles (Nyquist-plot) for the cells after completion of each of the five EXPS-1 steps and the normal operation step (overdischarge voltage = 1.0 V). Note that high frequency cell impedance increased slightly with increased dwell time at 1.0 V, while the reverse occurred on the low frequency side. This data, however, clearly show that both high and low frequency impedances of this cell increased after 100 cycles. Fig. 4B shows plots of the a.c. impedance values (mean
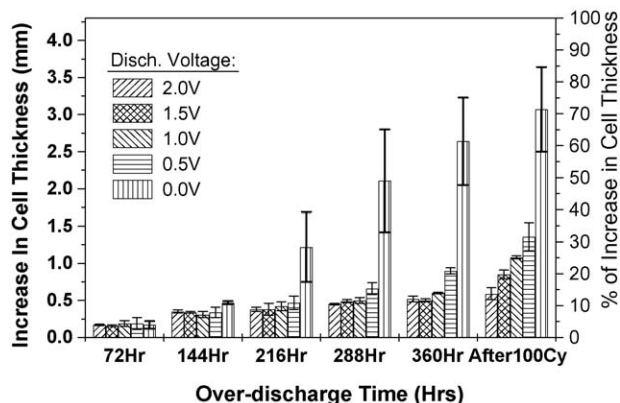

Fig. 5. Increase in cell thickness during EXPS-2 and 100 cycles of normal operation.

and standard deviation) for all overdischarged cells at high and low frequencies noted as points 1 and 2 in Fig. 4A. Note that the overall impedances of the 2.0, 1.5, 1.0 and 0.5 V cells were not significantly affected by repeated overdischarging to such low voltages. However, the impedance of the 0.0 V cells increased significantly, especially at low frequency after 216 h at 0.0 V. The stable high frequency impedance suggests that bulk electronic and ionic conductivity in the cell is unaffected by overdischarge. This increase in low frequency impedance suggests degradation in electrochemical charge transfer processes in the electrodes when overdischarged to 0.0 V.

Fig. 5 shows bar-chart plots of the cell thickness measured after each completion of the five EXPS-1 steps and the Normal Operation step (overdischarge voltage = 1.0 V). Note that the thickness of the 0.0 V cells increased more than others, especially after the third EXPS-1, which coincides with the high impedance growth of the cells after 216 h at 0.0 V. This sudden increase in both cell impedance and thickness can be indicative of events causing excessive gas generation and/or perhaps electrode swelling.
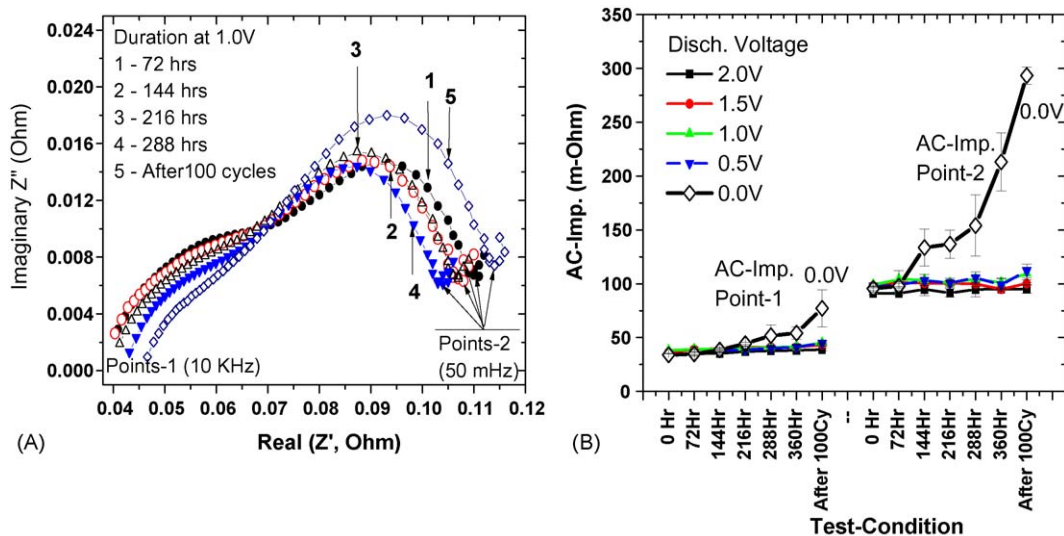

