

Abuse Response of 18650 Li-Ion Cells with Different Cathodes Using EC:EMC/LiPF₆ and EC:PC:DMC/LiPF₆ Electrolytes

E.P. Roth^a

^a Advanced Power Source R&D Dept., Sandia National Laboratories, PO Box 5800,
Albuquerque, NM 87185-0613, USA

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 are reported 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 LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ (Gen2), Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O₂ (Gen3), LiMn₂O₄ (spinel) and LiFePO₄ (nano-phosphate). 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 LiPF₆ and ethylene carbonate: propylene carbonate: dimethyl carbonate (EC:PC:DMC)(1:1:3)\1.2M LiPF₆.

CosMX

EX1009

Page 1 of 23

Electrolyte additives were also examined to determine the effect on low-temperature stability, flammability and overcharge protection. The range of materials studied under the ATD program is summarized in the Table below:

Table 1 Li-ion cell materials tested for the ATD program

➤ **Cathode materials:**

- ☐ LiCoO_2
- ☐ $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ (Gen1)
- ☐ $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (Gen2)
- ☐ $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$; $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ (Gen3)
- ☐ LiMn_2O_4 (Spinel)
- ☐ LiFePO_4

➤ **Anode materials:**

- ☐ MCMB (Gen1 and 3)
- ☐ MAG10 (Gen2)
- ☐ GDR (Gen2)

➤ **Electrolytes/salts:**

- ☐ EC:EMC (3:7) 1.2M LiPF_6
- ☐ EC:PC:DMC (1:1:3) 1.2M LiPF_6
- ☐ LiBOB, LiBETI

➤ **Additives:**

- ☐ SEI enhancer – Vinyl ethylene carbonate (VEC); Vinylene carbonate (VC)
- ☐ Flame retardants– e.g. Phosphazene-based “Phoslyte” from Bridgestone, phosphate TPP, ...

Cylindrical cells were wound in our laboratory in the 18650 configuration (18 mm dia. by 65 mm length) as shown in Figure 1, using coated electrodes with these anodes and cathode compositions resulting in cells with nominal 0.9–1.2 Ah capacity. This cell size allows accurate determination of cell material properties in a configuration that is relatively simple to measure but representative of actual cells in commercial applications.

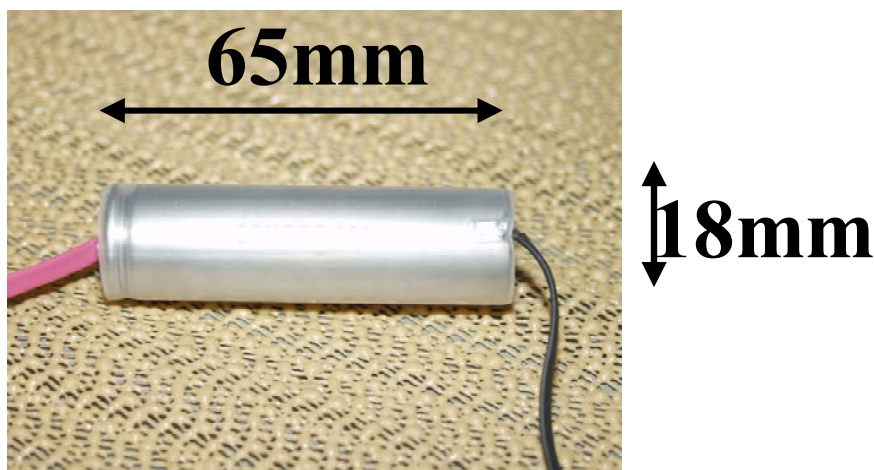
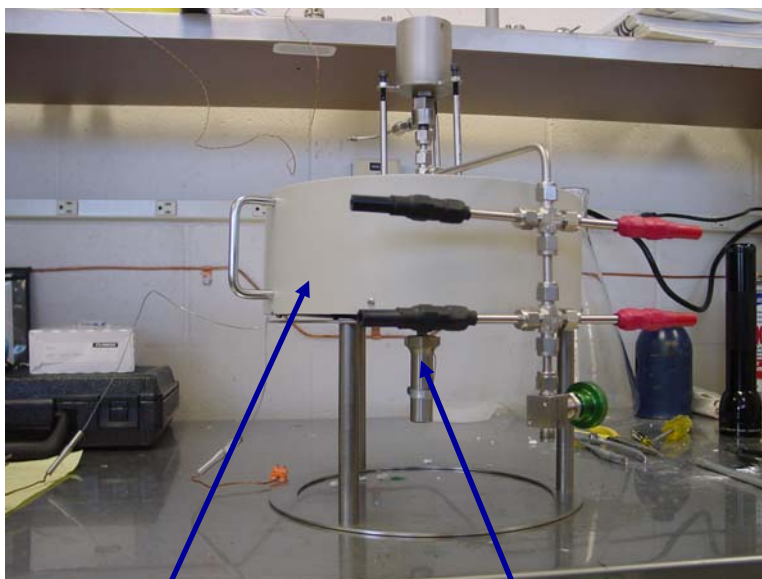


Figure 1. 18650 Li-ion wound cylindrical cell.

Measurement Techniques

Accelerating Rate Calorimeter. 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. Pressure and temperature data were used with measured system volumes to determine the moles of gas and volume at standard temperature and pressure throughout the run.



Top Heater **Cell
Holder**

Figure 2. 18650 cell holder mounted to upper heater for ARC apparatus (not shown).

Thermal Ramp Apparatus. Cells were 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. A layer of insulating glass tape was placed between the cell and the thermal block to allow measurement of cell self heating which resulted in a temperature differential between the cell and the block. The rate of cell heating was calculated using the time derivative of the temperature differential throughout the thermal ramp. The block heating rate was usually set at either 5°C/min or 10°C/min. Flammability of the vent gases was measured using spark ignition sources placed around the fixture. Video recordings of the cell venting and vapor ignition allowed comparison of the abuse response of cells with varying chemistries and designs.

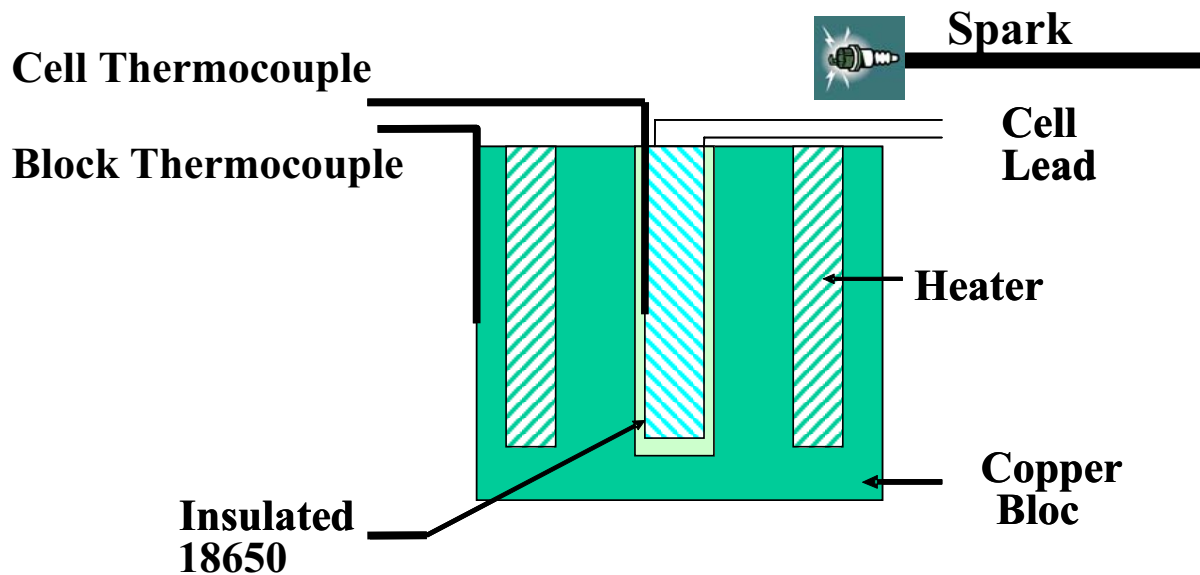


Figure 3. Schematic of thermal ramp apparatus with 18650 cell and external ignition source.



Figure 4. Thermal ramp apparatus with 18650 cell.

Cell Heat Generation Measurement. Cell electrical and thermal responses were measured during charge and thermal runaway using a thermally calibrated cell fixture as shown in Figure 5. The cell was placed in an inner metal sleeve which was wrapped with a layer of insulating glass tape and placed in an outer metal cylinder for protection. Thermocouple pairs were placed on the both sides of the insulating tape in three locations. The thermal resistance of this layer was calibrated initially using a cartridge heater inserted for the cell and the temperature differential used to calculate the heat flow. Quantitative measurements were made of cell heat generation and temperature profile during charge or thermal events. The cell and fixture were placed in a sealed, transparent container that also allowed 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.

