Impact of Battery Material on Safety and ways of mitigating the thermal runaway of Lithium Batteries for Automotive Application

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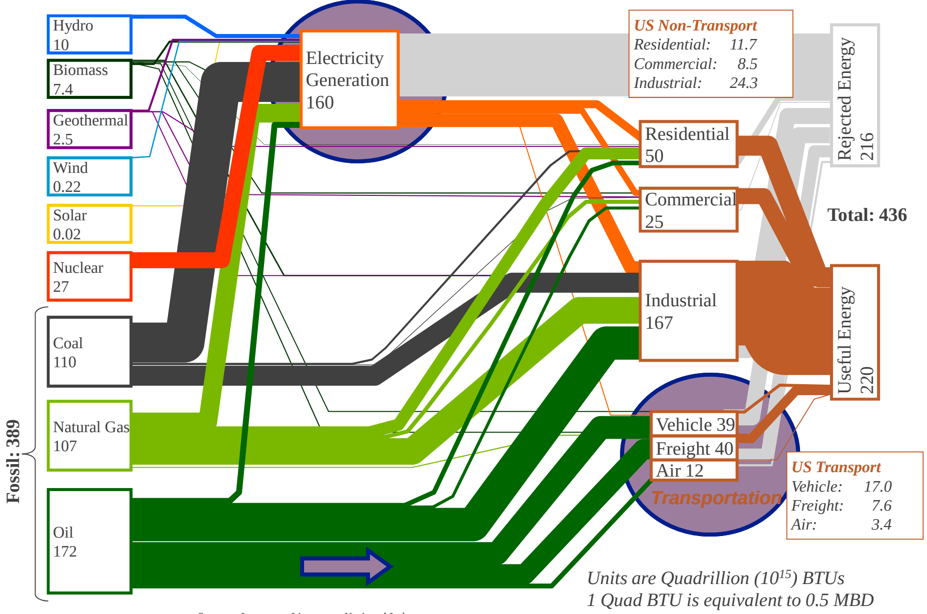
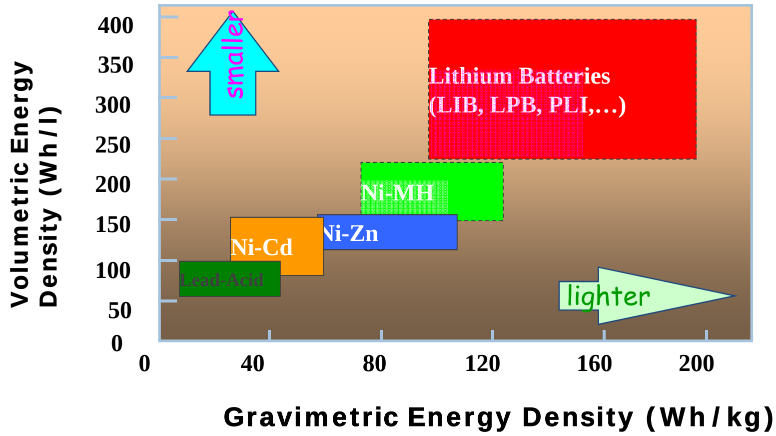
2009 Global Human-Activity Energy Flows

- *Transportation the only major industry dependent on only 1 energy supply chain*
- *Electricity serves as unifying energy carrier for diverse energy resources*

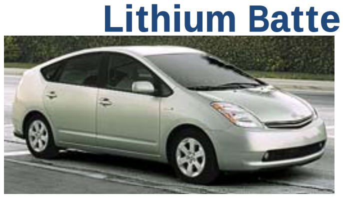


Source: Lawrence Livermore National Laboratory

Why Lithium Ion Battery is so attractive



Key Barriers that need to be overcome to enable Lithium Batteries in HEVs, PHEVs and EVs

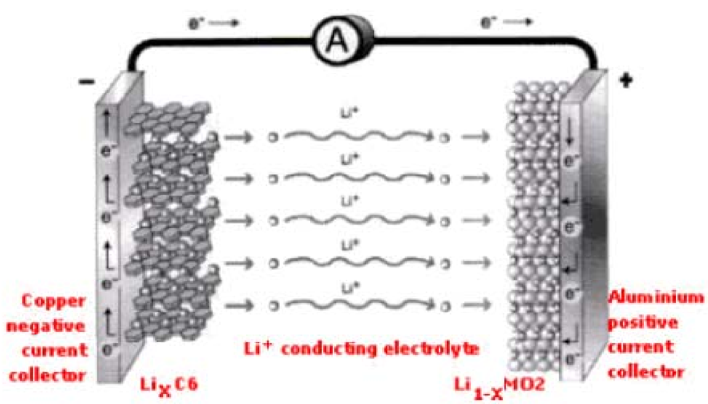


- **Calendar Life:** 15-year life
- **Cost:** ($20/kW).
- **Abuse Tolerance:** Tolerance to overcharge, crush, and high temperature exposure.
- **Low Temperature Performance:** -30°C cold cranking

- **Argonne leads the DOE applied program to develop advanced batteries technologies for transportation**
  - Spinel-$MnLi_{1+x}Mn_{2-x}O_4$ system
  - $LiNi_xMn_yCo_zO_2$ (NMC) system
  - $LiFePO_4$ system

One of the major Technical Barriers for Current Lithium Ion Batteries is safety

Which components in Lithium battery is responsible for safety?



