

# Overcharge studies of carbon fiber composite-based lithium-ion cells

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## Abstract

Prototype lithium-ion pouch cells of 5.5 Ah have been fabricated with carbon fiber composite anodes, LiCoO<sub>2</sub> cathodes, and LiPF<sub>6</sub> electrolyte to investigate the overcharge characteristics of these cells at the 1C rate. The cells were made with anode to cathode capacity (A/C) ratios of 1.0 and 1.1. The cells were first examined for charge–discharge characteristics at different rates in order to determine the delivered capacity, specific energy and energy density and rate capability, and to ensure that the cells are suitable for overcharge studies. The current, voltage, and temperature responses during overcharge to 12 V were recorded. Maximum temperatures of 65 and 85 °C were observed with the cells with A/C equal to 1.1 and 1.0, respectively. The overcharged cells were dissected in an inert atmosphere and their components were analyzed using scanning electron microscopy and x-ray fluorescence spectroscopy. It is believed that a relatively low amount of heat is generated with carbon fiber composite-based lithium-ion cells and a separator shutdown mechanism is operative in the cell system which prevents fire or explosion during overcharge.

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**Keywords:** Carbon fiber composite; Lithium-ion battery; Overcharge; Anode–cathode ratio; Heat generation; Shut-down mechanism

## 1. Introduction

Lithium-ion batteries are widely used in portable electronic devices. Their lack of safety when operated under abusive conditions, however, prevents other avenues of application. One of the most important safety issues for the present state-of-the-art lithium-ion batteries is related to overcharge, which can lead to thermal runaway and ultimately to fire or explosion of the batteries. To protect a battery from overcharge, the lithium-ion battery industry uses a number of safety measures, such as overcharge protection circuits, positive temperature coefficient resistors, pressure sensitive rupture disks, temperature sensitive separators, etc. The use of these safety devices not only increases the cost of lithium-ion batteries but also lowers their specific energy and energy density. For small capacity and relatively low voltage batteries, the above measures to protect the battery and users are found to be acceptable. For high capacity, multi-cell high voltage batteries, such as are being considered for military, aerospace, and vehicular applications, a battery chemistry that is resistant to abusive conditions, such as overcharge is desirable so that if the battery is accidentally exposed to overcharge

due to electronic malfunction, there still will not be any safety concerns.

Several complex energy-related processes are involved during overcharge of a lithium-ion cell:

- (a) Electrical energy due to injected current is released which may: (i) increase cell temperature, (ii) decompose electrolyte solvent(s), (iii) dissolve cathode material, (iv) deposit metallic lithium on the carbon anode, (v) shrink separator, etc.
- (b) Heat energy associated with undesirable side-reactions of: (i) anodes and (ii) cathodes is released.
- (c) Dissipation of heat energy from the cell to the ambient environment occurs.

The difference in the heat energy gains and losses determine whether the heat that remains within the cell is rising or falling and this determines the ultimate fate of the overcharged cells. If a lithium-ion cell is designed and developed in such a way that the total retained heat energy is sufficiently low so that it does not trigger thermal runaway, overcharge-related safety incidents can be avoided. One can, therefore, address the overcharge related safety issues by using one or a combination of the following approaches:

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- (a) Increasing the exposed surface area of the cell so that most of the generated heat energy can dissipate to the ambient environment.
- (b) Eliminating/minimizing side-reactions that generate heat.

Present day applications, however, often require compact cell design and, therefore, step (a) is rarely acceptable. The battery scientists are, therefore, in search of a cell chemistry that provides step (b).

There have been a number of papers published on the side-reactions that generate heat from lithiated anodes [1–6] and delithiated cathodes [3,5,7] during cell temperature rise. From accelerated rate calorimetry (ARC) measurements of a lithiated carbon anode, Richard and Dahn [2,4] showed two exotherms—the first one corresponded to the decomposition of a metastable SEI layer at around 100 °C and the second exotherm at around 150 °C was due to the reaction of  $\text{LiC}_x$  with the electrolyte. For both the exotherms, the amount of heat generation depends on the surface area of the carbon anode—the higher the surface area, the higher the heat generation. It has been shown that the reactions of lithiated carbon with PVDF binder [3,8] are exothermic. MacNeil and Dahn [7] investigated the thermal decomposition of  $\text{Li}_{0.5}\text{CoO}_2$  using accelerated rate calorimetry and X-ray diffraction (XRD) and concluded that loss of oxygen from  $\text{Li}_{0.5}\text{CoO}_2$  occurs only above 200 °C. The involvement of the cathode in a safety incident during overcharge, therefore, occurs only if the cell temperature is close to 200 °C. Takeuchi and co-workers [9] concluded from their overcharge studies of 1.5 Ah cells that the  $\text{Li}_x\text{CoO}_2/\text{Li}_y\text{C}_6$  system itself can produce the high temperature reactions that lead to rupture of the cell.

