Cell Comp't Thermal Reactivity & Improvements

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Objectives of the work

- Identify the role of each cell material/component in the abuse characteristics of different cell chemistries.
- Identify and develop more stable cell materials that will lead to more inherently abuse tolerant cell chemistries.
- Secure sufficient quantities of these advanced materials (and electrodes) to supply SNL for validation and quantification of benefits in 18650 cells.

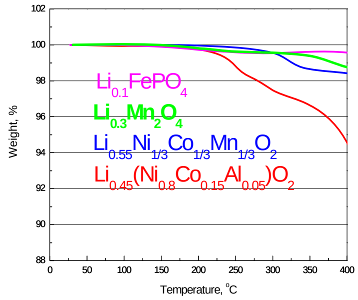
Approaches for understanding the role of each cell material on the safety of the battery

- Correlate the loss of oxygen from the charged cathode "$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiMn_2O_4$, and $LiFePO_4$" with the heat generated from the oxidation of the electrolyte
- Investigate the heat generated from cathodes during high rate charge and discharge
- Investigate the effect of surface area and morphology of cathodes on the safety of the cell
- Understand the role of the SEI film breakdown from carbon surface on the thermal behavior of the cell
- Investigate the relationship between the surface area of the carbon and the heat from SEI breakdown
- Investigate the relationship between the particle morphology of the carbon and the heat from SEI breakdown
- Quantify the role of the SEI breakdown by studding anodes that doesn't require SEI such as $Li_4Ti_5O_{12}$
- Investigate the possible oxidation of the separator from the oxygen release from the oxide cathode.

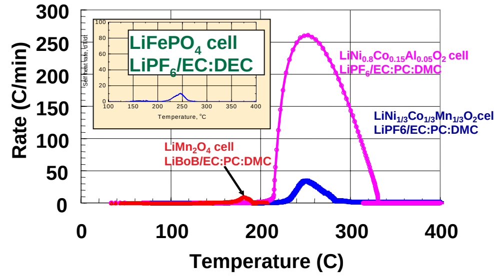
Approaches for identifying & developing stable chemistry for better abuse tolerance

- Coating cathode particle with stable nano-films of Al-oxide or Al-fluoride that act as a barrier against electrolyte reactivity with cathodes
- Investigate the effect of new functional electrolyte additives that forms stable passivation film at the carbon surface which can lead to the reduction of the overall heat generated from the SEI breakdown.
- Investigate the effect of new ANL redox-shuttle on improving the overcharge protection of lithium batteries

Amount of oxygen release from the cathode impact significantly the cell safety



Arc on 18650 cells, source SNL



In general the cathode play dominant role in the thermal runaway of the cell. Cathodes that generate less oxygen provide better safety characteristics

$LiFePO_4$>$LiMn_2O_4$>NMC>NCA>$LiCoO_2$

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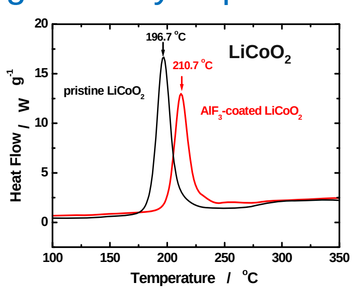
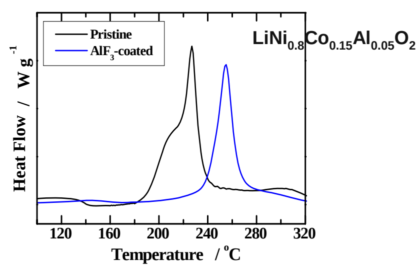
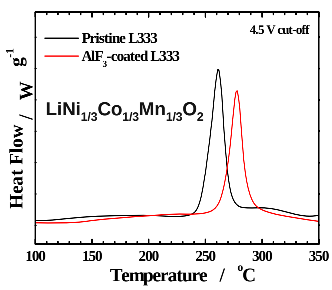
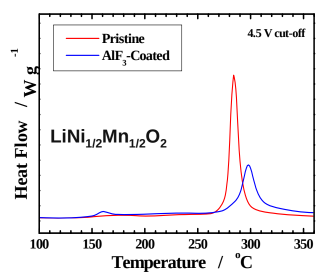
Increased cathode surface stability with AlF_3 coating can significantly improve the abuse tolerance of the cathode

DSC Scans









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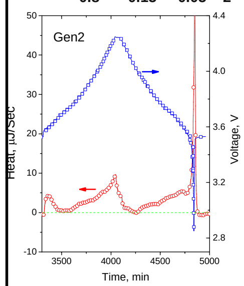
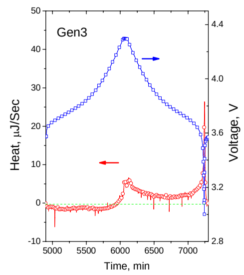
Heat profiles from Isothermal microcalorimeter different cathode materials during cycling

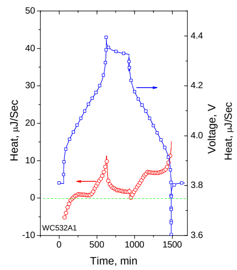
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$



