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# Performance Loss of Lithium Ion Polymer Batteries Subjected to Overcharge and Overdischarge Abuse

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# 1. Executive Summary

Lithium-ion polymer (LiPo) batteries are rechargeable energy storage devices which power a variety of unmanned ground and aerial vehicles throughout the Department of Defense. Thin form factors make LiPo cells ideal for assembling in large strands or stacks to make a high voltage and high energy batteries. However, faulty connections between cells or improper cell balancing during routine charge/discharge can lead to overcharge or overdischarge of an individual cell, thus reducing performance and safety. This report presents the performance loss of commercial LiPo cells subjected to repeated overcharge and overdischarge abuse.

The following conclusions are made:

- LiPo cells charged within the recommended voltage limits can provide hundreds of charge/discharge cycles at relatively high rates.
- Charging and discharging LiPo cells outside of their recommended voltage window causes physical degradation and performance loss. These effects increase with the severity of overcharge/overdischarge voltage and are compounded with repeated abusive cycling.
- The usable cycle life of LiPo cells is dramatically reduced with repeated overcharge/overdischarge abuse.
- Overcharge and overdischarge causes material and component decomposition within the cell producing gaseous species causing swelling of the LiPo pouch.

## List of abbreviations, acronyms and formulas

LiPo: lithium-ion polymer battery

OC: overcharge

OD: overdischarge

DOD: depth of discharge

SOC: state of charge

Li: lithium

HF: hydrofluoric acid

LiCoO<sub>2</sub>: lithium cobalt oxide

LiMn<sub>2</sub>O<sub>4</sub>: lithium manganese oxide (spinel)

LiPF<sub>6</sub>: lithium hexafluorophosphate

EC: ethylene carbonate

DEC: diethyl carbonate

DMC: dimethyl carbonate

PC: propylene carbonate

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Ocpwuetkr v'cr r tqxgf "Ugr vgo dgt"32."42340'

## 2. Introduction

Lithium-ion polymer (LiPo) batteries are power sources which provide high specific energy and high energy density, in thin, high aspect-ratio form factors (Linden and Reddy 2002). LiPo cells are a derivative of standard lithium-ion chemistry but use a polymer gel electrolyte. Like traditional lithium-ion batteries, LiPos are rechargeable, capable of delivering thousands of high energy discharge cycles. During cycling, lithium ions shuttle between the positive and negative electrodes which are separated by a polymer gel electrolyte. LiPo cells are typically packaged as wound prismatics or pouches that lack a rigid outer casing. The pouch construction offers advantages over cylindrical cells, such as better cell-to-cell packing for battery fabrication and superior heat dissipation.

LiPo batteries have been power sources for programs of record in a variety of applications across the Department of Defense and NASA. Within the Navy and Marine Corp., unmanned air vehicles (UAV) Dragon Eye (2004) and Raven (2007) were powered by LiPo cells coupled together to produce 25.9 V (5.7 Ah) and 22.2 V (3.8 Ah) batteries respectively for propulsion and communications power. Unmanned ground vehicles (UGV) Toughbot and Throwbot utilized LiPo batteries to power remote video and audio reconnaissance equipment (Govar, Fuentevilla et al. 2007). Larger format LiPo batteries have been employed in Air Force aircraft, UAV and ground power applications. LiPo cells of exceptional manufacturing quality can provide thousands of discharge cycles making them ideal candidates for space missions. Their thin form factor and high cell voltage make LiPos ideal power sources for NASA miniature spacecraft (Simon 2005).

The nominal specifications (voltage, energy and power) of a LiPo cell are determined by the chemistries of the integral battery components: cathode (positive electrode), anode (negative electrode) and electrolyte. The most common commercially available LiPos consist of a  $\text{LiCoO}_2$  cathode and graphite anode. Polymer electrolytes are polymer gels with an ionic conductive salt such as  $\text{LiPF}_6$ .

Single cells are often bundled together into various geometric arrays. The most common configurations of cells are the planar or stacked array which typically joins multiple cells together in series to increase the battery voltage (given in Appendix Figure A.1). Eight cells in series are denoted as an 8s1p strand. Planar or staked arrays joined together in parallel increases the capacity of the battery. A typical planar battery array with parallel strands, also given in Figure A.1, would be termed 8s2p where “s” is the number of cells in series (8) and “p” is the number of strands connected in parallel (2).

### *Example 1*

Standard LiPo cells of nominally 3.7 V and 300 mAh joined together in the 8s2p planar array. Eight LiPos cells joined together in series provide 29.6 V ( $3.7 \text{ V} \times 8 \text{ cells} = 29.6 \text{ V}$ ). Two planar strands joined in parallel doubles the capacity to provide 600 mAh ( $300 \text{ mAh} \times 2 \text{ strands} = 600 \text{ mAh}$ ).

When cells are assembled in battery packs there is always a distribution of cell capacity which increases the susceptibility of the cells to abusive conditions such as overcharge and overdischarge. The extent of capacity distribution widens with cycling and increasing the severity of the overcharge and overdischarge abuses. Defective connections between cells or faulty charging circuits can lead to cell overcharge (Xu, He et al. 2012) while leakage currents in the battery circuitry can lead to overdischarge (Maleki and Howard 2006).

Overcharge and overdischarge are the most common abuses imposed upon LiPo cells. Abuse can manifest itself as a decrease in performance (limiting mission capability) and/or decrease in safety. Each type of LiPo has a recommended voltage window where the upper and lower voltage bounds are specific to the chemistry of the cathode, anode and electrolyte materials. Deviation outside of these boundaries

are thus termed overcharge (charge above voltage limit) and overdischarge (discharge below voltage limit). **This report presents the performance loss of commercial LiPo single cells subjected to repeated overcharge and overdischarge abuse.**

### 3. Definitions

*Cycle life* is the number of charge/discharge cycles a cell provides before losing functionality. In practice throughout DoD and elsewhere, end of the usable cycle life is reached when the cell delivers less than 80% of the rated ampere-hour capacity.

*Overcharge* occurs when a cell is charged above its recommended capacity or voltage cutoff often the result of improper charging practices or faulty cell balancing of LiPo packs. Typically, cells overcharge when the charge cutoff voltage is increased above the recommended limit (voltage driven). However, overcharge may also occur during prolonged periods of current draw even within the recommended voltage window (current driven).

*Overdischarge* occurs when a cell is discharged below its recommended capacity or voltage cutoff. Faulty cell balancing may produce cells below the average state-of-charge (SOC) of the entire battery pack. These cells are susceptible to overdischarge once an electric load is applied to the battery pack. Below the normal voltage endpoint, the cell may be forced into polarity reversal greatly affecting the future performance of the cell. Overdischarge can also be voltage driven or current driven.

### 4. Material Components of LiPo Cells

*Aluminized Polyester Pouch* is a three-layer laminate packaging material often used for LiPo cells. The interior and exterior layers are non-conductive polyester polymer with an impermeable internal aluminum foil layer.

*Aluminum foil* is the metallic current collector used to facilitate electric contact from the positive electrode materials to the cell terminal. Aluminum maintains a stable passivation layer in voltage range of the cathodic half-cell reaction.