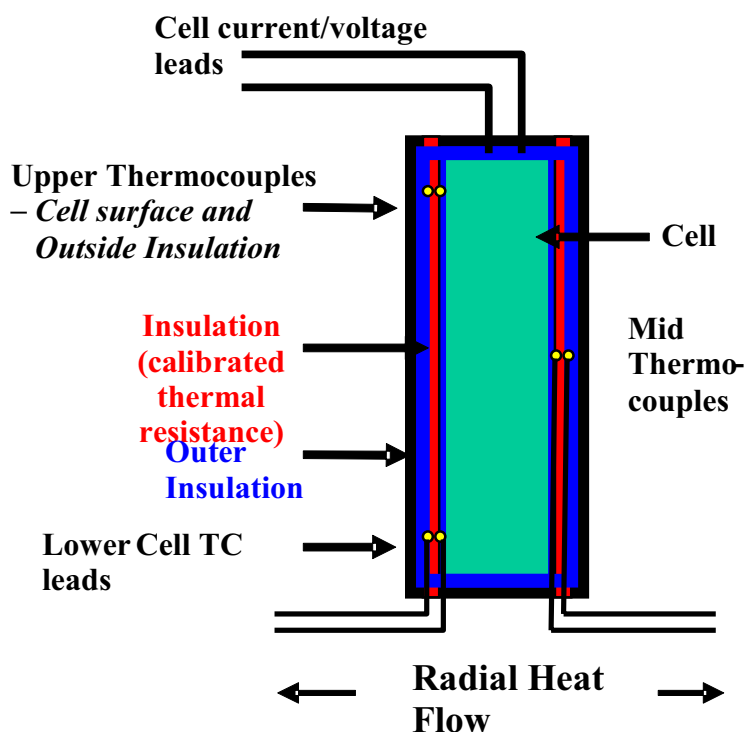
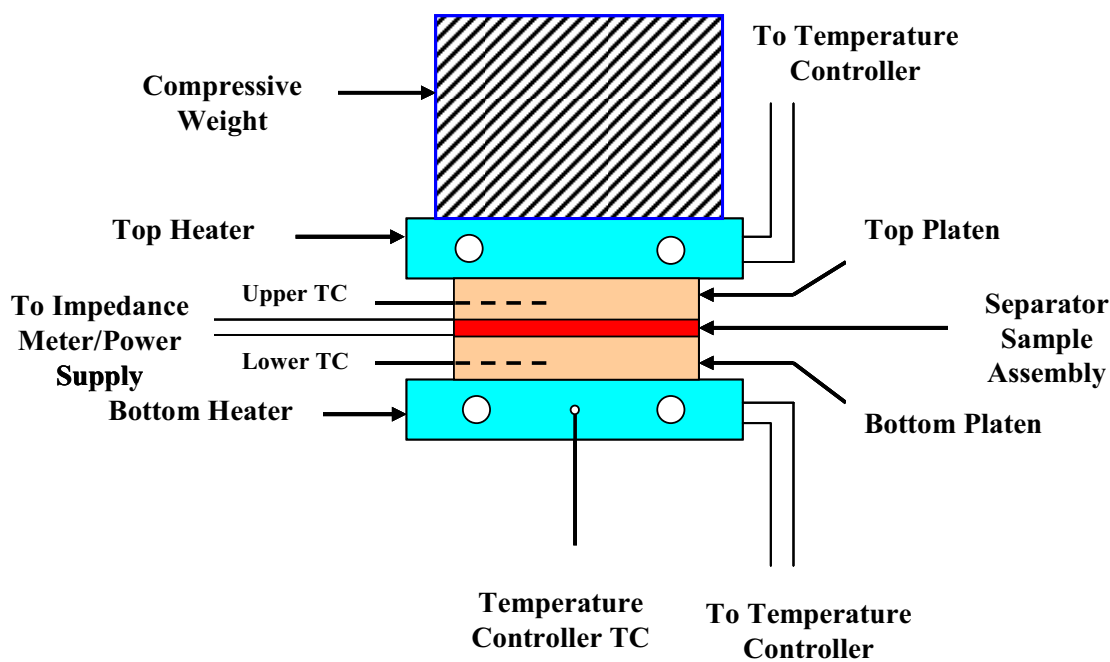


Figure 5. Overcharge fixture for measuring heat flow from 18650 cell.

Separator Characterization. The separator characterization apparatus measured the impedance of an electrolyte-soaked separator sandwiched between two 1.9 cm dia. nickel electrodes as shown in Figure 6. Measurements were made at multiple frequencies (1kHz, 5kHz and 10kHz) while ramping the temperature up to 200°C at rates from 10°C/min up to 60°C/min. An automated data acquisition and control system was designed to allow measurement of the multiple frequency impedance as well as temperatures above and below the sample assembly. Several electrolytes were tested with the most reproducible results obtained with either EC:EMC\1.2MLiPF₆ or a high-temperature electrolyte consisting of 1 M lithium trifluoromethanesulfonimide (HQ-115, 3M Co.) in a 1:1 by volume solution of propylene carbonate and triethylene glycol dimethyl ether. The separator was kept in compression using an external weight to simulate internal cell pressures. Separate measurements were performed on the separator materials to

determine stability above shutdown temperatures with external applied voltage. The cell resistance was measured as a function of time and temperature with different parameters such as applied voltage, pressure, electrolyte composition and surface roughness of the electrodes. This measurement simulated cell conditions of series cell strings where a single cell has gone into shutdown and experiences high potentials from the other cells or external power sources due to the high cell impedance.



Separator Measurement Fixture

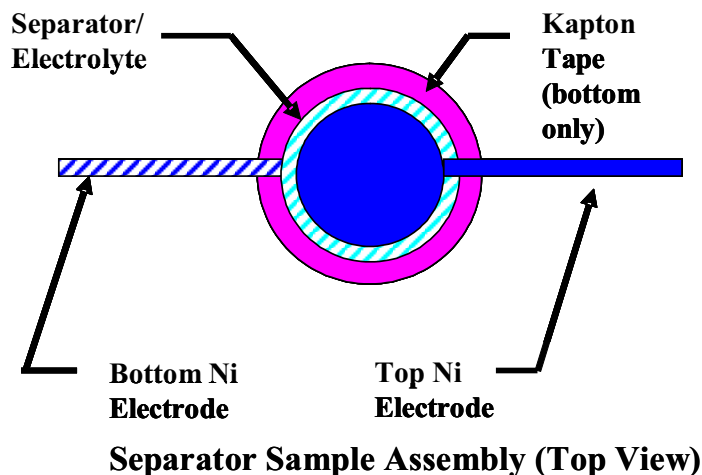


Figure 6. Schematic of separator impedance and voltage breakdown apparatus for separator characterization.

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 7.

- **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**

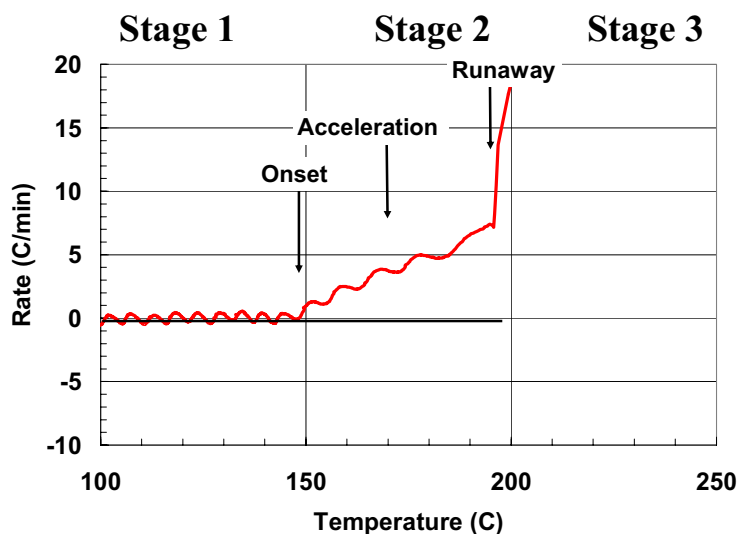


Figure 7. Cell heating rate during a thermal ramp test showing the three stages of thermal runaway.

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 break down, 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 8 shows the ARC thermal runaway profile for three cell chemistries. Cathode composition ranged from LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, 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.

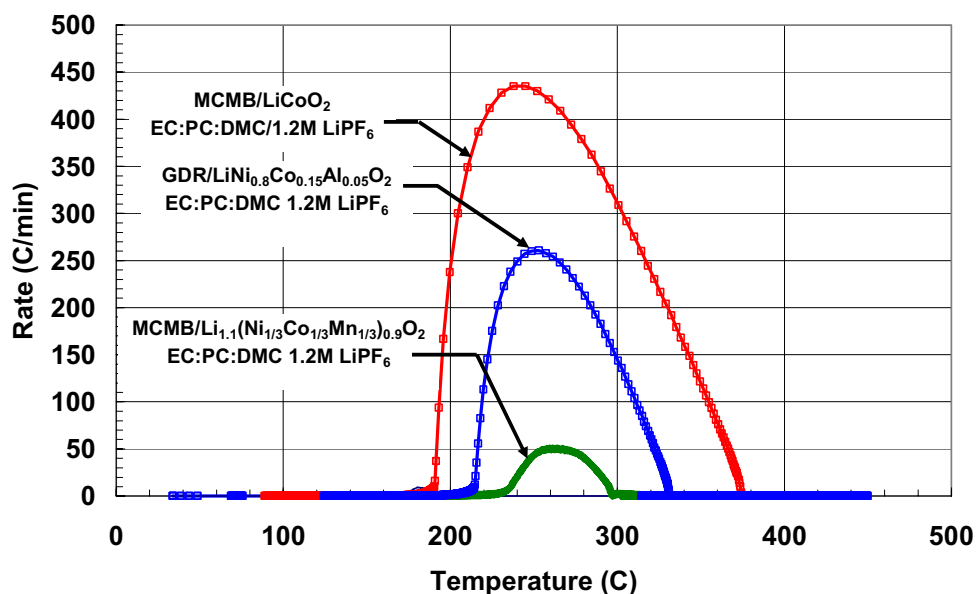


Figure 8. ARC thermal runaway profiles showing Stage 3 runaway for three cathode chemistries showing improved runaway responses.