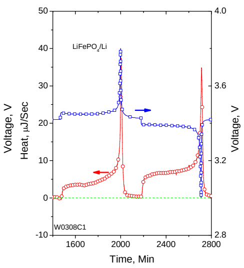
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$



$LiMn_2O_4$



$LiFePO_4$



✓Gen 2 shows increasing exothermic heat during charge and discharge
✓At the end of discharge significant heat is observed

✓Gen 2 shows endothermic heat during charge and small exothermic heat during discharge
✓At the end of discharge small heat is observed

✓Spinel shows endothermic heat during charge and small heat afterward
✓At the end of the discharge very small heat is observed
✓Spinel when overcharged shows very small heat

✓Olivine shows increasing exothermic heat during charge & discharge
✓At the end of the charge & discharge significant heat is observed

Internal cell temperature using infrared camera of cylindrical $LiFePO_4$ olivine/carbon cell when discharged at 13 C rate

62.5°C

<66.7°C

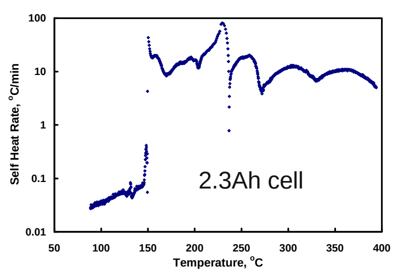
13C Discharge rate

The observed heat inside the olivine cell could be caused by the heat coming from the carbon as well as $LiFePO_4$

Role of carbon anode on the safety of lithium batteries

- Cathode reactivity with the electrolyte was shown to be the dominate reaction in the cell
- Recent study using over 2.3 Ah cell comprising a stable $LiFePO_4$ cathode and carbon anode shows that the cell want on mild thermal run away.
- Role of carbon anode in a big cell can't be ignored regardless of the choice of the cathode chemistry

Heat from the carbon anode can induce a thermal runaway in olivine cell

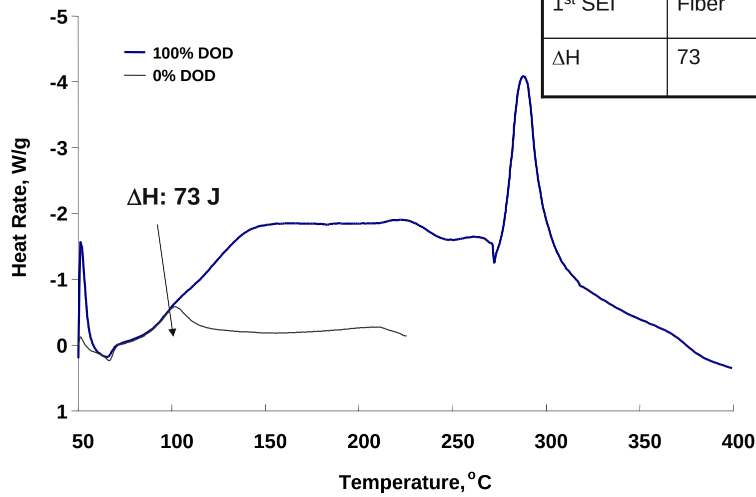


Olivine cells could go to thermal runaway.

Carbon can also play a significant role on safety of lithium ion batteries

Heats profile from primary and secondary SEI decomposition in graphite

1st SEI	Fiber	MCMB
ΔH	73	62.3



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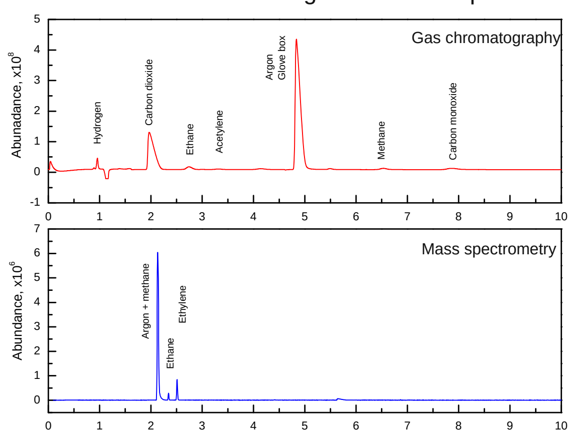
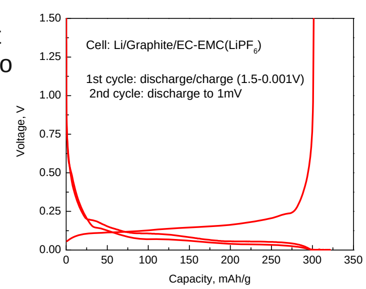
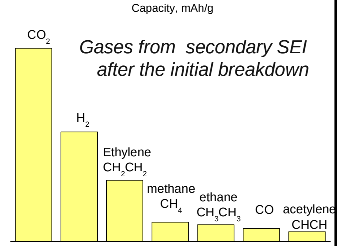
Gas from the formation of the secondary SEI Layer on carbon