*Lithium cobalt oxide* ( $\text{LiCoO}_2$ ) has been the most ubiquitous positive electrode material for lithium-ion and LiPo cells for portable electronic devices due to its high energy density, voltage and cycleability. All of the LiPo cells tested in this report contain the  $\text{LiCoO}_2$  positive electrode chemistry.

*Separator* is a micro-porous polymer membrane which electrically isolates the electrodes while allowing ionic conduction between the electrodes while maintaining electric isolation (Love 2011).

*Electrolyte salt* is an inorganic lithium salt, typically  $\text{LiPF}_6$ , capable of providing ionic conductivity and miscible within the electrolyte solvents.

*Electrolyte solvents* are typically aprotic organic solvents with electrochemical stability within a voltage range of 0 to 5.0 V vs. Li.

*Graphite carbon* (C) is typically used as the negative electrode material and commonly coupled with  $\text{LiCoO}_2$  and other transition metal oxides and phosphate positives.



*Copper foil* is the metallic current collector used to facilitate electric contact from the negative electrode materials to the cell terminal. Copper maintains a stable passivation layer in voltage range of the anodic half-cell reaction.

## 5. Background

### 5.1 Origins of Cell Voltage and Acceptable Limits

Lithium-ion batteries rely on the reversible intercalation/extraction of Li ions from positive and negative electrode materials. The electrochemical couple between the two materials will determine a cell's voltage boundaries to achieve 100% SOC (full delithiation of positive) and 100% DOD (full lithium extraction from positive). The open-circuit voltage,  $V_{oc}$ , is given by the difference in lithium chemical potential ( $\mu_{Li}$ ) between the positive and negative electrodes:

$$V_{oc} = \frac{\mu_{Li(p)} - \mu_{Li(n)}}{F}$$

where  $F$  is the Faraday constant, 689,000 C/V (Coulombs per Volt). A high  $\mu_{Li(p)}$  and low  $\mu_{Li(n)}$  provide the greatest operating voltage window for the electrochemical couple.

#### *Example II*

Consider the electrochemical couple utilized in LiPo cells. LiPos typically consist of a lithium cobalt oxide ( $\text{LiCoO}_2$ ) positive electrode and a graphite negative electrode. It is necessary to identify the electrochemical reactions occurring at each electrode or the half-cell reactions first to understand the voltage limitation of the full cell. The voltage limitations provide the recommended upper and lower voltage limits for cell operation.

#### Positive electrode reaction:



#### Negative electrode reaction:



The acceptable cell voltage will be limited to the difference between the potential windows of the half-cell reactions, ie: the low voltage boundary is the difference of  $3.0 - 0.2 \text{ V} = 2.8 \text{ V}$ ; the upper boundary is the difference of  $4.2 \text{ V} - 0 \text{ V} = 4.2 \text{ V}$ . Therefore the full cell reaction can be written as follows with the acceptable operating voltage,  $V_{cell}$ :

#### Full cell reaction:



### 5.2 Operating Outside of the Acceptable Voltage Limits

In an overcharged state, Li ions are removed from the positive electrode material in excess leading to instability of the crystal structure and the potential for oxygen release. During an overcharge, the negative electrode becomes over saturated with Li ions which plate lithium metal dendrites on the negative electrode surface. These dendrites grow with repeated cell cycling (even under normal voltage conditions) until reaching a critical length capable of reaching the positive electrode and shorting the cell resulting in uncontrolled heat and energy release (Lisbona and Snee 2011). Performance loss and capacity fade can result from numerous external abuses or internal side reactions (Arora, White et al. 1998).  $\text{LiCoO}_2$  charged above 4.2 V causes irreversible damage leading to capacity loss and an increased

safety threat. The various degradation mechanism associate from the overcharge (delithiation) of  $\text{LiCoO}_2$  positive electrode materials have been described elsewhere (Love and Swider-Lyons 2012). The removal of greater than 0.5 mol of lithium causes degradation of the crystal structure of the material, the release of oxygen gas and the oxidation of cobalt to the unstable  $\text{Co}^{4+}$  valence.

The effects of voltage-driven overcharge are typically corrosion of the cells metallic components and breakdown of the electrolyte solvents. Prolonged charging above 4.30 V forms plating of metallic lithium on the negative electrode, while the cathode material becomes an oxidizing agent, loses stability and produces carbon dioxide ( $\text{CO}_2$ ). Above 4.5 V electrolyte solvents decompose to form lithium carbonate,  $\text{Li}_2\text{CO}_3$ , which blocks lithium migration on the electrode surfaces.

Table I illustrates the effect of current and voltage driven overcharge on the stability of the internal components in a typical LiPo cell.

Improper cell balancing may produce cells below the average state-of-charge (SOC) of the entire battery pack. These cells are susceptible to overdischarge once an electric load is applied to the battery pack. Deep discharge of  $\text{LiCoO}_2$  forms  $\text{Li}_2\text{O}$  and Co. Upon charging, these compounds form  $\text{CoO}$ ,  $\text{Co}_3\text{O}_4$  and  $\text{Li}_x\text{CoO}_y$  on the surface of the cathode reducing capacity performance. Voltage driven overdischarge, below the prescribed cut-off voltage, results in corrosion processes which decrease performance and present safety hazards to personnel and equipment. Overdischarge below 1.5 V causes the dissolution of copper from the anode current collector, forming mobile Cu ions. Copper ions may then deposit on the anode surface or even penetrate through the separator forming an electric shunt (Maleki and Howard 2006; Lee, Chang et al. 2008). Below the normal voltage endpoint, the cell may be forced into polarity reversal greatly affecting the future performance of the cell.

Table II illustrates the effect of current and voltage driven overdischarge on the stability of the internal components in a typical LiPo cell.