Improvements in the thermal runaway heating rate profile have been obtained using other solvent combinations in the electrolyte. Figure 9 shows ARC profiles for Gen2 cells in electrolytes using solvent compositions of EC:EMC, EC:DEC and EC:PC:DMC, all with LiPF_6 salt. The onset temperatures remained fairly constant as were the temperature widths of the peak runaway region indicating equal enthalpies of reaction during the peak reaction regime. However, the peak reaction rates showed significant variation for the solvent compositions and with the EC:PC:DMC solvent showing the lowest reaction rate. This effect was also measured in other cell chemistries. Figures 10, 11 and 12 show comparisons of ARC runs of LiCoO_2 , Gen2 and Gen3 cells using either EC:EMC/1.2M LiPF_6 or EC:PC:DMC/1.2M LiPF_6 . The cells with PC containing electrolyte showed reduced heating rates for all three cathode chemistries. However, the effect of the PC containing electrolyte showed the greatest reduction with decreasing reaction activity of the cathode, i.e. LiCoO_2 showed little effect while the Gen3 cathode cell showed significant improvement.

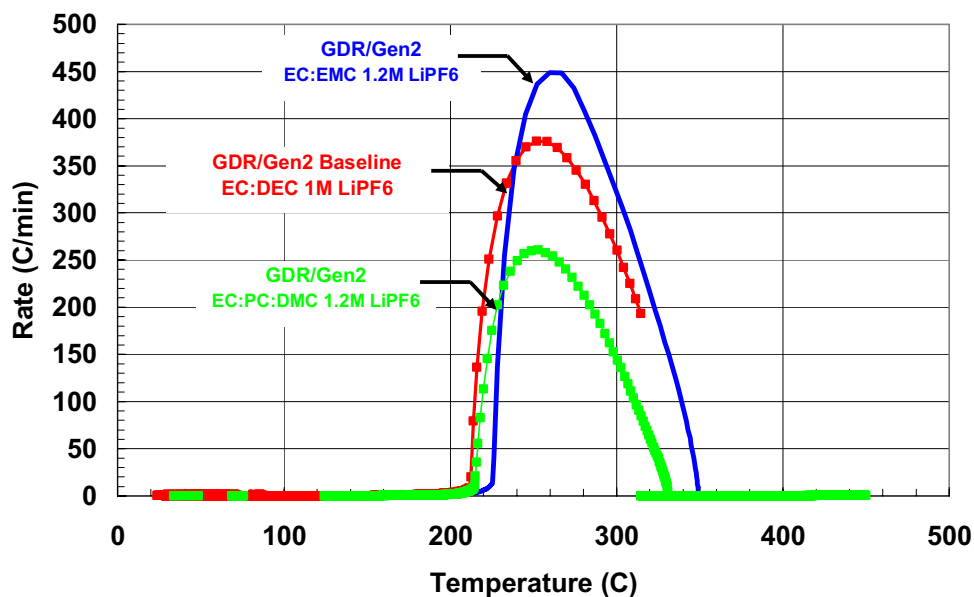


Figure 9. Comparison of ARC profiles for Gen2 cells with different electrolytes.

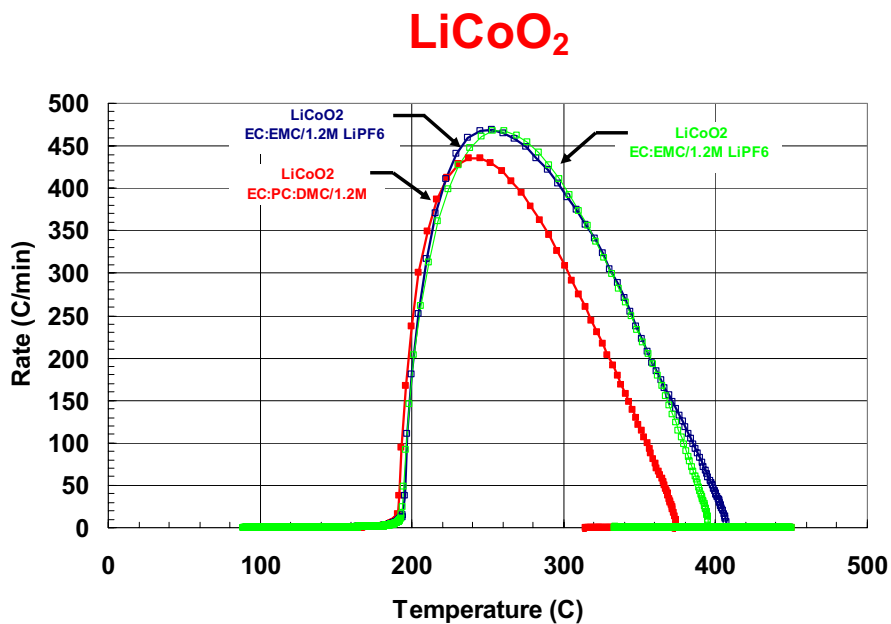


Figure 10. ARC profile comparison for LiCoO₂ cells with EC:EMC\LiPF₆ and EC:PC:DMC\LiPF₆ electrolytes showing reduction in heating rates for PC containing electrolyte. A repeat run for a cell with EC:EMC is shown to show reproducibility.

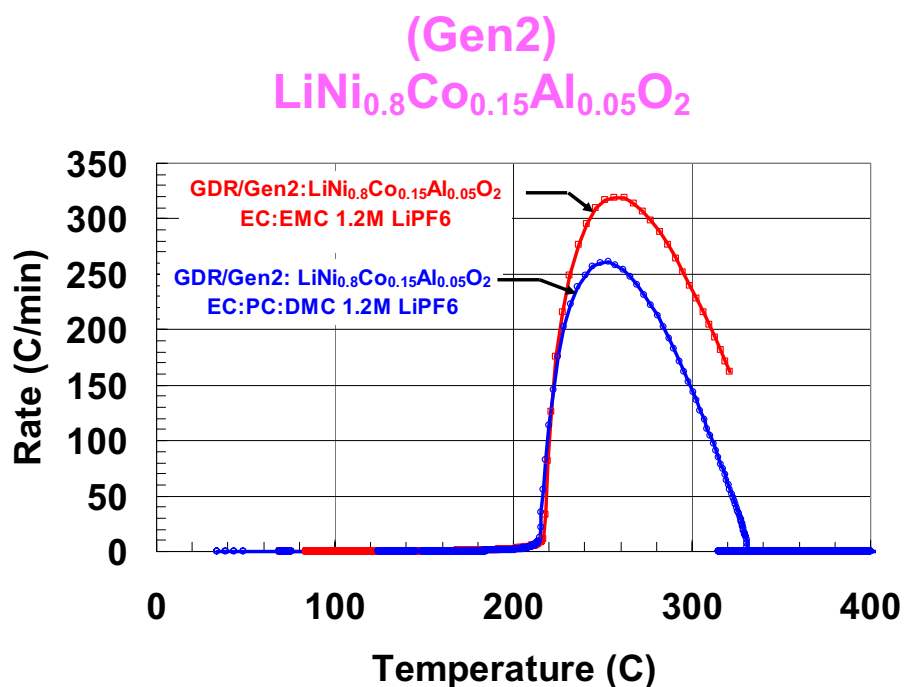


Figure 11. ARC profile comparison for Gen2 cells with EC:EMC\LiPF₆ and EC:PC:DMC\LiPF₆ electrolytes showing reduction in heating rates for PC containing electrolyte.

