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

Zonghai Chen, Yan Qin and K. Amine

Argonne National Laboratory

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Project ID: esp_23_amine

Overview

Timeline

- Start - October 1st, 2008.
- Finish - September 30, 2009.
- 50%

Barriers

- Barriers addressed
  - Safety of the cathode
  - Safety of the anode
  - Overcharge abuse

Budget

- Total project funding
  - DOE share: 440K

Partners

Interactions/ collaborations:
Zonghai Chen, Yan Qin , P. Roth (SNL), Hitachi Chemical

Project lead: Khalil Amine

Objectives of the work

- Identify the role of each cell material/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) to supply SNL for validation and quantification of safety 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 (demonstrated in the past meetings)
- 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 solid electrolyte interphase (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 the 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
- 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

- Coat cathode particle with stable nano-films of Al-oxide or Al-fluoride that act as a barrier against electrolyte reactivity with cathodes
- Explore 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.
- Explore new redox-shuttle to (a) improve the overcharge protection of lithium batteries, and (b) for automatic capacity balancing of battery packs
- Quantify the role of the additives and surface area of carbon on 18650 cell in collaboration with SNL
- Investigate the role of flame retardant and none flammable solvents of the safety of lithium battery

FY 2009 plans & schedule

- Investigate the effect of nano-coating of active materials on the safety of lithium ion batteries (Sep 2009)
- Investigate of the effect of breakdown of the Secondary SEI on battery safety using 18650 cells having $LiFePO_4$ cathode and different carbon made in the same way but have different surface area (Sep 2009)
  (Argonne has shipped 10 kg $LiFePO_4$ and provides design specification to Hitachi for making 18650 cells using graphites with the same grade but different morphology and surface area).
- Investigate the role of additive in improving the safety of carbon and quantify its effect in 18650 cells (Sep 2009)
- Investigate the effect on safety of new non flammable solvent and flame retardant. (Sep 2009)
- Investigate new ANL redox shuttle recently discovered (Sep 2009)
- Screening other redox shuttles from industry (Sep 2009)

Recent Accomplishments and Progress

- ***Safety investigation of lithiated carbon anodes***
  - Lithiated carbon anodes are thermodynamically unstable
  - A stable SEI layer is crucial for better safety and life.
  - Additive is critical to provide stable SEI film.

- Safety investigation of delithiated cathodes
  - Delithiated cathodes are also unstable in non-aqueous environments.
  - Reactivity of delithiated cathodes can also be mitigated by surface modifications.

- Improvement on the overcharge tolerance using different redox shutlle
  - $Li_2B_{12}F_{12-x}H_x$ (x=1,2,3,…12) redox shuttles
  - 3M's redox shuttles – aromatic compounds
  - Argonne's redox shuttles – aromatic compounds

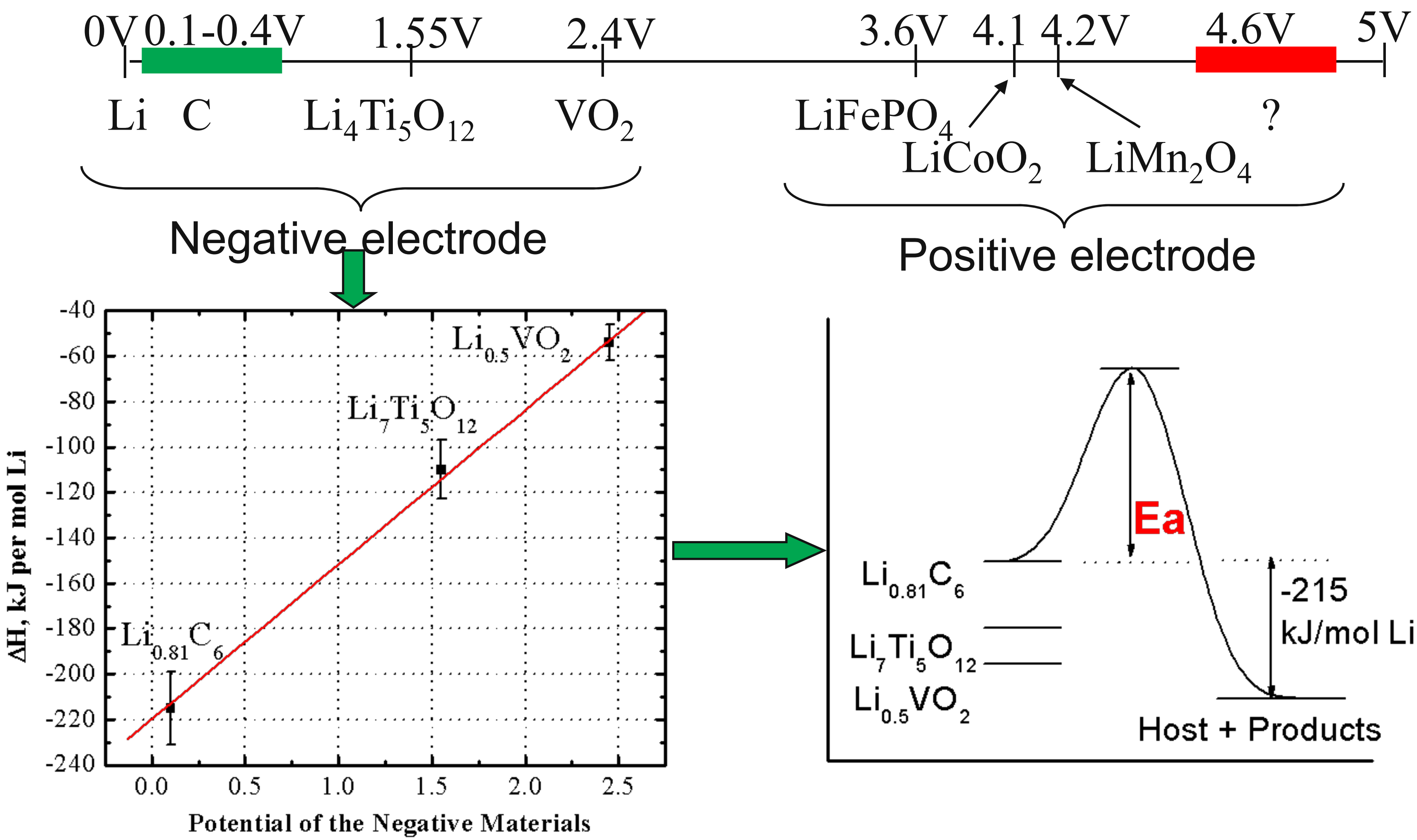
Approaches for the investigation of anode safety

