Develop & evaluate materials &additives that enhance thermal & overcharge abuse

Khalil Amine (PI)
Zonghai Chen, Y. Qin, L. Zhang, W. Weng and J. Zhang
Argonne National Laboratory
June 10th, 2010

Project ID: ES035

Overview

Timeline

- Start: 10/01/2008
- End: 09/30/2014
- 30% completed

Budget

- Total project funding
  - DOE - $880K
  - Contractor - $ 0
- Funding received in FY09
  - $440K
- Funding for FY10
  - DOE - $440K

Barriers

- Barriers addressed
  - Cell safety
  - Cell flammability

Partners

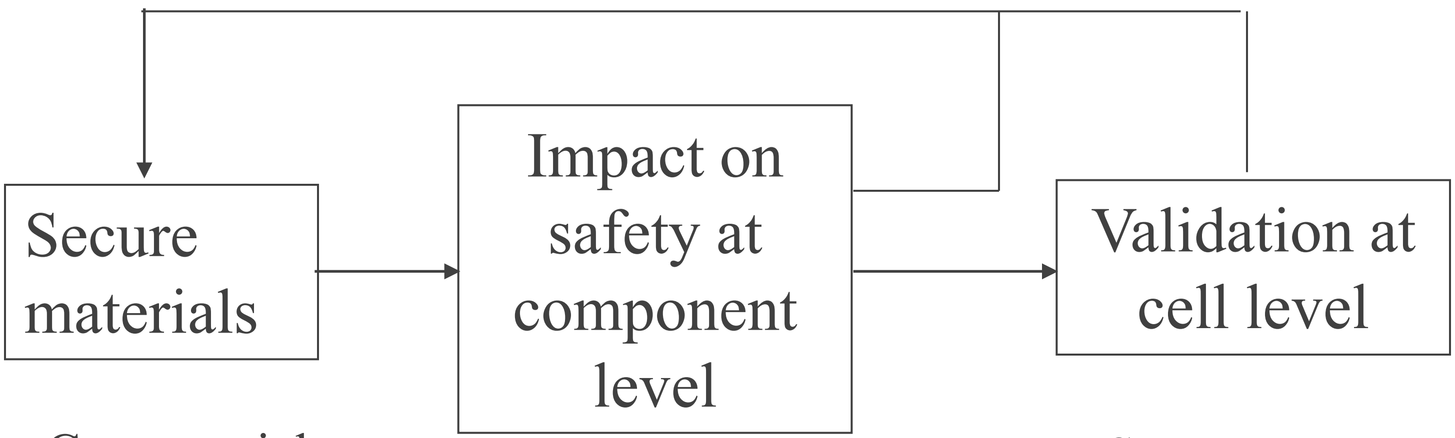
- Sandia National Laboratory
- EnerDel
- Hitachi Chemicals
- ECPRO

Objectives of the work

- Identify the role of each cell components 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) & supply them to SNL for validation of safety benefits in 18650 cells.

Approach

Current targets: a) Safer electrode materials – cathode and anode
b) additives for stable SEI on anode
c) surface modification for safer cathode
d) safer electrolyte components – solvent and salt
e) redox shuttles for overcharge protection



- Commercial source
- Partners
- In-house synthesis

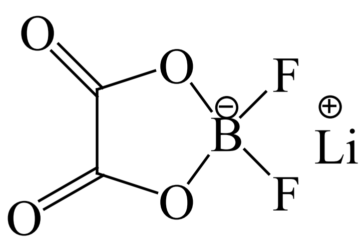
- Thermal analysis
- Electrochemical analysis

- SNL
- Industrial partners

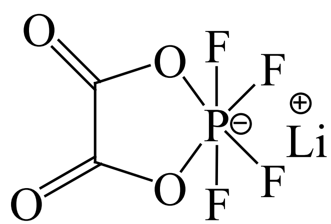
Recent Accomplishments and Progress

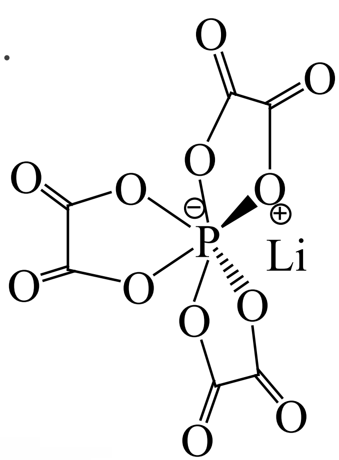
- **SEI formation on different carbon anodes**
  - Material investigated: MCMB-1028, 3 types of surface modified graphite from Hitachi, and Hard carbon
  - 18650 cells using $LiFePO_4$ and different carbons were secured and sent to SNL for ARC study.
  - Both DSC(ANL) and ARC (SNL) data agreed that the type of carbon anode significantly impact the safety of lithiated carbon.

- **Electrolyte additive for stable SEI layer**
  - Three electrolyte additives were identified to provide stable SEI on graphite and hence improve the safety of lithium ion cells.
  - Better capacity retention with the electrolyte additives.
  - SNL is quantifying the impact of LiDFOB at the 18650 cell level.



