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Effect of Cathode Composition on Abuse Response of 18650 Li-Ion Cells

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Abstract: 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. Anode, cathode, and electrolyte interactions have been measured for chemistries chosen to meet the high-power requirements of the DOE Advanced Technology Development (ATD) Program. The peak thermal runaway response is largely determined by the oxygen release from high-temperature cathode decomposition while the importance of anode reactions increases for the more stable cathodes. We report here on quantitative measurements of the reaction enthalpies during thermal runaway for cells with several of the leading cathode chemistries used for Li-ion applications.

Keywords: Li-ion; abuse tolerance; cathode composition

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]. 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 under abusive conditions of over-temperature to determine the effects of new materials on intrinsic abuse response and these responses correlated with measured cell material thermal properties.

Experimental

MATERIALS - Anodes used consisted of intercalating carbon materials such as MCMB while cathode materials were used that are representative of current and future Li-ion cells as shown below. 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 $LiPF_6$.

18650 test cells have been constructed using:

Anode:	MCMB
	Natural graphite (GDR)
Cathode:	$LiCoO_2$, $LiMn_2O_4$
	$LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (Gen2)
	$Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$ (Gen3)
	$LiFePO_4$
Electrolyte:	EC/EMC (3:7)\1.2M $LiPF_6$
	EC:PC:DMC (1:1:3)\1.2M $LiPF_6$
Separator:	Celgard 2325, Tonen

Cells were wound in our laboratory in the 18650 configuration using coated electrodes with these

cathode compositions and using either GDR or MCMB anodes resulting in cells with nominal 0.6–1.5Ah capacity. In addition, some commercial 26650 cells were also measured for comparison.

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 runway. 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. Cells were also measured in a thermal ramp apparatus that allowed measurement of cell heat generation and observation of cell venting and thermal events. Possible ignition of the vent gases were measured using ignition sources placed around the fixture. Real-time gas analysis using FTIR and mass spectrometry allowed determination of the gas species during the overcharge.

Results and Discussion

The ARC thermal runaway profiles for several cathode chemistries are shown in Figures 1 and 2 ranging from the highly-reactive $LiCoO_2$ to the stable $LiFePO_4$. The reaction enthalpies and kinetics decreased with decreasing oxygen generation at high temperatures and the onset for runaway moved to higher temperatures. This correlation with oxygen release is shown by comparison with TGA data for two of the main cathode chemistries (Gen2 and Gen3) as shown in Figure 2. TGA runs were performed for charged cathode materials that had been washed and dried to remove any electrolyte components. Three runs were made on each with increasing ramp rate. The more reactive Gen2 material, Figure 4, showed the greater mass loss and higher decomposition kinetics as shown by the similarity of the mass loss with increasing ramp rate. The more stable Gen3 material showed the lower mass loss, especially in the peak reaction region up to 350°C and also showed lower kinetics as seen in the lower mass loss at higher ramp rate as shown in Figure 5.

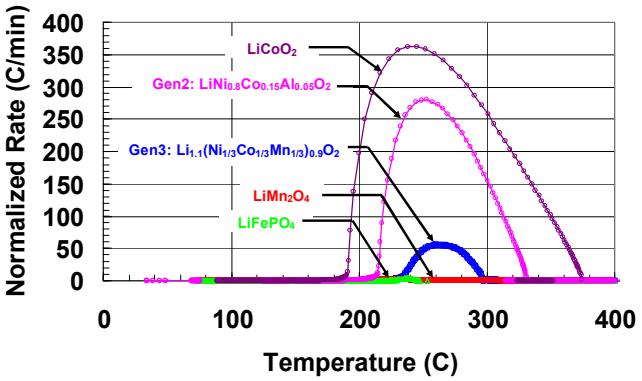

Figure 1 ARC thermal runaway profiles for 18650 cells with increasing cathode stability.

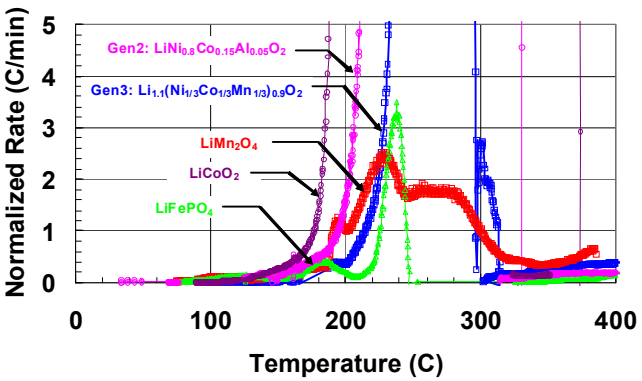

Figure 2 Expanded view of ARC thermal runaway profiles showing low-rate reactions by $LiMn_2O_4$ and $LiFePO_4$ cathodes.