- Using kinetics of undesired reaction as an indicator of stability.

- Investigated the impact of electrolytes additives (LiBOB and LiDFOB) that can provide stable SEI films.

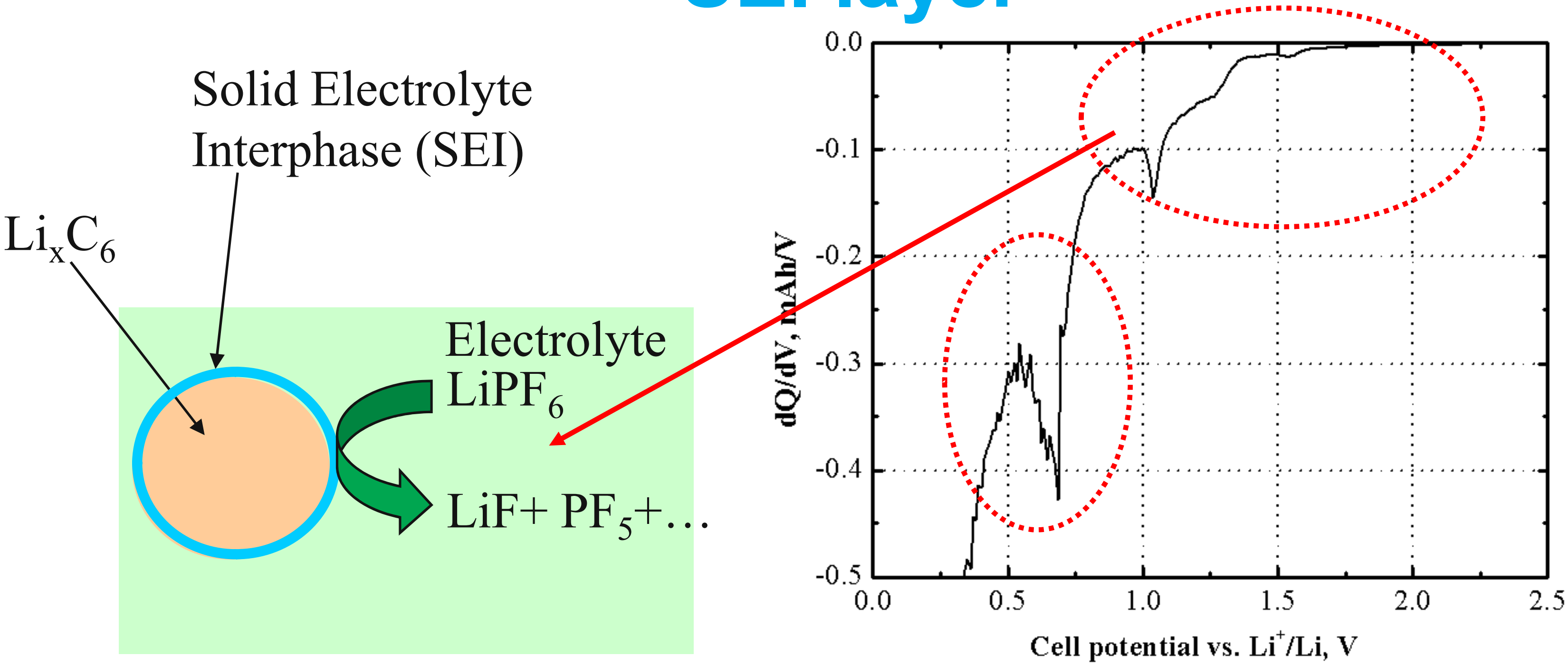
- Additional additives will be investigated in the near future.