**Table I: Effects of Current and Voltage Driven Overcharge on the Stability of LiPo Battery Components and Materials**

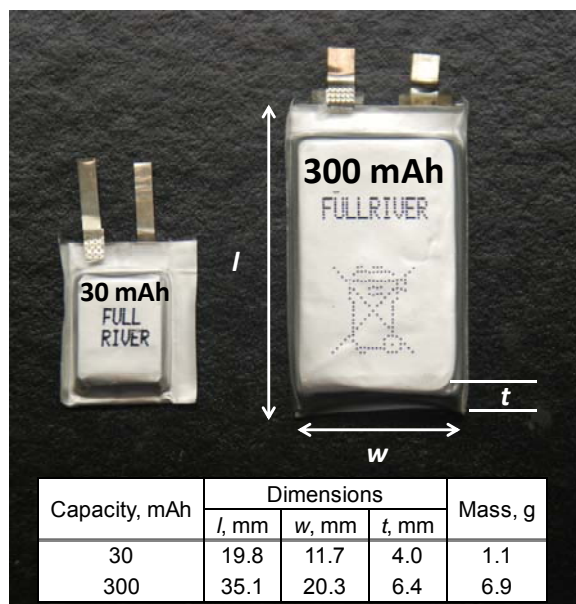
Material	Current Driven Overcharge, $\text{Li}_x\text{CoO}_2$ $x < 0.5$	Voltage Driven Overcharge, $V > 4.2$ V
Aluminized Polyester Pouch	none	none
Aluminum Foil		passivation to 5.0V above 5.0 V electrolyte salt degradation formation of HF
Cathode Materials LiCoO <sub>2</sub> LiMn <sub>2</sub> O <sub>4</sub>	oxygen loss: $3\text{CoO}_2 \rightarrow \text{Co}_3\text{O}_4 + \text{O}_2$ change/loss of crystal structure exothermic reactions	oxygen loss: $3\text{CoO}_2 \rightarrow \text{Co}_3\text{O}_4 + \text{O}_2$ change/loss of crystal structure exothermic reactions
Separator	none	none
Electrolyte Salt LiPF <sub>6</sub>	decomposition reaction: $\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5$ $\text{PF}_5 + \text{H}_2\text{O} \rightarrow 2\text{HF} + \text{PF}_3\text{O}$	reactive with cathode at high voltage formation of HF $> 4.0$ V
Electrolyte Solvent EC DEC DMC PC	oxidation of solvents at cathode: (DEC) $(\text{C}_2\text{H}_5\text{O})_2\text{CO} \rightarrow 5\text{CO}_2 + 5\text{H}_2\text{O}$ (DMC) $\text{CH}_3\text{OCO}_2\text{CH}_3 + 3\text{O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O}$	formation of C <sub>2</sub> H <sub>2</sub> from oxidation of C <sub>2</sub> H <sub>4</sub> on cathode surface $> 4.5$ V $\text{C}_2\text{H}_2 + 3\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$
Anode Materials Graphite	rupture of passivation layer lithium plating on anode surface hydrogen evolution from anode	rupture of passivation layer lithium plating on anode surface hydrogen evolution from anode
Copper Foil		copper corrosion occurs with the formation of HF and water

**Table II: Effects of Current and Voltage Driven Overdischarge on the Stability of LiPo Battery Components and Materials**

Material	Current Driven Overdischarge, $\text{Li}_x\text{CoO}_2$ $x > 1.0$	Voltage Driven Overdischarge, $V < 2.8$ V
Aluminized Polyester Pouch	none	none
Aluminum Foil	LiAl alloying deposition of dissolved $\text{Al}^{3+}$	pitting corrosion potential $< 3.5$ V vs. $\text{Li}/\text{Li}^+$ Corrosion above $4.3$ V vs. $\text{Li}/\text{Li}^+$
Cathode Materials $\text{LiCoO}_2$ $\text{LiMn}_2\text{O}_4$	$\text{LiCoO}_2 + x\text{Li}^+ \rightarrow \text{Li}_{1+x}\text{CoO}_{2-y} + \frac{1}{2}y\text{O}_2$ $\text{Li}_{1+x}\text{CoO}_{2-y} \rightarrow \text{Li}_2\text{O} + \text{Co}$	
Separator	none	none
Electrolyte Salt		
Electrolyte Solvent EC DEC DMC PC		decomposition to form $\text{CO}_2$ & $\text{CO}$
Anode Materials Graphite		
Copper Foil	Cu plating on cathode surface	cell voltage $< 2.5$ V corrosion begins cell voltage $< 0.4$ V $\text{H}_2\text{O}/\text{HF}$ accelerate corrosion formation of $\text{CuO}$ and dissolution to form $\text{Cu}^+$

## 6. Experimental Details

Full River LiPo pouch cells (30 and 300 mAh) were purchased from a domestic vendor, BSD Micro RC LLC (Carthage, MO). Full River batteries are manufactured in China. The cell consists of a  $\text{LiCoO}_2$  cathode material on an aluminum foil current collector. The anode material is a carbon composite on a copper foil current collector. A polymer gel electrolyte-soaked polyolefin separator electrically isolates the electrodes. A photograph of 30 and 300 mAh Full River LiPo cells and nominal cell dimensions are given in Figure 1.



**Figure 1: Photograph of Full River 30 and 300 mAh LiPo cells. Inset: table of nominal cell capacity, dimensions and mass.**

Electrochemical cycling was performed by a Maccor Series 4300 battery tester. All tests were performed under constant current at a rate of 1C or 10C (the current necessary to fully charge/discharge the cell within the normal voltage boundaries in 1 hour or  $1/10^{\text{th}}$  of one hour, respectively). A 1C current is equivalent to the nominal capacity of the cell divided by 1 hour. Thus, a 1C current used to charge/discharge the 30 mAh LiPo cell was 30 mA or 0.03 A. A 10C discharge rate is the amount of current needed to discharge in  $1/10^{\text{th}}$  of one hour or 6 minutes. The 10C discharge current for the 30 mAh LiPo cell was 0.3 A. The recommended voltage boundary for all cells is between 2.8 – 4.2 V.

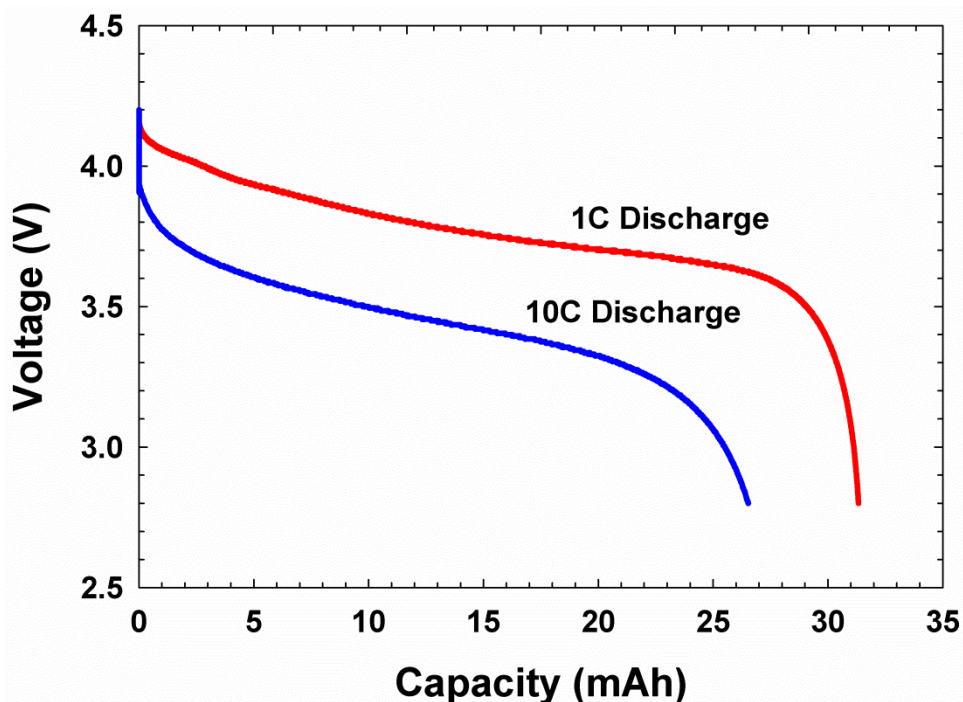
Abuse testing was done by voltage driven overcharge where the voltage window was extended outside of the normal range above 4.2 V while the discharge voltage cutoff was lowered below 2.8 V for voltage driven overdischarge tests. Current driven overcharge and overdischarge were not performed in this report however the degradation mechanisms and performance loss characteristics are related (as shown in Table I & II).

