

Effects of additives on thermal stability of Li ion cells

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Available online 1 June 2005

Abstract

Li ion cells are being developed for high-power applications in hybrid electric vehicles, because these cells offer superior combination of power and energy density over current cell chemistries. Cells using this chemistry are proposed for battery systems in both internal combustion engine and fuel cell-powered hybrid electric vehicles. However, the safety of these cells needs to be understood and improved for eventual widespread commercial applications. The thermal-abuse response of Li ion cells has been improved by the incorporation of more stable anode carbons and electrolyte additives. Electrolyte solutions containing vinyl ethylene carbonate (VEC), triphenyl phosphate (TPP), tris(trifluoroethyl)phosphate (TFP) as well as some proprietary flame-retardant additives were evaluated. Test cells in the 18,650 configuration were built at Sandia National Laboratories using new stable electrode materials and electrolyte additives. A special test fixture was designed to allow determination of self-generated cell heating during a thermal ramp profile. The flammability of vented gas and expelled electrolyte was studied using a novel arrangement of a spark generator placed near the cell to ignite vent gas if a flammable gas mixture was present. Flammability of vent gas was somewhat reduced by the presence of certain additives. Accelerating rate calorimetry (ARC) was also used to characterize 18,650-size test cell heat and gas generation. Gas composition was analyzed by gas chromatography (GC) and was found to consist of CO₂, H₂, CO, methane, ethane, ethylene and small amounts of C1–C4 organic molecules.

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Keywords: Abuse testing/tolerance; Electrolyte additives; Li ion cell; Block temperature

1. Introduction

The thermal-abuse tolerance of Li ion cells is a complex function of the interactions of the cell components at elevated temperature that generate gas and heat, which if not interrupted, may lead to uncontrolled thermal runaway of the cells. Anode, cathode and electrolyte interactions have been measured for chemistries chosen to meet the high-power requirements of the US Department of Energy (DOE) Advanced Technology Development (ATD) Program [1], which is an element of the FreedomCAR and Vehicle Technologies Program [2]. Heat-generating reactions are initiated below 100 °C as low-rate reactions at the anode followed by accelerating reactions above 150 °C due to solid electrolyte interface (SEI) decomposition and electrolyte reduction [3]. High-rate

reactions at the cathode begin around 180 °C followed by decomposition reactions of the electrolyte at the anode between 180 and 225 °C. Consequently, onset of uncontrolled cell thermal runaway occurs in this elevated temperature regime with venting of the decomposition gases and the expulsion of unreacted electrolyte, often resulting in ignition of these flammable materials [4]. Aging of cells can reduce the magnitude of the exotherms, but the gas composition is relatively unchanged [5]. Lower state of charge reduces the heat output in all Li ion cell chemistries we have studied. Additionally, anode carbon morphology has a profound impact on onset temperature and the magnitude of exothermic reactions, with small particle size flaky graphite being much more reactive than rounded particle MesoCarbon Micro Beads-type materials [6]. We have shown that additives can also reduce the magnitude of exothermic reactions at low temperatures in small (110 mAh) cells [7], but it was still unclear whether these additives would have a similar effect with larger capacity cells.

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Thermal-abuse tolerance was investigated in 18,650-size test cells with carbon anode, Ni/Co/Al-mixed metal oxide cathode and standard alkyl carbonate-based electrolyte with the addition of additives and alternative solvent mixtures. The effect of additives can be classified [8] as:

- (1) stabilizing the anode (e.g., enhancing the stability of the anode solid electrolyte interphase (SEI) passivation film);
- (2) imparting other beneficial effects to the electrolyte (e.g., flame-retardant agents, overcharge protection, etc.);
- (3) protecting the cathode materials (e.g., barrier to solubility or oxidation of the solvent).

The cell thermal-abuse tolerance was measured using a fixture specially designed for measuring the self-generated heating of the cell during a forced thermal ramp into open room atmosphere. The flammability of the vented gas species was studied using a novel arrangement of a spark generator placed near the cell during thermal ramp to 200 °C in a copper block so that ignition of vent gas would occur if a flammable gas mixture was present.