LiDFOB





Recent Accomplishments and Progress (cont'd)

- **Role of $LiPF_6$ for the thermal reactivity of cathodes**
  - The reaction of delithiated NMC with electrolyte components studied with DSC.
  - $LiPF_6$ was investigated against pure solvents, $LiBF_4$, LiTFSI and $Li_2B_{12}F_{12}$.
  - $LiPF_6$ has negative impact on safety of cathode by reducing the onset temperature from ~310^oC to about ~230^oC.

- **Surface coating of cathode materials**
  - Al_2O_3 coating was shown to be beneficial to the electrochemical performance of NCA.
  - 18650-cells using NCA and Al_2O_3 coated NCA were secured from industrial partner to verify the impact of coating at the cell level.
    - Some cells were provided to INL/ANL for life test.
    - 10 cells were shipped to SNL for abuse tests.
    - 10 cells were shipped to EnerDel for overcharge and nail penetration test.

Recent Accomplishments and Progress (cont'd)

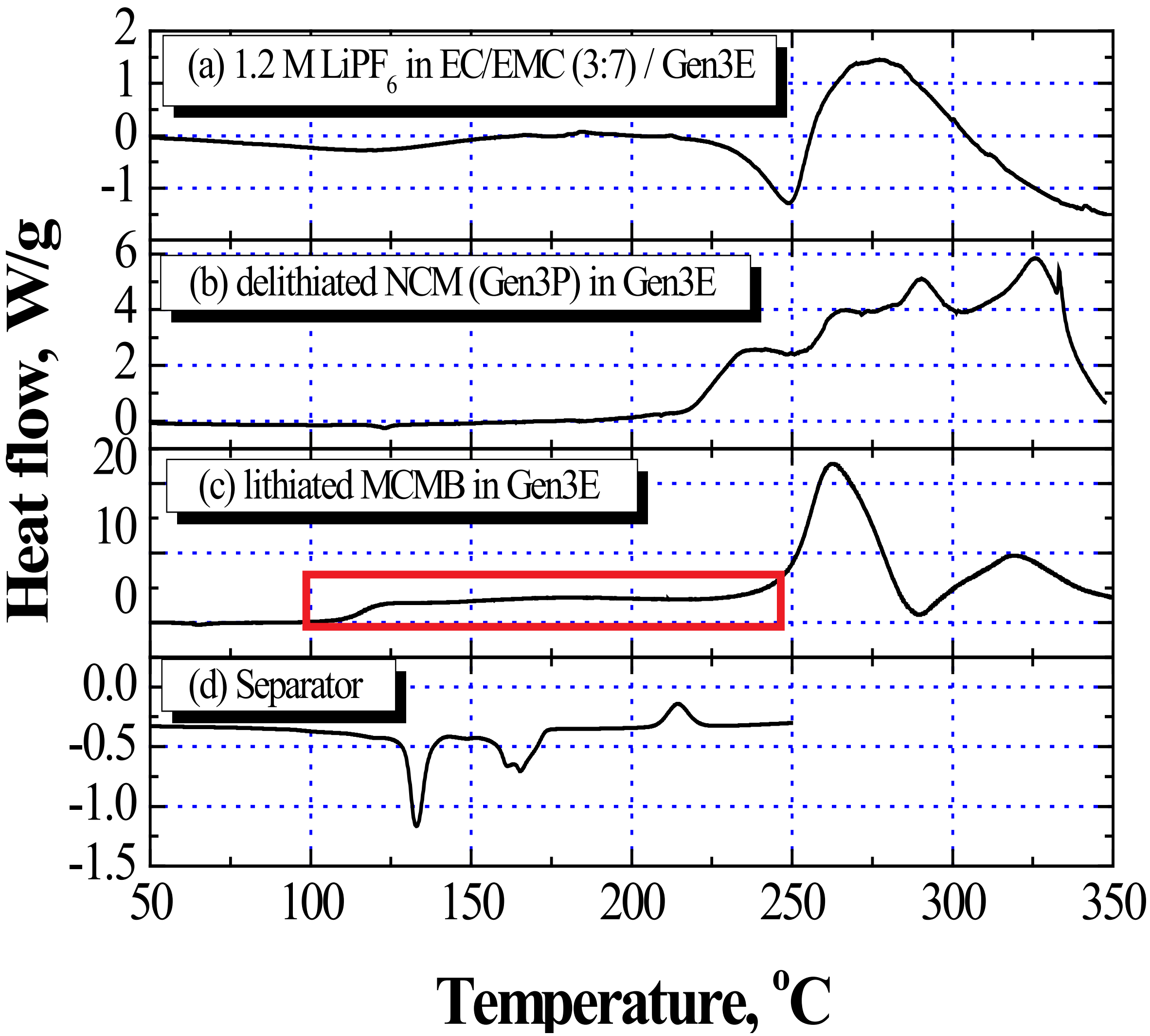
- **Redox shuttles for overcharge protection**
  - Three new aromatic redox shuttles with a redox potential of 4.17, 4.2 and 4.85 V vs. Li^+/Li were synthesized at ANL.
  - Their overcharge protection functionality was confirmed in coin cells.
  - The structures of redox shuttle are in the process of being patented, and might be disclosed at the merit review.

Only 2 of 5 areas are selected for oral discussion today.

(1) SEI decomposition reaction on different carbons.