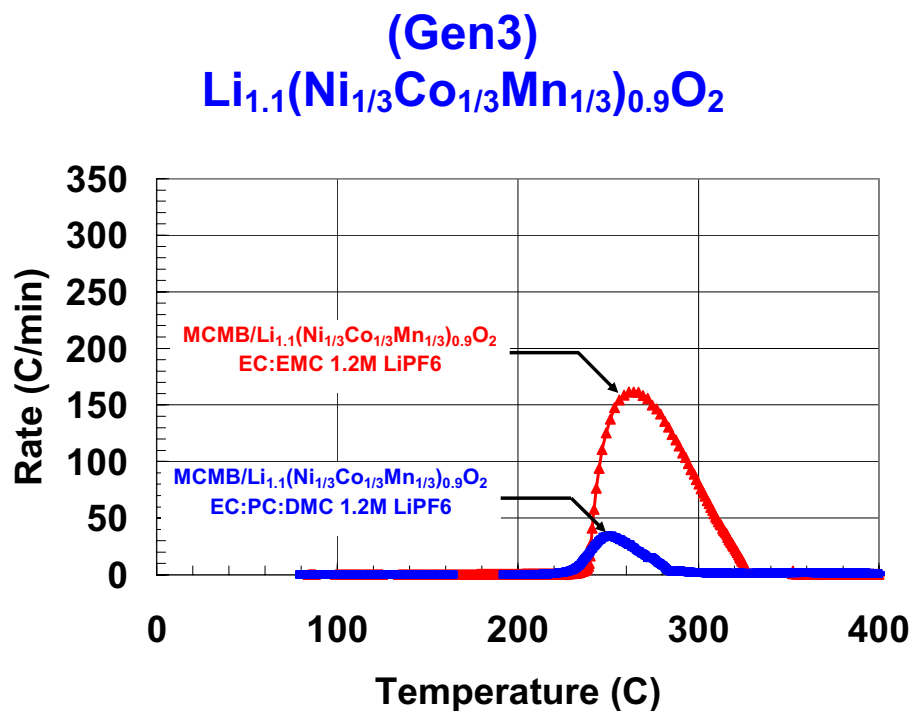


Figure 12. ARC profile comparison for Gen3 cells with EC:EMC\LiPF₆ and EC:PC:DMC\LiPF₆ electrolytes showing reduction in heating rates for PC containing electrolyte.

Electrode Contributions to Full Cell Thermal Runaway

The contributions of the individual anode and cathode components to the full cell thermal runaway were investigated for both the Gen2 and Gen3 cell chemistries. Fully charged 18650 cells were disassembled in an argon glove box and the individual electrodes removed in the fully charged state. The electrodes were resealed in 18650 cans in the presence of the same electrolyte as the cell (EC:EMC\1.2MLiPF₆) using approximately equal amounts of electrolyte for each electrode (2g) which added up to the total cell electrolyte weight (~4g).

Figure 13 shows the ARC profiles for the Gen2 full cell and Gen2 cathode. As can be seen, the cell thermal runaway response is dominated by the cathode for this chemistry. Detailed examination of the lower temperature rates show that the anode did contribute to the early runaway response of the cell but the cathode peak reaction rates determined the cell peak runaway response. Figure 14 shows the data for the Gen3 cell and electrode components. Both anode and cathode electrodes are compared to the full cell. The lower reaction rate of the Gen3 cathode chemistry is clearly evident. The anode and cathode show comparable contributions to the full cell peak reaction response with the anode showing lower temperature onset for runaway compared to the cathode. The anode electrode measurement had excess electrolyte in the 18650 can and thus also showed the electrolyte decomposition reaction starting around 200°C. In a full cell, there is little free electrolyte and this peak is not normally observed. These results show that as improvements are made in cathode reaction rate and enthalpies, the anodes must still be accounted for in the full cell response.

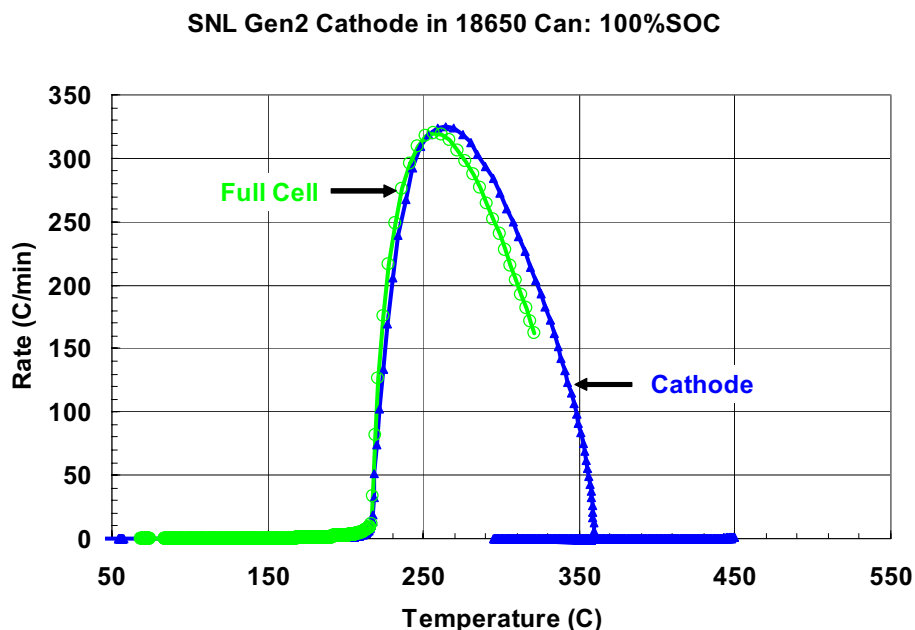


Figure 13. Comparison of ARC profiles of a full 18650 Gen2 cell and the cathode electrode removed from a charged cell and resealed in an 18650 can with EC:EMC\LiPF₆ electrolyte.

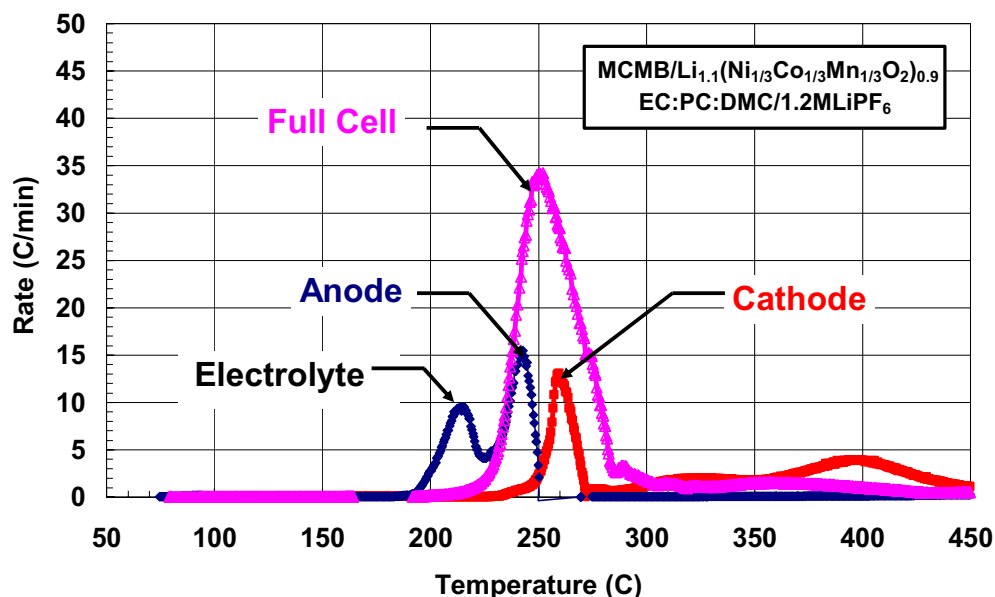


Figure 14. ARC profiles of a full 18650 Gen3 cell and the individual electrode components removed and resealed in 18650 cans with EC:PC:DMC/LiPF₆ electrolyte.

Gas Generation

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 15) which serves to aerosolize the cell electrolyte, resulting in a strong flammable source if ignited. The volume of gas generated during the Stage 3 runaway was less than half of the total volume generated for complete reaction to high temperatures (Figure 16) but this volume has the most effect on cell thermal abuse response. The composition of this vent gas was determined using gas chromatography of grab samples taken after the ARC run. The main gas species generated was CO₂ as shown in Figure 17. Other species included H₂, 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 CO₂ decreased with temperature while the amount of H₂, methane, and ethylene increased. The gases released during cell decomposition have also been compared with gases from decomposition of pure electrolyte and found to be almost identical. The contributions of each electrode to the total gas evolved were also measured during the runs of the individual anode and cathode. Figure 18 shows that for the Gen2 cell and individual electrodes, the anode and cathode contributed almost equally to the total gas evolved. Similar runs for the other cell chemistries (LiCoO₂, Gen3, LiMn₂O₄) showed the same result of equal gas contributions from each electrode. These results represent the gas evolution for electrodes with equal volumes of electrolyte showing that the electrolyte decomposition determines the volume of gas evolved.