Fig. 4. (A) The a.c. impedance (10 kHz to 50 MHz) of fully charged cells measured after each EXPS-1 step (overdischarge voltage = 1.0 V) and after 100 cycles of normal operation; (B) plots of the high and low frequency impedance values (overdischarge voltage = 2.0–0.0 V) at points 1 and 2 in Fig. 4A.
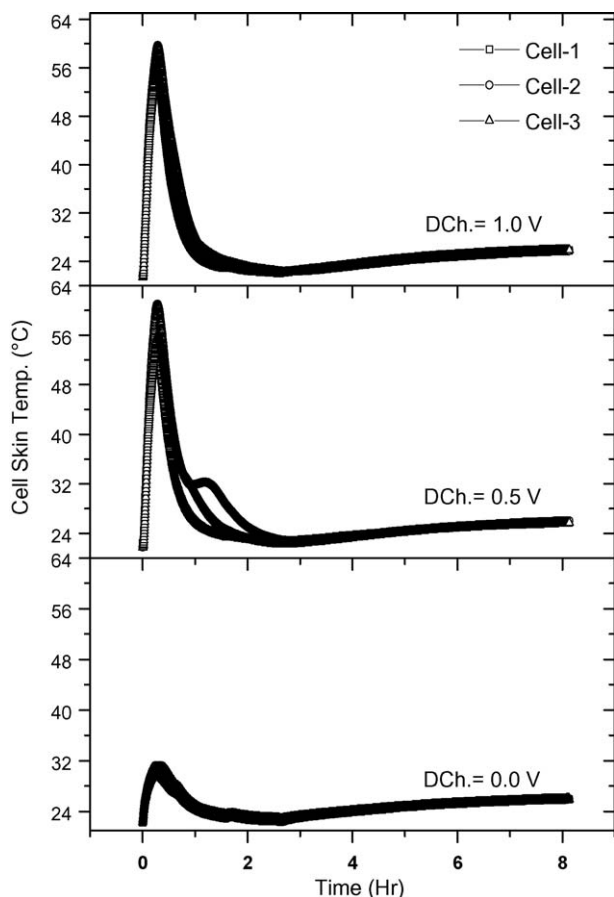
Fig. 6. Temperature vs. time profiles of cells overcharged (4.6 V/3 A) after completion EXPS-2 (undercharge voltage = 1.0, 0.5 or 0.0 V) and 100 cycles of normal operation.

Table 1
Initial capacity before, and temperature rise of cells during, overcharge tests

Cell under discharge voltage	No. of cells tested	Cap. values (mA h)	Cell skin temperature rise (°C)
1.0 V	1	662	33.6
	2	657	38.1
	3	560	35.1
0.5 V	1	588	37.9
	2	645	40.9
	3	525	35.6
0.0 V	1	169	9.5
	2	120	8.1
	3	89	7.72

and reformation, because of repeated overdischarge to 0.0 V, led to gas generation and consequently swelling of the Li-ion cells that we investigated.

Fig. 6 shows overcharge test results (temperature versus time profiles) for the cells after the normal operation step. Table 1 gives values for recoverable capacity of cells before, and temperature rise during, the overcharge tests. Note that the temperature of the 1.0 and 0.5 V cells increased by 34 and 41 °C, respectively, and the 0.0 V cell by only ~10 °C. This behavior must be attributed to the higher recoverable capacities for the higher voltage cells.