The upper voltage boundary was raised during overcharge testing (4.4, 4.6, 4.8, 5.0 V) while the lower voltage boundary was held at 2.8 V. Conversely, the lower voltage limit was decreased during overdischarge testing (2.0, 1.8, 1.2 V, 1.0 V) with the upper voltage limit held at 4.2 V. All measurements were collected at room temperature,  $\sim 23^\circ\text{C}$ . Thickness measurements were taken with a Mitutoyo micrometer at various locations along the cell surface.

## 7. Results

### 7.1 Normal Voltage Boundaries

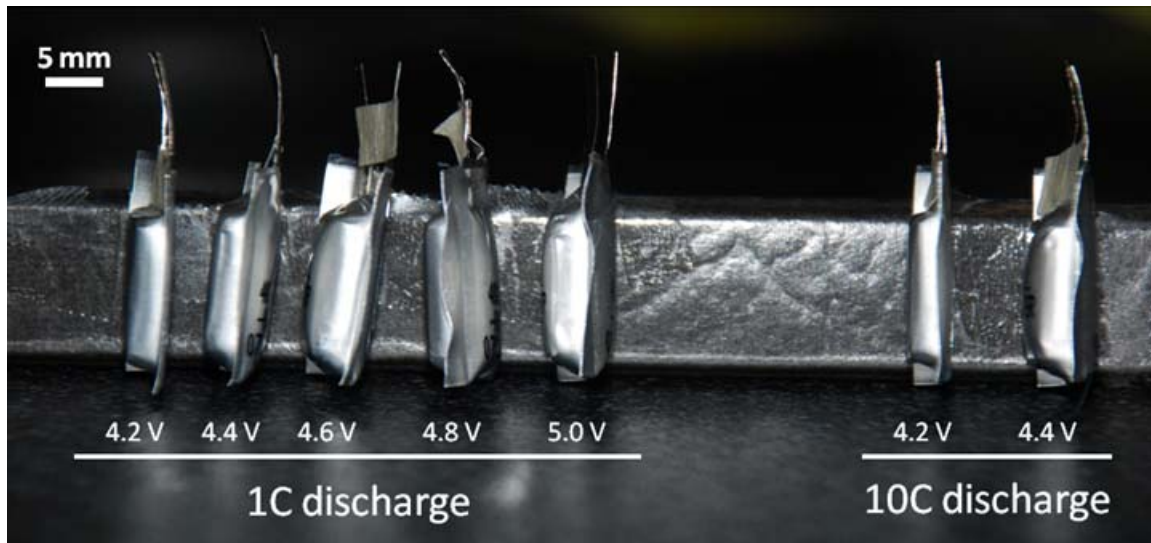
The discharge rate capabilities of LiPos have been previously reported (Stux and Swider-Lyons 2007). Figure 2 provides a sample of the discharge capability of 30 mAh Full River LiPo cells at 1C (0.03 A) and 10C (0.3 A) discharge rates. Both cells were charged at constant 1C (0.03 A) rate to the manufacturer prescribed voltage cut-off of 4.2 V. Each cell was discharged to the recommended discharge voltage of 2.8 V. A decrease in discharge capacity is clearly seen at the higher discharge rate. Constant 1C discharge yields a capacity of 31.3 mAh. However, increasing the rate 10x to 10C rate (0.30 A) decreases the capacity by 14.7% to 26.7 mAh.



**Figure 2: Discharge curves representative of 30 mAh Full River LiPo batteries discharged at constant current, 1C (0.03 A) and 10C (0.30) rates, between normal voltage range, 4.2 – 2.8 V. The charge rate was constant for both cells, 1C (0.03 A).**

### 7.2 Overcharge Abuse

When charged to the recommended 4.2 V voltage limit, no significant dimensional changes are observed in the LiPo cells, even after 200 cycles. However, the LiPo cells swell with increasing overcharge potential in the thickness ( $z$ ) direction, as shown in Figure 3, indicating the formation of a gas product inside the cell pouch. The cell dimensional changes at various states of overcharge are given in Table III, and increase linearly to 4.6 V, as has also been shown by Belov and Yang for a prismatic Li-ion (Belov and Yang 2008). The Full River cells in this study reached a maximum thickness at 4.6 V, due to the elastic stiffness of the packaging material and geometric constraints of the cell. The mass of the cells after testing equal that of the “as-received” cells, indicating no electrolyte venting or leakage during or after overcharging, even after the most severe overcharge.



**Figure 3: Photograph of LiPo cells after 200 charge/discharge cycles at 1C charge rate. The discharge voltage was held constant at 2.8 V while the charge voltage varied between 4.2 V state-of-charge and 4.4 – 5.0 V states-of-overcharge.**

When the overcharged cells were disassembled, the electrode materials were delaminated from the aluminum cathode and copper anode current collectors, most severely in the cells charged to 5.0 V. The carbon negative electrode material that remained on the copper foil appears pitted and rough. Electrode materials delaminate from current collectors during overcharge because moisture and oxygen from decomposed electrolyte corrode the current collector foils (Belov and Yang 2008). XRD of a positive electrode charged to 5.0 V and discharged to 2.8 V, did not reveal any significant structural deviation from the initial  $\text{LiCoO}_2$  with space group  $R\bar{3}m$ , confirming that oxygen release from delithiated  $\text{Li}_x\text{CoO}_2$  is not the source of gas in the swelled cells. This confirms electrolyte decomposition is the source of gas production causing cell swelling.

**Table III: Change in cell z-direction thickness of 30 mAh LiPo cells after 200 overcharge cycles. The severe overcharge condition to 5.0 V (+800 mV) was stopped after 12 cycles for safety reasons.**

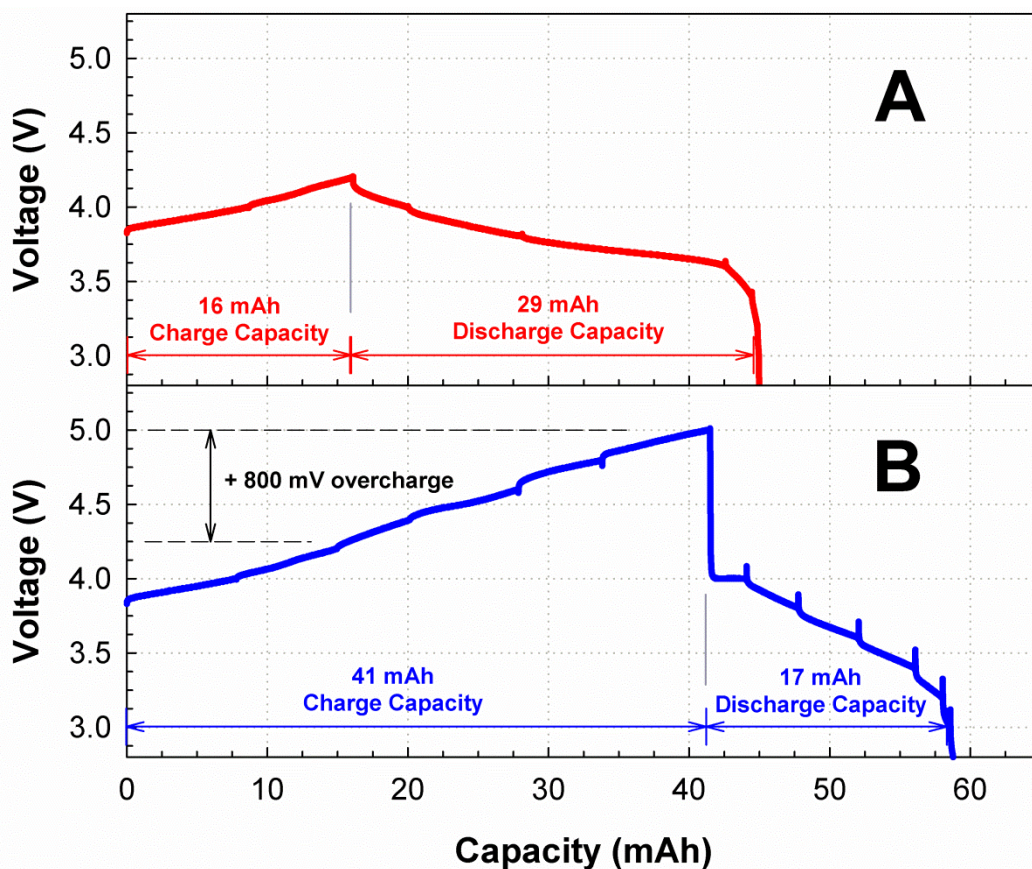
Upper Voltage Limit, V	$\Delta t$ , mm	
	1C discharge	10C discharge
4.2	0.005	0.005
4.4 (+200 mV)	1.93	2.56
4.6 (+400 mV)	2.53	-
4.8 (+600 mV)	2.57	-
5.0 (+800 mV)	1.30 (12 cycles)	-