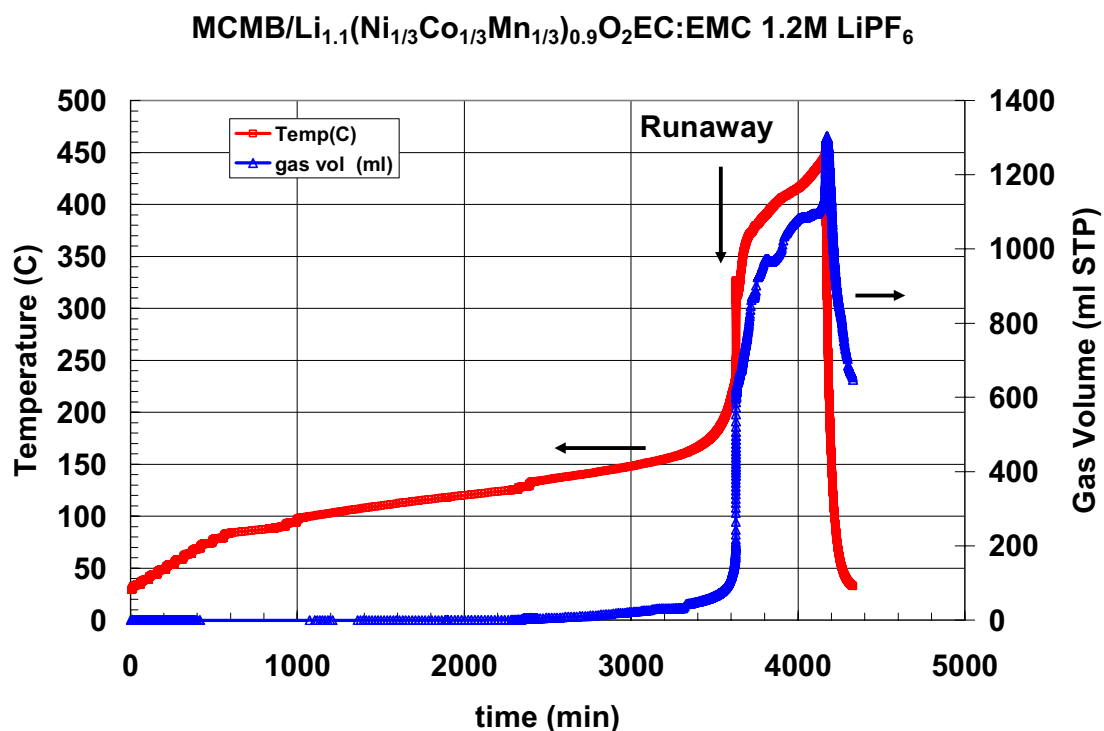


Figure 15. Temperature and gas volume profiles during ARC run of Gen3 cell.

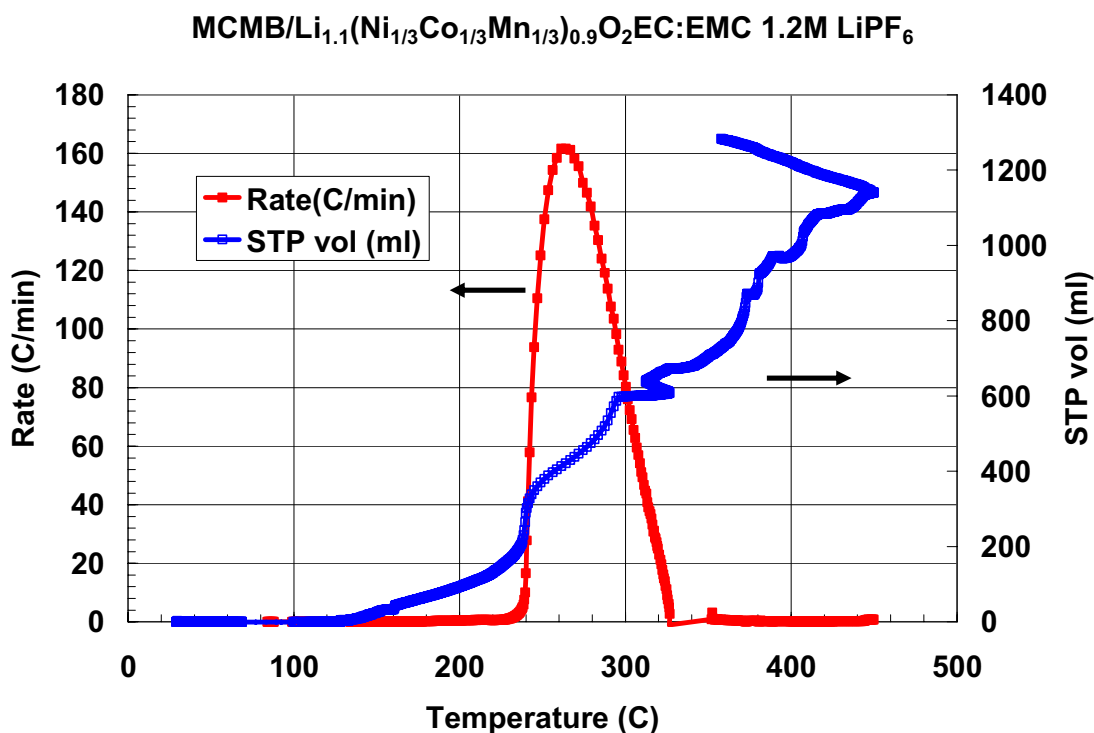


Figure 16. Heating rate and gas volume profiles during ARC run of Gen3 cell.

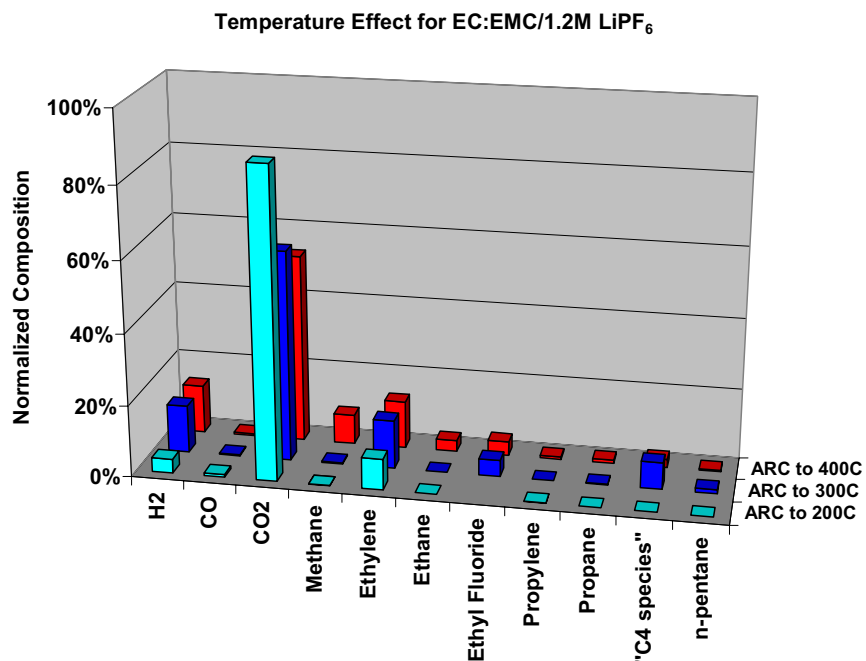


Figure 17. Composition of Gen2 cell gases after ARC runs as a function of final run temperature.

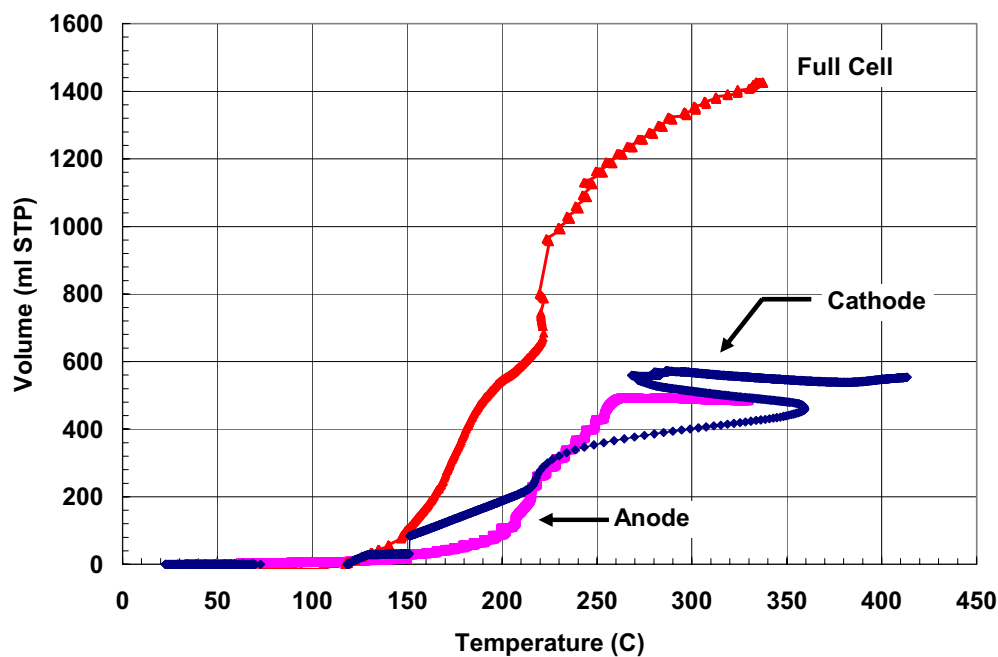


Figure 18. Gas volumes for full Gen2 cell and anode/cathode Gen2 cell components released during ARC runs showing equal contributions from anode and cathode.

Thermal Ramp Abuse Response

Cells were heated in the thermal ramp apparatus at a rate of 5°C/min to test for heat and gas generation under expected abuse conditions. The previous ARC measurements showed that cathode composition had a significant effect on cell self heating rate with the Gen3 material showing much lower heating rate and reaction enthalpy. This behavior was also observed in the thermal ramp measurements. Figure 19 shows that the Gen2 cathode cell experienced the onset of self heating around 140°C which was the beginning of Stage 2 thermal runaway. The rate accelerated until the cell went into Stage 3 runaway at around 190°C where the cell exhibited high-rate generation of gases which were ignited by the external spark ignition sources. As the cell was generating heat, the actual cell internal temperature was higher than the measured cell skin temperature due to the limited heat transfer through the cell to the fixture. The Gen3 cell also showed an onset for self heating near 140°C but the heating rate during Stage 2 was significantly lower. The cell started venting around 190°C and went into Stage 3 thermal runaway at about 225°C which corresponded well to the ARC thermal runaway temperature of 225°C. The gases from the Gen3 cells all ignited almost immediately upon venting.