Anode Electrolyte cathode

Impact of Cathode on safety

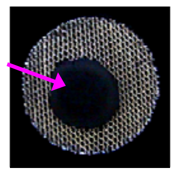
The role of each component of the $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode was investigated by DSC using the following study :

- Charged $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ positive powder without binder and carbon
- Charged $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ positive powder with binder only
- Charged $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ positive with carbon additive only
- Charged $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ positive electrode (with binder and carbon additive)

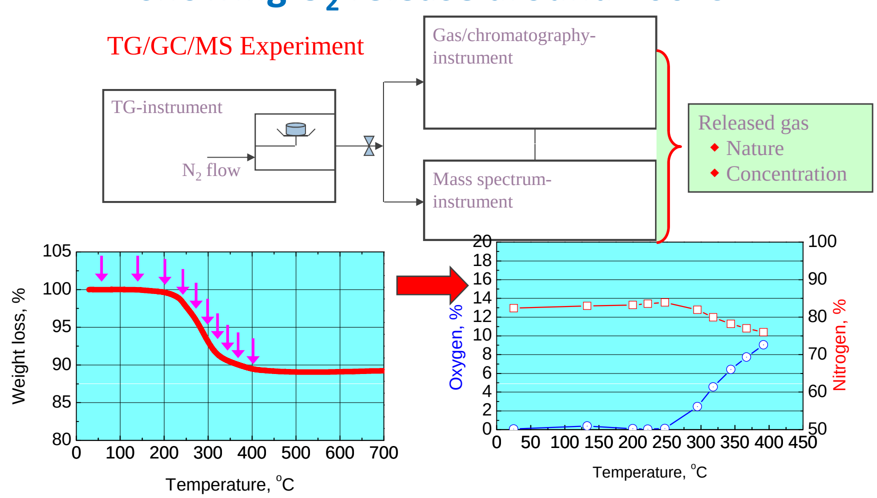
<u>Electrolytes used:</u>

- 1.2 M $LiPF_6$ in (EC:EMC) (3:7) (Gen 2 electrolyte)
- EC alone
- EMC solvent alone
- $LiPF_6$ salt alone

active powder is pressed against a mesh and then charged vs Li/Li^+ . Capacity obtained after charge is similar to that in a normal electrodes (150mAh/g)

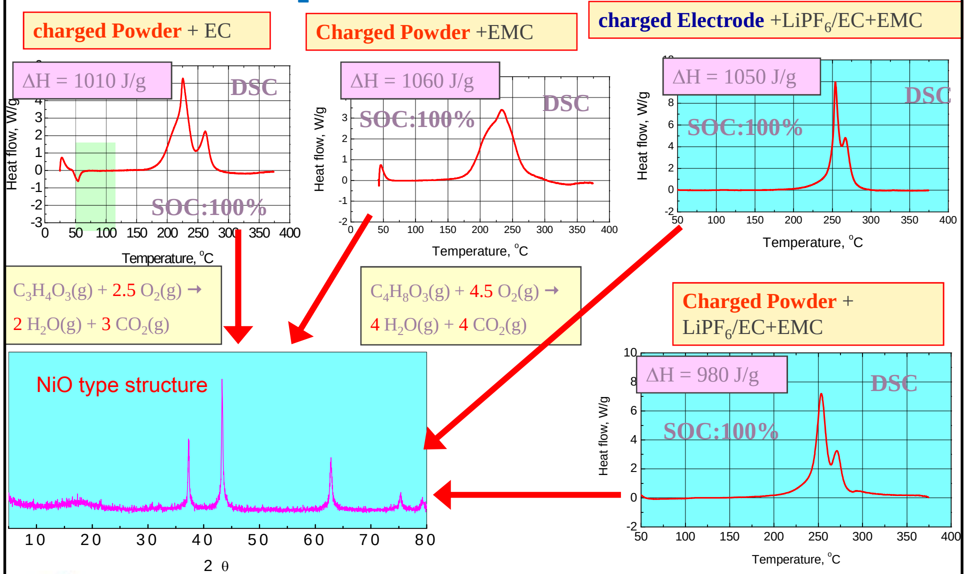


TG/GC/MS of charged cathode Powder showing O_2 release around 200°C



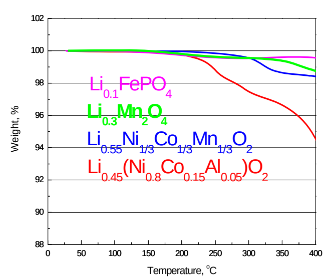
Oxygen release from charged cathode powder

