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... for a brighter future

Advanced battery chemistries for PHEV and EV Applications

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US Department of Energy

U.S. Department of Energy

THE UNIVERSITY OF CHICAGO

A U.S. Department of Energy laboratory managed by The University of Chicago

Vehicle Technologies Program

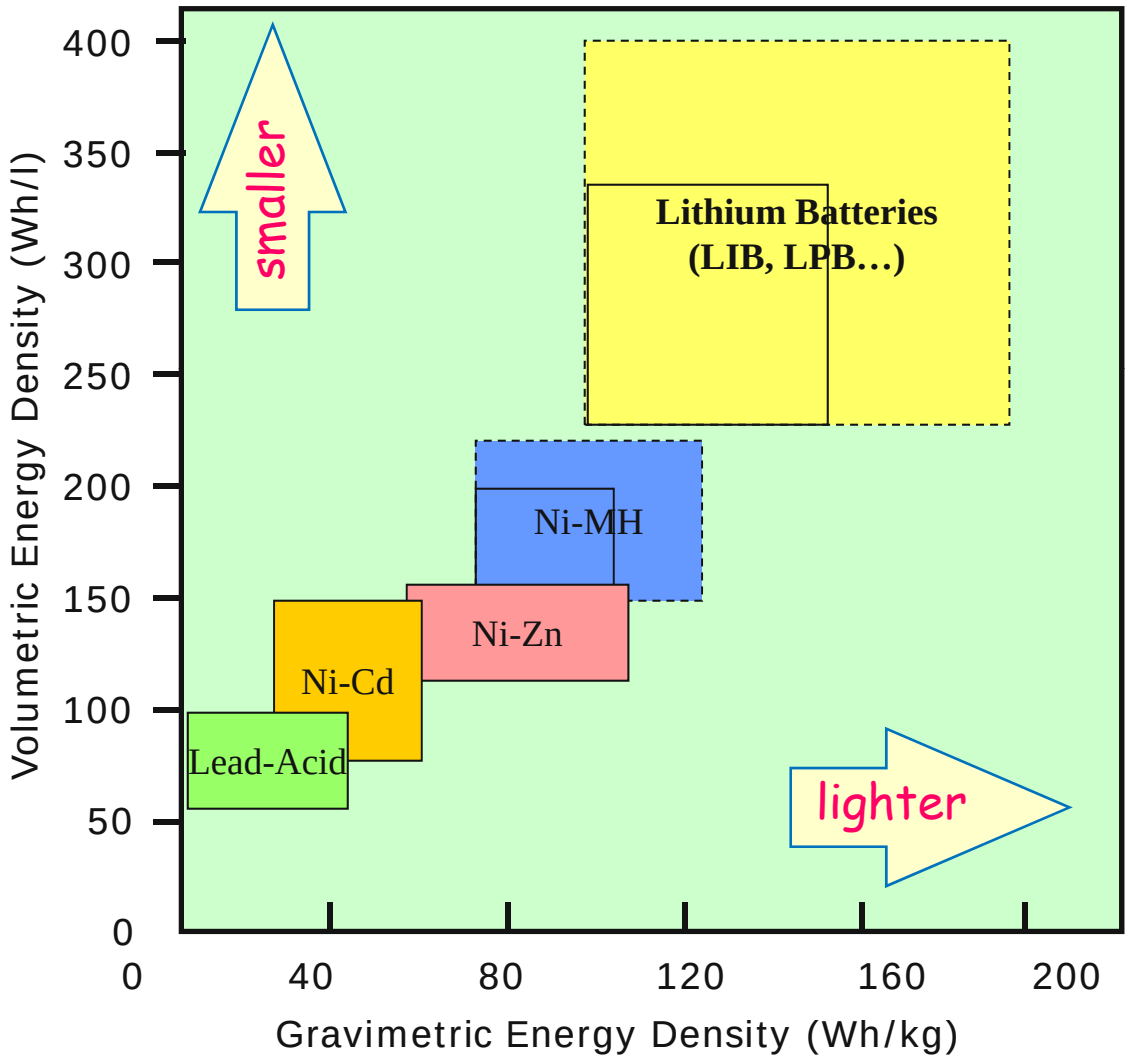
Why Li-ion cells for Transportation (HEVs, PHEVs, EVs)? Higher cell voltage & higher energy/power densities

Frequently Used Terms

Capacity (Ah)

Energy (Wh=V*Ah)

Power (W)



Batteries technology candidates for PHEV and EV applications

Couple	NCA/ carbon	NMC/ Carbon	Mn spinel/ Carbon	Fe Phosphate/ carbon
Life	OO	OOOO	OOO	OOOO
Power	OOOO	OOOO	OOOOO	OOOOO
Energy	OOOO	OOOO	OOO	OO
Safety	OO	OOO	OOOO	OOOO

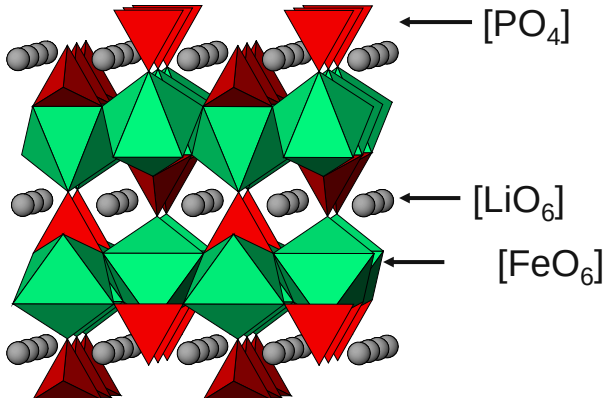
Advantages of $LiFePO_4$ for Application in PHEVs

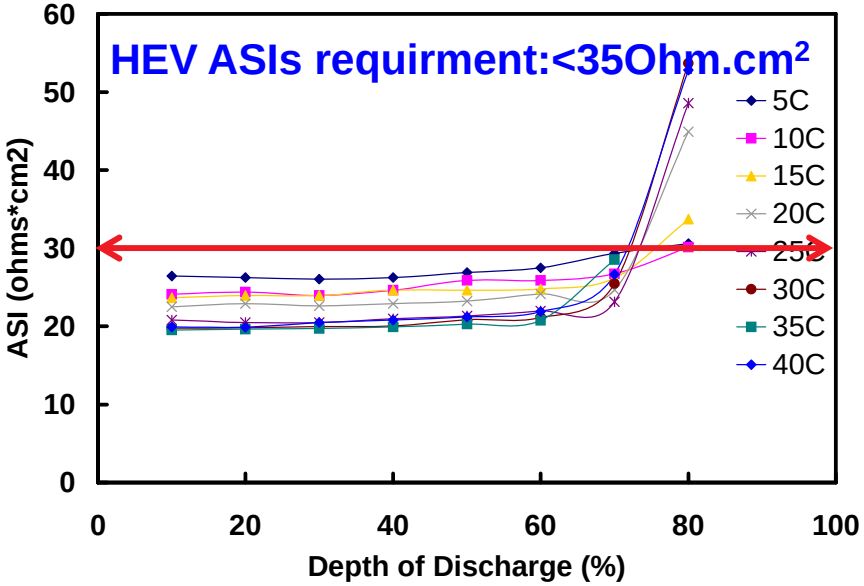
Advantage of phosphates:

- ✓ Low cost
- ✓ Over-charge & under-charge resilient (1 Li)
- ✓ Excellent structural stability (strong bond P-O)
- ✓Good cycle life
- ✓Thermally and chemically stable
- ✓Safe

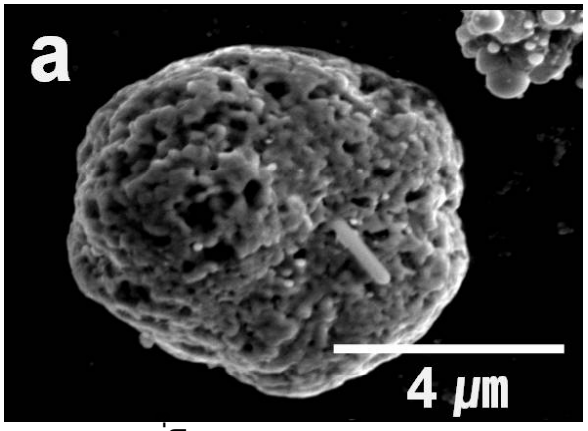
- $LiFePO_4$ has a flat 3.5V plateau and a capacity of almost 178mAh/g
- Charge cutoff voltage using the olivine system could be as low as 3.7 V. (good electrolyte stability specially at (37°C))
- Using nano powder concept and carbon coating, $LiFePO_4$ shows excellent power for HEV

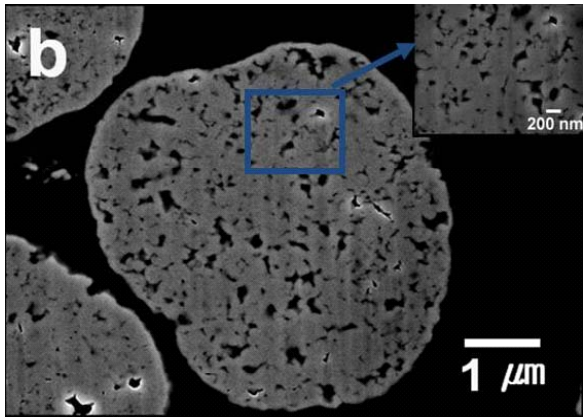
Olivine structure (orthorhombic)



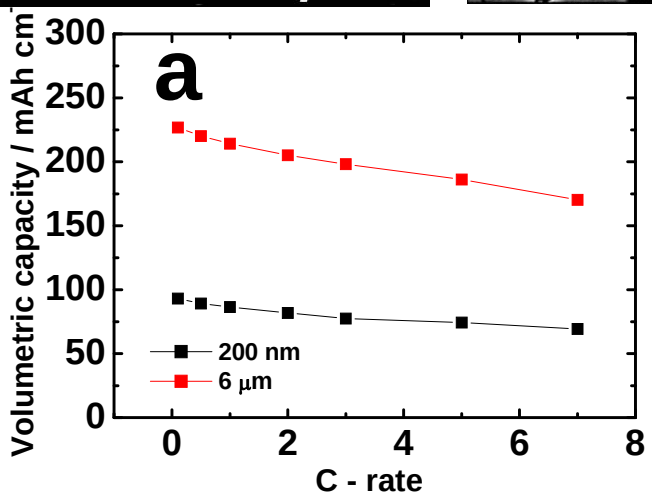


New micron size nano-porous C-$LiFePO_4$ with double the volumetric Energy density of the nano-$LiFePO_4$