Several gases from secondary SEI formation were observed after exposing charged carbon/Li cell at 100°C for several hours. These gases are similar to the one observed during the formation process







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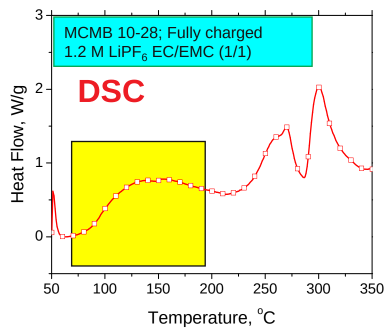
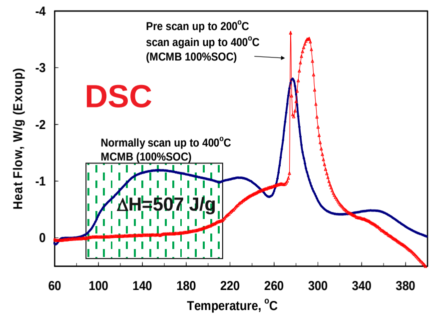
Heat generated from the decomposition of the secondary SEI can initiate the thermal runaway of the cell





- The thermal heat generated by the continuous breakdown and formation of the SEI (80ºC~200ºC) could trigger the early thermal run away observed in the cell

- This heat could be large enough to lead to the thermal runaway of the cell regardless of the nature of the cathode specially in large cells

MCMB : ΔH : 1552 J/g

Preheated MCMB: ΔH : 1045J/g

Heat from secondary SEI: ΔH=507 J/g

Investigate Role of Graphite/Carbon Properties

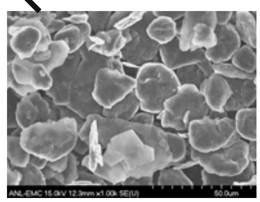
- SEI heat generation can depend on:
  - Morphology (spherical vs. flake) (effect on SEI)
  - Type of carbon (natural graphite, synthetic graphite, soft carbon, hard carbon)
  - Surface area (effect on SEI)
  - Particle size
  - Surface coating
- Effect of surface area and particle size were investigated using different graphites having the same morphology (same manufacturer)
- Effect of surface coating was investigated by studying same graphite before and after carbon coating

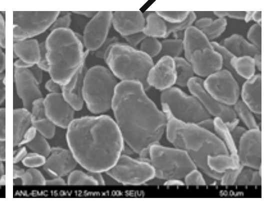
Hitachi Chemical Graphite Materials used in Study

Natural graphite samples were recently obtained from Hitachi Chemical for use in this study. They are coated with soft carbon, possess similar morphology, and cover an average particle size range from 7-20 µm.

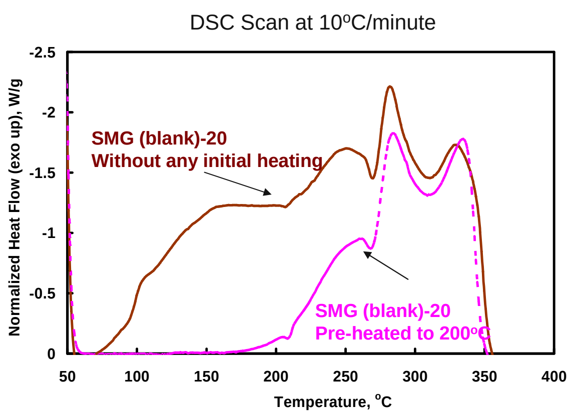
Material	*Unit*	*MCMB*	*SMG-NAL1-20C*	*SMG-NAL1-15C*	*SMG-NAL1-10C*	*SMG-NAL1-7C*	*SMG (blank)-20*
Average Particle Size	µm	25	23.4	17.4	11.9	7.8	19.8
S.S.A	x10^3 m^2/kg	1.3	2.0	2.9	4.2	6.3	5.0