Accelerating rate calorimetry (ARC) was also used to determine the onset of thermal runaway, relative peak reaction rates and gas generation. Quantitative measurements were made of the evolved gas volume during thermal runaway as well as the gas species composition at the end of the runaway event. Measurements were performed up to a maximum of 400 °C using a special fixture to contain the high-pressure gases and provide sensitive measurement of the cell-heating rate.

The baseline cells (referred to as Gen2 chemistry) consisted of a MAG-10 flaky graphite and a $\text{LiCo}_{0.15}\text{Ni}_{0.8}\text{Al}_{0.05}\text{O}_2$ (Fuji) cathode with an electrolyte that consists of 1.2M LiPF_6 dissolved in ethylene carbonate and ethyl methyl carbonate (EC:EMC) in a ratio of 3:7 (w/w). Additional cells were fabricated with the same cathode but with a different carbon and electrolyte; 6 wt.% carbon-coated natural graphite (GDR) and 1.2 M LiPF_6 dissolved in ethylene carbonate, propylene carbonate and ethyl methyl carbonate (EC:PC:EMC) in a ratio of 3:3:4. Extensive characterization of this chemistry has been performed using 18,650 cells as part of the ATD program [1,3–6]. The 18,650-size cells (0.91 Ah) were fabricated at Sandia National Laboratories [9] and consisted of a hermetic aluminum case with a machined vent. Coated electrodes were obtained from Quallion LLC [10].

The additives studied in this work are listed in Table 1.

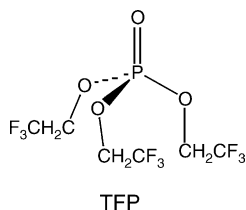
The thermal ramp experiment heated the cells at 6 °C per minute from room temperature to 200 °C in a copper block equipped with heating elements (see Fig. 1).

The test resembles a “hot box” test, but provides additional information. The block temperature was monitored during the test. The cell was wrapped with insulation, and its surface temperature was monitored. By analyzing the temperature difference between the cell surface temperature and the block temperature, we can estimate the onset temperature of

Table 1
Additive materials studied

	Proposed function	Description
1	Stabilizing the anode	Vinyl ethylene carbonate (VEC)
2	Imparting other beneficial effects to the electrolyte	Flame retardants
		Triphenyl phosphate (TPP)
		Army Research Lab (ARL) additive ^a
		Argonne National Lab (ANL) additives “B”, “C” ^a

^a The ARL additive is tris(trifluoroethyl)phosphate termed as TFP. The ANL additives B and C consist of phosphazene skeleton and with different types of substituents. These compounds were supplied from Bridgestone Corporation as a phoslyte (TM) additive.



self-heating. This test is complementary to an ARC test, but it can be performed under atmospheric conditions (i.e., with the presence of air to support flammability studies). Four spark sources (adapted from the ignition source for a natural gas cook stove) were mounted above the test fixture and were repeatedly energized during the test, providing a repetitive ignition source. With this configuration, if a flammable mixture of gas was present after the cell vented, we would observe a flame using digital video recording. Thus, our flammability test resembled “real world” conditions, and was a direct way to evaluate the effect of additives on flammability of vented gas and electrolyte vapors.

The ARC test fixture for 18,650-size cells has been described [7]. It is designed to contain the high-pressure gases from vented cells up to the maximum run temperature of 400 °C. The gas pressure was monitored throughout the run and was used to calculate the STP volume of the evolved gases using the calibrated system volumes. All cells were measured at a potential of 4.1 V (100% state of charge).

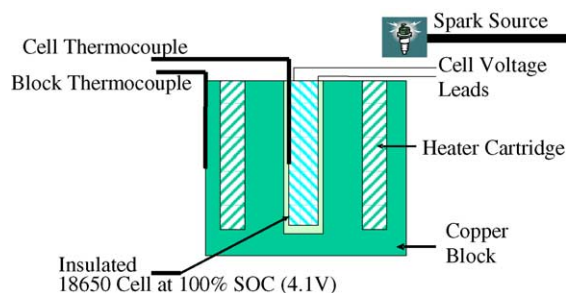


Fig. 1. Schematic of cell temperature ramp apparatus with spark source.