It is obvious that during overcharge: (i) more lithium-ions transfer from cathode to anode and if the anode does not have enough room to accommodate them, metallic lithium deposition may occur, (ii) the electrolyte decomposes and produces gaseous substances, and (iii) dissolution of transition metals (e.g., Co, Ni, etc.) occurs at the cathode. These metals transfer to the anode and cause soft shorting in combination with the deposited lithium metal.

The use and advantages of a carbon fiber composite as an anode material was disclosed by Hossain [10] in 2002 and is now considered one of the more effective high capacity anode materials for lithium-ion batteries [11–14]. The intercalation of lithium into carbon fiber through copper [15] and silver [16] films has also been reported by Takamura and co-workers. The physical properties of carbon fiber composite minimize the side-reactions that generate heat during overcharge. The low surface area, high thermal conductivity, absence of PVDF binder, the copper substrate (with the resulting absence of a thermal gradient) and the low coefficient of thermal expansion are some of the advantages. It has been shown from differential scanning calorimetry (DSC) [17] and accelerated rate calorimetry measurements [18] that carbon fiber composite generates much less heat than mesophase carbon microbeads (MCMB). As an additional advantage, a carbon fiber composite does not contain any inactive material (no binder or metal substrate). The entire composite electrode provides active sites for lithium-ion intercalation. This excess capacity of the composite anode [12], due

to the absence of a copper substrate and binder, can be utilized to accommodate more lithium ions during overcharge.

This paper describes overcharge studies of prototype 5.5 Ah lithium-ion pouch cells made with carbon fiber composite anodes and the subsequent analysis of the components of the overcharged cells.

## 2. Experimental

Several prismatic design prototype lithium-ion pouch cells were made with carbon fiber composite anodes,  $\text{LiCoO}_2$  cathodes and with 1.4 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) as the electrolyte. The carbon fiber composite was made from pitch-based carbon fibers heat-treated to 2850 °C under an inert atmosphere. The thickness of the composite was  $140 \pm 5 \mu\text{m}$ . The cell configuration was as follows:

C/2/S/A/S/C/S/A/S—C/S/A/S/C/2

where C/2 is the single-sided cathode, S the polyethylene separator (Tonen Chemical Corporation), A the carbon fiber composite anode, and C is the double-sided cathode. The total number of electrodes used for the development of the cells were C/2=2, C=9, and A=10. The dimensions of the anodes were 115 mm × 80 mm and those of the cathodes were 112 mm × 77 mm. The thickness of the separator was 25  $\mu\text{m}$ .

The carbon fiber composite electrodes were bagged with the separator. The bagged negative electrodes were then sandwiched in between positive electrodes. The positive electrode tabs were welded. Similarly, the negative electrode tabs were also welded. The resistance between the positive electrodes and the negative electrodes was measured to insure that the stack was not electrically shorted.

The electrode stack assembly was then placed in between three-layer packaging material (plastic foil/Al foil/plastic foil) and was sealed firstly on three sides of the stack excluding the side opposite to the electrode tabs. The sealed stack was then evacuated and filled with a measured amount of 1.4 M  $\text{LiPF}_6$  electrolyte. The cell was then fully sealed. All of these operations were carried out in a glove box ( $\text{H}_2\text{O} < 1 \text{ ppm}$ ). The seal of the plastic bag was checked several times prior removal from the glove box for electrochemical measurements.

The ratios of anode to cathode capacities (A/C) used in the cells were either 1.1 or 1.0 based on the specific capacities of the carbon fiber composite anode and the  $\text{LiCoO}_2$  cathode which were 300 and 140  $\text{mAh g}^{-1}$ , respectively. The higher anode to cathode capacity ratio is feasible in these practical lithium-ion cells due to the replacement of several inactive components (the copper substrate and binder) by anode material, which in turn, allows the anode to accommodate more lithium ions during overcharge and thus avoid deposition of metallic lithium.

A representative cell is shown in Fig. 1. The cells weigh approximately 105 g and their dimensions are 150 mm × 95 mm × 4.5 mm. The as-assembled uncharged open-circuit voltages (OCVs) of the prototype pouch cells were in the range of 5–30 mV. The pouch cells were “formed” using

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