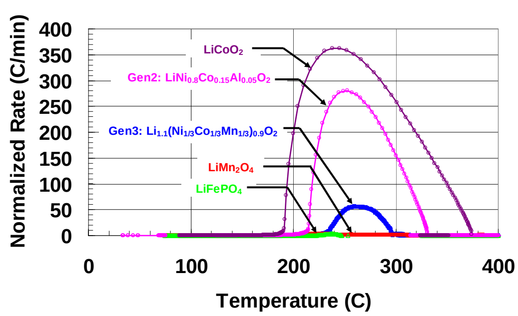
Reaction at the cathode is caused by the oxidation of solvent from O_2 generated from decomposed cathode



Different cathodes show different safety impact on lithium ion batteries

- **Oxidation of solvent from the O_2 generated by cathode is responsible for the thermal run away of lithium batteries**
- **Cathode that generate more oxygen could lead to unsafe lithium batteries**





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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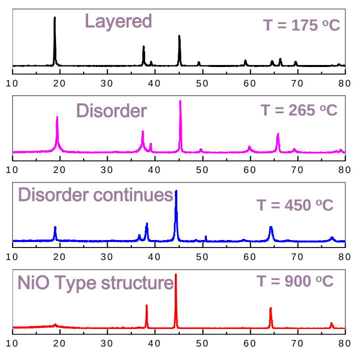
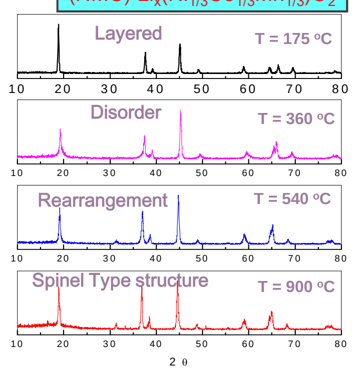
X-ray Diffraction of Delithiated NCA and NMC Cathodes at different temperatures

(NCA) $Li_x(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$



(NMC) $Li_x(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$

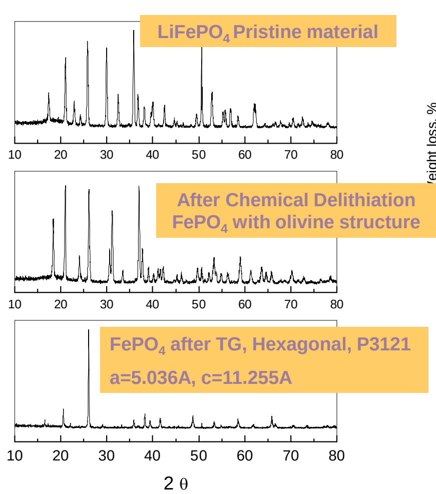


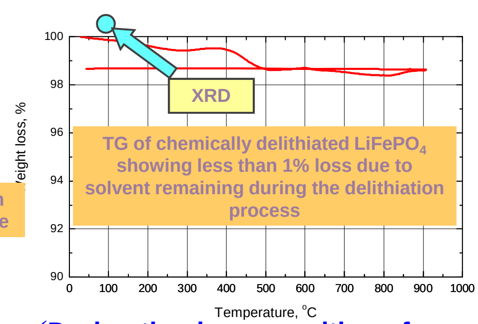
$(Ni_{0.8}Co_{0.15}Al_{0.05})O_2 \rightarrow (Ni_{0.8}Co_{0.15}Al_{0.05})O + 1/2\ O_2\uparrow$

$(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2 \rightarrow 1/3\ NiCoMnO_4 + 1/3\ O_2\uparrow$

The formation of the spinel structure during the decomposition of $Li_{1-x}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ is responsible for low O_2 gas release in this material

Olivine $LiFePO_4$ has the best thermal behavior because no oxygen is released during the decomposition of the material

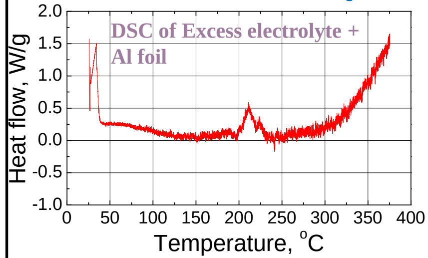


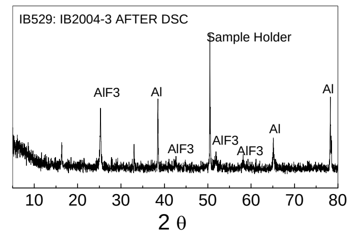


✓During the decomposition of delithiated $FePO_4$, a new stable $FePO_4$ with hexagonal structure is formed

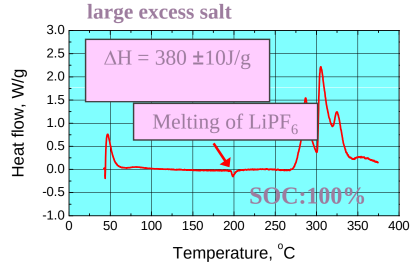
✓No oxygen is release during the decomposition process resulting in much better safety characteristics