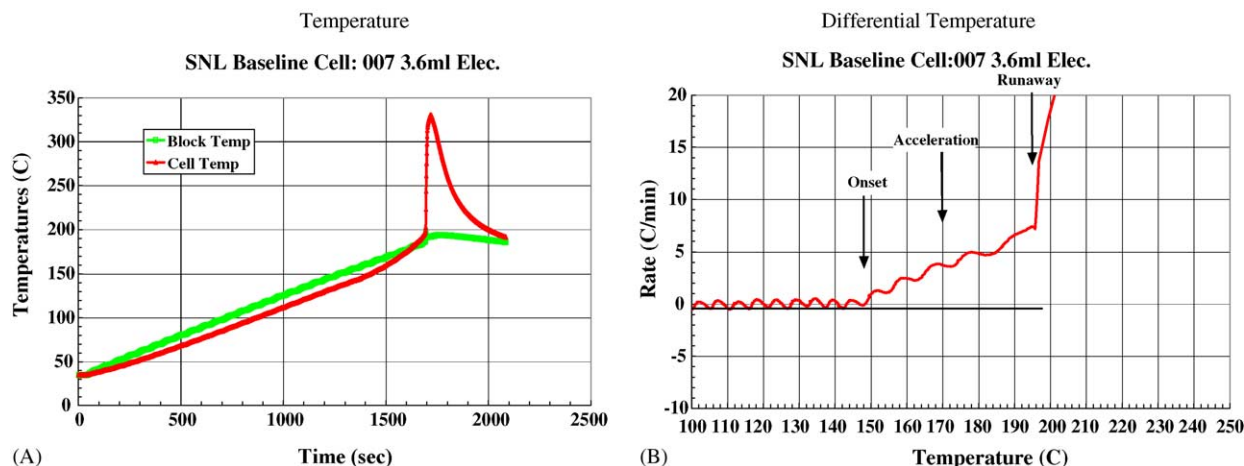


Fig. 2. (A) Temperature vs. time plot for block and cell temperatures for baseline cell. (B) Rate of change of differential temperature (cell-block temperature) vs. temperature for the same experiment.

2. Results and discussion

2.1. Thermal response of 18,650-size cells

The thermal ramp experiments provided information on two critical temperatures that indicate thermal-abuse response of cells: the onset and runaway temperatures. The Gen2 baseline cell was heated to 200 °C in the copper block apparatus and the observed temperature profiles are given in Fig. 2. The temperature differential between the cell and the thermal block shows the effect of self-generated heating.

The derivative of the temperature differential (Fig. 2B) more clearly shows the reaction regimes leading to thermal runaway. Note that the cell temperature lags the block temperature by a constant amount until 148 °C; this is defined as *onset temperature*. From 148 to 195 °C, the cell temperature increases faster than the heating rate of the block due to exothermic reactions within the cell. This range is termed *acceleration region*. At 195 °C, the cell-heating rate rises very rapidly, which is termed *runaway temperature*. The data for the cells in this study are presented in Table 2.

From the data in Table 2, we can see that the onset and runaway temperature of the cells is not improved by the additives. In fact, some of the additives substantially worsen the cell performance. In no case did the cells have higher onset or runaway temperature compared to the baseline cells. Cells with the ARL additive had similar onset and slightly reduced runaway temperatures compared to the baseline cell. Even though the number of cycles varies from test to test, cells with ANL additives B and C shared a common behavior; they had substantially lower runaway temperatures when the cells had only a modest number of cycles (20–36 for cells with additives B and C respectively) but had higher runaway temperature when higher number of cycles were applied (35–95 for cells with additives B and C, respectively). The early thermal runaway was accompanied by a high-rate gassing event immediately prior to runaway; the gas generation reactions appeared at higher temperature after cycling. The cause of the change in behavior for cells with ANL additives B and C has not been investigated at this time, but the stability of the additives during cycling should be studied. This premature runaway and gassing is a concern because it will make the cell more susceptible to venting and disassembly than the baseline cells.