Fig. 7A shows ARC test results (SHR versus temperature profiles) for all the cells, fully charged, after 100 cycles of the normal operation step. Results for a fully charged cell that was initially cycled 125 times between 3.0 and 4.2 V at 1.0 A are also included for comparison (reference cell). Note that the SHRs of the 2.0, 1.5 and 1.0 V cells were higher than the reference cell, which was cycled without being overdischarged. In contrast, the SHRs of the 0.5 and 0.0 V cells are lower than the reference cell. Fig. 7B highlights the SHR between 180 and 220 °C, where sudden cooling occurred because of cracked can/header welds (vent). This temperature increased with decreasing cell overdischarge voltage from 2.0 to 0.0 V. These two figures imply that the thermo-chemical reactivity of the cells overdischarged between

It is well known that abnormal operation of Li-ion cells leads to destruction and reformation of anode SEI-layer, especially at elevated temperatures. Such condition cause gaseous product build up and swelling of the Li-ion cells. Kishiyama et al. [10] have also noted that overdischarging of Li-ion cells to voltages <1.0 V can lead to dissolution of the anode SEI-Layer. Therefore, in this work, it is possible that the anode SEI-Layer dissolution
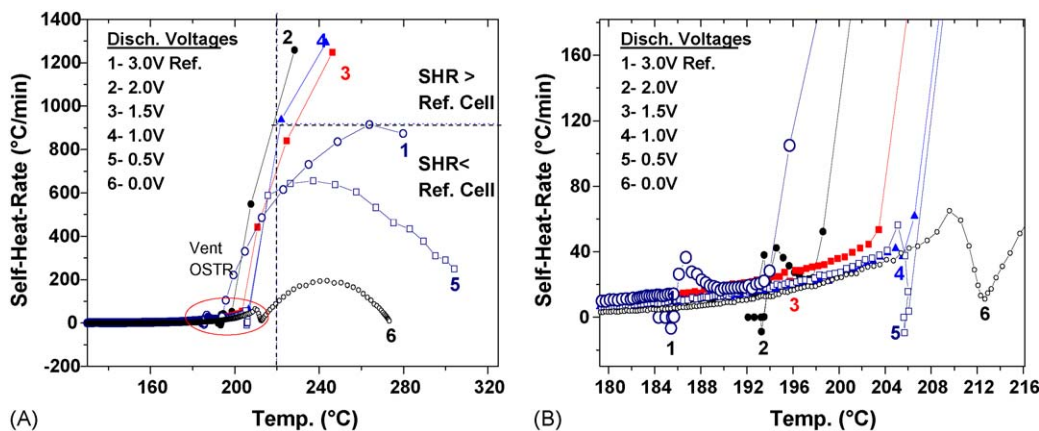

Fig. 7. (A) Self-heat-rate (SHR) of fully charged cells after completion of EXPS-2 (overdischarge voltage = 2.0–0.0 V) and 100 cycles of normal operation. SHR data for a fully charged Ref. cell (cycled 125 times under normal operation condition) are also included for comparison. (B) Detail of temperature range where sudden cooling occurred because of broken cell/header weld.

Table 2
Temperature values for vent and the point of no return from thermal runaway high heat generation

Cells discharges voltage (V)	Vent temperature (°C)	Point of no returned (°C)
3.0	185	193
2.0	193	197
1.5	197	196
1.0	207	205
0.5	204	205
0.0	209	212

The vent temperature is when cell's header weld breaks up, and point of no return is when cell's self-heating starts increasing at a very fast rate.

2.0 and 1.0 V is similar to or slightly higher than the reference cell; however, both total heat generation and thermo-chemical reactivity of cells overdischarged to 0.5 and 0.0 V are significantly lower than the reference cell. Table 2 gives temperature values for cells' venting points and the points of "no return" where their self-heating started increasing at rates faster than 20–40 °C min^{-1}.