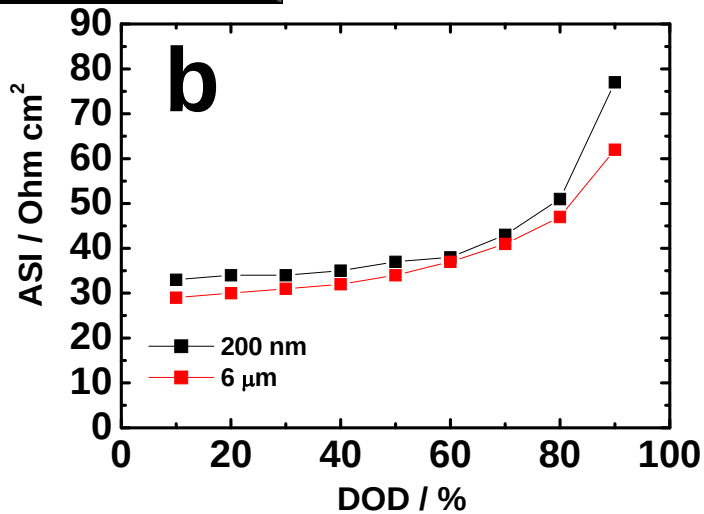




Tap density : 1.87g/cm3



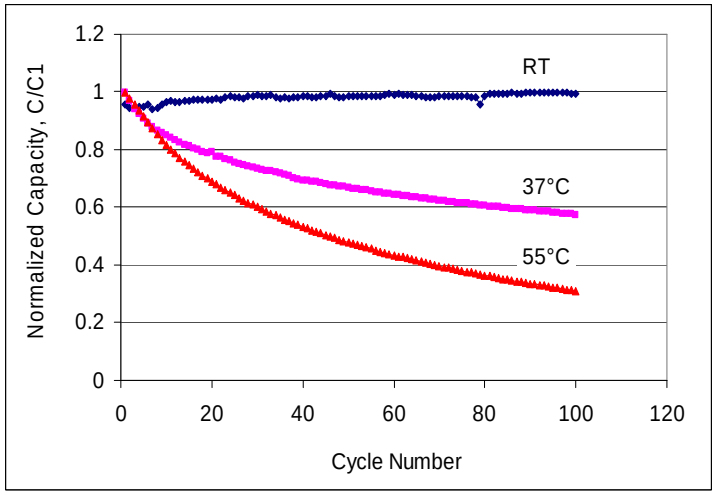
New material has the same power as the nano-material



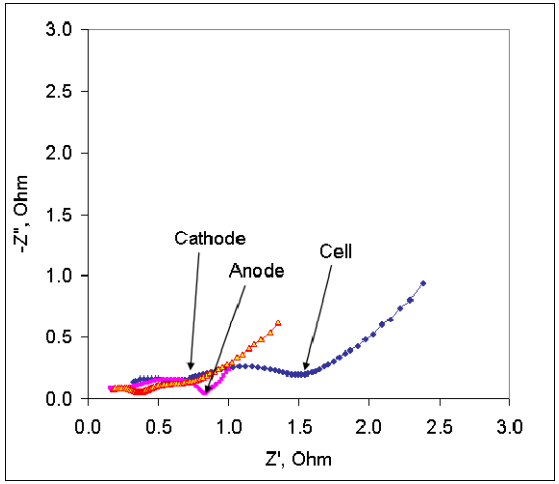
New material meets the pulse power needed for HEV and PHEVs

C-$LiFePO_4$ with Fe_2O_3 impurities shows poor performance at 55°C

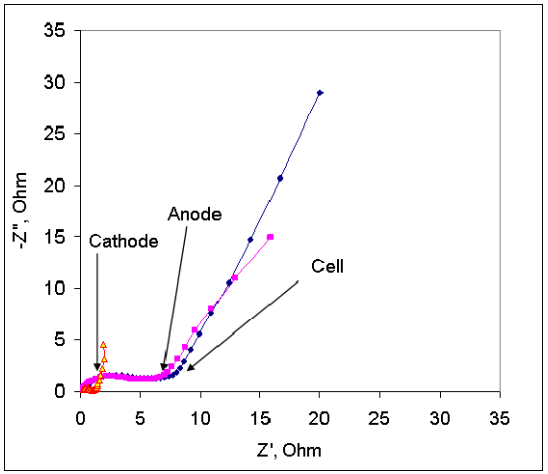
C-$LiFePO_4$ vs. MCMB

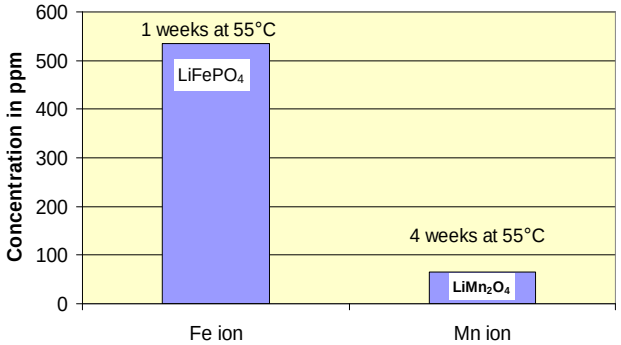


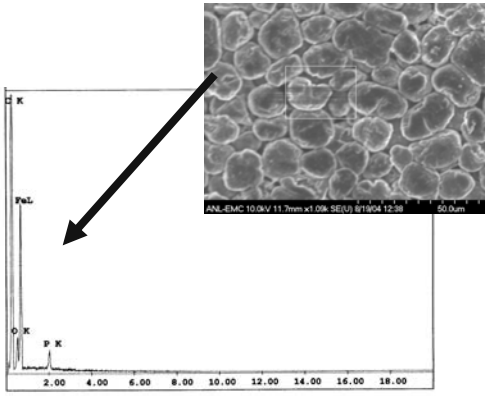
After 5cycles at 25°C



After 100 cycles at 55°C

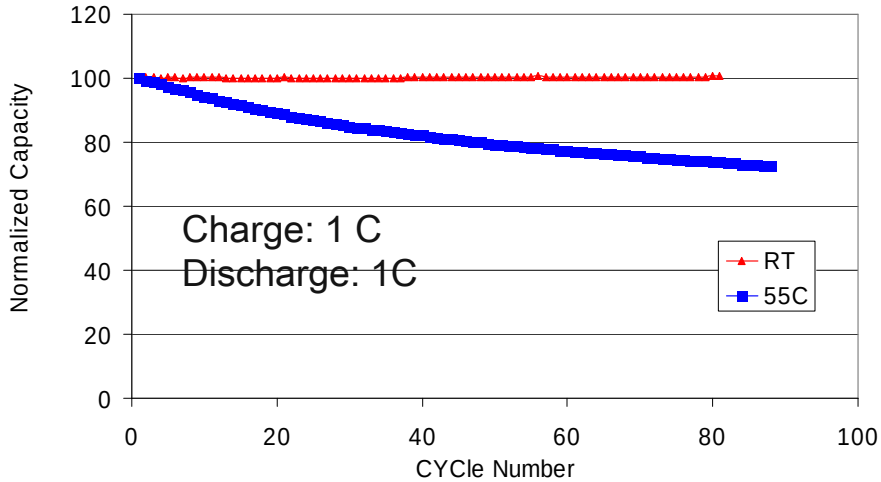


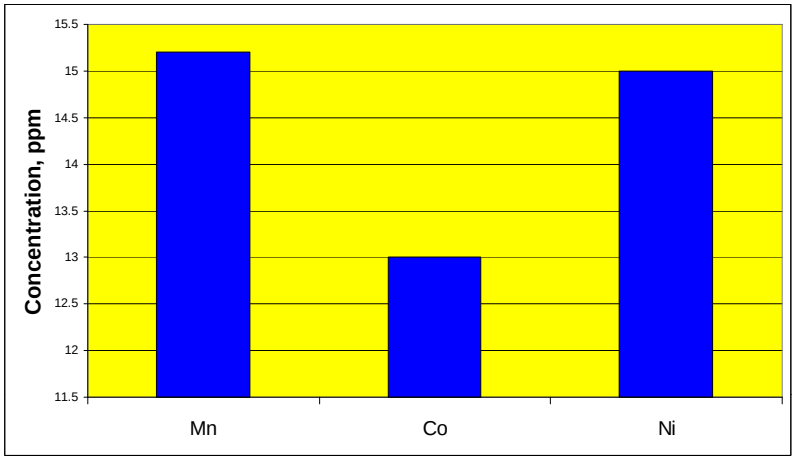


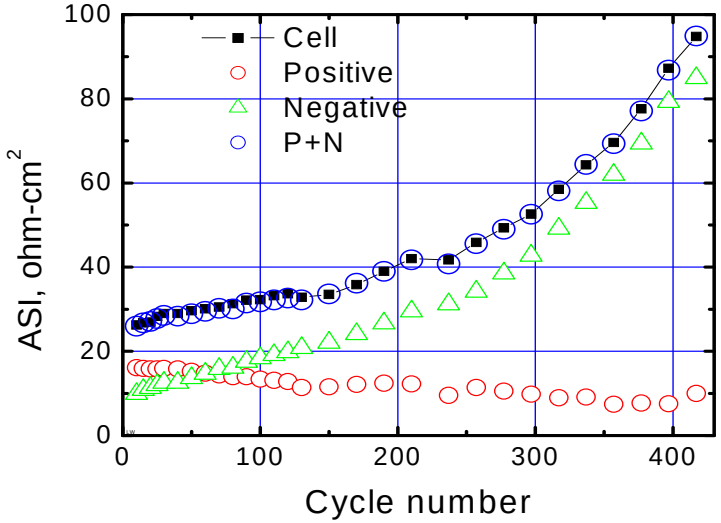


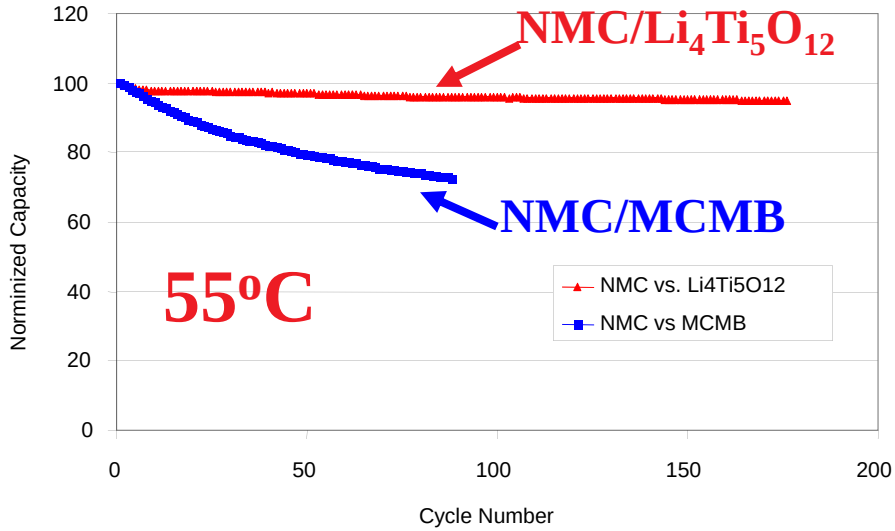
Fe dissolution from impurities are reduced at the carbon anode and causes a significant cell impedance rise

