

Thermal Response and Flammability of Li-Ion Cells for HEV and PHEV Applications

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ABSTRACT

Lithium-ion batteries are being considered as a high-energy density replacement for Nickel Metal Hydride (NiMH) batteries in Hybrid Electric Vehicles (HEVs) and in the new Plug-In Hybrids (PHEVs). Although these cells can result in significant reduction in weight and volume, they have several safety related issues that still need to be addressed. We report here on the thermal response of Li-ion cells specifically assembled in our laboratory to test new materials, electrolytes and additives. Improvements in the thermal abuse tolerance of cells will be presented and discussed in terms of the need for overall battery system safety.

INTRODUCTION

The DOE FreedomCAR & Vehicle Technologies program supports government-industry endeavors to develop more energy efficient and environmentally friendly highway transportation technologies that enable America to use less petroleum [1]. As part of this effort, five of the National Laboratories are working together under the Advanced Technology Development (ATD) program to address the issues of lifetime, cost and abuse tolerance of Li-ion cells. The thermal abuse tolerance of Li-ion cells is a complex function of the interactions of the cell components that result in gas and heat generation leading to uncontrolled thermal runaway of the cells [2]. The role of separator integrity has also been identified as a critical material property necessary for cell safety and stability. Anode, cathode, and electrolyte interactions have been measured for chemistries chosen to meet the high-power requirements for Hybrid Electric Vehicles (HEVs) and for the new Plug-In Hybrid Electric Vehicles (PHEVs). Cells have been measured during abusive conditions of over-temperature and overcharge to determine the effects of new materials on intrinsic abuse response.

EXPERIMENTAL DATA AND PERFORMANCE

MATERIALS - Anodes used consisted of intercalating carbon materials such as MCMB 2528. Cathode materials were used that are representative of current and future Li-ion cells including $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$,

$\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ and LiMn_2O_4 . The role of electrolyte solvent composition on thermal abuse response was also investigated for two representative compositions: ethylene carbonate: ethyl methyl carbonate (EC:EMC) (3:7)\1.2M LiPF_6 and ethylene carbonate: propylene carbonate: dimethyl carbonate (EC:PC:DMC) (1:1:3)\1.2M LiPF_6 . Electrolyte additives were also examined to determine the effect on low-temperature stability and on flammability.

Cylindrical cells were wound in our laboratory in the 18650 configuration (18 mm dia. by 65 mm length, Figure 1.) using coated electrodes with these anode and cathode compositions resulting in cells with nominal 1.0–1.2 Ah capacity. This cell size allows accurate determination of cell material properties in a configuration that is relatively simple to measure.

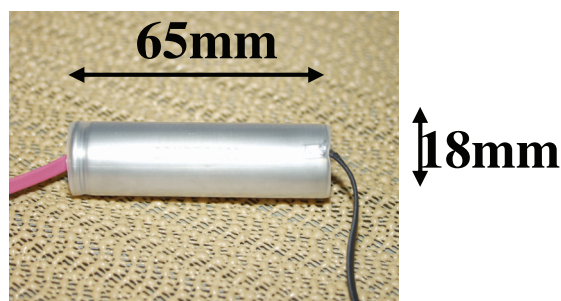


Figure 1. 18650 Li-ion wound cylindrical cell.

MEASUREMENT TECHNIQUES - The thermal abuse response of these cells was measured using calorimetric and thermal methods designed to quantitatively measure the heat and gas generation of the cells during thermal runaway. Accelerating Rate Calorimetry (ARC) is a technique used to measure the intrinsic thermal runaway of a cell under ideal, adiabatic conditions. We developed modified fixtures to allow complete containment of the generated gas during runaway allowing calculation of the total volume gas evolution profile as shown in Figure 2. Cells were also measured in a thermal ramp apparatus that allowed measurement of cell heat generation and observation of cell venting and thermal runaway, as shown in Figures 3 and 4. Possible ignition of the vent

gases were measured using ignition sources placed around the fixture. Overcharge electrical and thermal responses were measured using a thermally calibrated cell fixture as shown in Figure 5 that also allows control of the atmosphere surrounding the cell and determination of the flammability of the vent gases. Real-time gas analysis using FTIR and mass spectrometry allowed determination of the gas species during the overcharge.