All other reactions between the NCA cathode components are minor

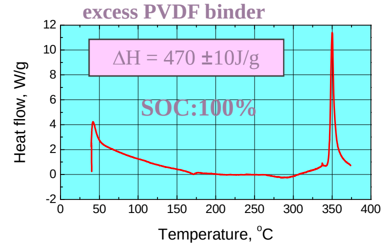




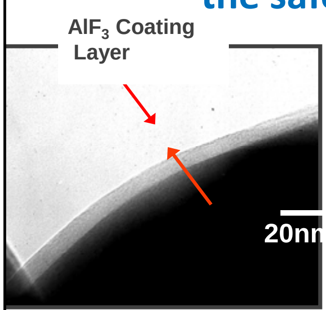
DSC of cathode powder + large excess salt



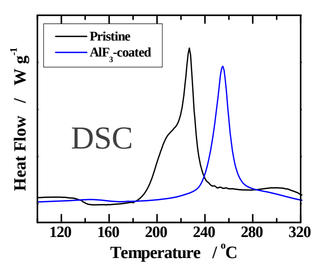
DSC of cathode powder + large excess PVDF binder



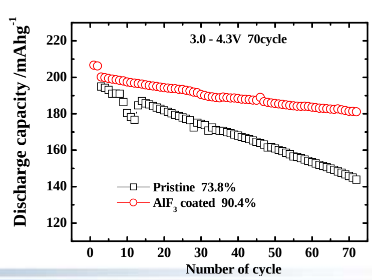
Coating the cathode particle with AlF_3 can improve the safety of the lithium battery



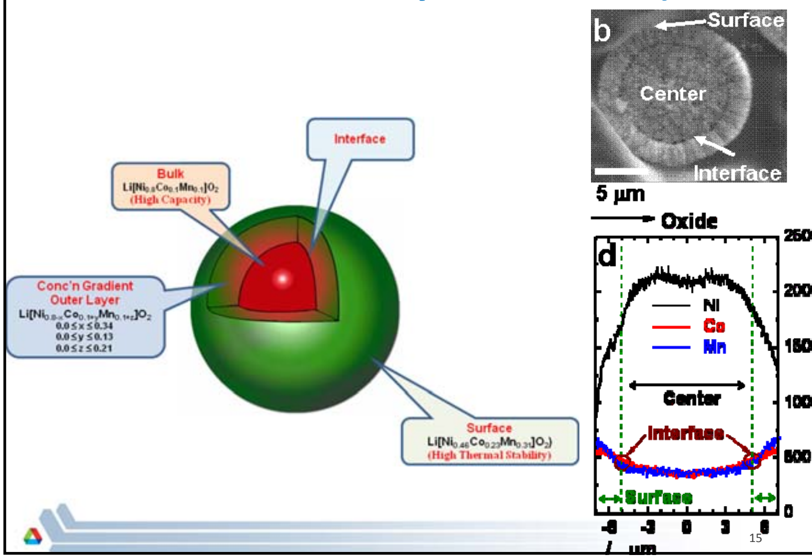
HRTEM of AlF_3 coated NCA



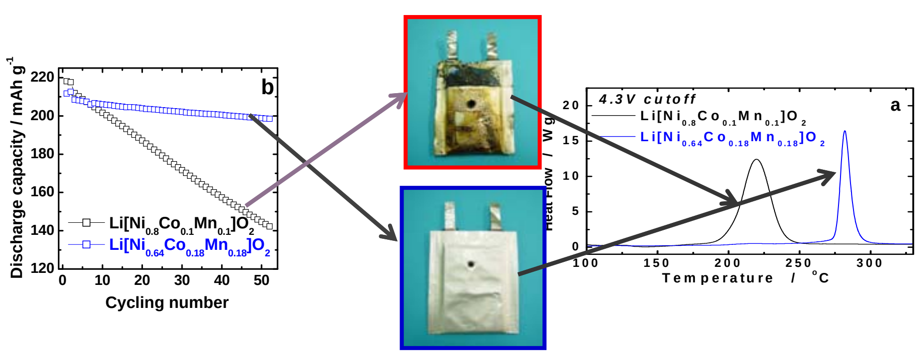
DSC of AlF_3 coated and non-coated NCA



Using Functional material design (Gradient concentration material to improve life & safety of cathodes)



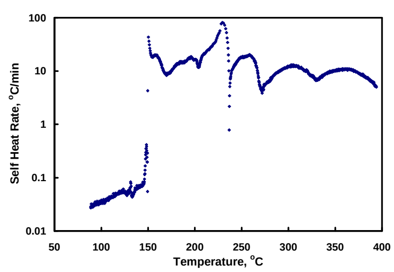
Gradient concentration material improves life & safety of cathodes



Possible mechanisms of reaction at the cathode

- ☑ The main reaction at the cathode is due to the oxidation of solvent by oxygen released from the cathode at high temperature.
- ☑ Cathodes that generate less oxygen during the thermal decomposition should exhibit better thermal behavior
- ☑ All other reactions with binder, salt, carbon additive, Al current collector are very minor
- ☑ Surface protection trough coating, functionality or additive improves significantly the safety of the cathode