Table 2

Onset temperature and runaway temperature for 18,650-size cells with various additives added to the electrolyte

Cell description	Temperature (°C)	
	Onset	Runaway
Baseline	148	195
5% ARL additive with 5 full charge/discharge cycles	145	188
2% VEC with 5% TPP with 30 full charge/discharge cycles	145	192
15% ANL additive B with 35 full charge/discharge cycles	145	192
20% ANL additive B with 21 full charge/discharge cycles	145	145
5% ANL additive C with 5 full charge/discharge cycles	141	141
5% ANL additive C with 95 full charge/discharge cycles	145	188
10% ANL additive C with 5 full charge/discharge cycles	144	145
10% ANL additive C with 35 full charge/discharge cycles	148	148

Table 3
Flammability of vent gas and expelled electrolyte for 18,650-size cells with various additives

Cell description	Flammability
Baseline	Sustained flame
5% ARL additive with 5 full charge/discharge cycles	Somewhat reduced flammability
2% VEC and 5% TPP with 30 full charge/discharge cycles	Substantially reduced flammability
15% ANL additive B with 35 full charge/discharge cycles	Somewhat reduced flammability
20% ANL additive B with 21 full charge/discharge cycles	Somewhat reduced flammability
5% ANL additive C with 5 full charge/discharge cycles	Somewhat reduced flammability
5% ANL additive C with 95 full charge/discharge cycles	Negligible flammability
10% ANL additive C with 5 full charge/discharge cycles	Somewhat reduced flammability
10% ANL additive C with 35 full charge/discharge cycles	Somewhat reduced flammability

2.2. Flammability studies

The flammability of the vent gas/expelled electrolyte was observed during the thermal ramp. The evaluation of this

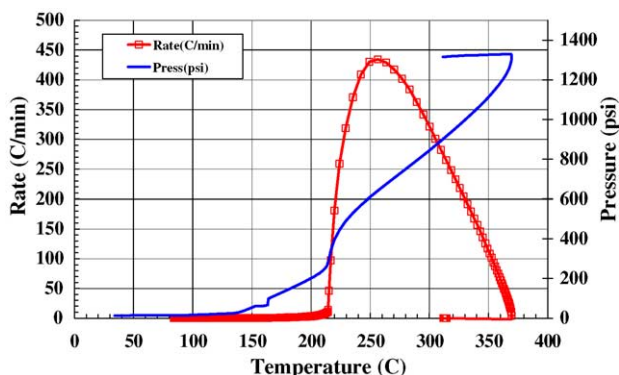


Fig. 3. Typical ARC run of 18,650 cell showing heating rate and pressure through thermal runaway.

characteristic of the cell is somewhat subjective. To compare the results we observed, we will characterize the flammability as sustained flame (i.e., similar to the baseline), somewhat reduced flammability, substantially reduced flammability and negligible flammability. In the latter case, the vent gas and expelled electrolyte did not support a sustained flame at any time during the test. Table 3 gives the results of our observations. All of the additives had some effect, but usually the magnitude was small. The cell with 2% VEC plus 5% TPP had substantially reduced flammability, and the cell with 5% ANL additive C (after 95 cycles) had the greatest reduction in vent gas flammability.

2.3. Gas analysis

Cells with similar composition and cycling history were studied in the ARC to quantitatively measure the onset temperature and vent gas composition. A typical ARC run, shown in Fig. 3, illustrates the cell adiabatic heating rate

