Development and Characterization of Li-Ion Batteries for the FreedomCAR Advanced Technology Development Program

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Abstract—High-power 18650 Li-ion cells have been developed for hybrid electric vehicle applications as part of the DOE FreedomCAR Advanced Technology Development (ATD) program. Cells have been developed for high-power, long-life, low-cost and abuse tolerance conditions. The thermal abuse response of advanced materials and cells were measured and compared. Cells were constructed for determination of abuse tolerance to determine the thermal runaway response and flammability of evolved gas products during venting. Advanced cathode and anode materials were evaluated for improved tolerance under abusive conditions. Calorimetric methods were used to measure the thermal response and properties of the cells and cell materials up to 450 °C. Improvements in thermal runaway response have been shown using combinations of these materials.

Keywords—Li-ion, abuse tolerance, hybrid vehicles, safety

I. INTRODUCTION

The Advanced Technology Development (ATD) Program was established by DOE as part of the FreedomCAR program to assist industrial developers of high-power lithium-ion batteries to overcome key barriers in the areas of abuse tolerance, calendar life, and cell packaging cost. One goal of this project is to rapidly develop high-power lithium-ion cell chemistries, using commercially available materials that can be shared with the industrial battery developers. A second goal is to establish the performance, life, and thermal abuse characteristics of these cells. Abuse tolerance has been a major concern limiting the application of advanced Li-ion chemistries in the consumer market. Abuse environments can be categorized as physical abuse (crush, nail penetration), electrical abuse (short circuit, overcharge) and thermal abuse (overheating, thermal runaway). Of these conditions, understanding the response of cells to thermal abuse is most crucial, since electrical and mechanical abuse often generate heat and cause a cell to experience a thermal abuse condition. Thermal abuse can result from relatively normal operating conditions when the heat generation rate of the cells exceeds the heat removal from the battery system. Cell thermal runaway has been described by other researchers [1-4] and found to be sensitive to the particular cell chemistry and operating conditions such as state of charge (SOC) and history.

The response of cells to abuse environments is determined by engineering choices in cell construction as well as materials selection. In this work, we focus on the materials response to abuse environments. In order to study the technical barriers of abuse tolerance, it is necessary to have detailed knowledge about the cell chemistry and the cell performance under a wide range of abusive conditions. The mechanisms leading to poor abuse tolerance need to be understood to allow development of advanced cell chemistries which meet all the requirements for performance, life, cost, and safety. The Thermal Abuse Tolerance Program at Sandia has concentrated on studying the behavior of cells and cell materials that have been specifically designed to meet these safety and power requirements. Cells of the 18650 configuration have been built incorporating new, stable materials to allow detailed study and comparison of lifetime, performance, and safety. Cells were constructed both at Quallion [5] and at Sandia National Laboratories. The cell chemistries were chosen to best meet the program performance requirements after screening numerous commercially available material combinations by program partners at Argonne National Laboratory. The 18650 cell configuration was chosen to allow quick and economical cell manufacture in a meaningful cell size.

II. EXPERIMENTAL

Thermal abuse tolerance was studied using calorimetric techniques on full cells and on cell components. Accelerating Rate Calorimetry (ARC) was used to measure the thermal runaway and gas generation response of full cells and cell components. Differential Scanning Calorimetry (DSC) was also used to compare the thermal response of the cell components. Flammability was measured using a thermally ramped block apparatus containing the cell in open room air with an external ignition source in the cell vent area. We report in this brief paper only on the ARC characterizations.

A. Cell Composition

Cells were constructed in the 18650 configuration with 0.9 Ah nominal capacities. Initial cells (Gen1/Gen2) were based on the Li/Ni/Co oxide composition for the cathodes. Gen1 cells consisted of LiNi$_{0.85}$Co$_{0.15}$O$_2$ while the Gen2 cells
used a stabilized LiNi_{0.80}Co_{0.15}Al_{0.05}O_{2} material. Gen1 anodes used an artificial MCMB carbon with a spherical geometry while Gen2 used a flaky carbon morphology (MAG10). Electrolytes were either EC:DEC (ethylene carbonate: diethyl carbonate) (Gen1) or EC:EMC (EC:ethylmethyl carbonate)(Gen2) and LiPF₆ for the salt. Table I lists the cell compositions for all of the cells tested in this program.

Advanced cells were constructed at Sandia using electrodes coated at Quallion. These cells consisted of new cathode materials designed for improved thermal stability as well as lifetime and power requirements. Advanced Cell 1 consisted of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, an oxide with greater thermal stability and reduced oxygen generation [6,7]. Advanced Cell 2 consisted of a stabilized LiMn₂O₄ spinel with a 6% amorphous carbon coating. This carbon is believed to have much of the stable thermal properties seen for MCMB but at reduced cost. Improved electrolytes were also tested consisting of different linear carbonate solvent compositions and new salts. Table I again lists the detailed film compositions and electrolytes used.