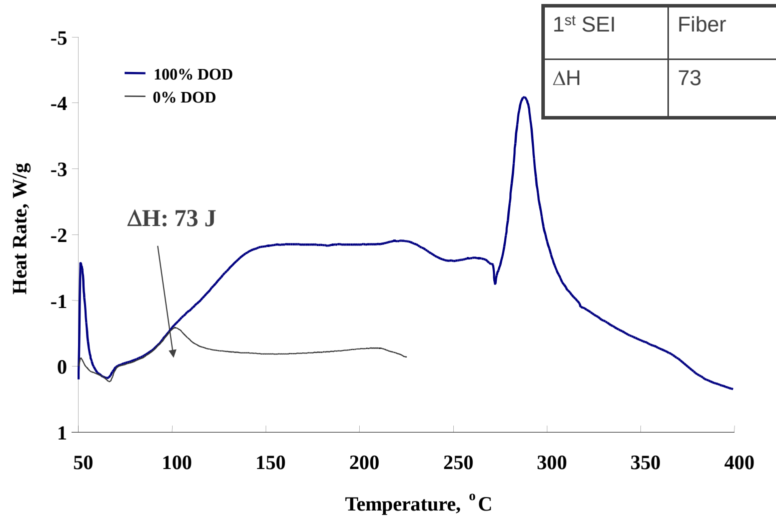
Heat from the high surface area carbon anode can induce a thermal runaway in olivine cell



Olivine cells could go to thermal runaway if the cell has high surface area Carbon

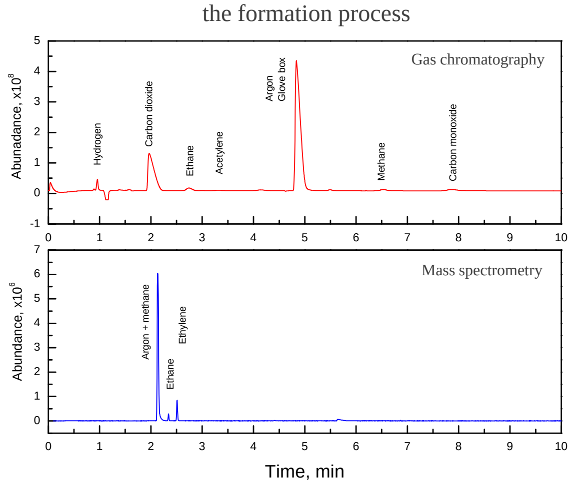
Heats profile from primary and secondary SEI decomposition in graphite

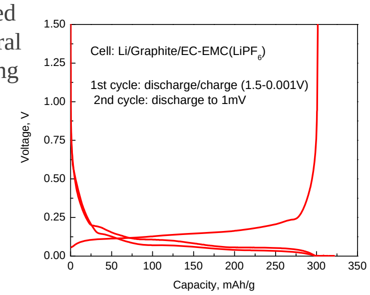
1st SEI	Fiber	MCMB
ΔH	73	62.3

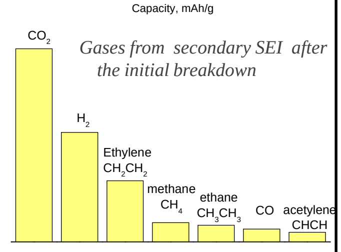


Gas from the formation of the secondary SEI Layer on carbon

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



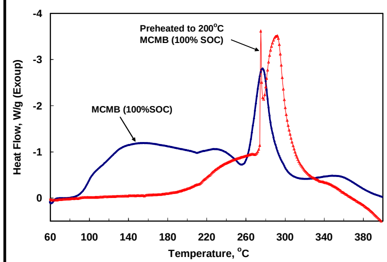




Gases from secondary SEI after the initial breakdown

Effect of graphite surface area on the amount of heat generated by the decomposition of SEI film (primary and secondary)

DSC of charged MCMB , and charged MCMB that has been first preheated in the electrolyte to 200°C

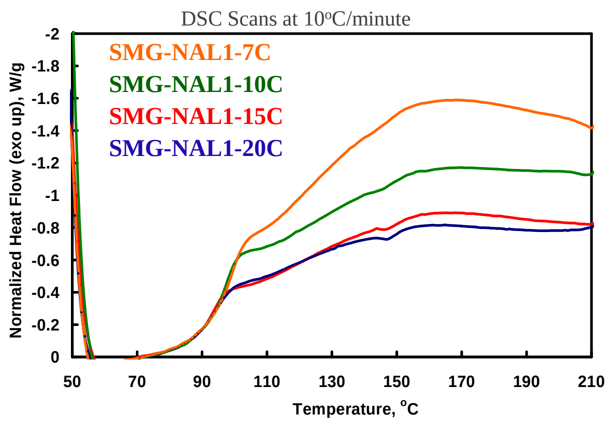


MCMB :ΔH : 1552 J/g
Preheated MCMB:ΔH : 1045J/g
Heat Generation from second SEI (80°C to 200°C) 507 J/g

