Ovecharge Abuse Response of 18650 Li-Ion Cells

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Overcharge abuse response is one of the main safety concerns for use of Li-ion cells in the commercial market. Continual removal of Li from the cathode during overcharge can result in a highly unstable, reactive structure. Reaction with the electrolyte is highly exothermic and can drive the cell into thermal runaway. The highly lithiated anode is also more reactive and contributes to cell thermal runaway. Studies have been performed on 18650 Li-ion cells under overcharge conditions as part of the DOE Advanced Technology Development (ATD) Program. Quantitative measurements have been made of the cell heat output, temperature profile, runaway behavior and gas generation. The cell overcharge response has been measured under various charging and thermal conditions.

The cells (referred to as Gen2) consisted of a MAG-10 flaky graphite anode and a $LiCo_{0.15}Ni_{0.8}Al_{0.05}O_2$ cathode with a 1.2M $LiPF_6$ EC:EMC (3:7) electrolyte with a nominal 900 mAh capacity [1]. The cells were initially charged to 4.1V for the 100% state of charge (SOC) starting state. A special fixture was built to enclose the cell and measure the temperature differential across a calibrated insulation layer allowing determination of the heat generation by the cell. The cell was placed in a Lexan enclosure and flushed with inert gas (He or N_2). Real-time gas analysis was performed using FTIR, MS and GC.

Figure 1 shows the voltage and temperature response for a cell charged at a 1 amp (1.1C) rate in a He atmosphere which served as an effective heat removal gas. Increasing heat output was observed beginning at 125%SOC. The cell voltage increased steadily from 4.1V and peaked at 5.1V at 145%SOC. Gas evolution was detected from the venting cell beginning at the peak in cell voltage and consisted of H_2, CO, CO_2 and EMC solvent vapors. Heat generation increased up to about 225%SOC, reaching a maximum cell skin temperature of 105˚C and heat output of 8W. Separate measurements of the cell internal temperature during overcharge showed a 15˚C temperature differential indicating that the internal cell temperature reached 120˚C during this measurement, well below the separator melt temperature.

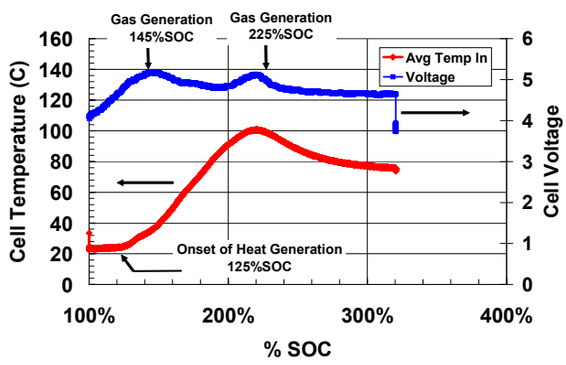

Figure 1. Cell voltage and temperature during 1.1C overcharge.

The cell did not go into thermal runaway and eventually the heat output stabilized such that the heat out equaled the power input to the cell.

Figure 2 shows the heat output response of a cell with increasing charge rates from C/2 up to 3C. Rates at 1C and below which resulted in cell temperatures below the separator shutdown temperature did not go into thermal runaway. The higher 3C charging rate heated the cell to 130˚C at which temperature the voltage across the cell and the resultant input power increased due to the high cell impedance and the cell went into thermal runaway.

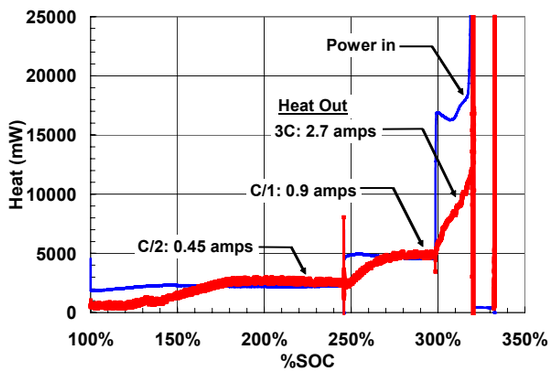

Figure 2. Heat output for cell at increasing charging rate until thermal runaway.

The structure and thermal properties of the overcharged cell components have been studied by disassembling cells in an Argon glove box. Cells overcharged to the first voltage peak at 150%SOC were analyzed first. XRD was used to measure the crystallographic state of the anode and cathode while DSC was used to measure the thermal response of the overcharged materials. The overcharged cathode was seen to maintain the R3m structure but with a significant reduction in the c-axis dimension. The anode material clearly showed incomplete lithiation due to the cathode limited cell design. DSC analysis showed reduced onset temperatures for the main exotherm reaction peak in the cathode and increased high-temperature peak reaction rates in the anode. Details of these measurements and analyses will be discussed in the presentation.

Acknowledgments

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References

1. E. P. Roth, D. H. Doughty, J. Power Sources 128 (2004) 308-318.