Reference Material



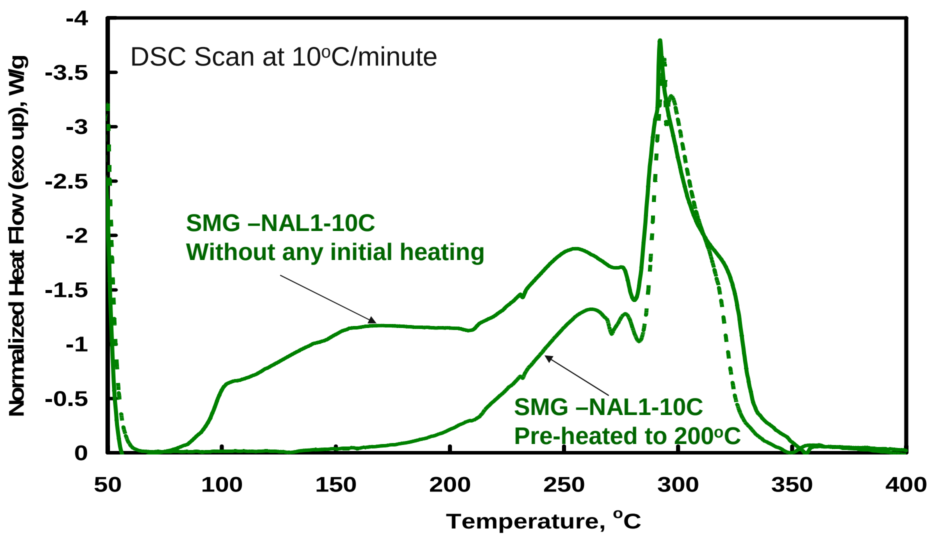


Determination of SEI Heat from Fully-Lithiated SMG (Blank)-20

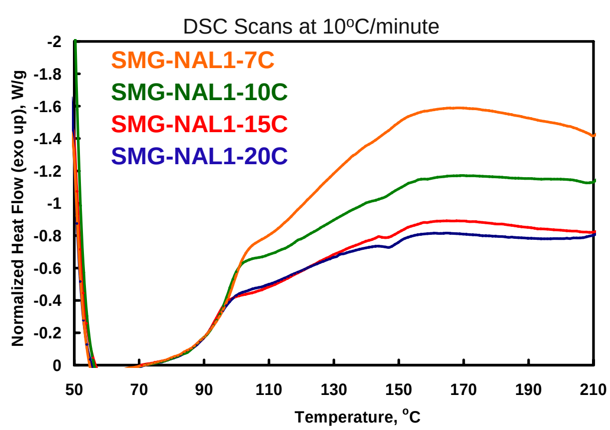


The heat from the breakdown of the SEI was determined contrasting total heat from two DSC scans on the same lithiated graphite. In one case, the lithiated graphite was preheated to 200ºC to decompose and react the SEI prior to running the DSC scan.

Determination of SEI Heat from Fully-Lithiated SMG-NAL1-10C

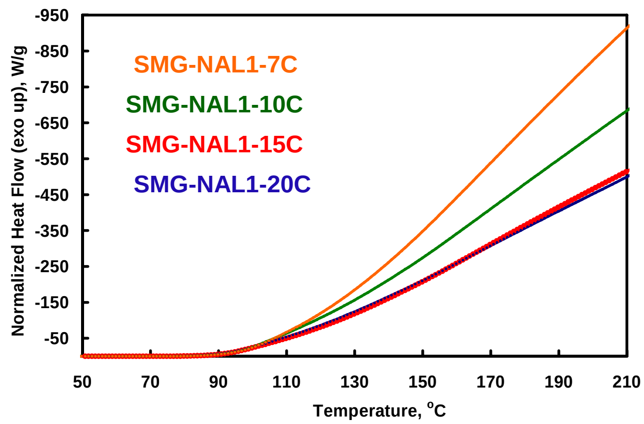


Comparison of SEI Decomposition Heats from Hitachi Graphites



Large particle size and low surface area reduces SEI decomposition heat generation between 80 to 200ºC

Comparison of Accumulated Heat Flow



Large particle size and low surface area reduces SEI decomposition heat generation between 80 to 200ºC

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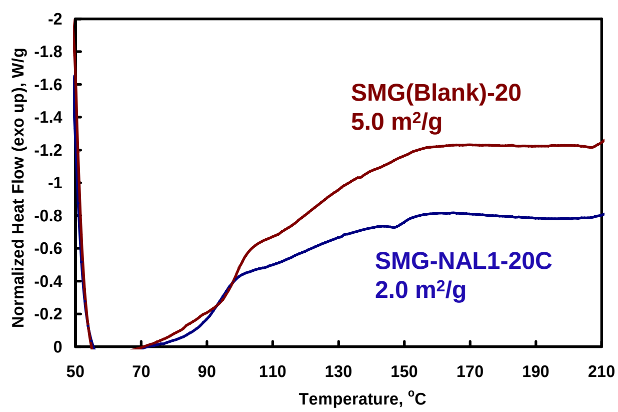
Effect of Carbon Coating & Reduced Surface Area

DSC Scan at 10ºC/minute



The soft carbon coated material has a lower surface area and exhibits improved thermal behavior between 80 and 200ºC

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Summary Information on Hitachi Graphite Samples

Material	Unit	MCMB	SMG-NAL1-20C	SMG-NAL1-15C	SMG-NAL1-10C	SMG-NAL1-7C	SMG (blank)-20
Average Particle Size	µm	25	23.4	17.4	11.9	7.8	19.8
S.S.A	x10^3 m^2/kg	1.3	2.0	2.9	4.2	6.3	5.0
Capacity Obtained	mAh/g	345	354	355	331	327	339
Irreversible capacity	mAh/g	45	42	56	52	51	55
Heat due to SEI Decomposition	J/g	-507	-716	-762	-1149	-1222	-993
Ratio of SEI heat to total heat	%	29	29	40	49	61	55

These 2 materials exhibit lowest SEI heat and lowest ratio of SEI/Total heat.