Fig. 8 shows photos of separators (both anode and cathode faces) recovered from cells overdischarged to 1.0, 0.5 V, as well as a cell overdischarged to 0.0 V that continuously lost capacity throughout the five EXPS-1 repetitions until complete capacity depletion. All separators have some level of residue on them. Table 3 gives results for EDX elemental analysis (wt.%) of the cathodes and separators of these cells. Statistically insignificant amounts of copper were detected in these cases.

Fig. 9A shows photos of the separator from the cell that lost most of its capacity at the early stages of repeated overdischarging to 0.0 V and finally shorted internally near the end of EXPS-2. Fig. 9B is magnified photo of the circled location on the separator's anode side, taken using a light transmission microscope. The bright spot at the center of the photo indicates that more light is passing through the separator, which implies that the separator has degraded at this location. Results show that this separator has significantly more residue than those in Fig. 8, especially on its anode side. However, Fig. 9C shows EDX elemental maps of the circled areas on the separator's anode and cathode sides. Note that these are at the same location, but on
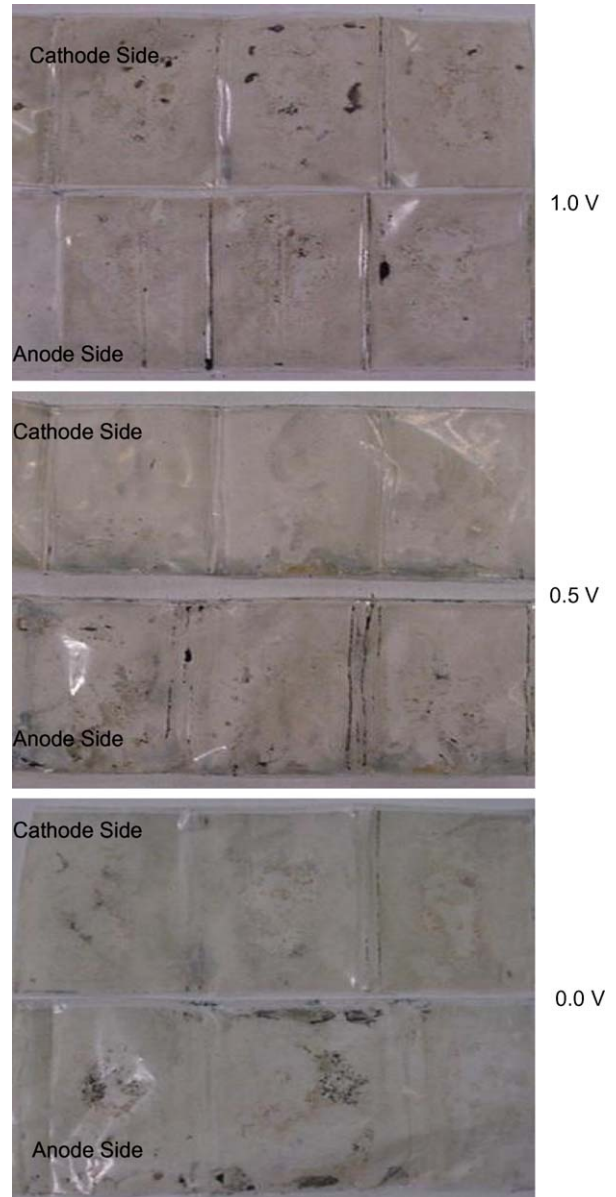

Fig. 8. Photos of two separators recovered from cells after completion of EXPS-2 (overdischarge = 1.0 and 0.5 V) and 100 cycles of normal operation and a separator from the cell that gradually lost its full capacity during the five EXPS-1 steps (voltage = 0.0 V).