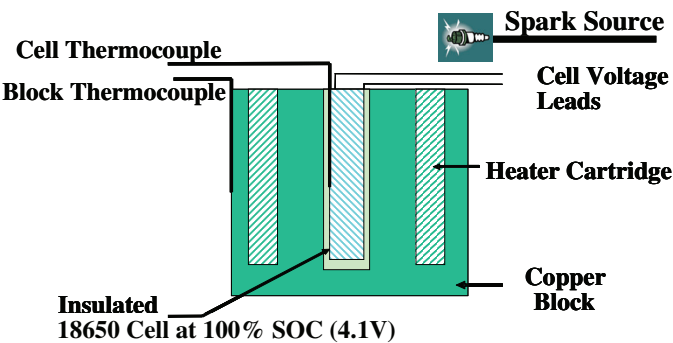
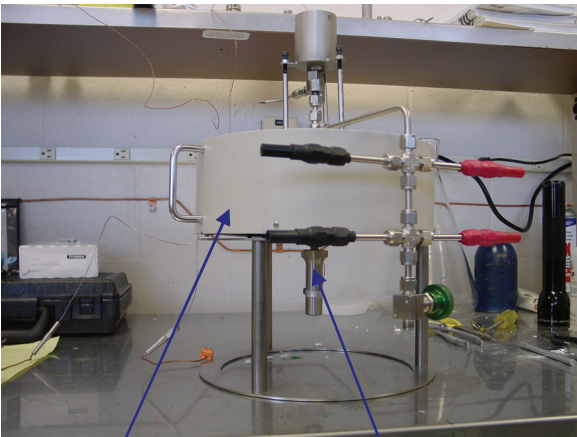


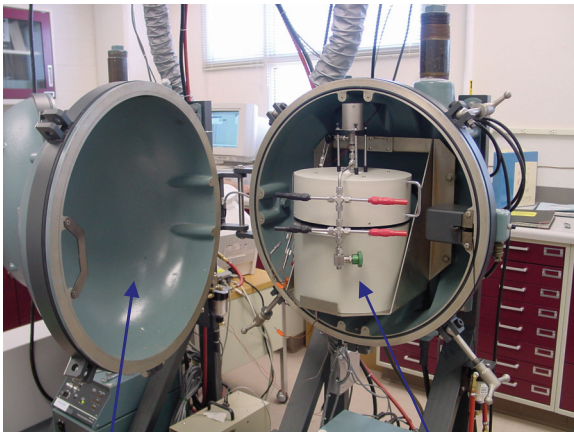
Figure 3. Schematic of thermal ramp apparatus with 18650 cell and external ignition source.



Top Heater Cell Holder



Figure 4. Thermal ramp apparatus with 18650 cell in center.



Blast Shield Heating Unit

Figure 2. ARC heater with sample holder.

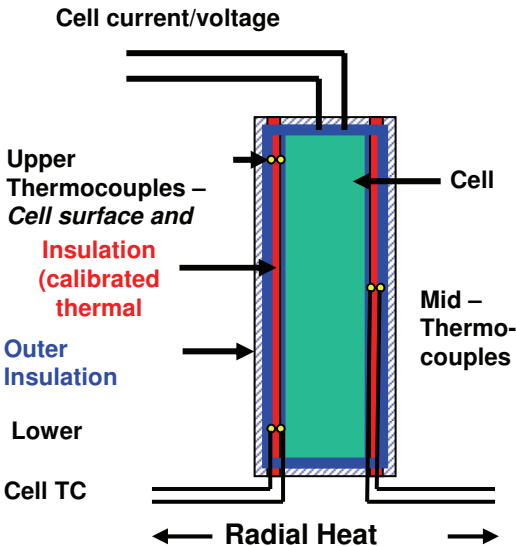


Figure 5. Overcharge fixture for measuring heat output from 18650 cell.

THERMAL ABUSE RESPONSE – Cell abuse can occur from several sources including mechanical abuse (crush, penetration), electrical abuse (short circuit, overcharge), and thermal abuse (over-temperature). Most of these abuse events eventually result in a thermal excursion in the cell resulting in a thermal runaway reaction. Thermal runaway can be broken down into three stages as indicated by the heating rate of the cell as shown in Figure 6.