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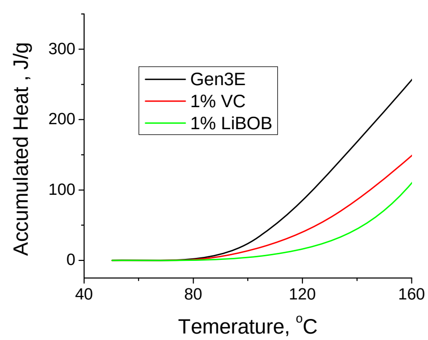
Use of electrolyte additives could be very effective in reducing the heat caused by the secondary SEI breakdown



The use of electrolyte additive to stabilize the SEI can reduce the initial heat generated from the carbon below 180°C

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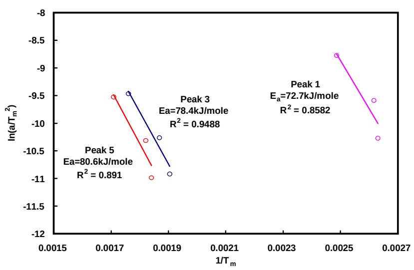
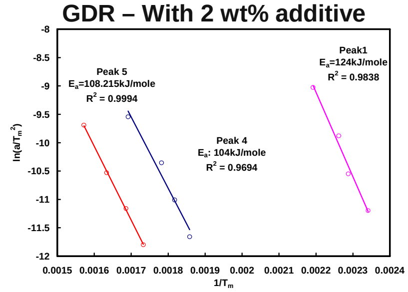
Carbon with stabilized SEI and round morphology improves the safety of lithium batteries



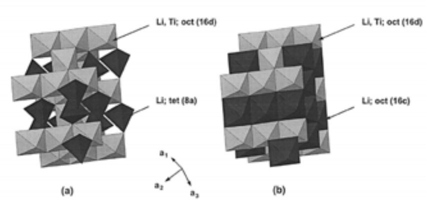


Arrhenius plots for different peaks in the DSC scans of GDR-spherical anode

Thermal parameters	Mag-10		GDR	
	w/o	w	w/o	w
$T_{onset\ T}$ °C for SEI	83	83	84	115
E_a kJ/mol	21	78.1	72.7	124

additive reduces significantly the self heat from SEI and increases the activation energy of reaction with electrolyte

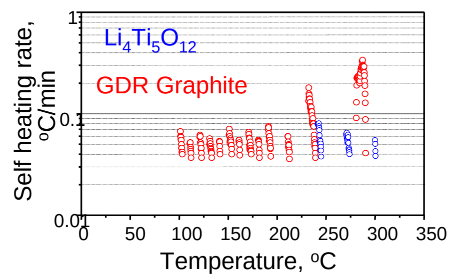
Alternative anode such as $Li_4Ti_5O_{12}$ can impact significantly the safety characteristics of lithium batteries



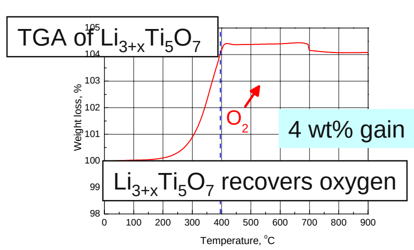
$Li_{8a}[Li_{1/3}Ti_{5/3}]_{16d}O_4$;
a = 8.36 Å*

+ Li →

$[Li_2]_{16c}[Li_{1/3}Ti_{5/3}]_{16d}O_4$;
a = 8.35 Å



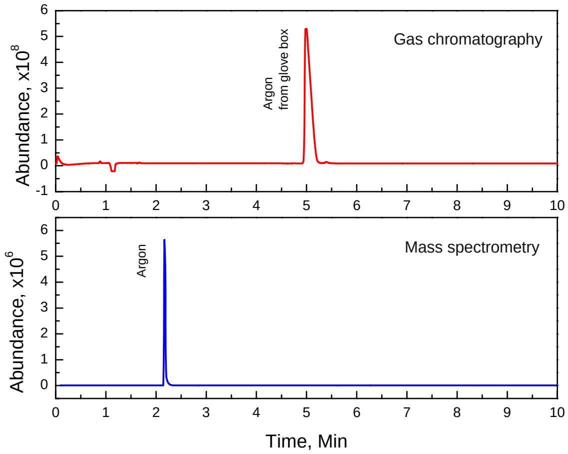
$Li_4Ti_5O_{12}$ + 3 LiC_4H_9/C_6H_6 → $Li_7Ti_5O_{12}$
Spinel — Rock salt



✓No heat is generated below 200°C in $Li_4Ti_5O_{12}$. Safety of the cell will depend on the choice of the cathode

✓$Li_7Ti_5O_{12}$ react with Oxygen and could impact the safety of the cell in a positive way (Oxygen release from the cathode and the oxidation of the electrolyte is responsible for thermal run away)

Heat generated from SEI breakdown could be prevented by using anode that doesn't require SEI to work



No gas is observed after exposing charged $Li_{4+x}Ti_5O_{12}$/Li cell at 100°C for several hours. Only Ar from dry box is detected by GCMS