Table 3
Constituents (wt.%) of cathode and separator samples (facing both anode and cathode) recovered from cells after completion of EXPS-2 and 100 cycles of normal operation

Elements (K-shell)	Cells discharged to 0.0 V			Cell discharged to 0.5 V			Cells discharged to 1.0 V		
	Cathode	Separators, anode side	Separators, cathode side	Cathode, 0.5 V	Separators, anode side	Separators, cathode side	Cathode, 1.0 V	Separators, anode side	Separators, cathode side
Carbon	14.7	93.28	91.16	14.14	80.65	63.93	14.24	85.74	76.2
Oxygen	23.66	1.21	2.4	26.71	7.785	19.28	26.47	2	5.55
Cobalt	61.6	0.46	1.22	58.03	0.05	0.96	58.93	0	0.13
Copper	0.04	0.0	0.0	0.22	0.0	0.00	0.00	0.00	0.13
Aluminum		0.07	0.04	0.66	0.0	0.0	0.3	0.01	0
Phosphor		1.06	1.05	0.24	10.49	0	0.07	2.34	3.45
Fluorine		3.92	4.14			15.64		9.91	14.67
Silicon				0.13	0.18				

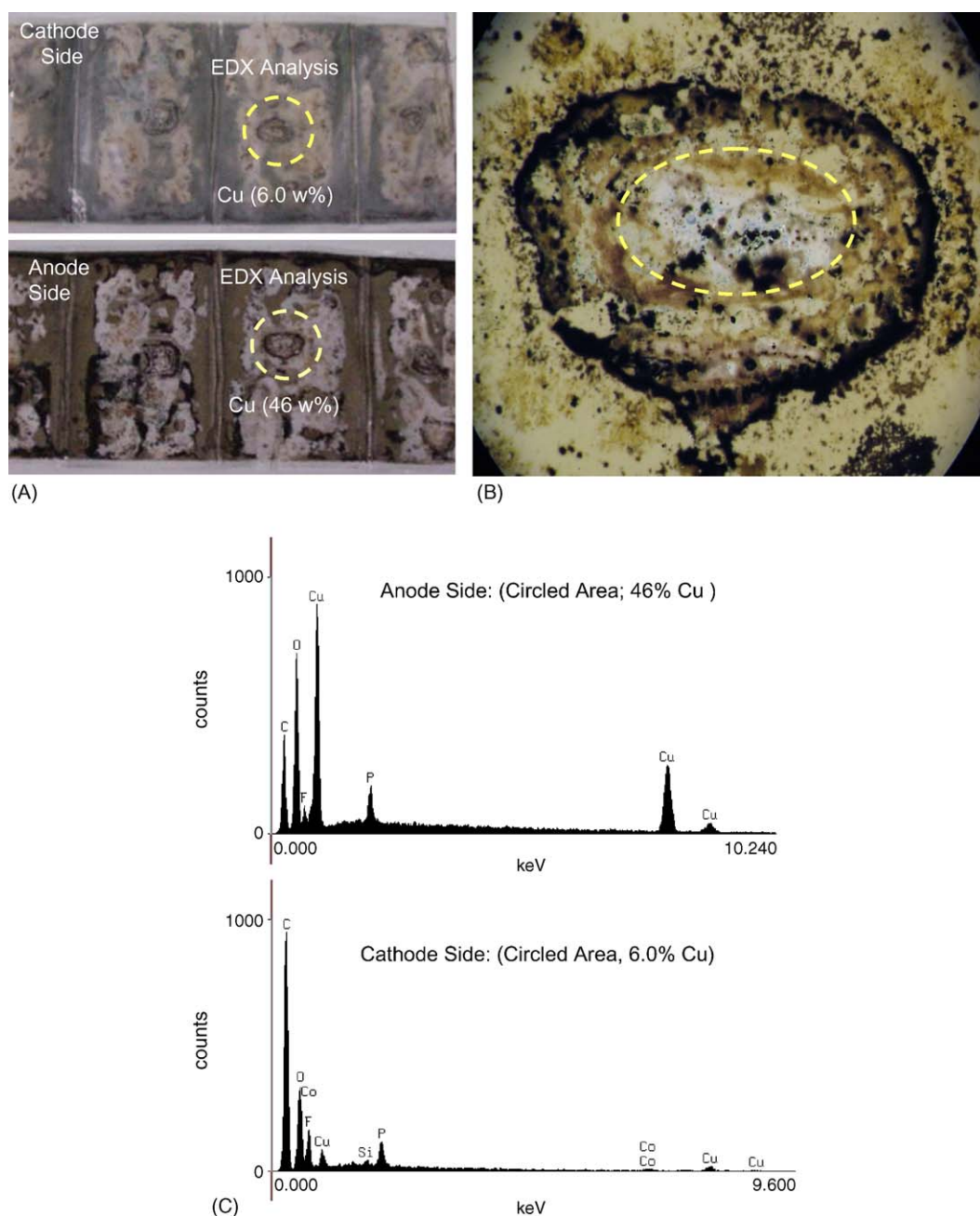Data obtained using EDX analysis (sensitivity limit > 1000 ppm).