Same issue with NMC/MCMB

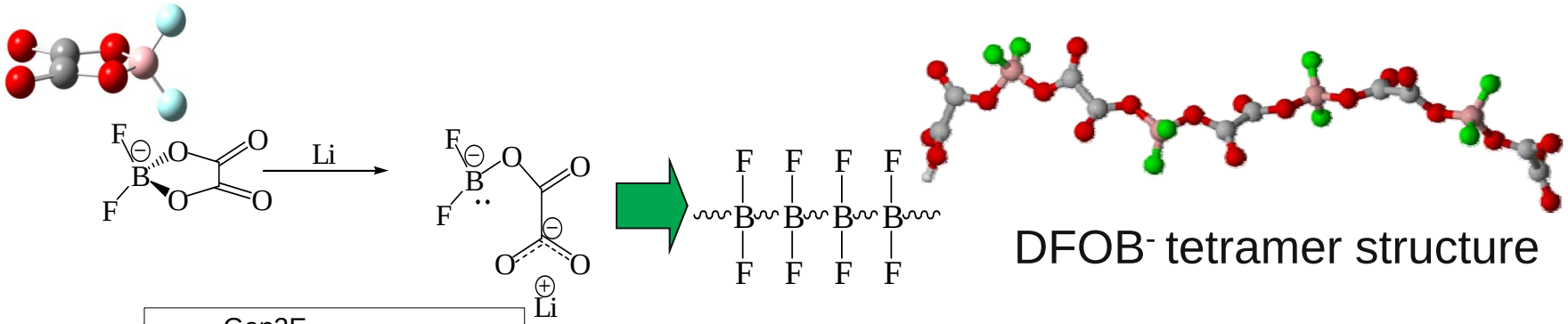


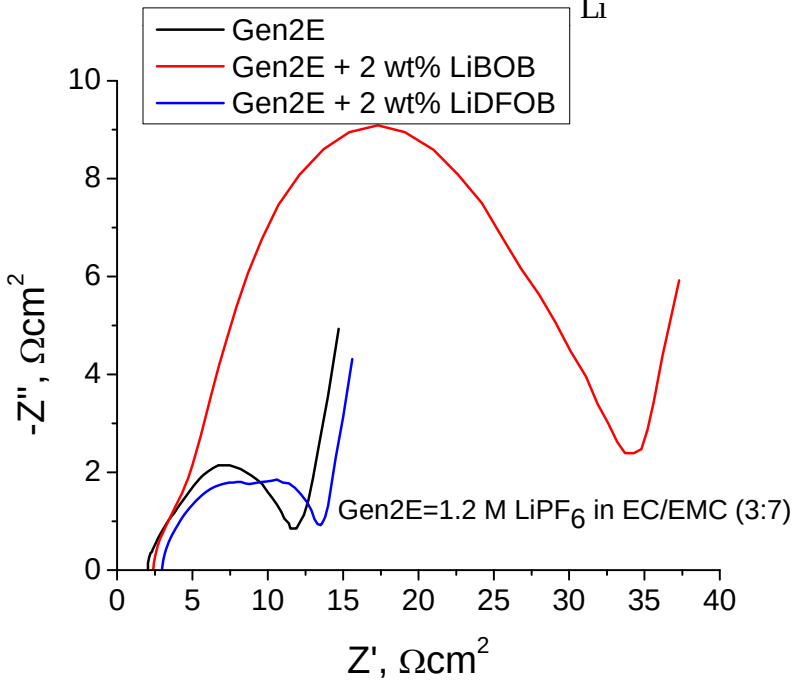






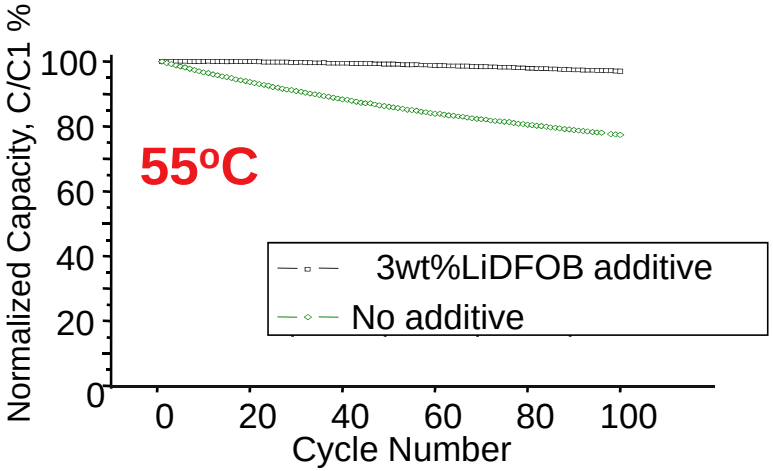
Use of Additives such as LDFOB can resolve this problem

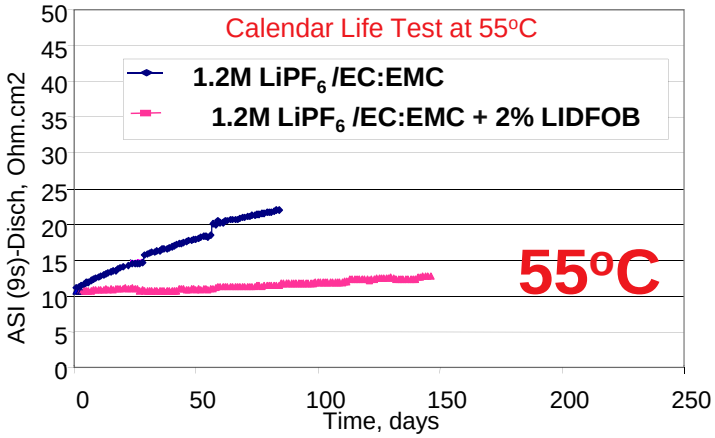


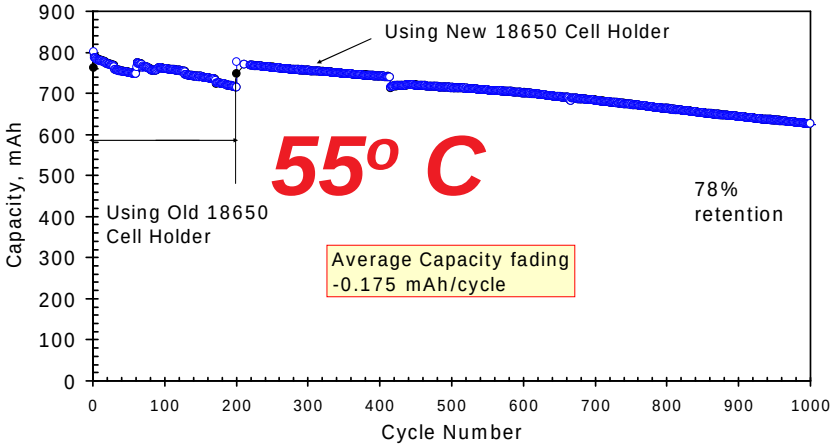


- **Density functional calculations show that fluorine termination prevents 3-D polymeric structure growth. This explains the low observed impedance for LiDFOB compared LIBOB**

Performance of $Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$/ Graphite Cell using Additive

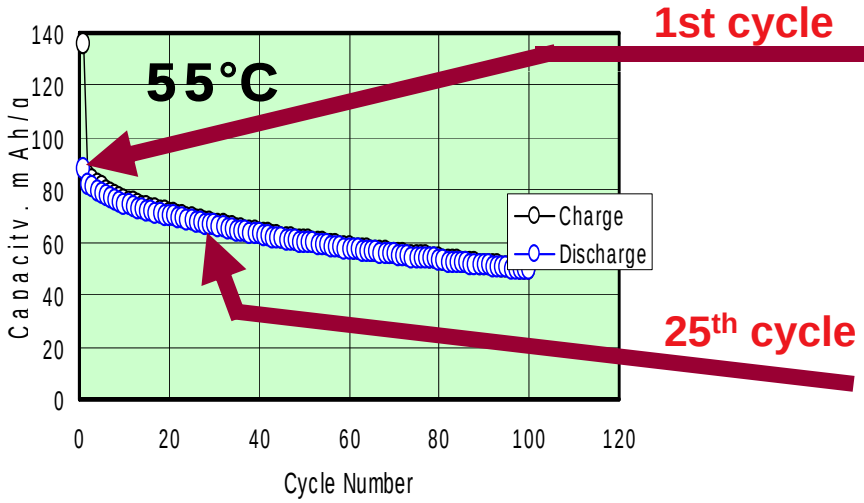


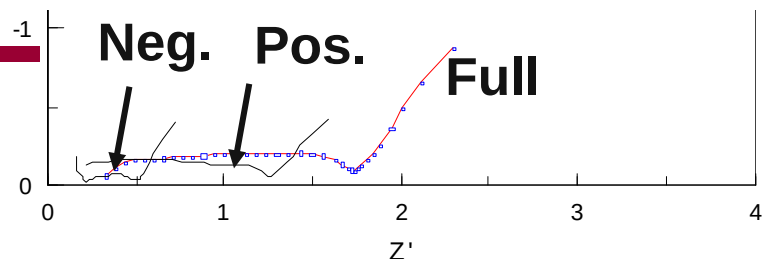


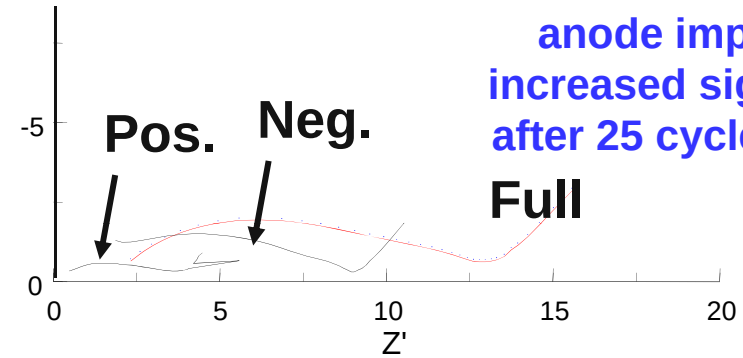


NMC/MCMB cells based on a new LIBDF additive (at 3 wt%) show low initial ASIs, good capacity retention and limited impedance rise during calendar life test at 55°C.

Issues of Mn-spinel/carbon system during cycling and aging at 55ºC using $LiPF_6$/EC:DEC

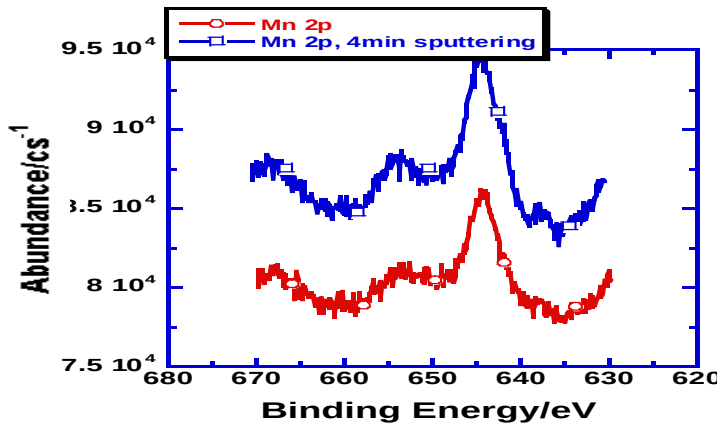






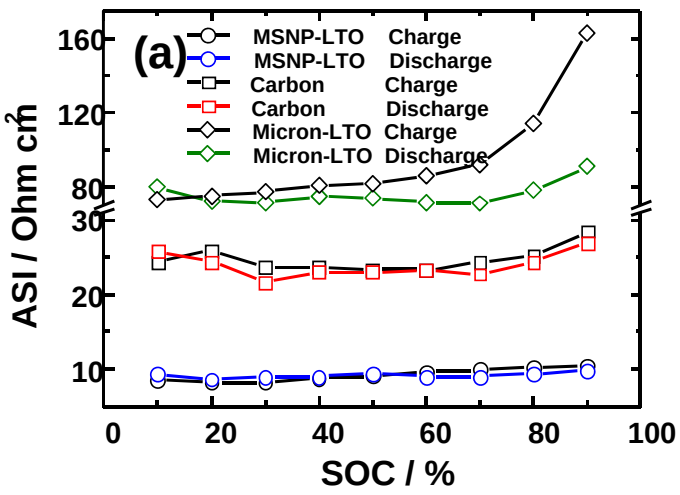
anode impedance increased significantly after 25 cycles at 55ºC