Representative galvanostatic charge and discharge data are shown in Figure 4 for cells charged to cut-off voltages of 4.2 V and 5.0 V. Each cell had an initial open circuit voltage around 3.805 V. The cell charged to 4.2 V had an initial discharge capacity of greater than 30 mAh, the rated capacity for the cell. A high discharge capacity was maintained throughout 200+ charge/discharge cycles for cells charged to 4.2 V. Self-charging and self-discharging of the cell (as evident by the sharp peaks at 0.2 V increments)



occurs when the cell was allowed to relax (no current flow). Overcharging to 5.0 V produces a severe voltage loss to 4.0 V and a 43% coulombic efficiency.

The long-term cycleability performance of LiPo cells with repeated overcharge is illustrated in Figure 5. The capacities of overcharged Li-ion cells after the 1<sup>st</sup>, 12<sup>th</sup>, and 200<sup>th</sup> discharges are given in Table IV. All cells were charged at a constant 1C (30 mA) rate. After 200 cycles, only a  $\pm 2.4$  mAh fluctuation from the initial discharge capacity is observed for cells charged to 4.2 V upper voltage limit at 1C charge and discharge rates. Increasing the discharge rate to 10C causes the cells with a 4.2 V voltage limit to lose 4.0 mAh after 200 cycles. The discharge capacity increased initially for cells overcharged to 4.4 – 4.8 V. However, after just 53 charge cycles to 4.4 V (+200 mV) the cell's discharge capacity decreases to 80% of its initial capacity. The number of cycles to reach 80% discharge capacity is independent of discharge rate. Capacity retention continues to decrease with increasing overcharge voltages of 4.6 V (+400 mV) and 4.8 V (+600 mV). After a single overcharge to 5.0 V (+800 mV), the cell retains only 57% of its initial discharge capacity (17 mAh). After 18 cycles to 5.0 V, the cell had no charge or discharge capacity. Capacity fade increases with the severity of the overcharge voltage.



**Figure 4. Polarization loss after a single (A) charge to 4.2 V and (B) overcharge to 5.0 V for a 30 mAh Full River LiPo cell. The spikes in the charge/discharge profile are the voltage changes during rest periods where no current was flowing. The severity of the spikes indicate the extent of polarization losses and irreversible damage caused by the 5.0 V charge cutoff (+ 800 mV overcharge).**



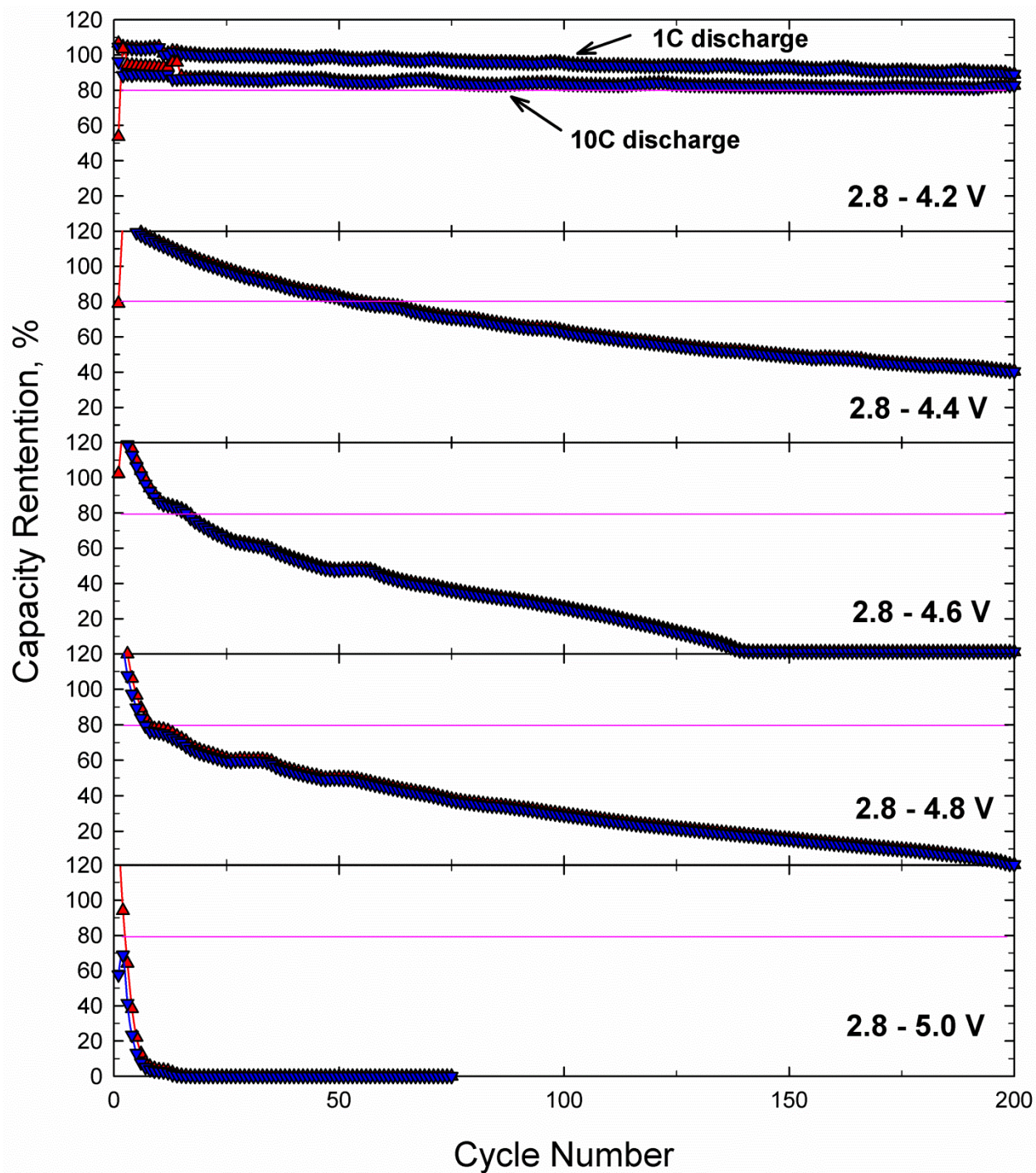


Figure 5: Capacity retention behavior of 30 mAh Full River LiPo cells under normal charging conditions and exposed to overcharge potentials: 4.4 V (+200 mV), 4.6 V (+400 mV), 4.8 V (+600 mV), and 5.0 V (+800 mV) during 1C (0.03 A) and 10C (0.30 A) discharge rates. Symbol key:  $\blacktriangle$  denotes charge capacity and  $\blacktriangledown$  denotes discharge capacity. The pink solid line indicates the 80% nominal capacity limit.