(2) Redox shuttles for overcharge protection.

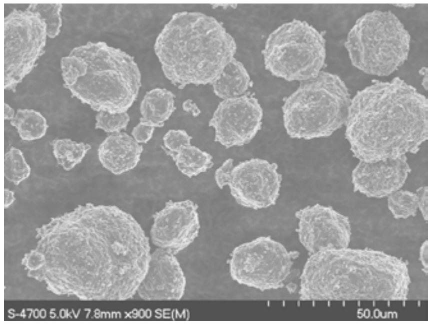
Importance of SEI on graphite safety



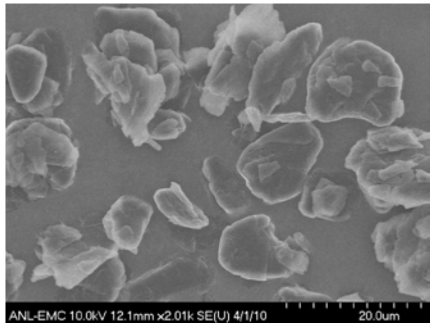
- Thermal runaway of LIB can be triggered at about 140-180°C.
- SEI decomposition is the only exothermal reaction below 200°C.
- The continuous SEI decomposition plays a critic role in triggering the major reaction of cathode with electrolyte at above 200°C.
- **A good SEI is expected to decompose at high temperature and generate low exothermal heat flow.**