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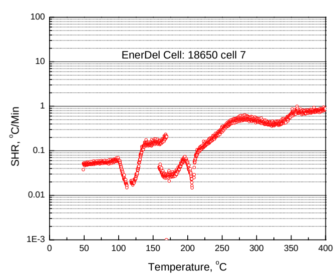
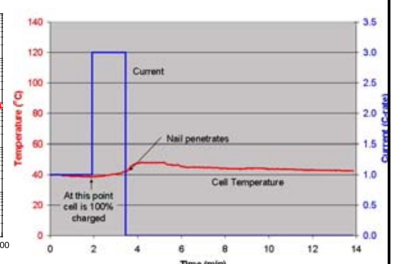
Result of $Li_{1.06}Mn_{1.94}O_4$/$Li_4Ti_5O_{12}$ cell after different safety test

Before ARC After ARC

Photo of the cell before & after Arc test



ARC test shows extremely low heat generation Within the noise of the ARC



Nail penetration after 15%overcharge of the cell shows no even happening. Cell temperature increased by 7°C

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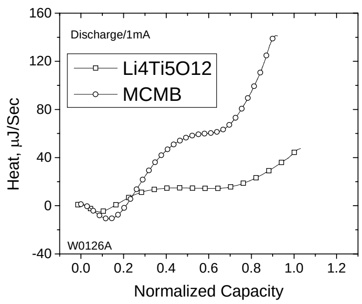
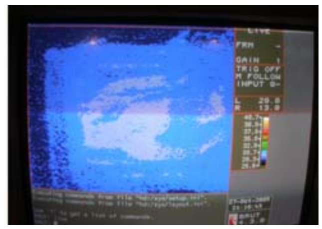
Entropy change and heat generation during cycling of $Li_4Ti_5O_{12}$ and MCMB graphite



Heat generation from Isothermal microcalorimeter during 1C discharge of $Li_4Ti_5O_{12}$ and MCMB based cells

31°C



$LiMn_2O_4/Li_4Ti_5O_{12}$ (50C) continues Discharge

The heat from cells containing $Li_4Ti_5O_{12}$ generate very little heat when charged and discharged at very high rates

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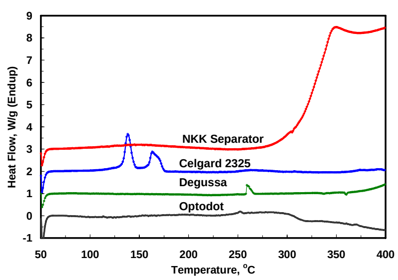
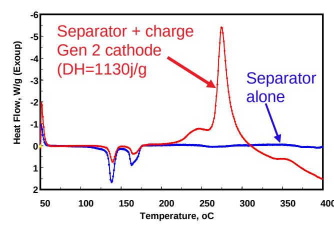
Reactivity between charged cathode " $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$) and separator is not negligible



DSC of different separator without the presence of charged Gen 2 cathode



DSC of Celgard separator as it is and in the presence of charged Gen 2 cathode. (oxidation of separator is significant & initiated at 200°C)

The reactivity between the charged cathode and the separator can't be ignored. However, this reaction take place at high temperature and could add to the violence of the thermal run away of the cell

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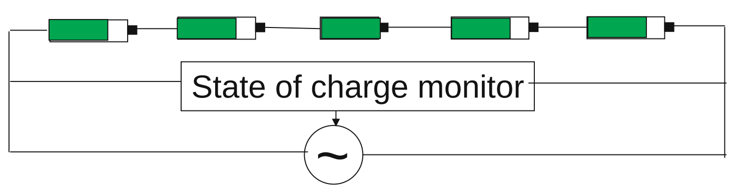
ANL new stable redox shuttle to improve overcharge tolerance of lithium ion batteries

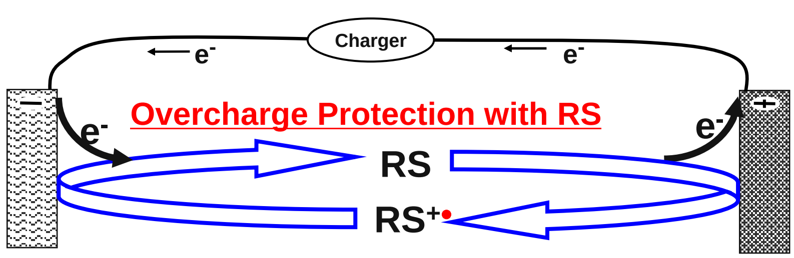
- Overcharge is one of the most severe abuses for lithium-ion batteries that can result in thermal runaway.