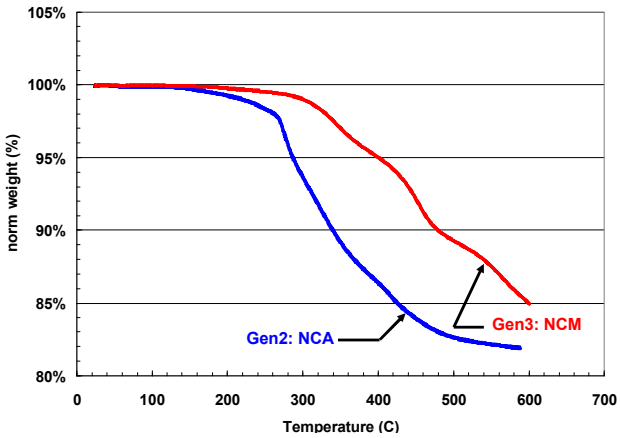

Figure 3 TGA profiles for Gen2 and Gen3 cathodes showing decreasing oxygen release at high temperatures.

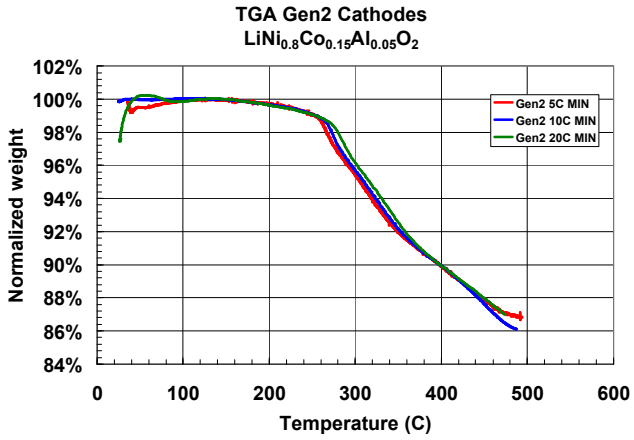

Figure 4 TGA profiles for Gen2 cathodes.

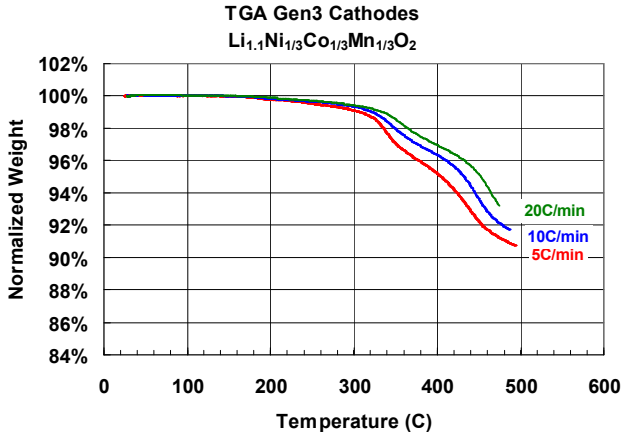

Figure 5 TGA profiles for Gen3 cathodes.

Cells were also ramped at 5 °C/min in an open block apparatus to measure thermal runaway and flammability of the vent gases. Figure 6 shows the temperature\time profile showing cell thermal runaway during the ramp.

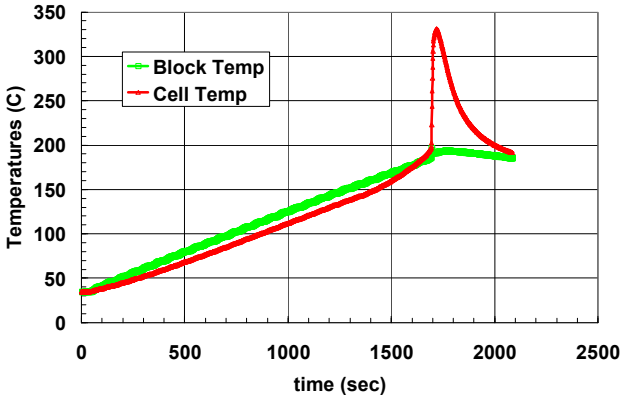

Figure 6 Thermal block and cell temperature during thermal ramp to runaway.

The improvement between Gen2 and Gen3 cathode chemistries is shown in Figure 7 where the heating rate for each cell is plotted as a function of cell temperature. The more stable Gen3 cathode shows a lower initial heating rate starting at 145°C leading up to thermal runway and also a higher thermal runaway temperature (225°C vs. 190°C).