Carbon anodes used for the safety study

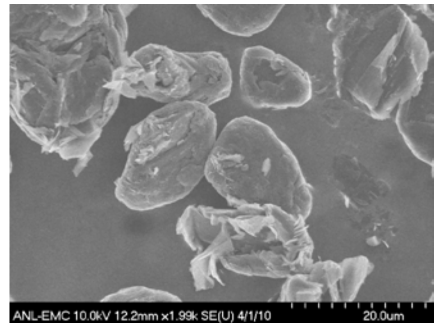
MCMB-1028



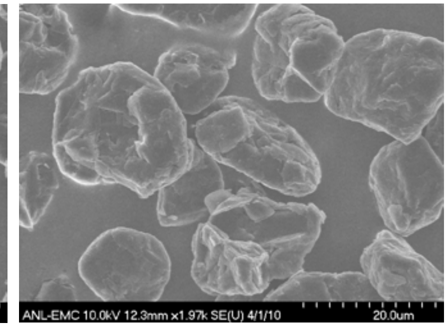
SMG-N-7b



SMG-N-20



SMG-Ns-15f

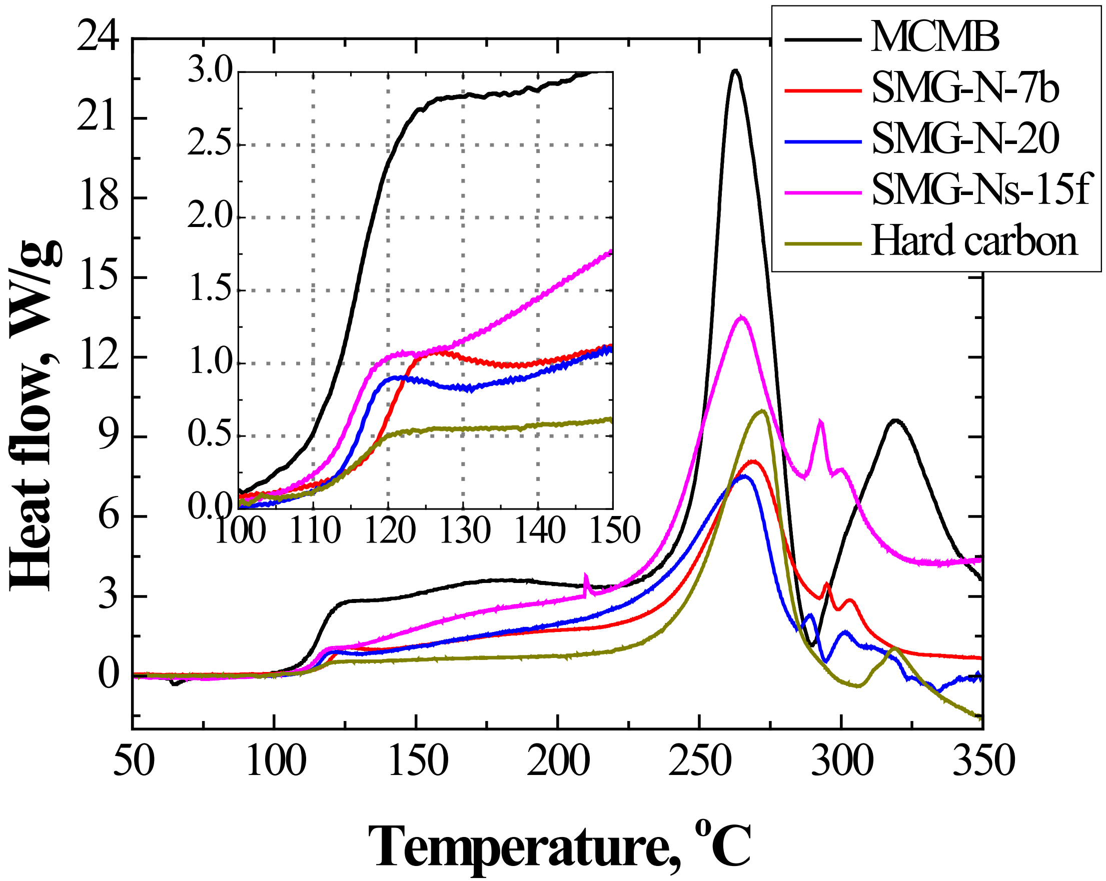


	MCMB-1028	SMG-N-7b	SMG-N-20	SMG-Ns-15f	HC
Description	MCMB	Surface modified	Nature graphite	Surface modified	Hard carbon
D_{50} (μm)	11.8	11.1	19.5	21.6	TBD
BET (m^2/g)	2.01	5.0	5.1	0.7	TBD

- Physical parameters investigated: bulk structure, particle size, surface area
- Physical characterization of hard carbon is ongoing.

Reaction of lithiated carbons with electrolyte

1.2M $LiPF_6$ in EC/EMC (3:7)



- Major exothermal reaction was observed above 220°C for all carbons.
- The focus is the SEI decomposition that trigger thermal runaway at low temperature.

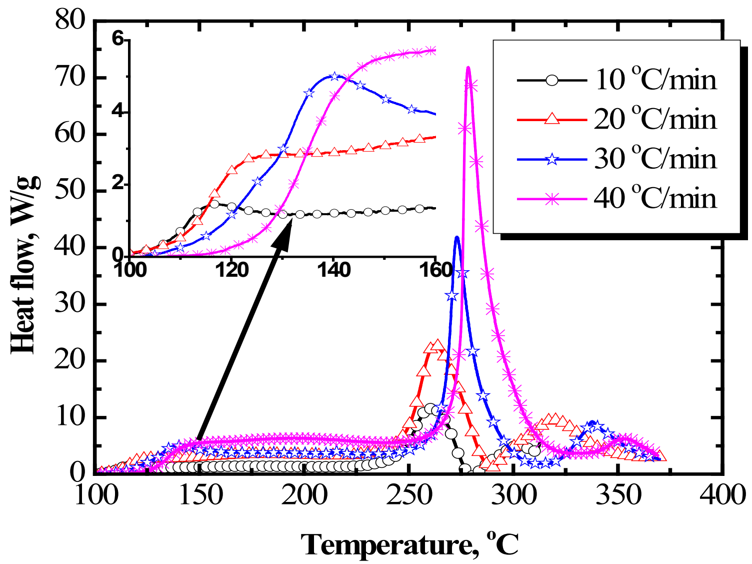
➢ At temperature below 200°C, MCMB generated more heat than surface modified graphite (SMG series). Hard carbon generate the least heat.

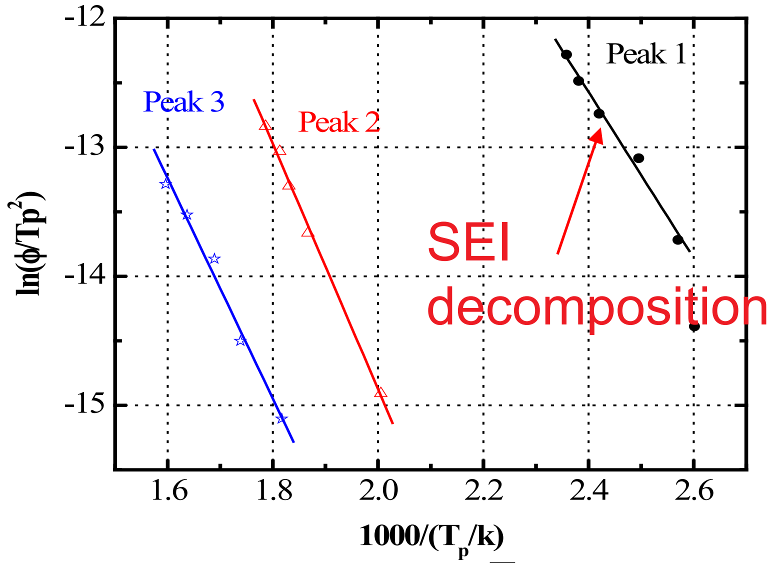
➢ Heat flow of SMG-N-20 is lower than SMG-N-7b, and SMG-Ns-15f.

➢ Kinetics of the SEI decomposition is another key parameter.

SEI Decomposition kinetics on different carbons

Lithiated MCMB-1028 with 1.2M $LiPF_6$ in EC/EMC(3:7)