- Redox shuttle role:
  - Provide intrinsic overcharge protection for lithium-ion batteries.
  - Improve performance (depending on redox shuttle potential)
  - Balance the cells in a battery configuration

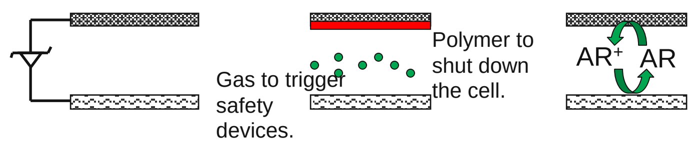
Mechanism of redox shuttle

•ANL have been investigating new redox shutle additives to prevent overcharge



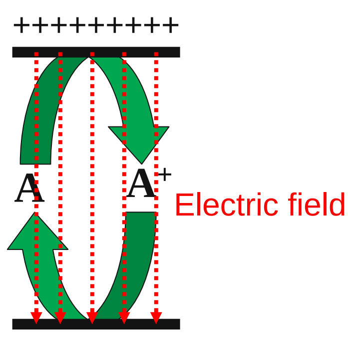


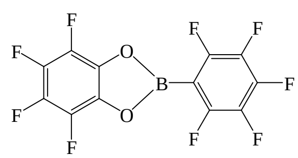
Overcharge protection strategies in lithium ion batteries



	External voltage regulation	Inactive agent	Redox shuttle
Physical device:	**External circuit**	**Electrolyte additive**	**Electrolyte additive**
Weight, cost and volume	**-----**	**++++**	**++++**
Mechanism:	**electronic regulation**	**Permanently inactivation gassing, polymerization**	**active protection reversible shuttle**
Heat management:	**++++**	**----**	**----**

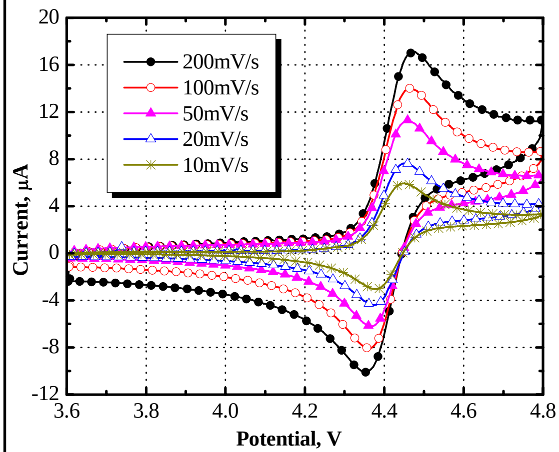
Efficiency of redox shuttles

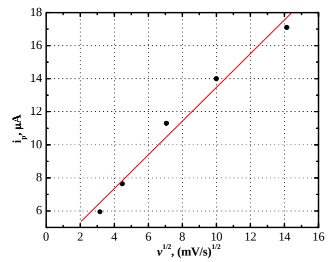




4.2V ANL-RS

Cyclic voltammograms of 5 mM ANL-RS in Gen3E



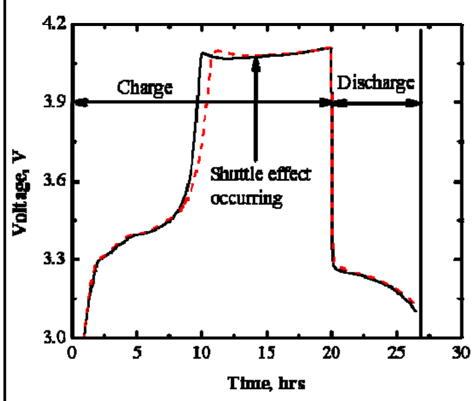


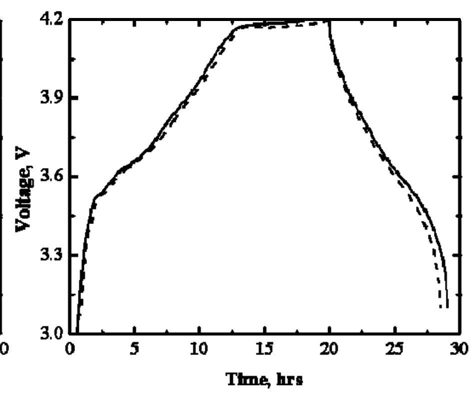
$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C$$

D≅1.4 × 10^{-6} cm^2/s

Gen3E= 1.2 M $LiPF_6$ in EC/EMC (3:7 by weight).

Voltage profiles of Lithium-ion cells when overcharged using ANL-RS

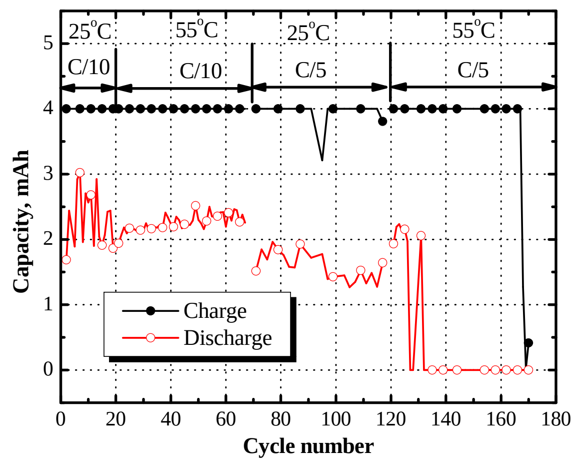




MCMB/$LiFePO_4$ with ANL-RS

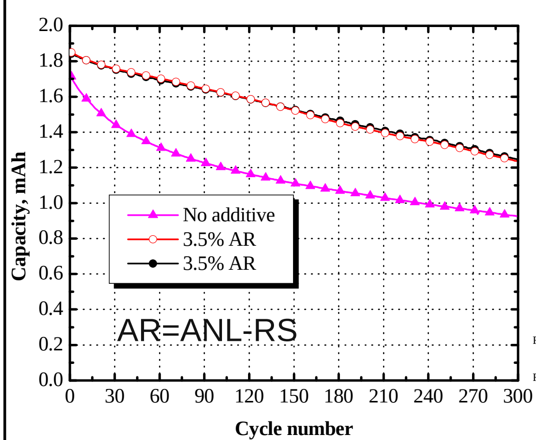
MCMB/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ with ANL-RS.