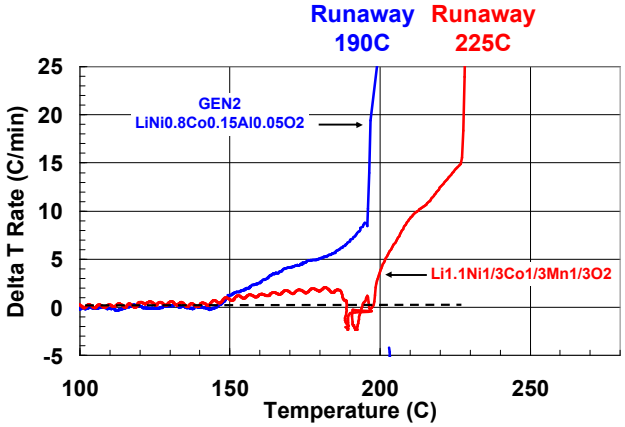

Figure 7 Cell heating rates during thermal ramp for Gen2 and Gen3 cathodes.

The contributions of the individual anode and cathode were measured by cutting open a fully charged cell in an argon glove box and removing the electrodes. The individual electrodes were resealed in 18650 cans with equal amounts of electrolyte and run in the ARC. Figure 8 shows the ARC profile for a full Gen2 cell and the corresponding cathode. The profiles are nearly identical indicating that the cathode dominated the runaway for the Gen2 chemistry.

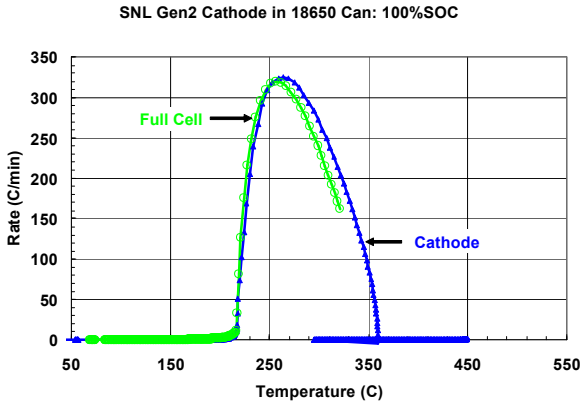

Figure 8 ARC profiles for a full 18650 Gen2 cell and just the Gen2 cathode electrode resealed in an 18650 can with electrolyte.

Electrodes for Gen3 cells were likewise measured. Figure 9 shows the ARC profiles for a full cell, anode, and cathode. The anode and cathode contributed equally to the cell thermal runaway peak. Also seen is the decomposition peak for the electrolyte which was added in excess for that run.

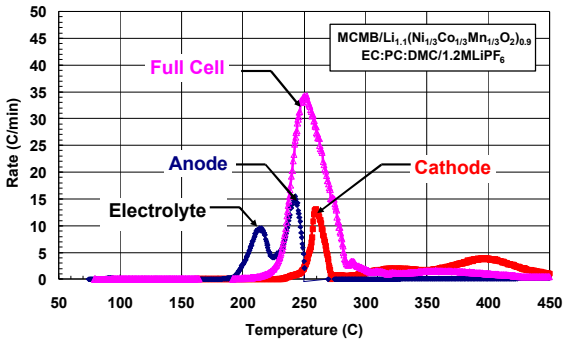

Figure 9 ARC profiles for full 18650 Gen3 cell, anode, cathode and electrolyte.

Figure 10 shows the cell thermal ramp self-heating rates for several cathode chemistries including two commercial 26650 cells with $LiFePO_4$ and a $LiMn_2O_4$ spinel cathode. Again, improved abuse response was seen for cathode chemistries with decreasing oxygen release indicated by the higher runaway temperatures. Even though the $LiFePO_4$ cathode does not release oxygen, a low-rate thermal runaway was observed at 240°C. The onset of thermal runaway was very similar to that for the $LiMn_2O_4$ cathode indicating that both cells were dominated by the anodes. Even though the heat generation was reduced, cell venting and ignition of the aerosolized electrolyte still occurred.

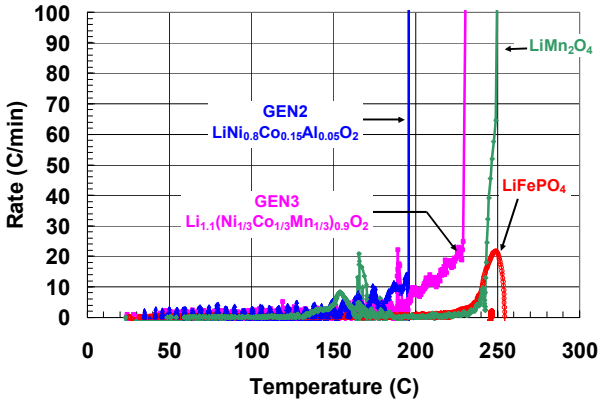

Figure 10 Thermal ramp cell heat generation profiles for 18650 cells with decreasing oxygen generation

Conclusions

Although significant improvements have been achieved in the abuse tolerance of Li-ion cells, several safety issues still remain. Anode reactivity needs to be reduced as well as electrolyte gas decomposition and flammability.

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.

Acknowledgements

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