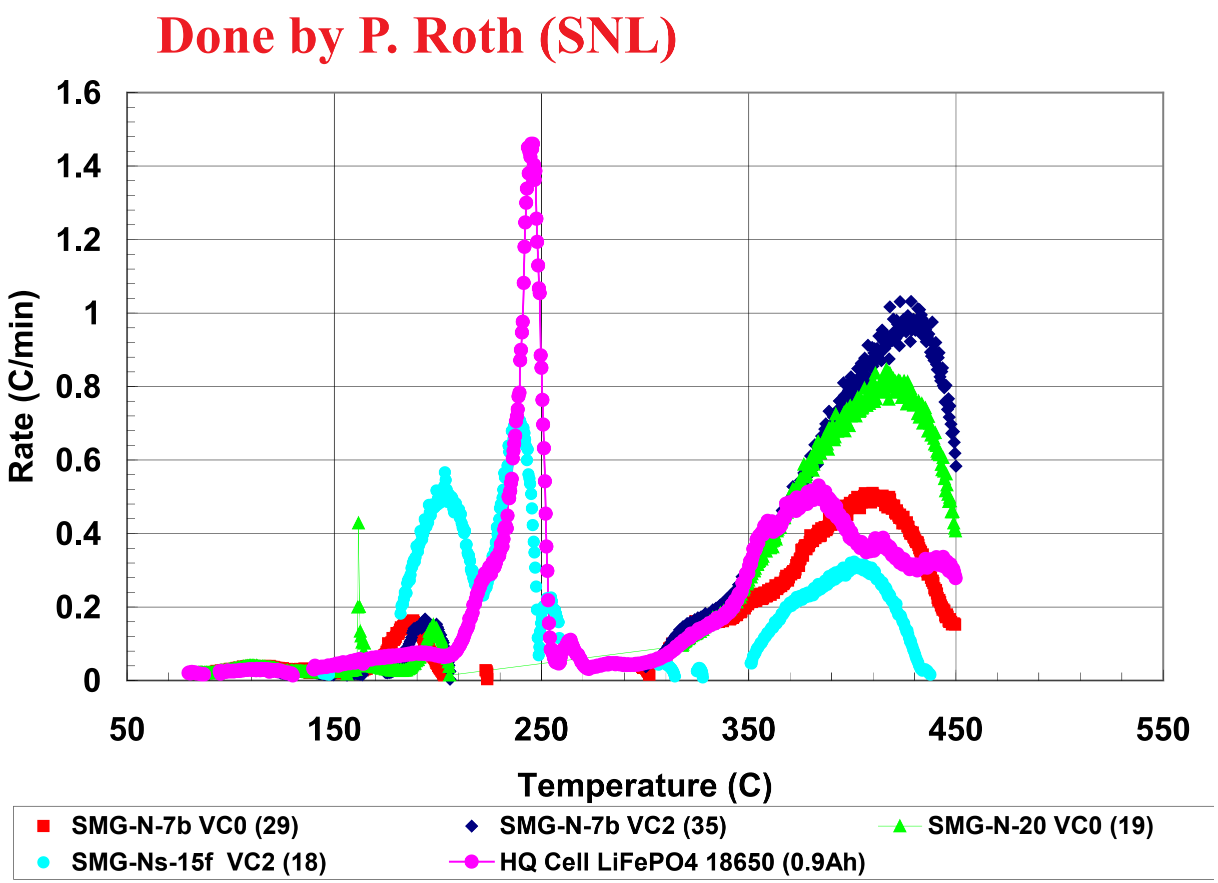


Model free kinetics determination: $$\ln(\phi / T_p^2) = k - \frac{E_a}{RT}$$

	MCMB-1028	SMG-N-7b	SMG-N-20	SMG-Ns-15f	HC
Ea (kJ/mol)	53.54	88.08	**92.66**	78.46	87.34

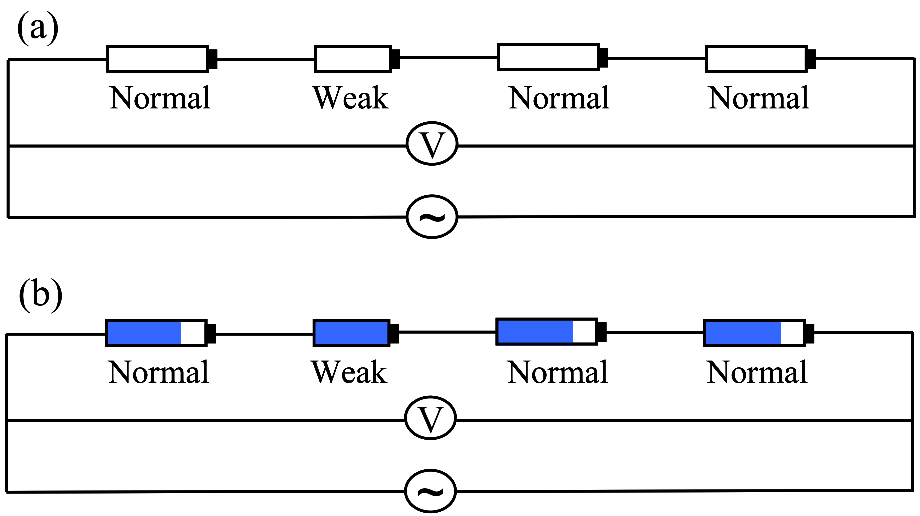
- **Kinetics: SMG-N-20 > SNG-N-7b ~ Hard carbon > SMGNs-15f > MCMB-1028**
- **How about the response at cell level?**