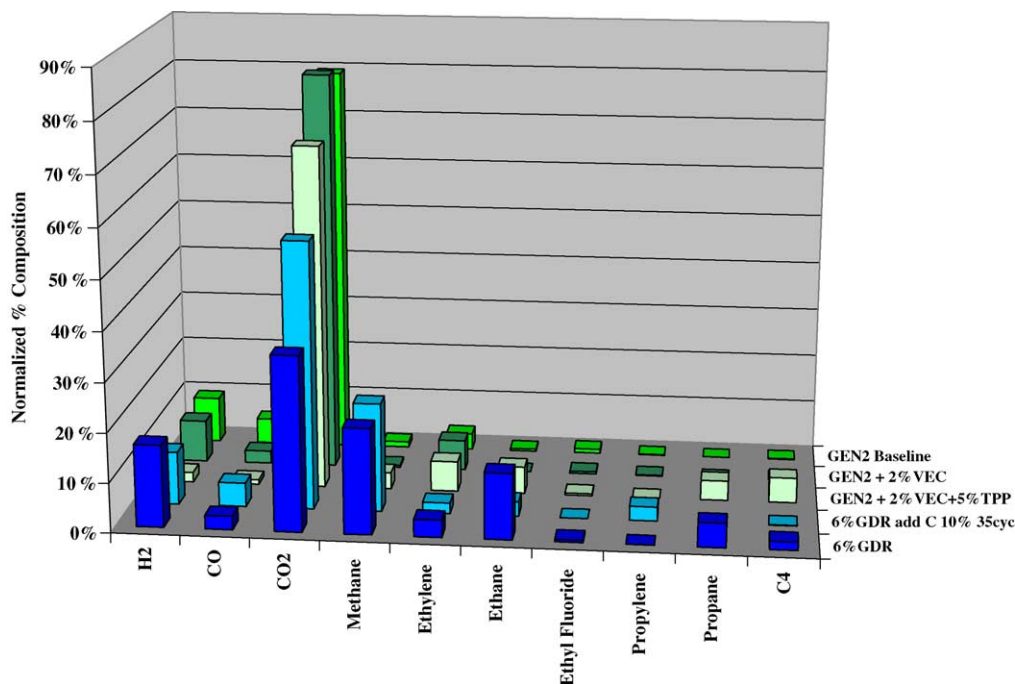


Fig. 4. Gas analysis of vented gas from thermal-abuse cells.

and pressure. Gas samples were taken from the sample fixture volume at the end of each ARC run. The gases were analyzed by gas chromatography (GC) and the relative gas species concentrations normalized to the volume of the evolved gases. The fixture volume was initially purged with nitrogen, which constituted a large part of the sampled gas and the effect was removed by normalization. The evolved gas species for the baseline and mitigation cells are shown in Fig. 4. The Gen2 baseline cell gases consist primarily of CO₂ (80%) with lower amounts of H₂ (10%), CO (5%) and ethylene (3%). Addition of the 2% VEC resulted in a relative increase in the amount of ethylene, possibly from decomposition of the VEC itself, but little change in the other evolved gas species. The addition of the 5% TPP primarily resulted in a decrease of CO and H₂ and an increase in the methane and ethane while the other gas species remained relatively constant. The cell with the 6% GDR anode showed a marked increase in the relative amount of H₂, methane, ethane and propane. Finally, the cell with the 6% GDR anode and EC/PC/EMC + 2% VEC electrolyte had gas products similar to the 6% GDR cell with Gen2 electrolyte but with increased CO and CO₂ and reduced amounts of H₂, methane, ethane and propane. The reduction in these light organic species may result from the reduced amount of the EMC linear carbonate in the solvent mix that is believed to be the prime source of the gas decomposition products [11]. It is interesting to note that although CO₂ is a major component of the vent gases, flammability is commonly observed. During the cell venting at elevated temperature, the CO₂ must dissipate rapidly as the remaining gases burn.

3. Conclusions

We have developed an improved technique to evaluate onset temperature, runaway temperature and the flammability of vent gas and expelled electrolyte in 18,650-size high power Li ion cells. In our tests, vented gas composition did not change significantly for the different additives and materials, and consisted mostly of CO₂ with lower amounts of H₂, CO and low molecular weight hydrocarbons. Onset temperature, runaway temperature and vent gas/expelled electrolyte flammability were measured for cells made with a variety of additives added to the electrolyte. While reduced flammability was observed for some additives, lower thermal runaway temperatures were also observed in some cases. This situation would prohibit the practical use of these materials in commercial cells, but points the way to improved additives.

These experiments demonstrate the need for more work in the area of additives to improve cell safety, including the

ability to tailor the flame-retardant additives to be more compatible with other components of the cell chemistry. These studies also point out the need for comprehensive safety testing of advanced Li ion cell chemistries. Lower flammability electrolyte is one factor that needs to be improved, but the solution to flammability cannot compromise other safety-related attributes.

Acknowledgements

We would like to thank Dr. Richard Jow of the US Army Research Lab for the TFP additive. We would also like to thank Bridgestone Corporation for the phoslyte (TM) additives and Bryan Sanchez for making the 18,650 cells. This work was performed under the auspices of DOE FreedomCAR and Vehicle Technologies Office through the Advanced Technology Development (ATD) High Power Battery Development Program. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. Argonne National Laboratory is under Contract no. W-31-109-ENG-38.

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