	Overall Heat Generation	(DH /SEI decomposition) (80 °C- 200°C) Normalized by Sample Weight	BET Area (m^2/g)	(DH from SEI decomposition) (80 °C- 200°C) Normalized By Area
MCMB 2528	1552 J/g	507 J/g	1.18 m^2/g	429 J/m^2
Carbon Fiber	2151 J/g	1171 J/g	2.8m^2/g	419 J/m^2

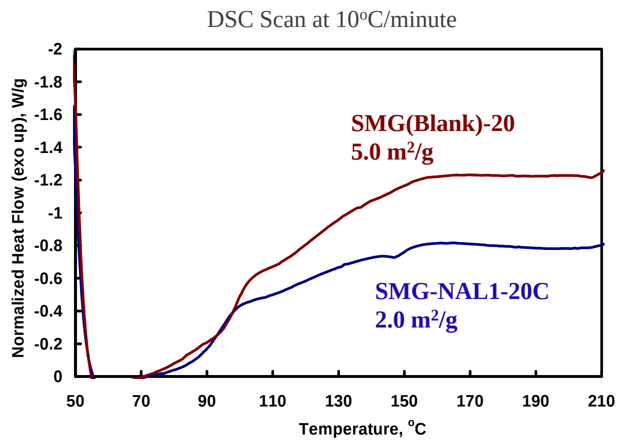
- ✓**Amount of heat genertated from the decomposition of primary and secondary SEI increases with the increase in surface area of graphite**
- ✓**Amount of lithium involve in the repeated formation of secondary SEI is the same regardless of surface area**

Comparison of SEI Decomposition Heats from Graphites having different surface areas



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

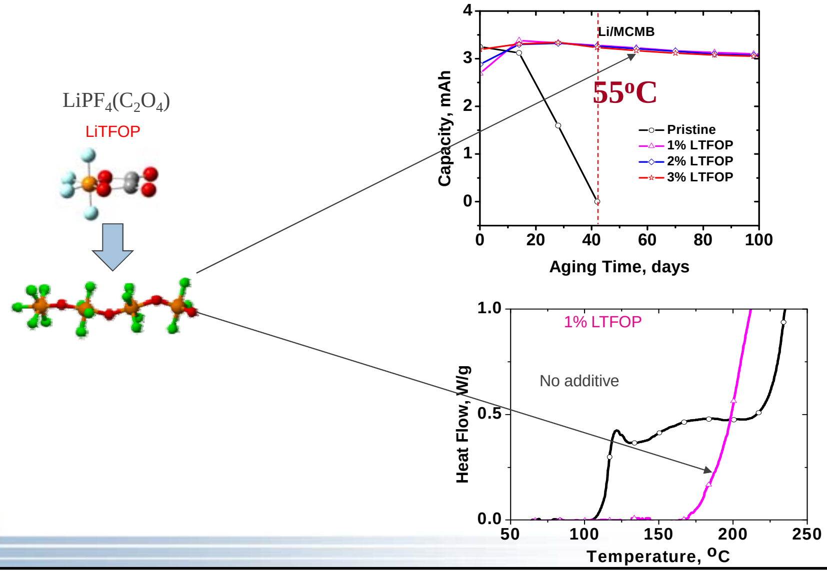
Effect of Carbon Coating & Reduced Surface Area on anode safety



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

Crash test of a PHEV Vehicle having 24kwh A123 LiFePO4/low surface area carbon chemistry

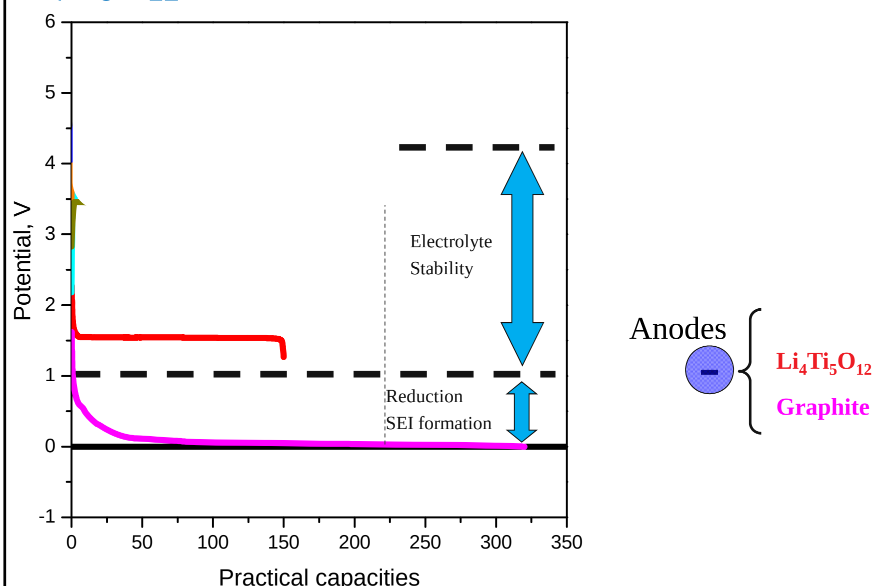
Stabilizing the Interface (stable SEI) using Functional Electrolyte Additives for Life & Safety improvement