DSC results confirmed by ARC study on 18650 cells



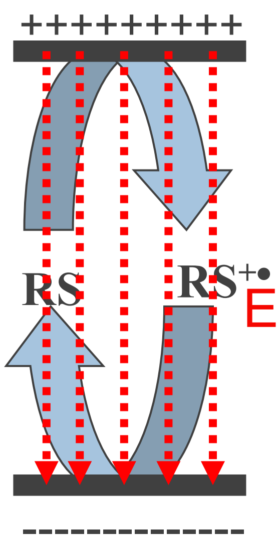
- $LiFePO_4$ was used as cathode to minimize the exothermal reaction on cathode side.
- Three carbons were examined: SMG-N-7b, SMG-N-20, and SMG-Ns-15f.
- SMG-N-20 > SMG-N-7b > SMG-Ns-15f
- Cell safety data is similar to components level safety data

Overcharge abuse of lithium ion batteries

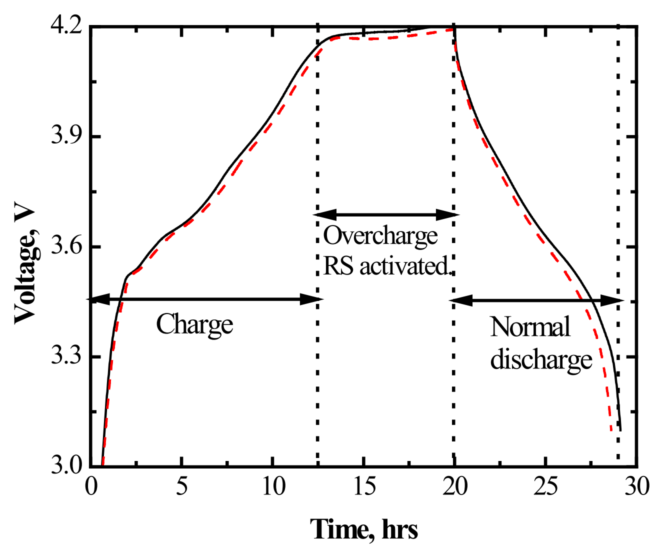


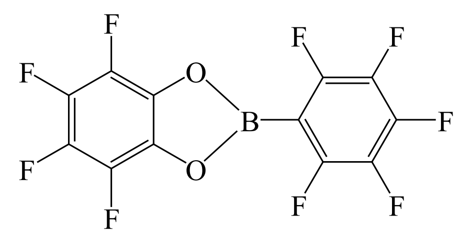
Possible consequences:

- Accelerate capacity/power fade; shortening life.
- Decomposition of cathode electrode.
- Lithium plating on anode.
- Heat generation; possibly triggering thermal runaway.
- Electrolyte decomposition and gassing; potential leakage.
- Internal short.



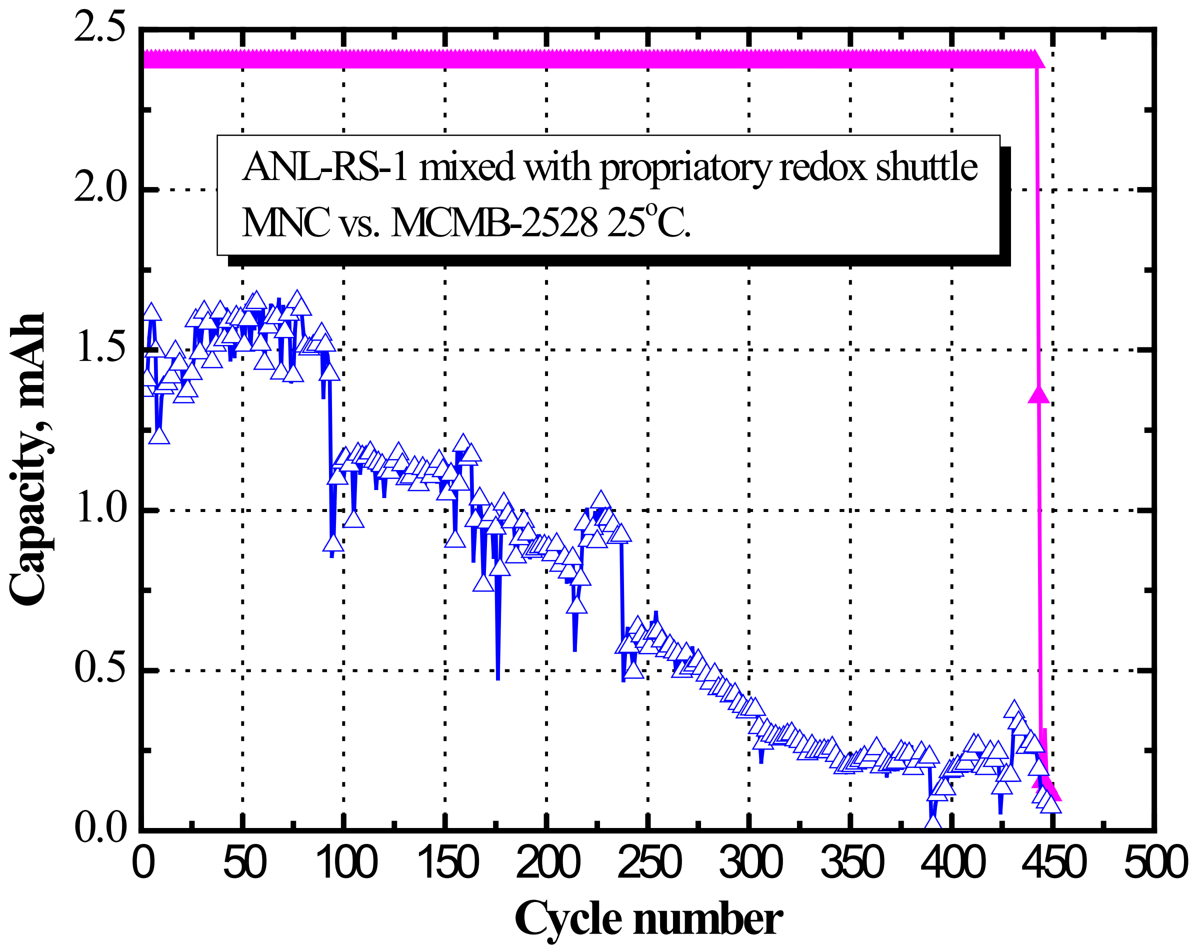
$MCMB/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$