**Table IV: Discharge capacity during the 1<sup>st</sup>, 12<sup>th</sup> and 200<sup>th</sup> discharge cycles following charging cycles to 4.2 and overcharge to 5.0 V for 30 mAh Full River LiPo. The lower cutoff discharge voltage was held constant at 2.8 V. The number of discharge cycles above 80% capacity (24 mAh) shows the long term capacity performance degradation following overcharge.**

Upper Voltage Limit, V	Discharge Rate <i>1C = 30 mA</i>	Discharge Capacity, mAh ( $\pm 0.2$ mAh)			Number of Cycles Reaching 80% Discharge Capacity
		1 <sup>st</sup> Cycle	12 <sup>th</sup> Cycle	200 <sup>th</sup> Cycle	
4.2	1C	29	31	27	200+
4.4 (+200 mV)	1C	38	33	12	53
4.6 (+400 mV)	1C	40	25	0.40	15
4.8 (+600 mV)	1C	45	22	0.37	6
5.0 (+800 mV)	1C	17	0.60	-	0
4.2	10C	29	27	25	200+
4.4 (+200 mV)	10C	32	28	19	53

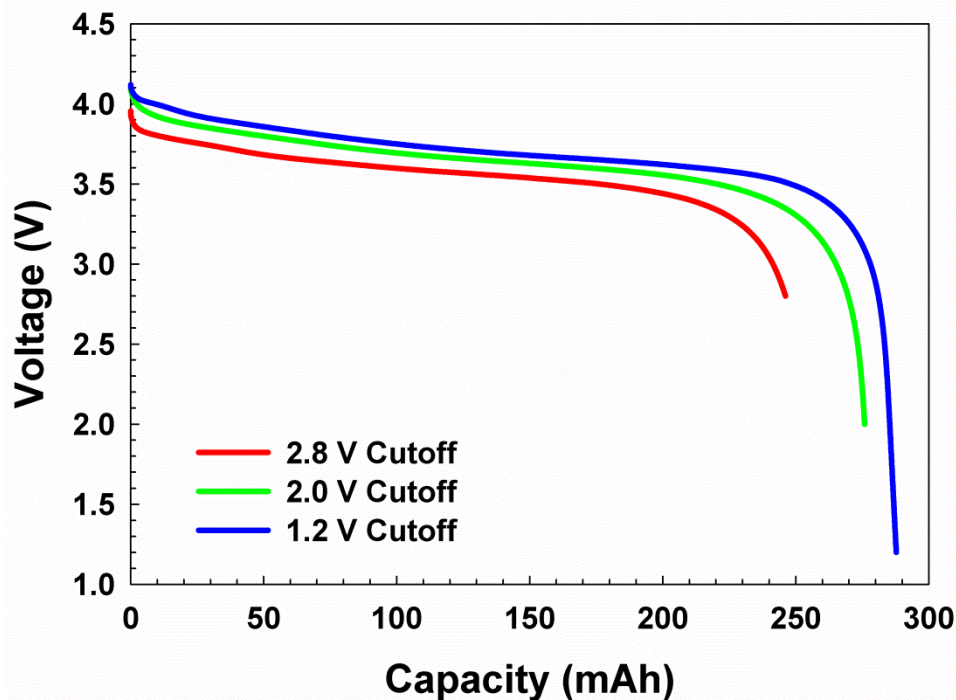
### 7.3 Overdischarge Abuse

Overdischarge of LiPo cells caused an increase in the thickness ( $z$ ) direction, as illustrated in Table V. Mild overdischarges of -800 mV only show a slight increase in the cell thickness. However, for the severe -1600 mV overdischarge (1.2 V cutoff) the thickness increases dramatically to 3.54 mm. This significant increase in cell thickness due to gas formation is over 50% of the cell's original thickness.

**Table V: Change in cell  $z$ -direction thickness of 300 mAh Full River LiPo cells after 200 overdischarge cycles.**

Lower Voltage Limit, V	$\Delta t$ , mm
2.8	0.01
2.0 (-800 mV)	0.11
1.2 (-1600 mV)	3.54

Representative galvanostatic discharge curves are shown in Figure 6 for 300 mAh Full River LiPo cells discharged to the recommended lower voltage limit of 2.8 V and overdischarged to 2.0 and 1.2 V. A severe voltage drop is observed when the lower voltage limit is decreased below 2.8 V. There are no gains in discharge capacity by decreasing the lower voltage limit. Two key features highlight the variability in the 300 mAh Full River LiPo cells. First, the voltage plateaus do not overlay one another. Even with changes to the end discharge voltage cutoff, the operating discharge plateau should be uniform as a result of the electrochemical couple between  $\text{LiCoO}_2$  and the carbon anode, as discussed previously. Second, all three cells are rated to 300 mAh, yet none of the cells actually reach the nominal capacity. This was observed for all of the cells tested in this report. Decreased voltage and capacity are the result of losses in the internal electrical contacts and loss of contact between the active electrode materials and the current collectors. The discrepancy in discharge capacity observed here highlights the importance for high quality cell manufacturing where cell to cell variability is minimized.



**Figure 6: Representative discharge curves for 300 mAh Full River LiPo cell discharged to normal cutoff voltage of 2.8 V and overdischarged to 2.0 V (-800 mV) and 1.2 V (-1600 mV). Notice all of the cells, even the cell under normal discharge conditions, fail to reach their nominal 300 mAh rating.**

The effect of repeated overdischarge on the long-term performance of 300 mAh LiPo cells is given in Figure 7. When charged and discharged within the recommended voltage boundaries, 2.8 – 4.2 V, the cell demonstrates high performance with 90% capacity retention even after 200+ cycles. For all cells tested, the capacity retention decreases with cycling. However the rate of performance loss increases with the severity of the overdischarge voltage cutoff. Mild overdischarges of -800 mV (2.0 V voltage cutoff) show capacity retention near 80% after 200 cycles. More severe overdischarge cutoff voltages, 1.2 and 1.0 V illustrate the significant effect of overdischarge abuse on the performance capacity of the LiPo cells. Table VI illustrates the performance losses in terms of discharge capacity during the 1<sup>st</sup>, 100<sup>th</sup>, and 200<sup>th</sup> electrochemical cycles. The useable life of a LiPo cell expires once the discharge capacity drops below 80% of the rated capacity. The LiPo cells can withstand mild overdischarge of -800 mV to 2.0 V and still supply 80% of the nominal capacity for 200 cycles. However more severe overdischarges of -1600 mV and -1800 mV restrict the usable life span of the cell to 57 and 8 cycles respectively.