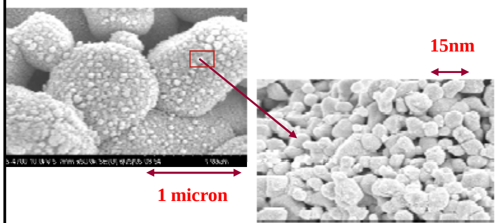
Nail Penetration of 20Ah cells based on NMC/Graphite system with and without additives

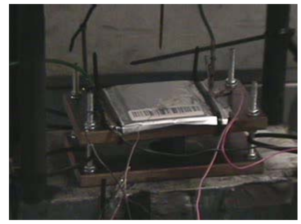
30 Meter drop test of 24Kwh pack having NMC/ low surface area Carbon with additives chemistry

$Li_4Ti_5O_{12}$ (LTO) without SEI as a very safe anode



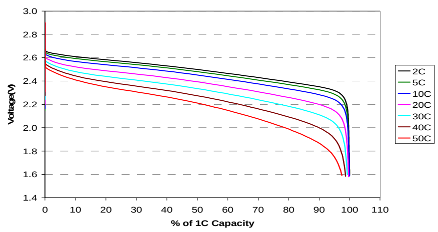
Safe, Long Life & Very High Power Characteristics of Nano-$Li_4Ti_5O_{12}$



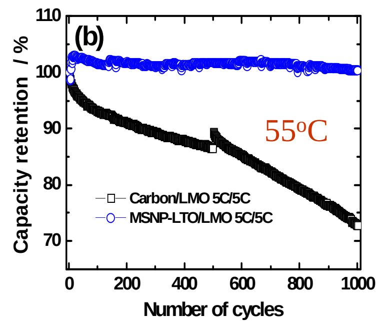


Unmatched safety

XRD of ANL made nano-$Li_4Ti_5O_{12}$ spinel

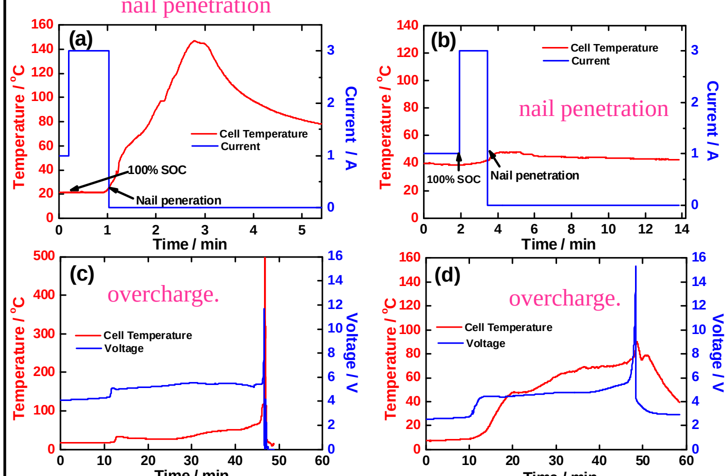


Excellent power LMO/LTO system can discharge within 1 minute



2008 R&D 100 award

Result of Nail penetration and overcharge for LMO/Carbon and LMO/$Li_4Ti_5O_{12}$

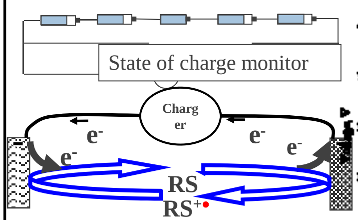


$Li_{1.06}Mn_{1.94}O_4$/nano-$Li_4Ti_5O_{12}$ shows outstanding safety characteristics both during nail penetration and overcharge.

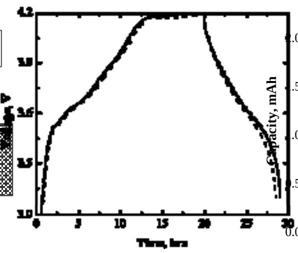
Redox shuttle to overcome overcharge abuse

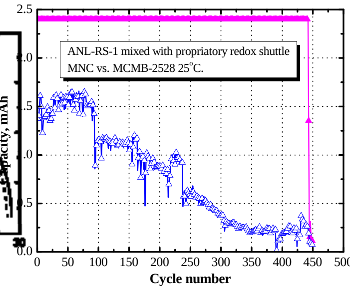
Redox shuttle role:

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



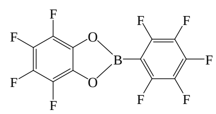
Overcharge Protection with RS



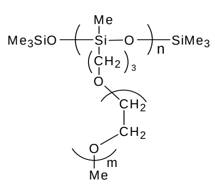


MCMB/NCA cells overcharged to 5.8V in the presence of ANL redox shuttle

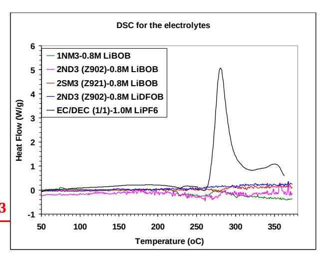
ANL redox shuttle is very stable & can sustain 500 of overcharge cycles a c/3