Fig. 9. (A) Photos of a separator recovered from the cell that failed at the early stages of the repeated undercharging to 0.0 V. Circles show the separator areas, facing anode and cathode, used for the EDX analysis. (B) Magnified photo of the circled location from the anode side, taken using transmission light microscope. Bright spot shows separator's weakened area allowing more light transmission. (C) EDX elemental maps of circled areas from Fig. 9A on the separator of the cell that failed/shorted at early stages of the five EXPS-1 to 0.0 V.

opposite sides of the separator. The dissolution of the copper current collector and migration of Cu^{2+} ions through the separator is clearly evident. While the EDX analysis detected ∼46 wt.% copper on the anode side, it detected ∼6.0 wt.% copper on the cathode side as well.

4. Conclusion

Overdischarge effects (15 days at voltages between 2.0 and 0.0 V) on cycle-life and thermal stability of a commercially available Li-ion cell (size, 4.3 mm × 34 mm × 50 mm) rated at

780 mA h have been investigated. Results indicate that overdischarging between 2.0 and 0.5 V can lead to permanent capacity loss and adversely affects cycle-life of this Li-ion cell under normal operating conditions. In this case, overdischarge between 2.0 and 1.5 V, and 1.0 and 0.5 V led to capacity losses of less than 2 and 18%, respectively. Subsequently, the same cells lost between 8 and 25% additional capacity when cycled 100 times between 4.2 and 3.0 V at 0.8 A (normal operation).

Overdischarge between 2.0 and 0.0 V also has no impact on thermal stability of this cell during overcharge conditions (4.6 V/3.0 A). Thermo-chemical reactivity of the cells

overdischarged between 2.0 and 1.0 V is close to or slightly higher than a normal cell. However, both total heat generation and thermo-chemical reactivity of cells overdischarged to 0.5 and 0.0 V are significantly lower than a normal cell, possibly because of the degraded capacity of the cell.

Behavior of this Li-ion cell is unpredictable when overdischarged to 0.0 V. Of the seven cells tested, four cells managed to withstand five consecutive repetitions of five cycles between 4.2 and 3.0 V and 3 days at 0.0 V, followed by 100 cycles of charge/discharge between 4.2 and 3.0 V at 0.8 A. However, three cells failed operation at different stages of repeated overdischarge to 0.0 V. Two of these cells exhibited no evidence of copper current collector dissolution. The third cell, however, showed a considerable amount of copper on the separator, with localized deposits greater on the anode side than the cathode side. This is indicative of the fact that dissolved copper (Cu^{2+}) can indeed migrate through the separator from the anode side to the cathode side and possibly cause an internal short.

Note: Additional investigations on this subject are currently being performed to address effects of self-discharge on cycle-life and thermal stability of Li-ion cells. Here, self-discharge was mimicked by connecting constant loads (12 kΩ resistor) across the positive and the negative poles of Li-ion cells, initially discharged to 2.35 V, for 36 days. Preliminary data suggest that slow discharging (self-discharge) of Li-ion cells to 0.0 V (OCV = 9–12 mV) leads to far less capacity loss ($17 \pm 2.3\%$)

than forced overdischarge to 0.0 V as discussed in this article.

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