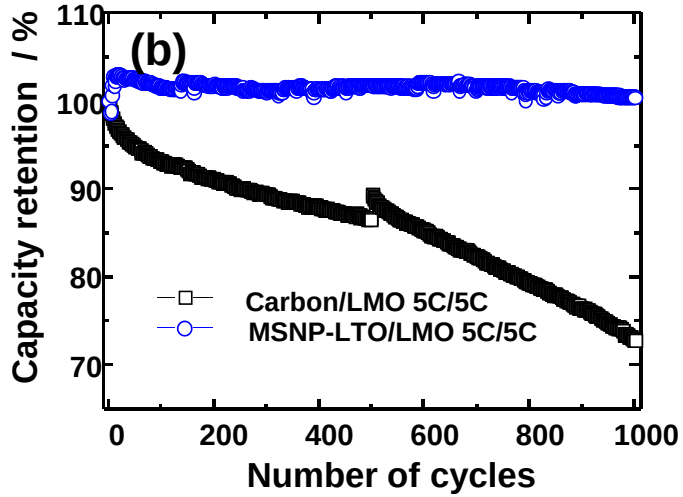
Small amount of manganese dissolution (5ppm) was reduced at the carbon and played a catalytic role that leads to the distraction of SEI and continues formation of a film at the carbon surface that causes the interfacial impedance increase at the carbon

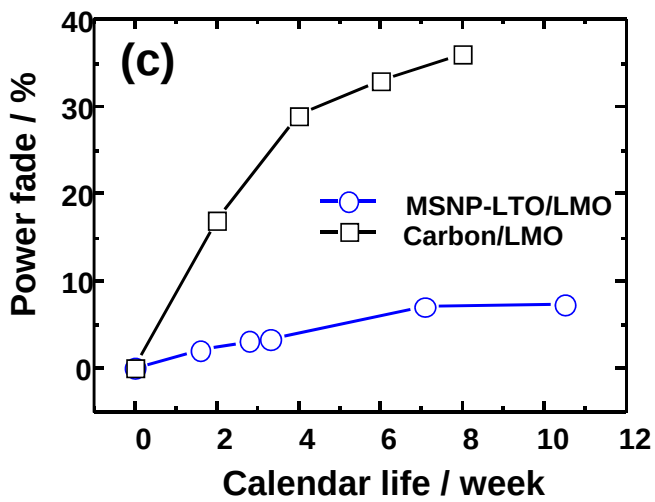


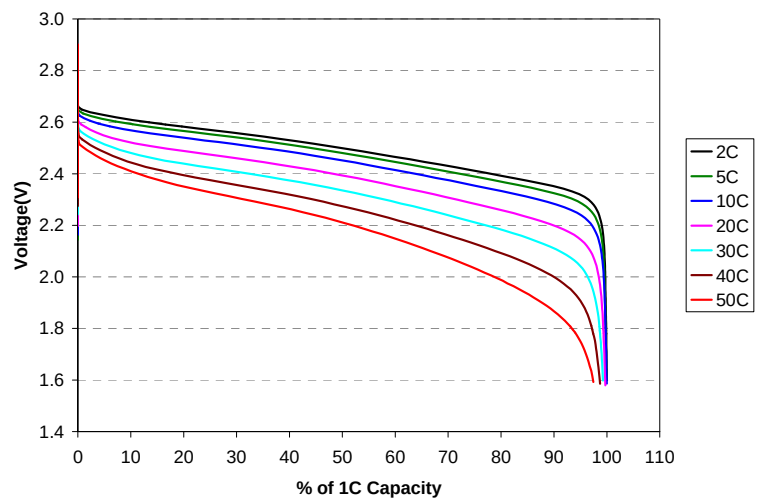
Mn-metal was observed at the carbon surface by XPS

Use of LTO can lead to long cycle life and unmatched safety





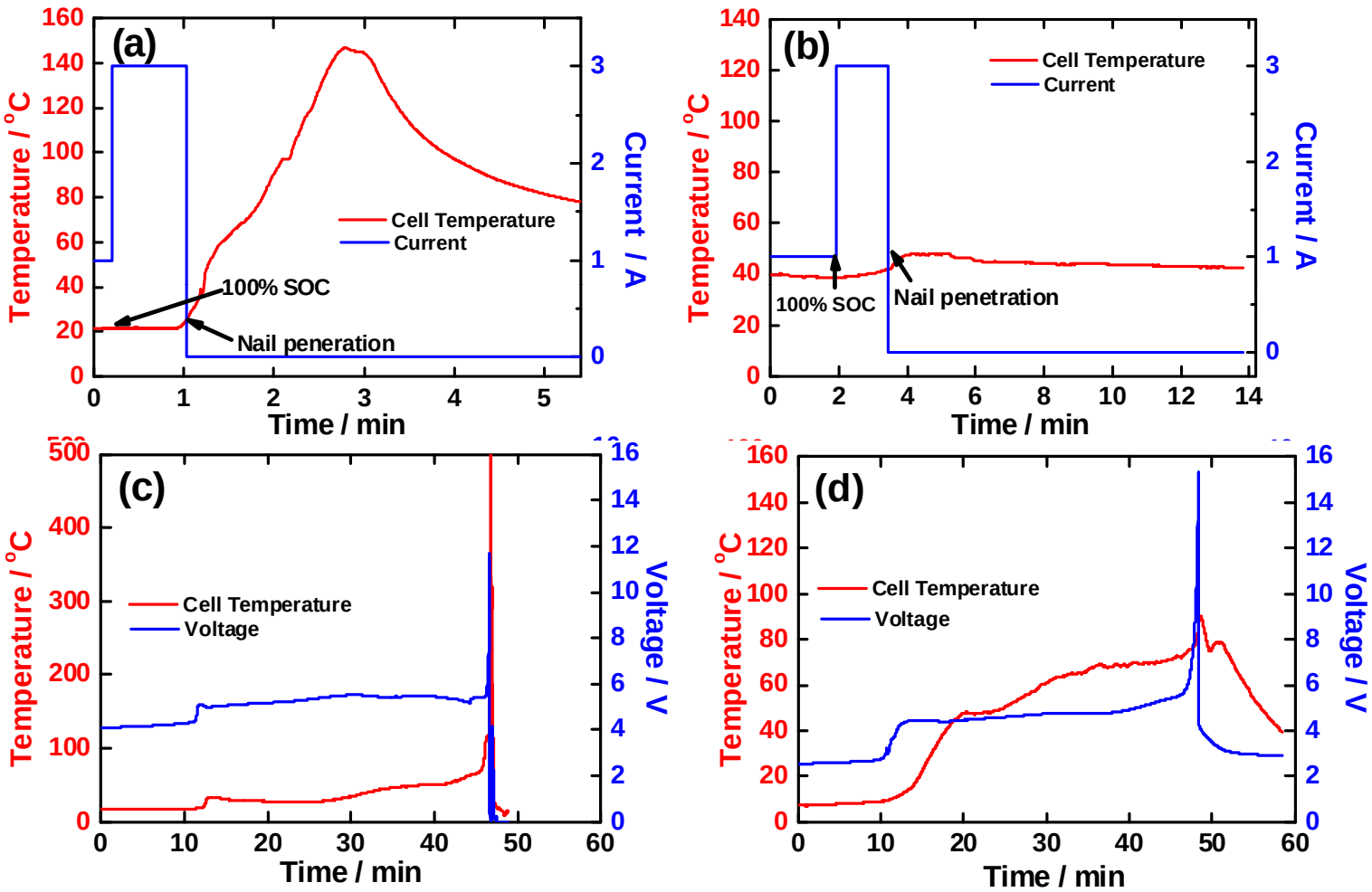




safety Test of Cells based on carbon and LTO

$Li_{1.06}Mn_{1.94}O_4$/Carbon

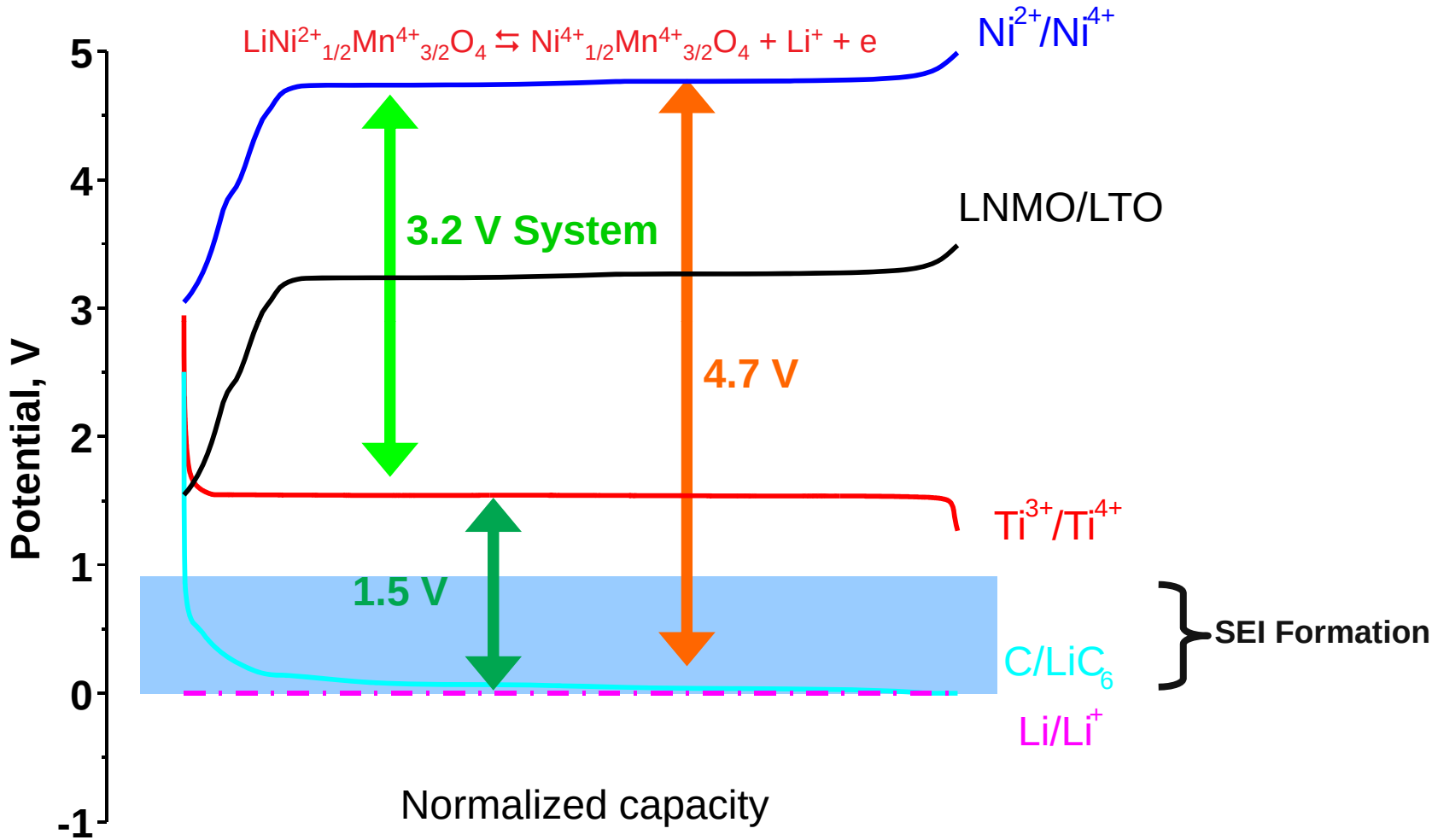
$Li_{1.06}Mn_{1.94}O_4$/nano-$Li_4Ti_5O_{12}$