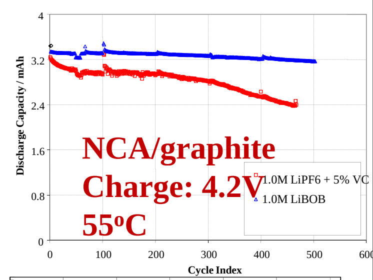


Stable Siloxane Electrolyte to Improve safety of Batteries for EV Applications

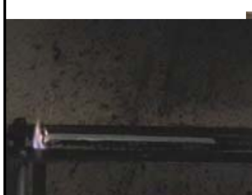


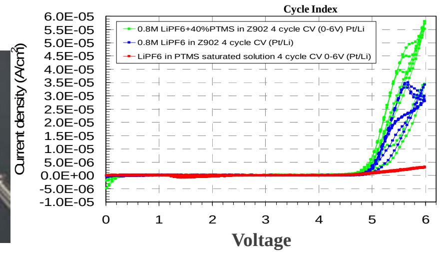
Conductivity =1.23x10^{-3}
Voltage >5.0V





NCA/graphite
Charge: 4.2V
55°C





Siloxane electrolyte exhibits high voltage stability

Carbonate electrolyte

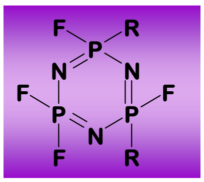
Siloxane electrolyte

K. Amine 2005 R&D 100 award

Phosphazine as promissing flame retardant additives

- Low viscosity almost same to that of conventional electrolyte.
- Additive can improve cell performance.
- Addition of small amounts can render the electrolyte non-flammable.

Phoslyte™



Ethoxypentafluorocycrotriphosphazene, $C_2H_5F_5N_3OP_3$
Phenoxypentafluorocycrotriphosphazene, $C_6H_5F_5N_3OP_3$

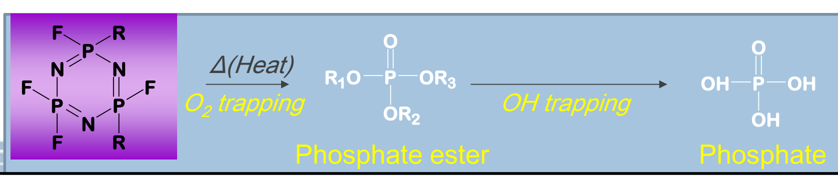
Flash point

Additive	Flash point (°C)
No additive	27.5
8wt%	34.5
≧9wt%	No-flash point

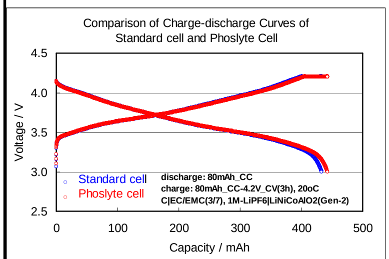
Oxygen Index

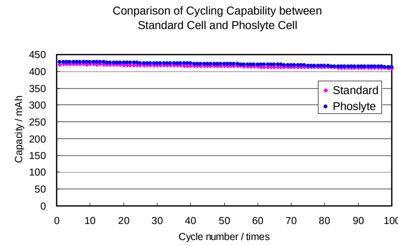
Additive	Limited Oxygen Index
No additive:	17.5
8 wt.% Phoslyte	22.8
20 wt.% Phoslyte	25.4

➢ Mechanism of Fire-extinguish ability

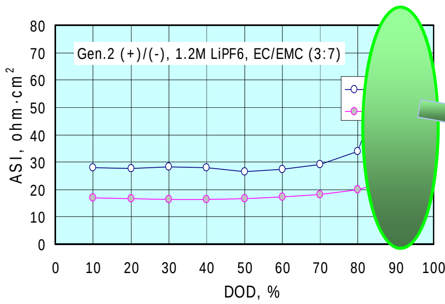


Phoslyte improve the power performance of Lithium battery because of its excellent wetting characteristics

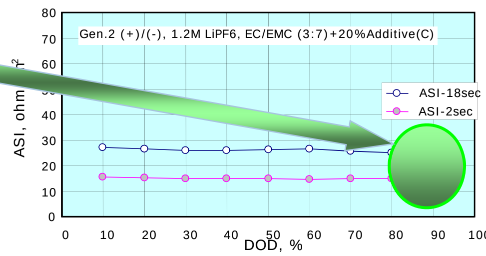




Standard Cell



Phoslyte Cell



Spark ignition test under cell heating

(NMC Standard)

NMC with Phoslyte

Conclusions

- **Cathode reactivity with electrolyte is dependant on a degree of O2 release from the cathode**
- **Continous Breakdown and formation of SEI can accelerate the termal runaway in a lithium ion cell**
- **Additives to stabilize the SEI can improve significantly the safety of lithium batteries**
- **Flame retardant such as phoslyte can mitigate the flame when the cell goes on a thermal runaway**
- **Redox shuttles can be used as a backup against overcharge but also as potential cell balancing in a battery pack**

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