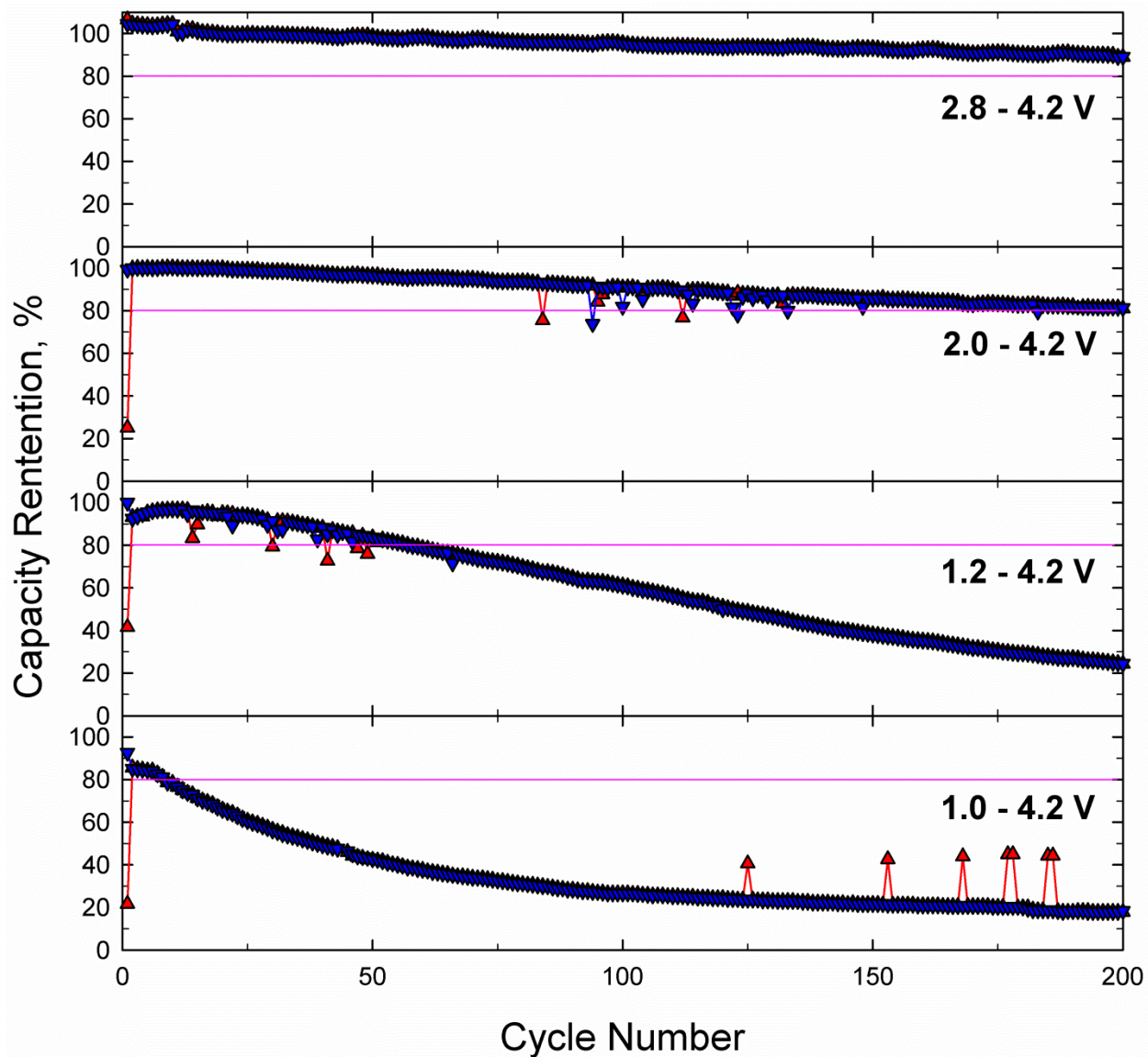


Figure 7: Capacity retention behavior of 300 mAh Full River LiPo cells under normal charging conditions (2.8 – 4.2 V) and exposed to overdischarge potentials: 2.0 V (-800 mV), 1.2 V (-1600 mV) and 1.0 V (-1800 mV) during 1C (0.3 A) charge and discharge rates. Symbol key:  $\blacktriangle$  denotes charge capacity and  $\blacktriangledown$  denotes discharge capacity. The pink solid line indicates the 80% nominal capacity limit.

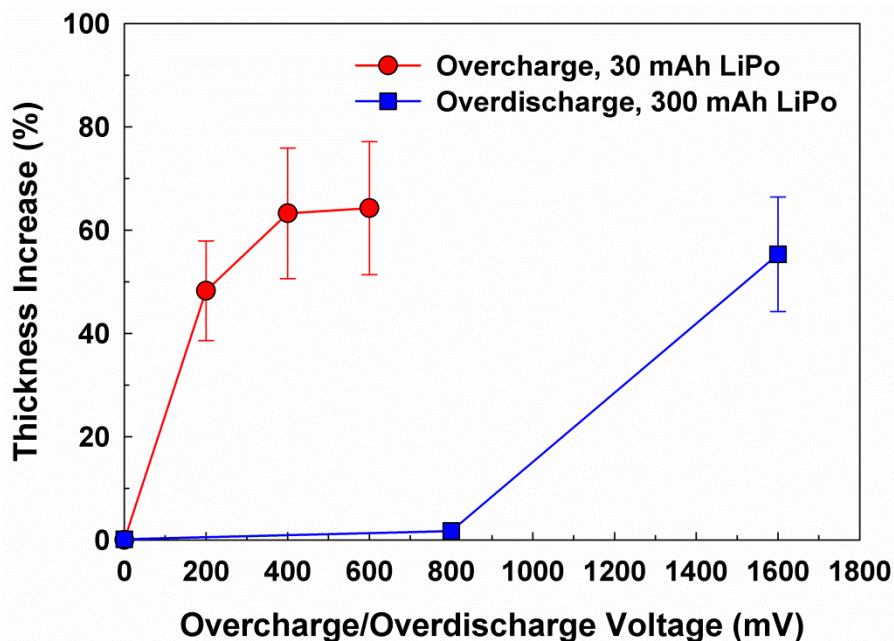


**Table VI: 1<sup>st</sup>, 100<sup>th</sup> and 200<sup>th</sup> discharge cycle capacity for 300 mAh Full River LiPo. The upper charge limit was 4.2 V while the lower cutoff discharge voltage varied from normal (2.8 V) to 2.0 V (-800 mV) and 1.2 V (-1600 mV). The number of cycles to reach 80% of the original capacity reports the effect of repeated overdischarge abuse on discharge capacity retention.**

Lower Voltage Limit, V	Discharge Rate <i>1C = 300 mA</i>	Discharge Capacity, mAh ( $\pm 1.2$ mAh)			Number of Cycles Reaching 80% Discharge Capacity
		1 <sup>st</sup> Cycle	100 <sup>th</sup> Cycle	200 <sup>th</sup> Cycle	
2.8	1C	315	285	267	200+
2.0 (-800 mV)	1C	276	253	226	200+
1.2 (-1600 mV)	1C	288	176	78	57
1.0 (-1800 mV)	1C	279	81	54	8