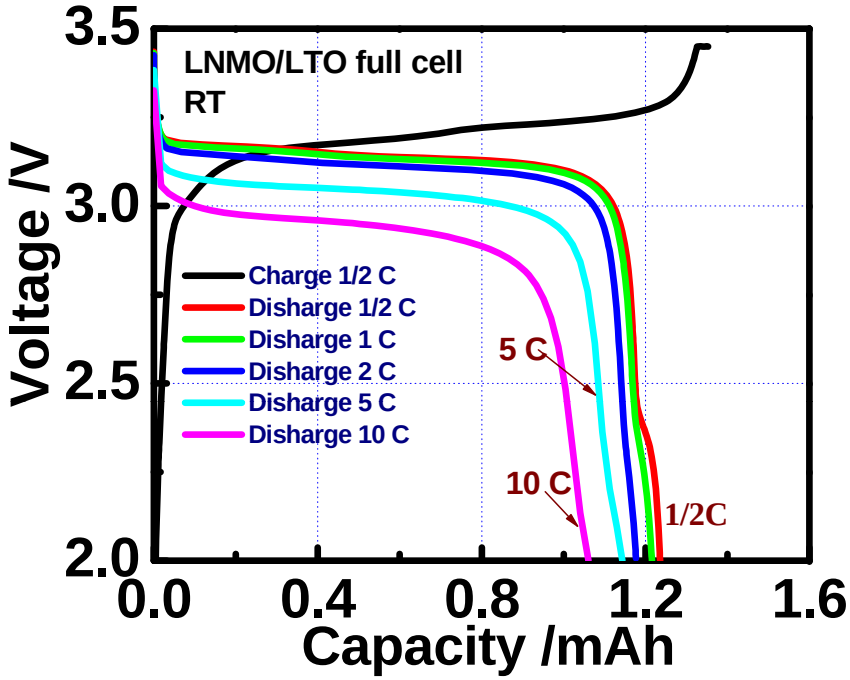
Nail penetration

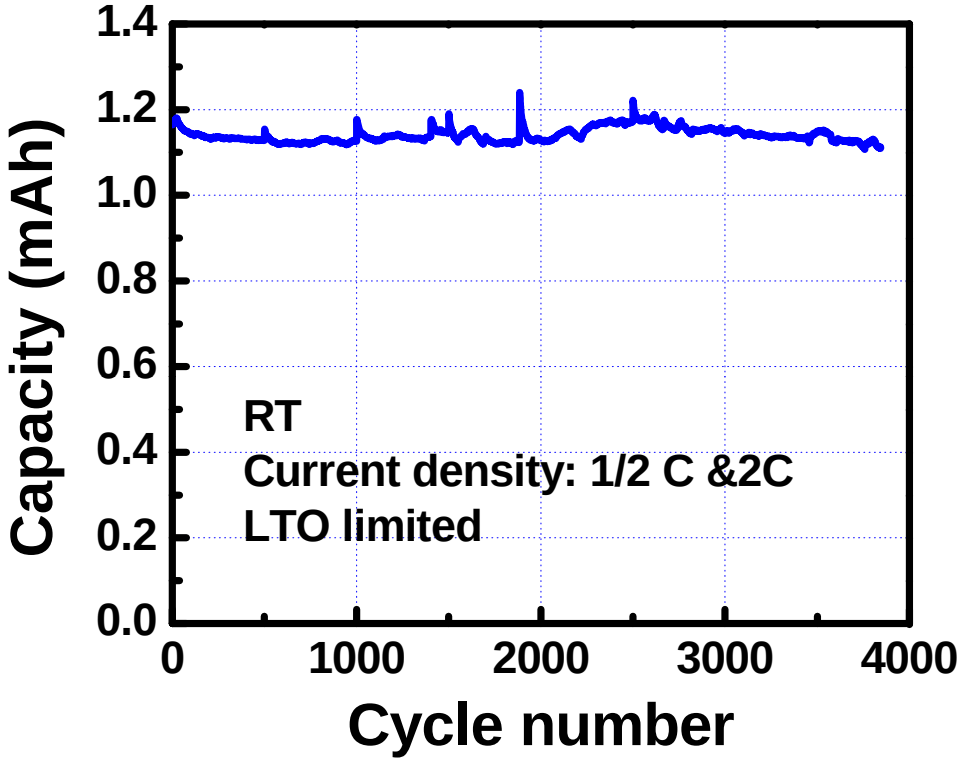
Overcharge

$LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ Battery System



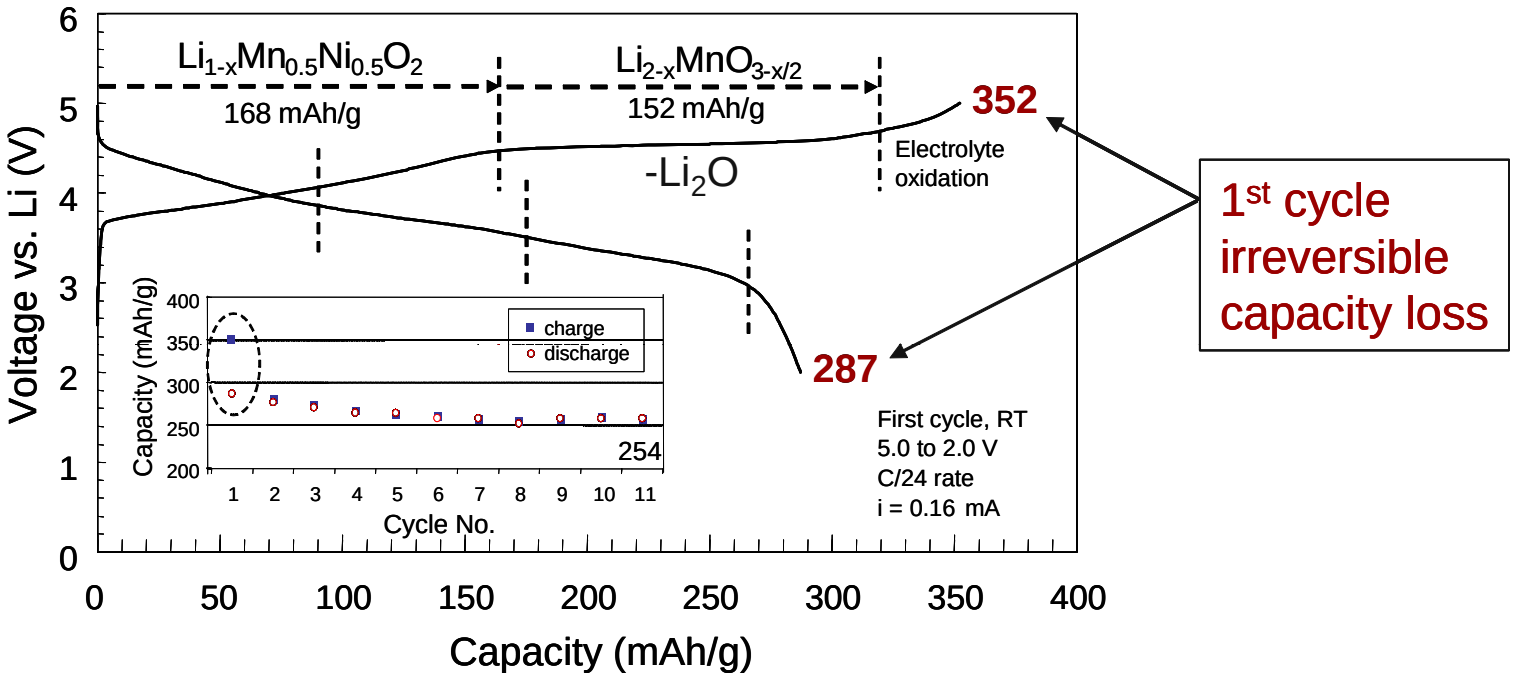
Power & cycle performances of LNMO/LTO cell





- At room temperature, LNMO/LTO battery shows outstanding Power & cycle performance.

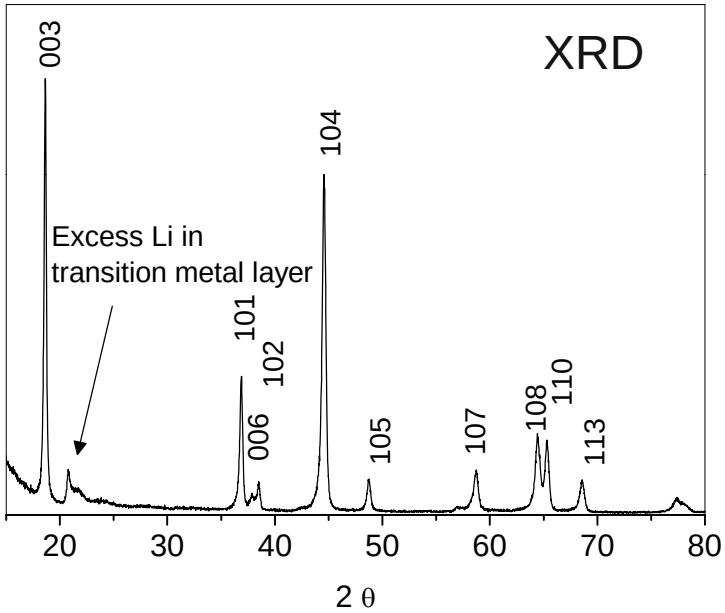
High Energy composite electrode [$xLi_2MnO_3 \bullet yLiMn_{0.5}Ni_{0.5}O_2$]

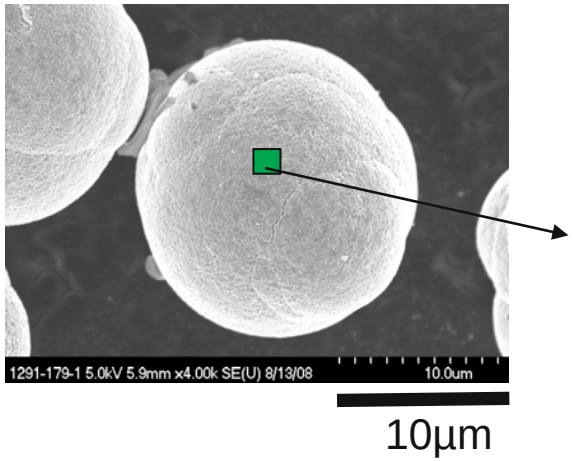


- Theoretical capacity of $LiMn_{0.5}Ni_{0.5}O_2$ Component: 184 mAh/g
- Theoretical capacity of Li_2MnO_3 Component: 158 mAh/g
- Theoretical charge capacity (total): 342 mAh/g
- Coulombic efficiency: 82% (1st cycle); >99% (10th cycle)
- Capacity (10th cycle): 254 mAh/g