### Table I. Cell Compositions

<table>
<thead>
<tr>
<th>advanced Cells</th>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gen1 Cells</td>
<td>75% MCMB-6-2800 Carbon 16% SFG-6 Graphite 9% PVDF Binder 84% LiNi_{2/3}Co_{1/3}Mn_{1/3}O₂ 4% Carbon Black,4% SFG6 8% PVDF Binder 1M LiPF₆, in EC:DEC (1:1)</td>
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<tr>
<td>Gen2 Cells</td>
<td>92% MAG10 Carbon 8% PVDF Binder 84% LiNi_{0.95}Co_{0.05}Mn_{0.05}O₂ 4% Carbon Black, 4%SFG6 8% PVDF Binder 1.2M LiPF₆, in EC:EMC (3:7)</td>
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<tr>
<td>Advanced Cell 1 (AC1)</td>
<td>90% GDR Carbon 10% PVDF 82% LiNi_{1.0}Co_{0.2}Mn_{0.2}O₂ 10% TB5500 carbon 8% PVDF 0.7M LiBOB or 1.2M LiPF₆ in EC:PC:DMC (1:1:3)</td>
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<tr>
<td>Advanced Cell 2 (AC2)</td>
<td>92% GDR Carbon 8% PVDF 82% stabilized LiMn₂O₄ 5% Super P carbon 5% SFG6 carbon 8% PVDF 1.2M LiPF₆, in EC:EMC (3:7)</td>
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B. Calorimetric Techniques

ARC testing was performed on full cells at 100% SOC (4.1 V). Cells were measured in a pressure tight fixture up to 400°C in the ARC apparatus (Arthur D. Little Model 2000, AD Little, Acorn Park, Cambridge, MA 02140). The ARC was operated in a heat, wait, search mode to allow determination of the onset of self-heating. The ARC increases the temperature in discrete steps, waits for the thermal transients to decay and then monitors the temperature of the cell for a fixed time period. If the cell temperature is not increasing above a threshold value, typically 0.02°C/min, the temperature is increased by another step and the process repeated. If the cell temperature increases at rate equal to or above the threshold value, the ARC switches to the exotherm mode during which the ARC temperature closely matches the cell temperature, thus maintaining the adiabatic state. The ARC matches the rate of temperature rise of the cell even at quite high heating rates. The normal mode of operation of the ARC terminates an experiment by cooling the sample once it reaches a set upper temperature limit. The ARC experiment closely simulates a thermal abuse environment that includes moderately high temperatures for relatively long periods of time.

### III. RESULTS AND DISCUSSION

A. ARC Runs

Thermal runaway occurs when heat generation by decomposition reactions in the cell exceeds the heat removal from the cell. The thermal runaway response of a cell can be divided into three stages. In Stage 1, even after heat generation begins in the cell, the cell spends a long period of time at relatively low heating rates before the final rapid thermal runaway. This stage can start at temperatures as low as 50°C, especially for highly charged cells. Stage 2 is characterized by accelerating heating rate and cell venting. This stage begins under 120°C and continues up to around 180°C-190°C. Cells in this heating regime can usually be prevented from going into thermal runaway if sufficient cooling is applied. Stage 3 represents uncontrolled thermal runaway, characterized by rapidly accelerating heating rates up to several hundreds of degrees per minute. The cell undergoes high-rate gas generation, often accompanied by internally generated sparks and ignition of the vented cell vapors. These stages are listed in Table II. During an ARC run the cell is maintained under adiabatic conditions and shows runaway behavior determined by the intrinsic properties of the cell materials. Figure 1 shows a typical temperature vs. time profile of an ARC run. Figure 2 shows the Stage 1 and 2 ARC heating rate profile as a function of increasing temperature for different cell chemistries while Figure 3 shows the Stage 3 high-rate runaway. The high-rate thermal runaway is not greatly influenced by the anode carbon material.

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Table II. Thermal runaway can be divided into three basic stages.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temperature Range</th>
<th>Response</th>
<th>Reaction Source</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>50 °C – 120 °C</td>
<td>Low rate heating</td>
<td>Anode reaction with electrolyte</td>
</tr>
<tr>
<td>2</td>
<td>120 °C - 180 °C</td>
<td>Accelerating heating rate and cell venting</td>
<td>Cathode and anode surface reaction with electrolyte</td>
</tr>
<tr>
<td>3</td>
<td>180 °C and above</td>
<td>High-rate runaway with possible cell disassembly</td>
<td>Cathode oxygen decomposition reacting with electrolyte</td>
</tr>
</tbody>
</table>