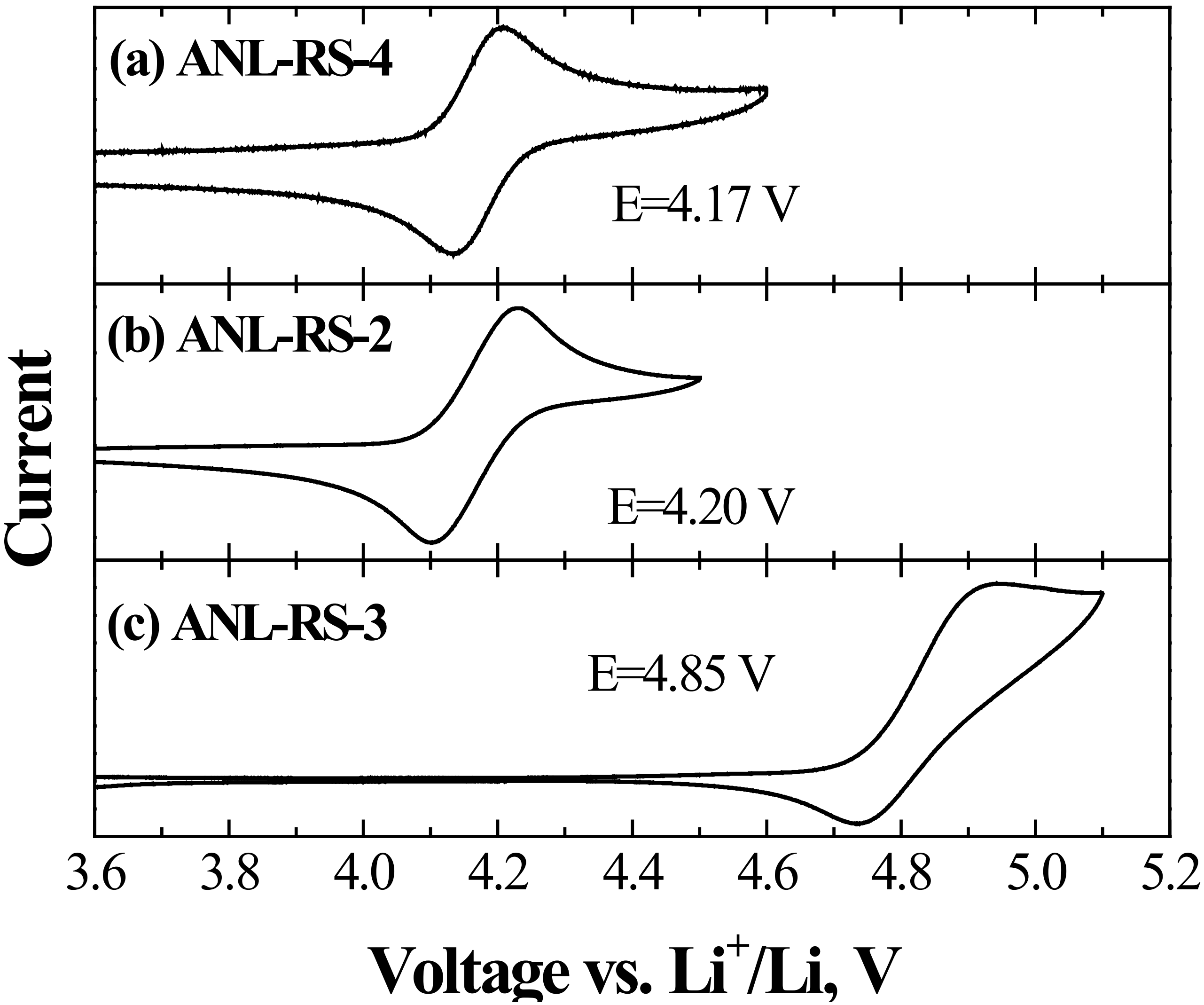
- The cell voltage can be properly capped with a stable redox shuttle.
- The redox potential of redox shuttle is required to be at least 0.2 V higher than the working potential of the cathode.
- Possible cell balancing with a shuttle

Unmatched long term overcharge protection



- Cathode: $Li_{1.1}[Mn_{1/3}Ni_{1/3}Co_{1/3}]_{0.9}O_2$
- Anode: MCMB-1028
- Current: C/3