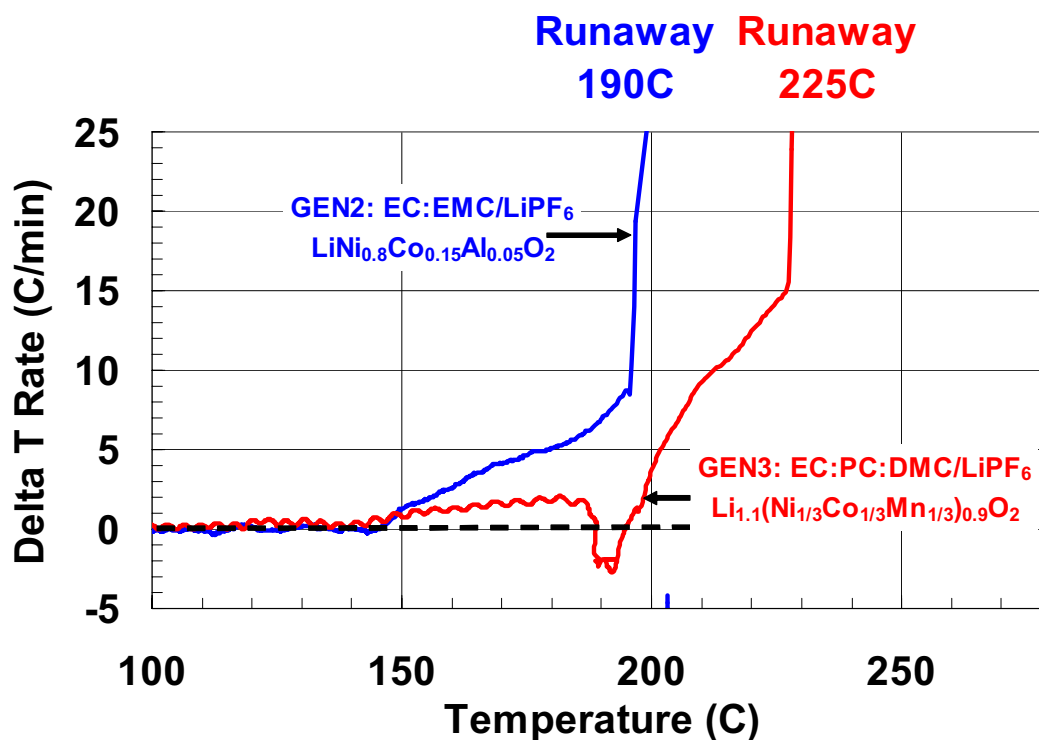


Figure 19. Thermal ramp cell self heating rates for Gen2 and Gen3 cells heated at 5°C/min.

Thermal ramp measurements were also made of commercial 26650 cells using cathode chemistries that show some of the greatest reductions in cathode reactivity: LiMn_2O_4 and LiFePO_4 (3). Figure 20 shows a comparison of the thermal ramp profiles for these two chemistries as well as comparison data of the 18650 Gen2 and Gen3 cells. The earliest runaway temperature was seen for the most reactive Gen2 ($\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) cathode chemistry. There was a steady increase in runaway temperature progressing from Gen3 ($\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$) to LiMn_2O_4 spinel and then to the most stable nano-phosphate LiFePO_4 . The spinel and the LiFePO_4 cells showed similar thermal runaway temperatures indicating that the onset of the peak thermal runaway was dominated by the anode reactions. However, the LiFePO_4 showed very low peak heating rates due to the lack of decomposition oxygen release and very low enthalpy for this cathode/electrolyte reaction. All cells, including the LiFePO_4 , showed venting and aerosolization of the flammable electrolyte.

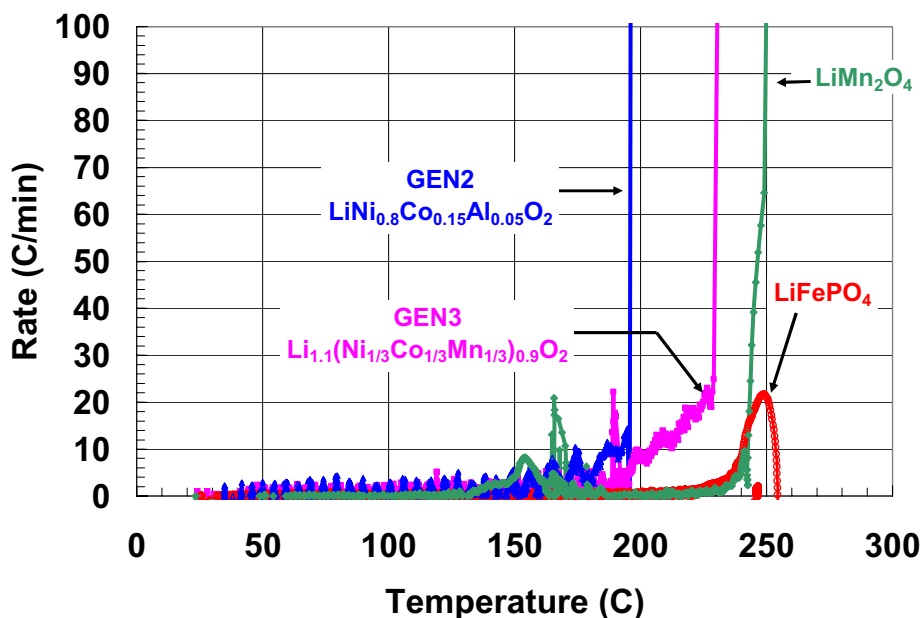


Figure 20. Thermal ramp cell self heating rates of several cell chemistries compared with LiFePO_4 cells.

Effect of Overcharge Shuttle on Improved Abuse Tolerance

One of the most potentially abusive conditions for a Li-ion cell occurs during overcharge. Overcharge can result in Li-plating on the anode, decomposition of the active cathode oxides and high-voltage breakdown of the electrolyte. In addition, heat generation during overcharge can result in separator shutdown which can then result in separator failure. An overcharge shuttle can limit the upper cell voltage by setting up an oxidation/reduction shuttle mechanism between the cathode and anode. This shuttle is activated at a cell voltage above the normal cell operating range and can provide a reversible mechanism to protect the cell from damaging voltage excursions.

Air Products has developed a family of new salts for use in Li-ion Rechargeable Batteries (4). The standard cell electrolyte was replaced with an electrolyte consisting of a 0.4M solution of $\text{Li}_2\text{B}_{12}\text{F}_9\text{H}_3$ and 0.1M LiPF_6 in 3EC:7DEC. The salts are believed to provide protection in overcharge conditions. Specifically, by tailoring the chemistry of the salt, the oxidation and reduction peaks of the salt can be varied around the 4.5V to 4.7V region, providing a shuttle mechanism that could provide overcharge protection.

18650 cells (880 mAh) were fabricated in our laboratory with Gen2 electrodes and using either EC:DEC\1M LiPF_6 baseline electrolyte or the Air Products (AP) electrolyte described above. The cells were placed in the heat flow cell fixture described earlier and overcharged at a 1C rate starting at 100% state of charge (SOC). Figure 21 shows the voltage profiles for the baseline and AP shuttle cells. The baseline cell showed a peak in cell voltage of 5.1V at about 150% SOC followed by a decrease in voltage. The cell heat output and temperature (Figure 22) increased during this overcharge until the cell temperature resulted in shutdown of the separator (Celgard 2325 trilayer). At shutdown, the voltage across the cell increased to the power supply limit of 20V and the cell went into thermal runaway. The AP shuttle cell showed activation of the overcharge shuttle at about 4.45V followed by reduction of cell voltage to 4.25V and then a gradual increase in voltage and heat output with continued overcharge. The cell for this measurement had been punctured to allow monitoring of cell gases so some electrolyte could have been lost resulting in the gradual voltage increase. The cell temperature remained below the separator shutdown temperature during extended overcharge up to 350% effective SOC at which time the run was terminated. Although the shuttle prevented overcharge of the cell, significant heat output resulted from activation of the shuttle. The heat output increased gradually with overcharge but remained below the peak, end-of-charge heat output seen for the baseline cell. Sufficient heat removal would have to be engineered into a final battery design to prevent cell over-temperature and runaway.