B. Anode Effects in Full Cells

Initial heat generation in the cell can be attributed to reactions at the cell anode between the lithiated carbon and the electrolyte. The anode initially has a protective layer called Solid Electrolyte Interface (SEI) which prevents continuous reduction of the electrolyte but allows ionic conduction of the Li ions. At temperatures above 100 ºC this layer begins to break down, resulting in increased heating of the cell by renewed electrolyte reduction. The morphology of the anode carbon particles greatly affects the stability range of the SEI. Particles with spherical morphology are more easily covered with the SEI and resist decomposition at the lower temperatures. Figure 4 shows SEM [8] micrographs of the three anode carbons used in construction of these cells. The Gen1 and GDR carbon particles show a definite smooth, spherical shape while the MAG10 particles are more flaky. The onset of heat generation shown in Figure 2 reflects these differences. The Gen1 and GDR anode cells both show similar ARC profiles with a long period of low-rate heating up to 140 ºC. Above this temperature the decomposition of the cathode material begins to dominate the cell response. The MAG10 carbon cell showed accelerated heating starting well below 100 ºC indicating that the SEI was not effective in coating the sharp edges of these particles.

C. Cathode Effects in Full Cells

Cathode decomposition reactions result from reactions of the electrolyte with the highly oxidizing cathode oxide particle surfaces and from decomposition of the cathodes to release free oxygen which in turn oxidizes the electrolyte [7]. Onset of these reactions can begin as low as 140 ºC but show a peak in reaction rate around 200 ºC depending on the exact metal oxide composition. Figure 5 shows the ARC profiles of cells with three different cathode oxides. The peak reaction rate and temperature excursion of the peak reaction reflect the total
enthalpy of the cathode reaction. Significant decrease in cell reactivity was shown in going from LiNi$_{0.80}$Co$_{0.15}$Al$_{0.05}$O$_2$, to LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, and then to stabilized spinel LiMn$_2$O$_4$.

D. Separated Anode and Cathode Responses

The contribution of each electrode to the full cell response was more clearly shown by disassembling fully charged cells under inert atmosphere conditions, dipping the electrodes in fresh electrolyte and resealing the individual electrodes in 18650 cans. ARC runs were performed on these isolated electrodes to determine the total heat and gas generation attributable to each electrode. Figure 6 shows the ARC profile for the anode run. The magnitude of the peak heating rate was very small compared to the total cell. Low-rate reactions were seen starting below 100 ºC confirming the SEI decomposition mechanism. However, the weak peak reaction around 200 ºC suggests that much of the lithiated anode either reacted at lower temperatures or was covered by reaction products which limited the high temperature reaction rates. The volume of gas generated during the run was calculated from the pressure increase of the sealed cell containment system and showed increased gas production starting just below 200 ºC. The majority of the gas production was complete by 250 ºC and yielded 800 ml of gas at STP.

The cathode decomposition reaction is shown in Figure 7. This reaction was quite energetic, peaking above 200 ºC at a rate of over 300 ºC/min. Gas evolution during the cathode reaction began around 120 ºC, increasing steadily throughout the run but not corresponding closely with the peaks in heat generation. The “S” shape in the gas curve at higher temperature resulted from cooling of the cell after it overshot the ARC temperature during the high-rate cooling. The cathode and full reaction rates are compared in Figure 8 showing that the high-rate reactions in the full cell are completely accounted for by the cathode reaction.

Calculation of gas generation of each electrode component, shown in each figure, revealed nearly equal amounts of gas evolution by the individual electrode even though the cathode was the source of the main high-rate heat generation. The total volume of gas from the individual electrodes was seen to be equal to that for the full cell. The composition of the full cell gases are shown in Figure 9. The main gas was CO$_2$ resulting from decomposition of the electrolyte. The same gas species were seen from the full cell and from just pure electrolyte decomposition.

IV. CONCLUSIONS

The thermal abuse response of 18650 cells built using advanced anode and cathode materials were measured using calorimetric techniques. Thermal runaway was characterized as occurring during three stages. The anode reactions were shown to determine cell response during the initial low-rate reaction regime (Stage 1 and 2) while the cathode decomposition reaction determined cell response during the high-rate (Stage 3) regime. The morphology of the anode carbon particles was shown to determine the stability and reaction rate of the anode SEI decomposition during Stage 1 while the cathode oxygen decomposition reaction was determined by the chemical structure and stability of the active metal oxide. Significant improvements in cell abuse tolerance has been shown using combinations of these new electrode materials.
Figure 6. ARC profile of full 18650 cell anode electrode in electrolyte (100% SOC).

Figure 7. ARC profile of full cell cathode electrode in electrolyte (100% SOC).

Figure 8. Comparison of ARC profiles of 18650 cell and just the cathode electrode.

Figure 9. Gas composition from ARC run of full cell compared with decomposition of electrolyte only.

ACKNOWLEDGMENT

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[5] Qualion LLC, PO Box 923127, Sylmar, CA 91392-3127.
[8] Micrographs provided by Daniel Abraham, Argonne National Laboratory, Argonne, IL.