Repeated overcharge of MCMB/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ with ANL-RS

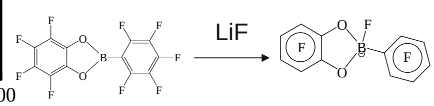


Additional functionality of ANL-RS –

MCMB/$Li_{1.1}[Mn_{1/3}Ni_{1/3}Co_{1/3}]_{0.9}O_2$ @ 55°C



ANL-RS helps to dissolve LiF generated during the formation and normal operation. Hence, ANL-RS can improve the performance of the lithium-ion cell as well.



FY 2007 Accomplishments & Conclusions

- Verified role of cathode materials on thermal abuse (w/SNL)
  - Oxygen released from cathodes reacts with electrolyte solvents to produce heat
  - Spinel generate low heat compared to layered or olivine cathodes during high rate cycling
  - Supplied electrodes, electrolyte and additives and in some cases cells to SNL
  - ANL result at the component level was verified/quantified in 18650 cells (via collaboration with SNL)
- Demonstrated improved thermal characteristics with AlF_3 coated cathode materials, via surface stabilization
- Quantify the role of carbon/SEI on thermal abuse
  - Initial data show that the breakdown of the conventional SEI on high surface area graphites/carbons can produce sufficient heat to trigger a major thermal event (need to verify/quantify at cell-level in collaboration with SNL)
- Initiated work on role of electrolyte additives in reducing heat from breakdown of SEI (between 80 and 170°C)
- Initiated work on redox shuttle to address overcharge abuse issues

Future Work

Graphite Anode Thermal Studies:

- Conduct detailed study on effects of carbon morphology on cell safety
- Investigate potential benefits of several electrolyte additives and study impact of surface area and particle size on effectiveness of the additives
- Investigate potential benefits of non-carbonaseous surface coatings
- Verify graphite SEI heat impact in 18650 cells, via collaboration with SNL
  - ANL will secure electrodes (for high energy design 18650 cells) using $LiFePO_4$ and different SMG graphites
  - Electrodes will be shipped to SNL for cell fabrication and abuse tests

Cathode Thermal Studies:

- Further investigate potential benefits of surface coatings (to expand on results obtained in FY 2007) and demonstrate the coating effect on the 18650 cells
- Investigate the effect of cathode morphology on safety (quantify the effect in 18650 cells)

Other Material-Level Studies:

- Investigate the effect of several redox shuttle on the safety of the cell
  - Provide samples to SNL for evaluation in 18650 cells
- Investigate new non-flammable electrolyte and ionic liquids developed by Bridgestone & Nippon Chemical via a collaborative work with ANL, and SNL,

Publications & patents

publications

1. Electrochemical and Thermal Investigation of Li4/3Ti5/3O4 Spinel
W. Lu, I. Belharouak, J. Liu, and K. Amine; **J. Electrochem. Soc. 154(2), A114-A118 (2007)**

2. Isothermal calorimetry investigation of Li1+*x*Mn2−*y*AlzO4 spinel
W. Lu, I. Belharouak, S.H. Park, Y.K. Sun, K. Amine; **Electrochimica Acta, 52, 5837–5842 (2007)**

3. Safety Characteristics of the Li4Ti5O12/LiMn2O4 Li-Ion Battery
I. Belharouak, W. Lu, D. Vissers, and K. Amine; **Mater. Res. Soc. Proc. Vol.972, 339-344 (2007)**

4-Bifunctional Electrolyte Additive for Lithium-Ion Batteries, Zonghai Chen, and K. Amine,
Electrochem. Commun., 9(4): 703-707 (2007).

5- Understanding the Stability of Aromatic Redox Shuttles for Overcharge Protection of Lithium-Ion Cells Zonghai Chen, Qingzheng Wang, and K. Amine,; **J. Electrochem. Soc., 153(12): A2215-A2219** (2006).

6. Investigation of Flame-Retardant Additives for Safety Usage of Lithium-Ion Batteries
M. Otsuki, T. Ogino and K. Amine***; ECS Transactions*, 1: 13-19 (2006).**

7. In Situ Thermal Study of Li[sub 1 + x][Ni[sub 1/3]Co[sub 1/3]Mn[sub 1/3]][sub 1 - x]O[sub 2] Using Isothermal Micro-clorimetric Techniques
W. Lu, I. Belharouak, and K. Amine; ***Journal of The Electrochemical Society*, 153: A2147-A2151 (2006**).

Patent:

1 patent issued and 2 patent applications

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