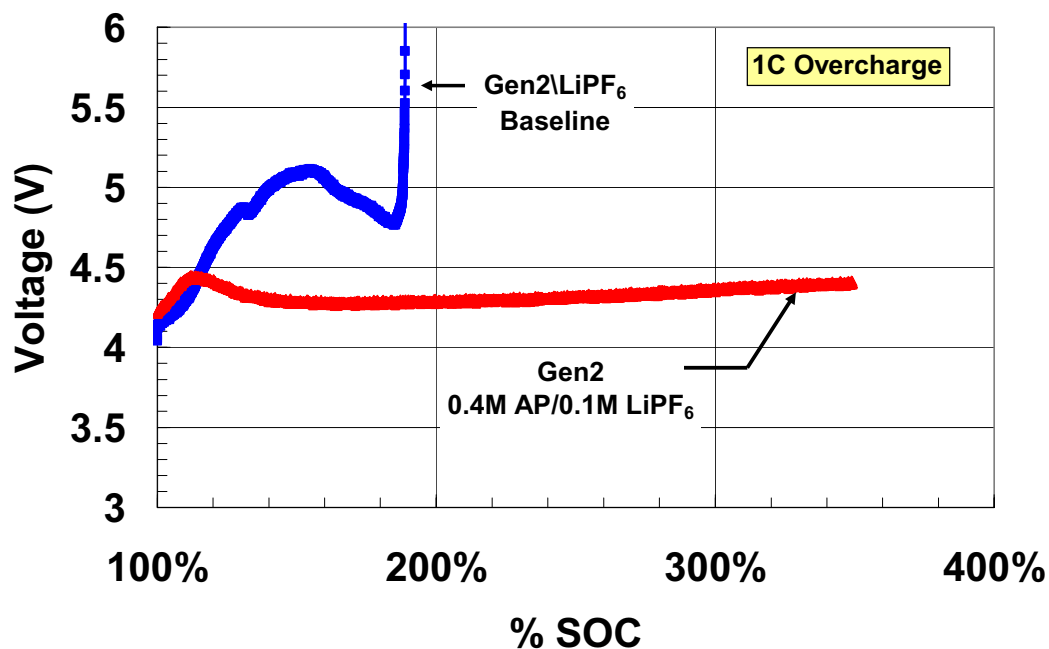


Figure 21. Overcharge voltage profiles for Gen2 cells with baseline EC:DEC\1M LiPF₆ and Air Products overcharge shuttle salt.

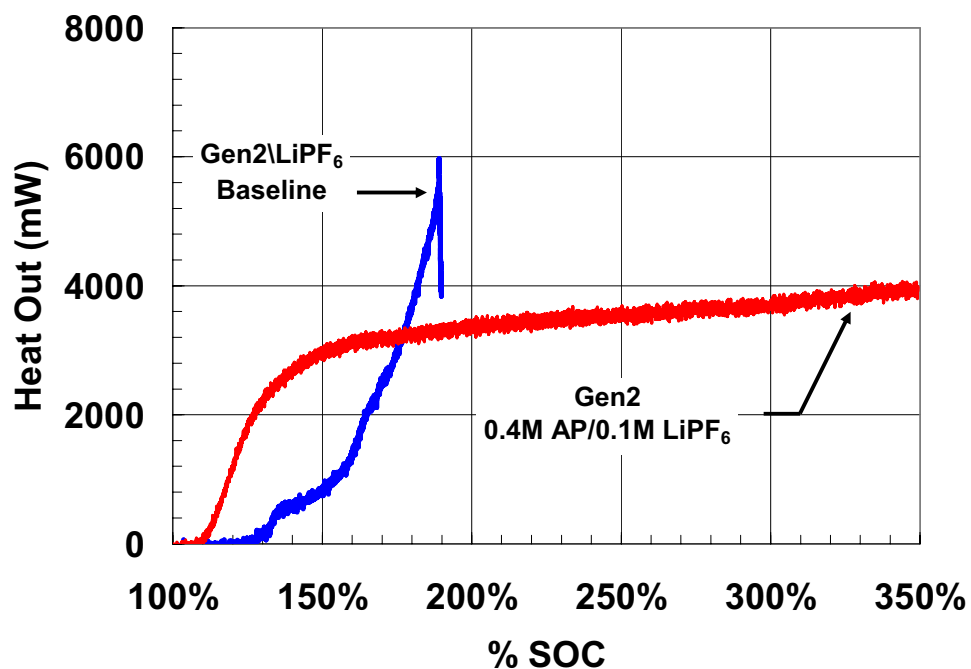


Figure 22. Overcharge heat output profiles for Gen2 cells with baseline EC:DEC\1M LiPF₆ and Air Products overcharge shuttle salt.

Effect of Separator Integrity on Abuse Response

The loss of separator integrity in a cell can lead to immediate, high-rate runaway due to the low-resistance shorting of the electrodes. This failure can occur rarely during normal operation due to an internal defect or more likely during an abuse condition after the separator has experienced melting of all or part of its structure. Three commercial separator materials were evaluated at the material and cell level to characterize this failure mode. Figure 23 shows the AC impedance at 1000Hz as a function of temperature for Celgard 2325, Entek Teklon GOLD LP, and Tonen separators (5-7). The separators shown here were soaked in the high-temperature electrolyte described earlier and measured in compression (~5psi) during a thermal ramp at 10°C/min.

The shutdown temperature varied from 131°C for the Celgard, 139°C for Tonen and 143°C for the Entek material. All of these separators incorporate polyethylene (PE) into their composition and thus showed similar shutdown temperatures at the PE melt temperature. During shutdown, the closed separator pores block ionic transport and thus restrict cell current flow. As the temperature increases the separator softens and pinholes can appear which can result in local conduction. As the separator material contracts at these temperatures, the pinholes can expand leading to a drop in resistance and eventually direct shorting of the electrodes. This final loss of electrode separation is the upper integrity limit of the separators. The Celgard material maintained integrity until above 160°C which corresponds to the melt temperature of the polypropylene component of this trilayer composition (PP/PE/PP). The Entek and Tonen materials both were based only on the PE polymer. The Entek material showed the highest impedance during shutdown but only had about a 10°C stability range. The Tonen material showed the widest stability range with an upper integrity temperature that was in the 190°C to 204°C range. The upper integrity temperature shows more variability due to variations in internal pressure points between the electrodes that cause local stress concentrations and compression of the soft separator. AC impedance measurements under low-voltage conditions gave the most stable shutdown properties for the materials. Measurements were also performed above the shutdown temperature with an applied DC potential (20V) representative of abuse conditions of real cells. The materials initially had to withstand the potential for a minimum of 30 minutes without shorting. Only the Celgard and Tonen separators passed this initial stability test. These materials were then heated at 5°C/min with the potential applied to determine the upper integrity temperature. With the DC potential, local currents through the pinholes can result in localized heating leading to accelerated failure of the separator. Figure 23 shows that the Celgard and Tonen both showed abrupt failure when these currents developed. However, the upper integrity temperatures were both only a few degrees lower than those seen from the AC impedance measurements.

The response of the separators above shutdown in full cells was also determined during overcharge abuse testing. During overcharge, the cell temperature continually increased until shutdown was reached and the voltage across the cell increased to the power supply voltage limit (20V). The cell was then monitored as a function of time until failure. Figure 25 shows the voltage/current profiles above shutdown for a cell with the Celgard separator charged at 1.4 amps (1C). Transition into the shutdown impedance state took almost one minute. The current then decreased slowly down to about 300 mA over a period of about two minutes at which time the separator failed. There was a brief increase in current and the cell then went into thermal runaway, ejecting the cell contents.

Figure 26 shows the cell temperature, cell heat output and electrical power input during this event. During the one minute transition into the shutdown state there was an increase in the power input to the cell but this transient power input did not result in any significant cell heating. The cell went into thermal runaway immediately at the temperature where cell shorting was observed. The cell skin temperature at shutdown was 110°C but the cell internal temperature was at the PE melt temperature of 135°C. Previous work with internal thermocouples confirmed that this amount of temperature difference can exist during overcharge. This cell separator response was in good agreement with the separator behavior observed for just the separator materials. Thus AC impedance and voltage breakdown screening is a useful tool for comparing separators and determining cell level response.

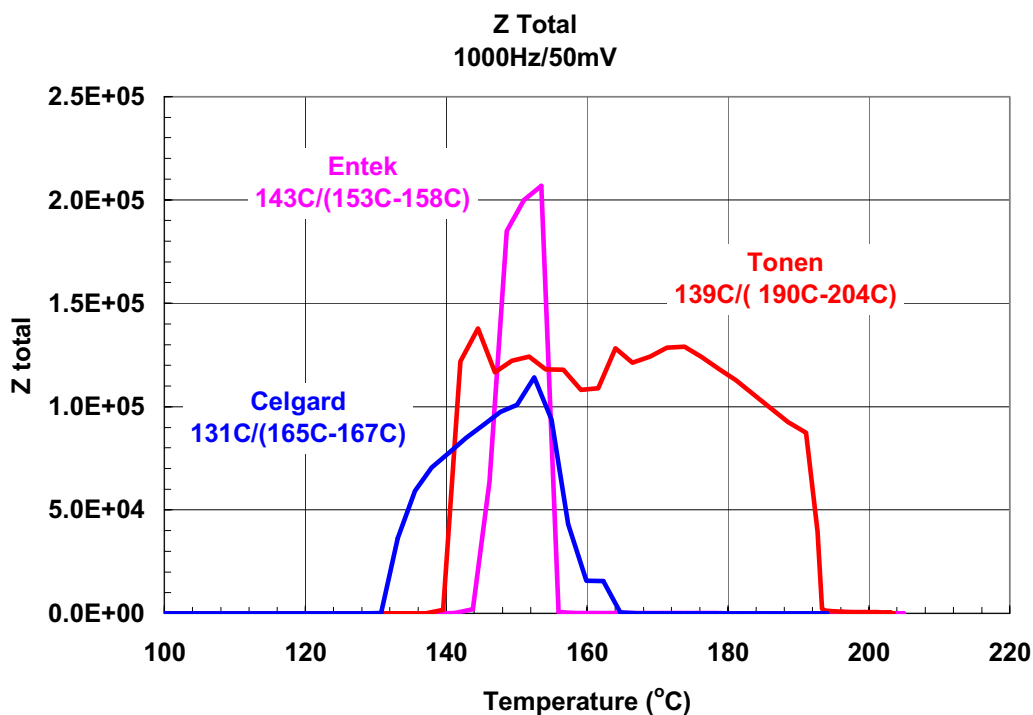


Figure 23. AC Impedance of three commercial separator materials.