## 8. Conclusions

We have shown the physical and electrochemical effects of LiPo cells subjected to overcharge and overdischarge abuses. LiPo cells charged within the recommended voltage limits can provide hundreds of charge/discharge cycles at relatively high rates. Charging and discharging LiPo cells outside of their recommended voltage window causes physical degradation and performance loss. These effects increase with the severity of overcharge/overdischarge voltage and are compounded with repeated abusive cycling. The usable cycle life of LiPo cells is dramatically reduced with repeated overcharge/overdischarge abuse. Overcharge and overdischarge causes material and component decomposition within the cell producing gaseous species causing swelling of the LiPo pouch. Figure 8 shows the percent pouch cell thickness increase as a result of cell swelling with repeated overcharge and overdischarge. Degradation processes inside of the cells produce gaseous products which cause the cells to swell. Dramatic LiPo cell swelling occurs after mild repeated overcharges (+200 mV). The degradation processes are not quite as severe for the case of overdischarge where the equivalent percent thickness increase is seen with -1600 mV.



**Figure 8: Normalized cell thickness increases after 200 cycles with overcharge and overdischarge voltage. The increases in cell thickness are due to the formation of gases produced as a result cycling outside of the recommended voltage boundaries. The nominal starting thicknesses of the cells are 4.0 mm (30 mAh) and 6.4 mm (300 mAh). Error bars indicate the error in the measurements taken at various locations along the cell surface.**

## 9. Acknowledgments

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## 10. References

- Arora, P., R. E. White, et al. (1998). "Capacity fade mechanisms and side reactions in lithium-ion batteries." *Journal of The Electrochemical Society* **145**(10): 3647-3667.
- Belov, D. and M.-H. Yang (2008). "Failure mechanism of Li-ion battery at overcharge conditions." *Journal of Solid State Electrochemistry* **12**(7): 885-894.
- Govar, C. J., D. A. Fuentevilla, et al. (2007). Advancements in Navy and USMC Power Systems. *Joint Power Sources Expo*.
- Lee, H., S. K. Chang, et al. (2008). "Li<sub>2</sub>NiO<sub>2</sub> as a novel cathode additive for overdischarge protection of Li-Ion batteries." *Chemistry of Materials* **20**(1): 5-7.
- Linden, D. and T. B. Reddy, Eds. (2002). *Handbook of Batteries*. New York, McGraw-Hill.
- Lisbona, D. and T. Snee (2011). "A review of hazards associated with primary lithium and lithium-ion batteries." *Process Safety and Environmental Protection* **89**(6): 434-442.
- Love, C. T. (2011). "Thermomechanical analysis and durability of commercial micro-porous polymer Li-ion battery separators." *Journal of Power Sources* **196**(5): 2905-2912.

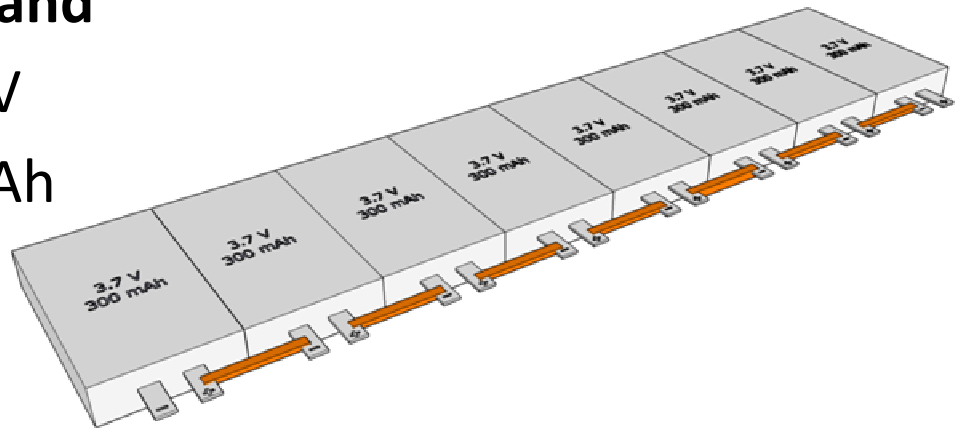
- Love, C. T. and K. Swider-Lyons (2012). "Impedance Diagnostic for Overcharged Lithium-Ion Batteries." Electrochemical and Solid State Letters **15**(4): A53-A56.
- Maleki, H. and J. N. Howard (2006). "Effects of overdischarge on performance and thermal stability of a Li-ion cell." Journal of Power Sources **160**(2): 1395-1402.
- Simon, E. (2005). Evaluation of Lithium Polymer Batteries. NASA Battery Workshop.
- Stux, A. M. and K. E. Swider-Lyons (2007). Survey of Commercial Small Lithium Polymer Batteries. Washington D.C., Naval Research Laboratory.
- Xu, F., H. He, et al. (2012). "Failure Investigation of LiFePO<sub>4</sub> Cells under Overcharge Conditions." Journal of The Electrochemical Society **159**(5): A678-A687.

## 11. Appendix

### 8s1p strand

29.6 V

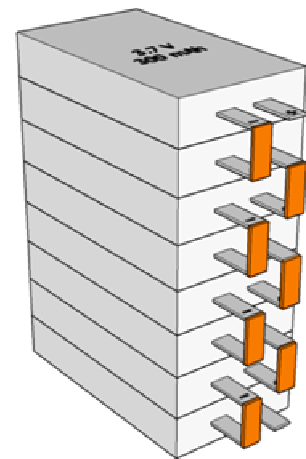
300 mAh



### 8s1p stack

29.6 V

300 mAh



### 8s2p strand

29.6 V

600 mAh

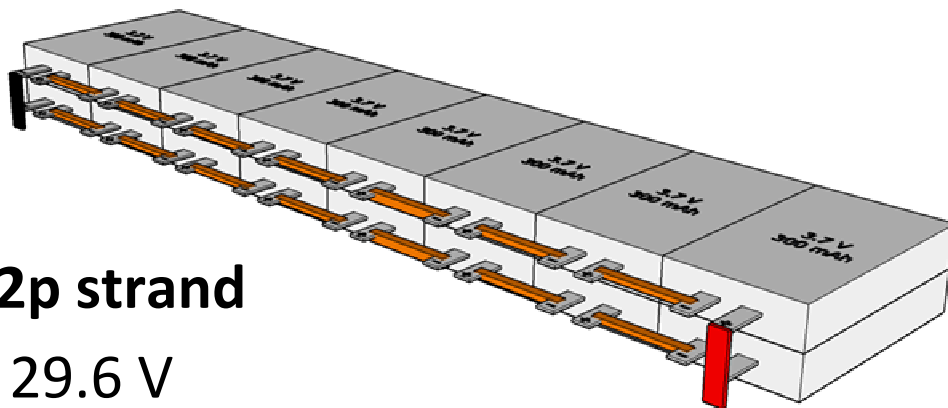


Figure A.1: Typical configurations of LiPo cells used to produce high voltage batteries. Cell to cell connectors are show in orange.