- **Stage 1: Room Temperature to 150°C – Onset of thermal runaway**
- **Stage 2: 150°C - 180°C – Venting and accelerated heating (smoke)**
- **Stage 3: 180°C and above – High-Rate venting/heating and possible flame and explosive expulsion**

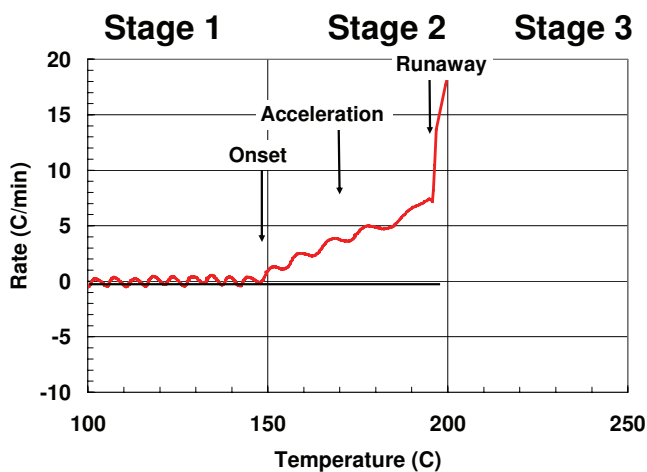


Figure 6. Cell heating rate during a thermal ramp test showing the three stages of thermal runaway.

Heat generation during each of these stages results from reactions of the electrode components with the cell electrolyte. Stage 1 reactions are dominated by the lithiated anode carbon reducing the electrolyte. A protective layer called the Solid Electrolyte Interface (SEI) layer begins to break down around 100°C resulting in low-rate heat generation. Without heat removal, the cell temperature increases resulting in accelerated breakdown of the SEI. When the cell temperature reaches about 150°C, oxidation reactions begin at the de-lithiated cathode particle surface. This reaction leads to accelerated heating rates and further reaction at the anode which characterize the Stage 2 region. Breakdown of the electrolyte also begins in the 150°C-160°C range generating decomposition gases which result in cell venting, aerosolization of the electrolyte and possible ignition of the electrolyte vapors. At temperatures above about 180°C, many cathode materials start to breakdown, releasing oxygen which reacts very exothermically with the electrolyte. This high-rate heat generation results in the Stage 3 runaway which is characterized by high-rate venting, flames and possible explosive expulsion of the cell contents.

The cell chemistry greatly determines the thermal response including onset temperatures, enthalpies of reaction and reaction rates. Figure 7 shows the Accelerating Rate Calorimetry (ARC) thermal runaway profile for three cell chemistries. Cathode composition ranged from LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}$, and $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ with decreasing reaction rate, enthalpy of reaction and higher onset temperature. Thermal gravimetric analysis of these cathode materials shows that the decreasing reaction results from decreasing amounts of O_2 released during high-temperature decomposition. Other cathode chemistries have even further reduced reactions rates such as the LiMn_2O_4 spinel and the LiFePO_4 olivine. The LiFePO_4 material is especially stable since it does not generate any O_2 at high temperatures.

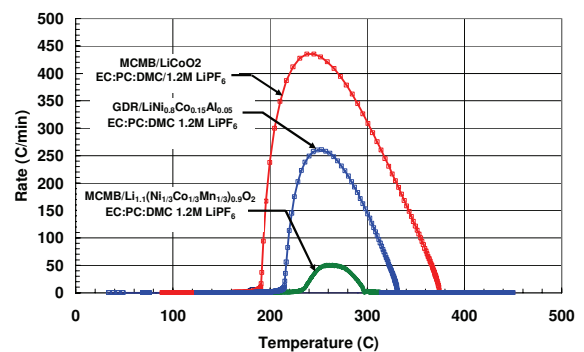


Figure 7. ARC thermal runaway profiles showing Stage 3 runaway for three cathode chemistries showing improved runaway responses.

Gas generation during thermal runaway is also very important in gauging the abuse response of the cell. Electrolyte decomposition begins around 160°C, increasing the cell internal pressure which can activate the cell vent, releasing flammable vapors. The thermal runaway reaction leads to high-rate gas generation (Figure 8) which serves to aerosolize the cell electrolyte, resulting in a strong flame source if ignited. The volume of gas generated during the Stage 3 runaway is less than half of the total volume generated for complete reaction to high temperatures (Figure 9). The composition of this vent gas was determined using gas chromatography of grab samples taken after the ARC run. The main gas species generated is CO_2 as shown in Figure 10. Other species include H_2 , CO , methane and ethylene though at much lower levels. Also shown in the figure are the gases taken at increasing temperatures from 200°C up to 400°C. The level of CO_2 decreased with temperature while the amount of H_2 , methane, and ethylene increased.

Improvements in the thermal runaway heating rate profile have been obtained using other solvent combinations in the electrolyte. Figure 11 shows a comparison of ARC runs of cells using either EC:EMC/1.2M LiPF_6 or EC:PC:DMC/1.2M LiPF_6 . The later electrolyte has shown