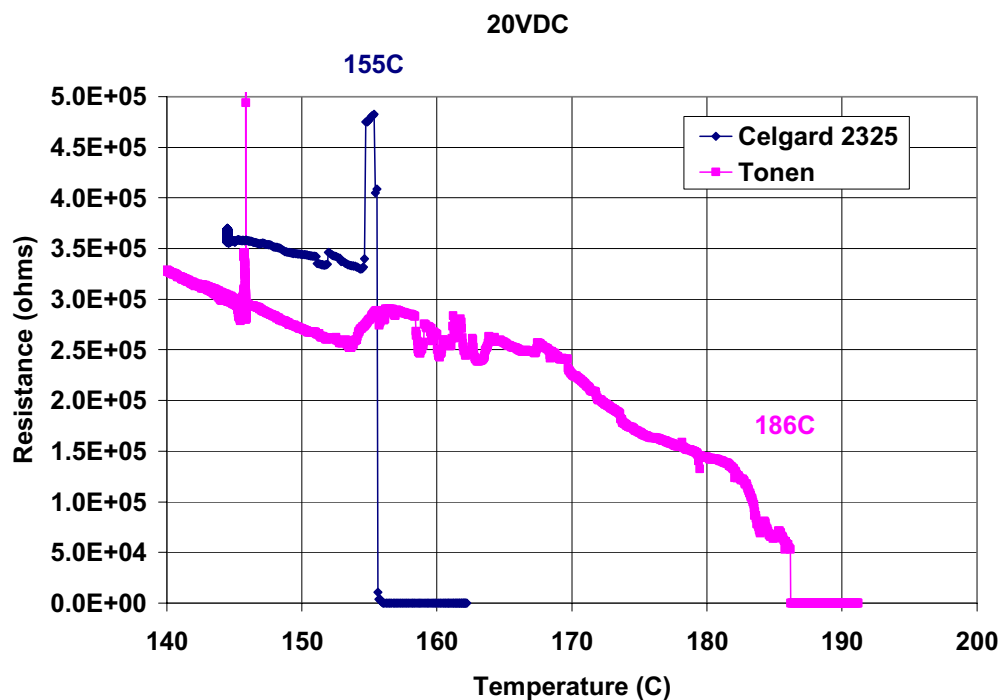


Figure 24. DC voltage breakdown at 20V of two separator materials above shutdown temperature.

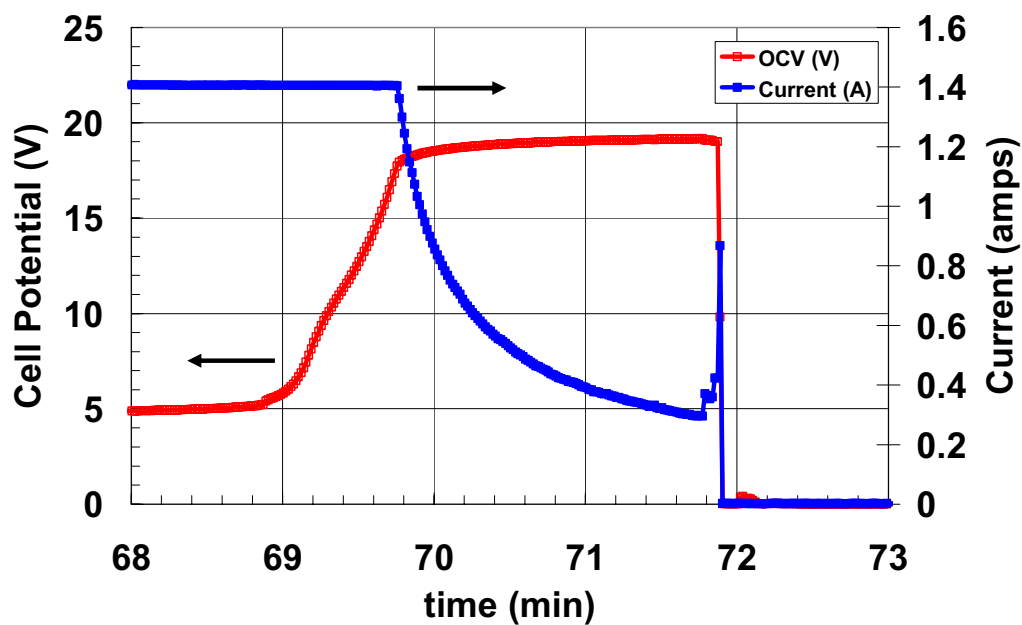


Figure 25. DC voltage breakdown at 22V for full cell above shutdown temperature with Celgard separator.

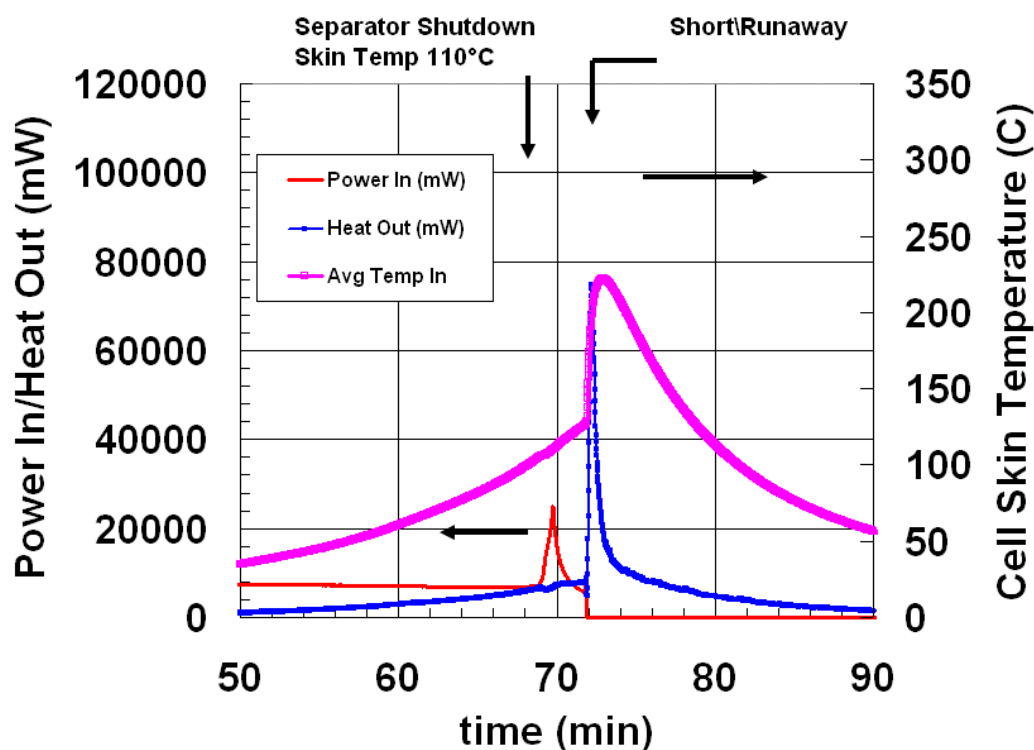


Figure 26. Thermal profile during DC voltage breakdown for full cell above shutdown temperature with Celgard separator showing temperature, heat output and power input.

Summary

The thermal abuse response of Li-ion cells has been shown to be a complex function of anode, cathode and electrolyte reactions. Separator integrity has also been shown to be critical to cell stability and abuse tolerance. Highly exothermic reactions can lead to high-rate thermal runaway, gas generation and combustion of the flammable electrolyte. New materials have resulted in steady improvement in the failure response of the cells, reducing the total reaction enthalpy and reaction rate. Cells are now exhibiting more graceful failures than the early chemistries which showed high-rate decomposition with ejection of the cell contents. New pack designs for plug in hybrids increase the total stored energy from the 1 kWh level to more than 10 kWh and will require greatly increased attention to safety and reliability.

Acknowledgements

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.

References

1. The FreedomCAR program description can be found at:
<http://www1.eere.energy.gov/vehiclesandfuels>
2. E. P. Roth, D. H. Doughty, J. Power Sources 128 (2004) 308-318.
3. A123 Systems, Inc., ONE KINGSBURY AVE.WATERTOWN, MA 02472
4. Air Products and Chemicals, Inc., 7201 Hamilton Blvd., Allentown, PA, 18195-1501
5. Celgard, LLC, 13800 South Lakes Drive, Charlotte, NC 28273
6. ENTEK Membranes LLC, 250 N. Hansard Ave, P.O.Box 127, Lebanon, OR 97355
7. Tonen Chemical Corporation (TCC), an affiliate of EXXONMOBIL CHEMICAL CO., 729 Pittsford-Palmyra Rd., Macedon, NY 14502