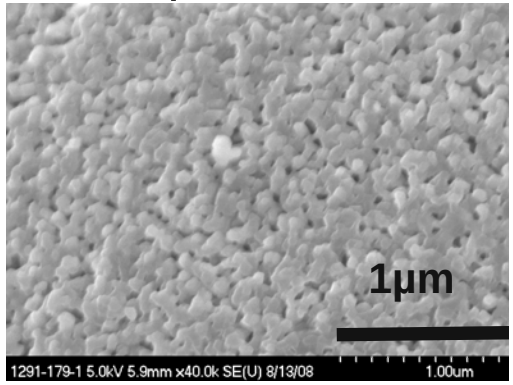
ANL composite electrode with highly dense nano-primary particles with improved rate capability

- Secondary particles: 10 μm
- Primary particles: 50~100nm





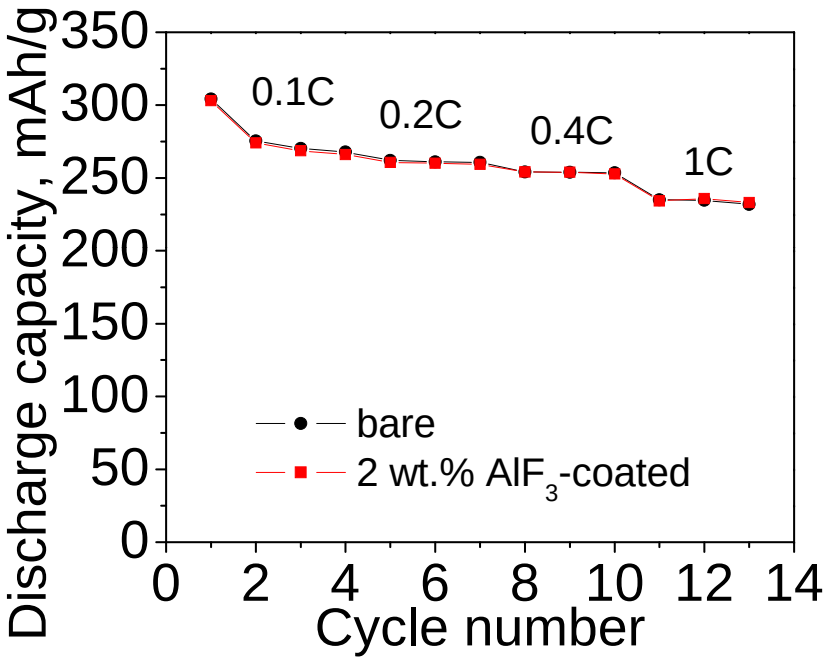
Primary particle

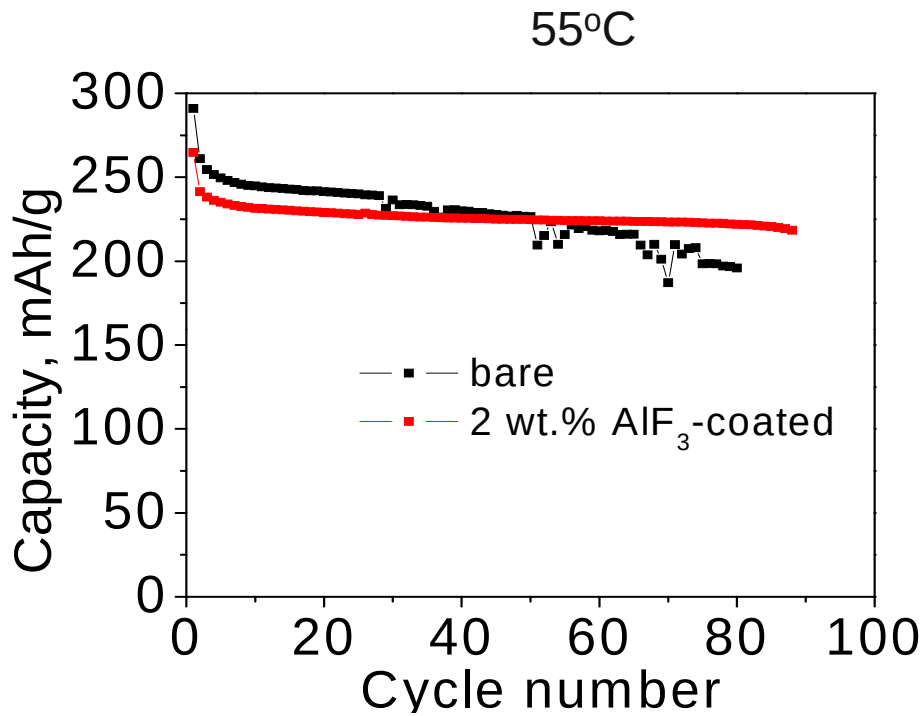


Tap density: 2.1g/cc

- Layered α-$NaFeO_2$ structure (R-3m)

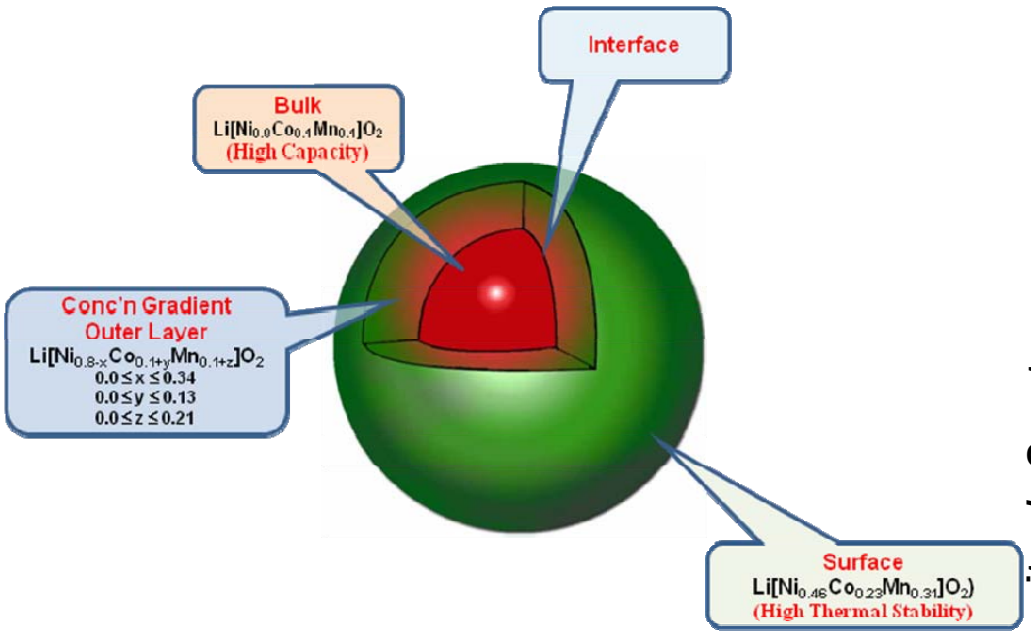
Effect of AlF_3-Coating on Rate and Cycle Life of high energy composite cathode at 55°C

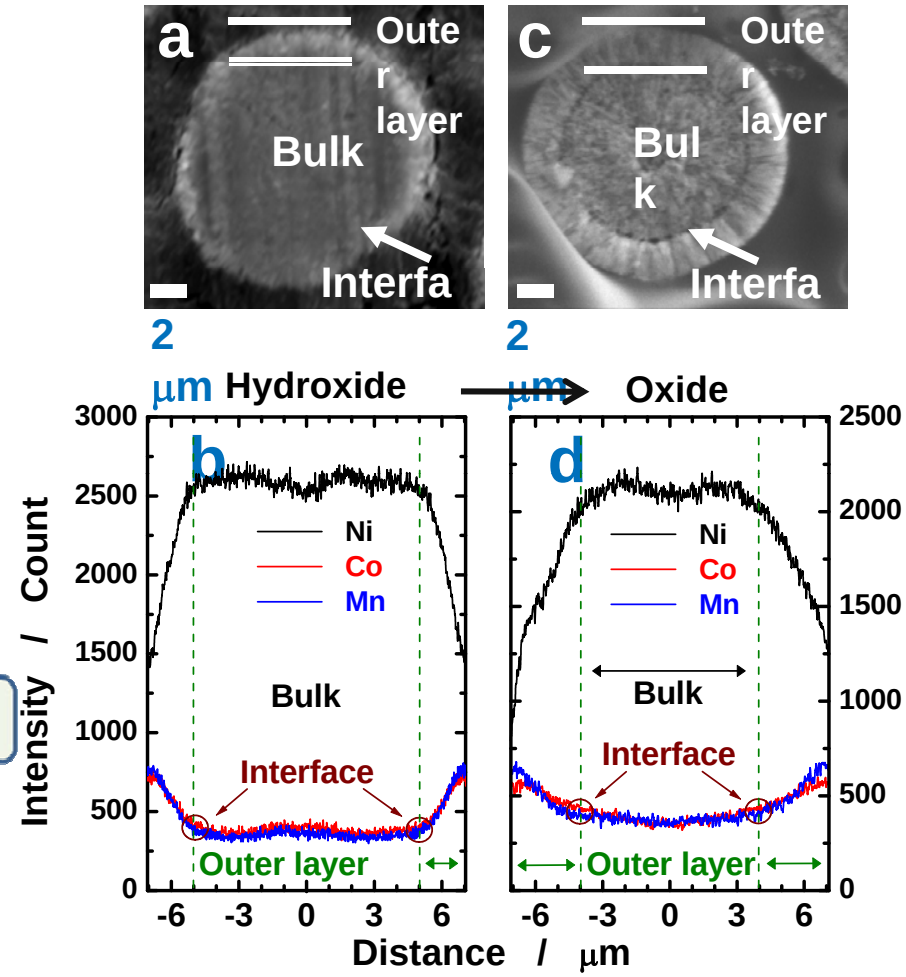




2 wt.% AlF_3-coated $Li_{1.395}Ni_{0.1875}Co_{0.125}Mn_{0.6875}O_{2.4475}$ showed improved cycling performance at 55°C performance.