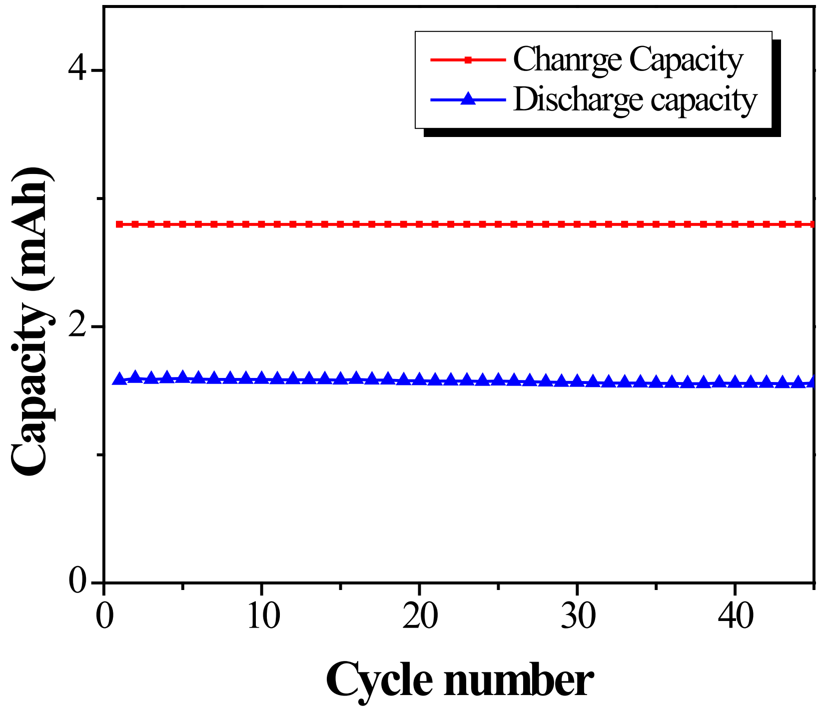
New redox shuttles synthesized at ANL



- Three new redox shuttles were synthesized at ANL (IP in the process of being generated)
- ANL-RS-2 and ANL-RS-4 are good candidates for 4 V class materials.
- ANL-RS-3 is promising for high voltage materials such us Composite electrode material.

Long term electrochemical performance of new redox shuttle (ANL-RS-4)

$LiFePO_4$/LTO; 1.2 M $LiPF_6$ in EC/EMC (3:7); 2.3 wt% of redox shuttle



•ANL-RS-4 showed excellent electrochemical performance in $LiFePO_4$/LTO cell. More study is needed for other lithium ion chemistry like oxides cathode and carbon anodes.

•Electrochemical study of ANL-RS-2 and ANL-RS-3 is ongoing, and will be reported later.

Collaborations

- **Partners**

  -Sandia National Laboratory: cell level verification of safety improvement using components identified at ANL.

  -EnerDel: overcharge abuse and nail penetration test of 18650 cells.

  -Hitachi Chemical: collaboration on the safety characteristics of carbon anodes and 18650 cell fabrication.

  -ECPRO: collaboration on 18650 cell fabrication using NCA based 18650 cells (Coated & non–coated NCA)

- **Technology transfer:**

  Collaboration with EnerDel & JCI to validate ANL's redox shuttles.

  - overcharge protection
  - cell capacity balancing

Proposed Future work

- Continue exploring electrolyte additive to reduce heat flow from SEI decomposition at low temperature.
- Investigate the safety of anode that doesn't require SEI
- Quantify the impact of $LiPF_6$ on the thermal stability of delithiated cathode and explore the possible safety mitigation techniques.
- Investigate the role of none flammable electrolyte & ionic liquid on the safety of lithium battery
- Investigate the effect of cathode composition, morphology and surface area on safety
- Systemic characterization of ANL's new redox shuttles, and continue exploring new shuttle structures.
- Work with SNL and industrial partner to validate new shuttles in a full cell configuration (focus on overcharge & cell balancing)
- Work with industrial partner to make 18650 cell using ANL composite electrode & investigate the safety performance of this high energy material in collaboration with SNL

Summary

•Several components were investigated for safety improvement:

(a) carbon anodes; Role of SEI

(b) electrolyte additives for more stable SEI layer;

(c) electrolyte components;

(d) redox shuttles for overcharge protection;

(e) oxide ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) coated with Al_2O_3

•SMG-N-20 and a hard carbon were identified as potentially safer anode than MCMB-1028.

•Three new stable redox shuttles discovered at ANL are promising for overcharge protection for 4 V class cathode materials.

Collaborations

- P. Roth (SNL) (provide materials and cells for cell level safety studies)
- Hitachi chemical (make 18650 cells based on LiFePO4 and several carbon made from the same process but have different surface area)
- ECPRO (make 18650 cells with Al_2O_3 coated and non coated NCA)
- EnerDel (Overcharge test, nail penetration of 18650 cells)
- EnerDel and JCI (shuttle validation and effect on cell monitoring)
- Daikin (provide new non flammable solvent and flame retardant)
- 3M (provided new shuttle for ANL for screening purpose)
- Many Japanese and Korean companies (supplied material that impact the safety of lithium batteries)