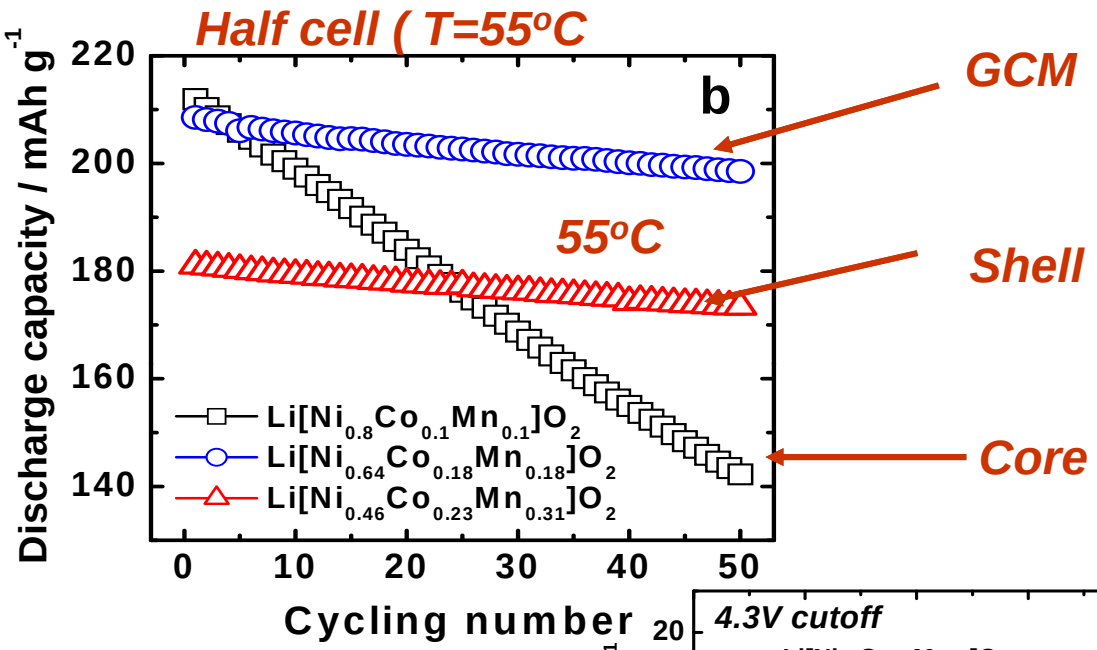
Gradient Concentration cathode material

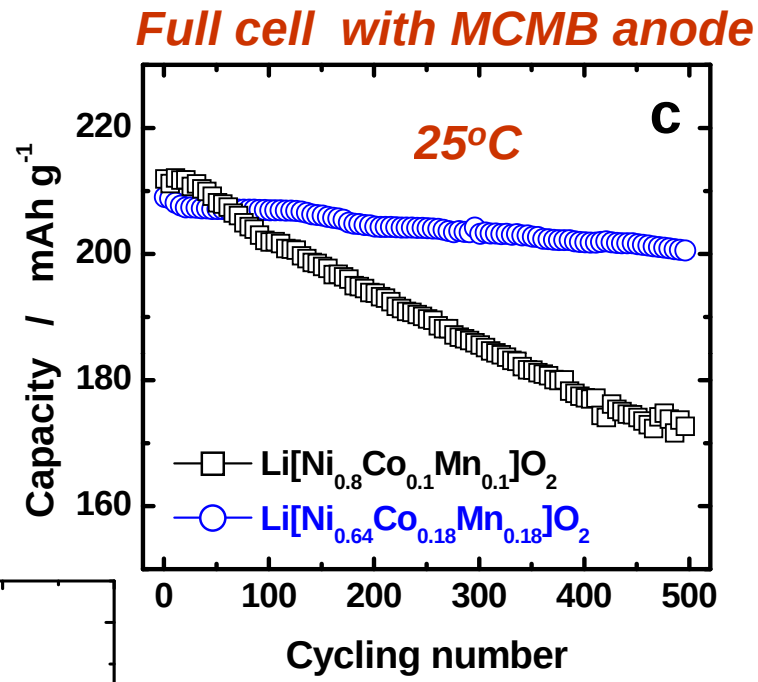


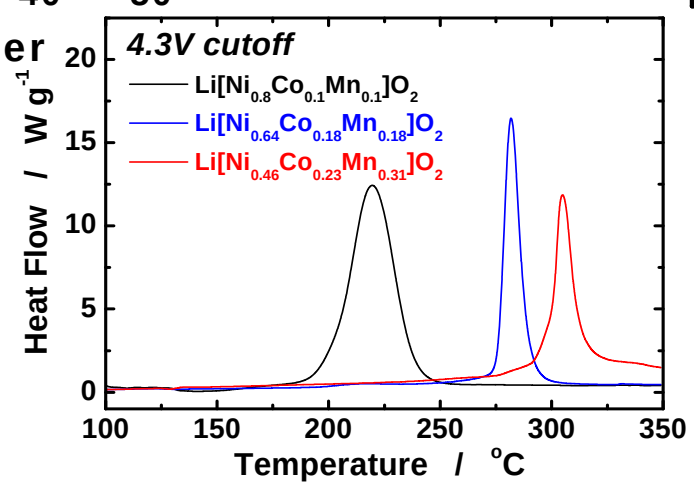


Y. K. Sun, K. Amine and al. Nature Material, 8(4): p. 320-324 (2009)

Comparison of performance of GCM ($LiNi_{0.64}Co_{0.18}Mn_{0.18}O_2$) $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (Core composition) and $LiNi_{0.46}Co_{0.23}Mn_{0.31}O_2$ (outer surface composition)



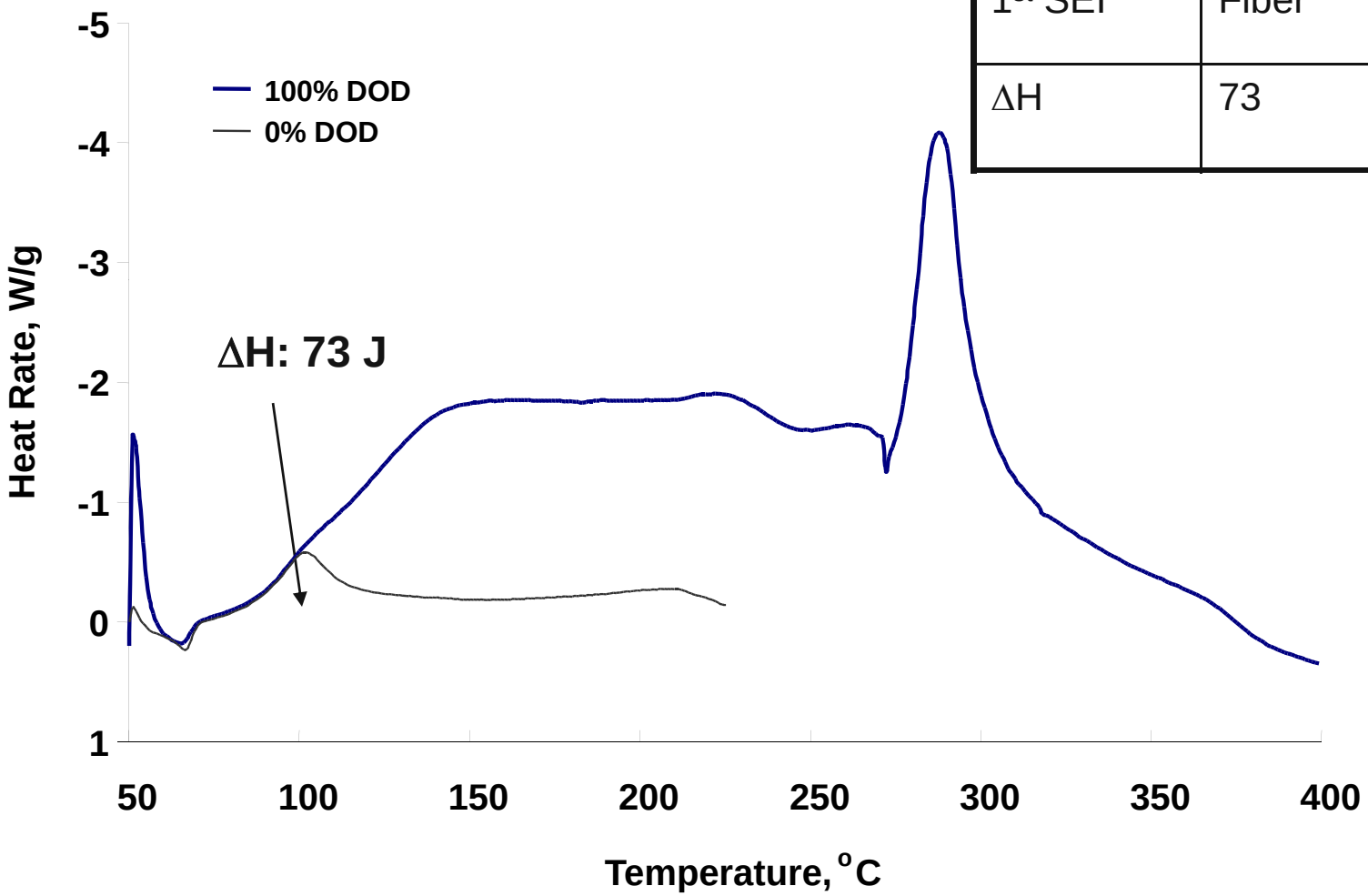




DSC of charged GCM, Core and shell materials

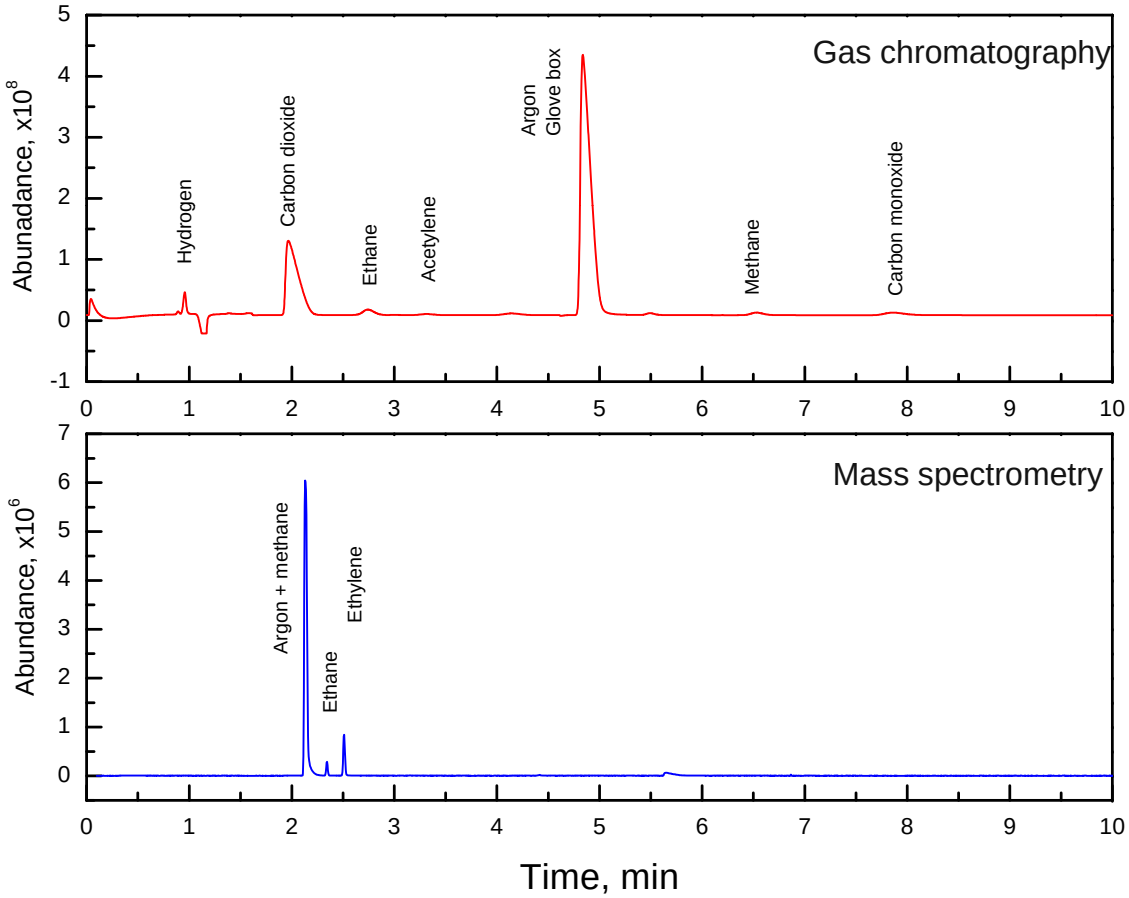
Heats profile from primary and secondary SEI decomposition in graphite

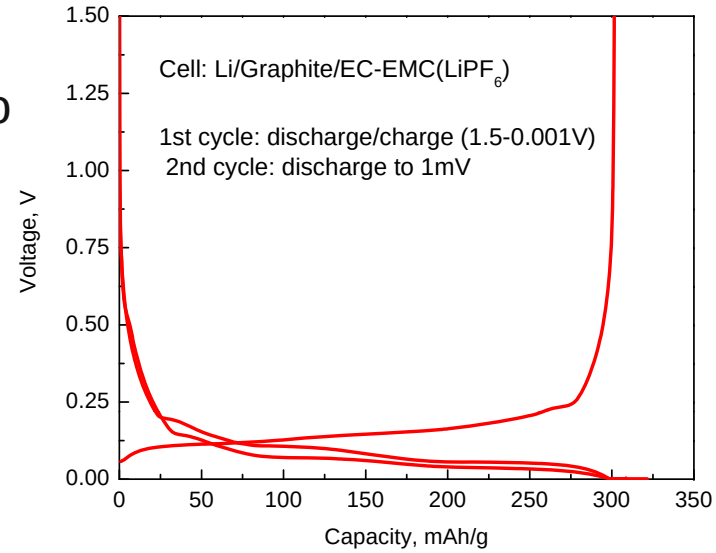
1st SEI	Fiber	MCMB
ΔH	73	62.3

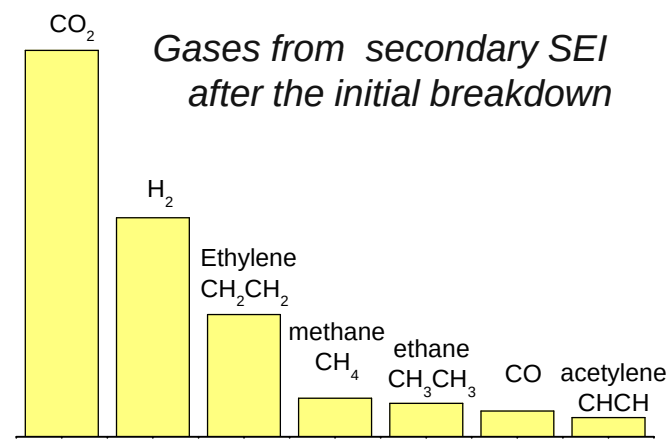


Gas from the formation of the secondary SEI Layer on carbon

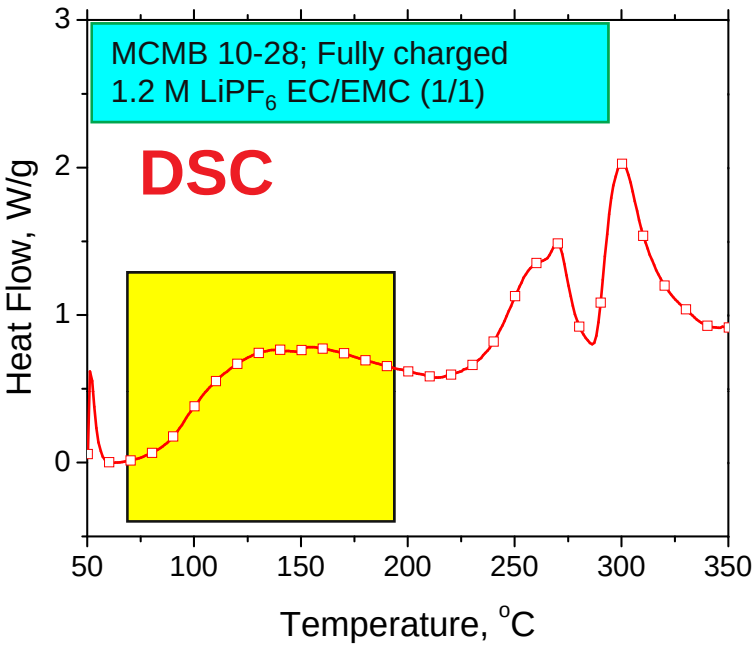
Several gases from secondary SEI formation were observed after exposing charged carbon/Li cell at 100ºC for several hours. These gases are similar to the one observed during the formation process

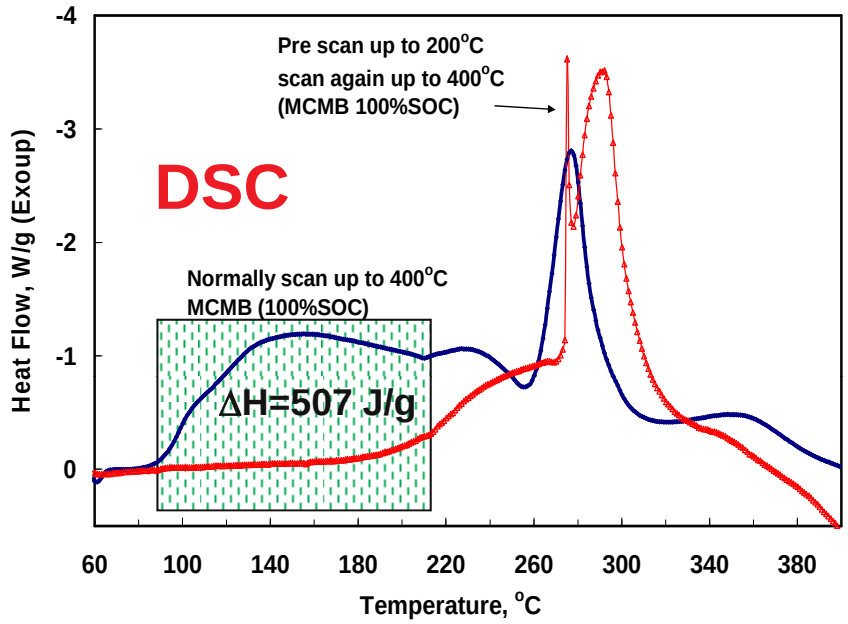






Heat generated from the decomposition of the secondary SEI can initiate the thermal runaway of the cell





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

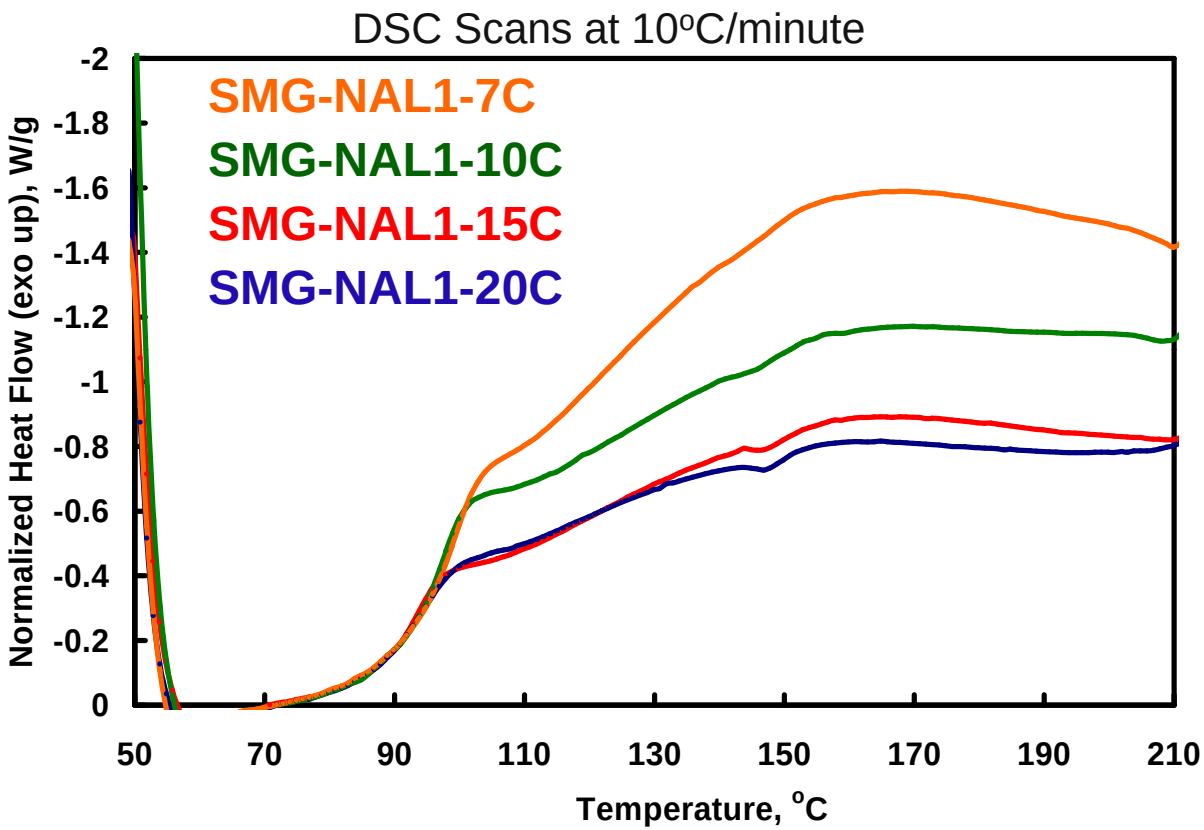
- This heat could be large enough to lead to the thermal runaway of the cell regardless of the nature of the cathode specially in large cells

MCMB : ΔH : 1552 J/g

Preheated MCMB: ΔH : 1045J/g

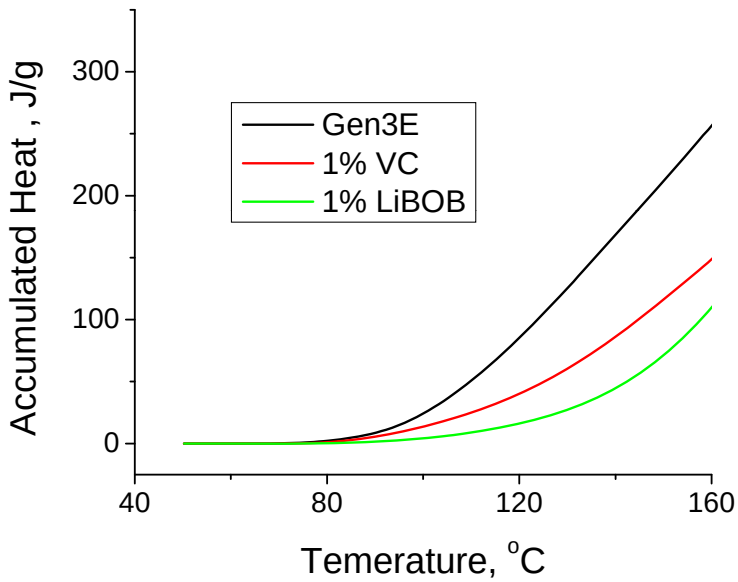
Heat from secondary SEI: ΔH=507 J/g

Comparison of SEI Decomposition Heats from Hitachi Graphites



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

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



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

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