Reactions between electrode materials and electrolyte



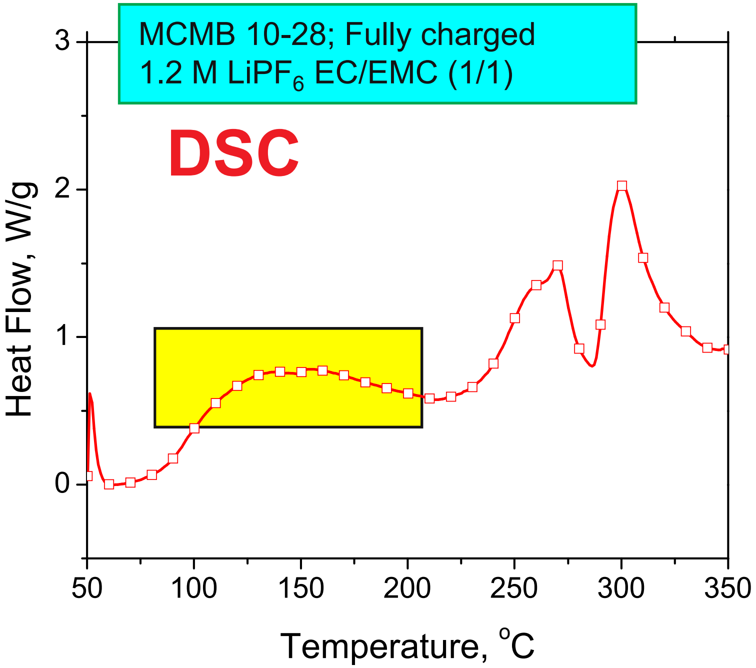
- All lithiated anodes react with non aqueous electrolyte and generate heat.
- Kinetics of the reaction is the key to the safety of batteries.

Lithiated carbon is kinetically stabilized by SEI layer



- Lithiated graphite is thermodynamically unstable in the non-aqueous electrolytes.
- Kinetic stability is achieved by the presence of SEI.
- A good SEI with higher activation energy (Ea) is critical to improve safety characteristics.

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

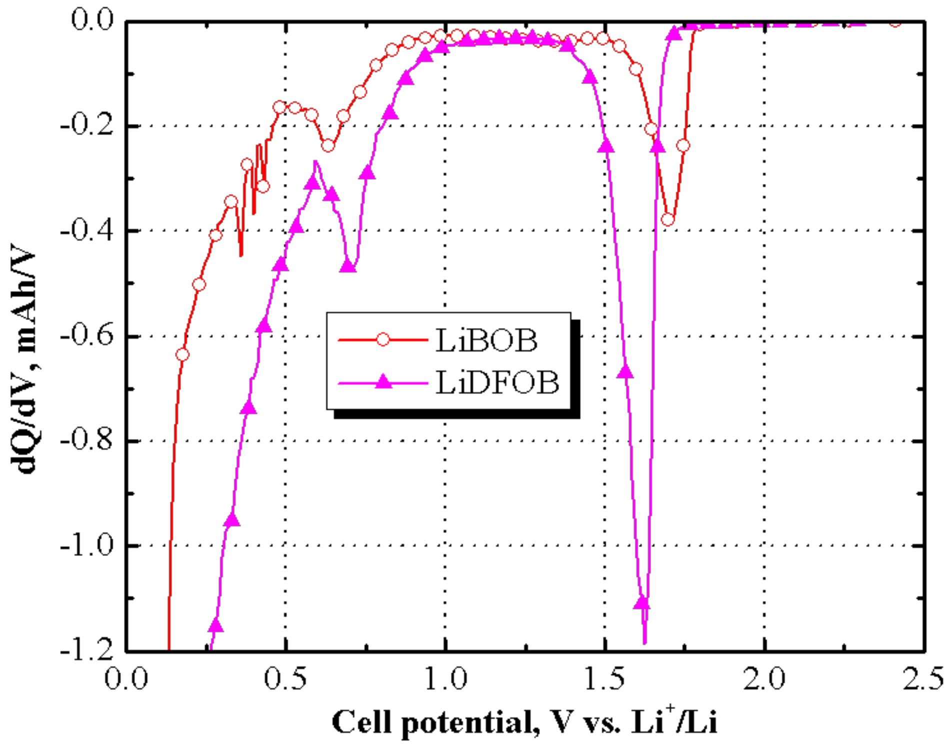


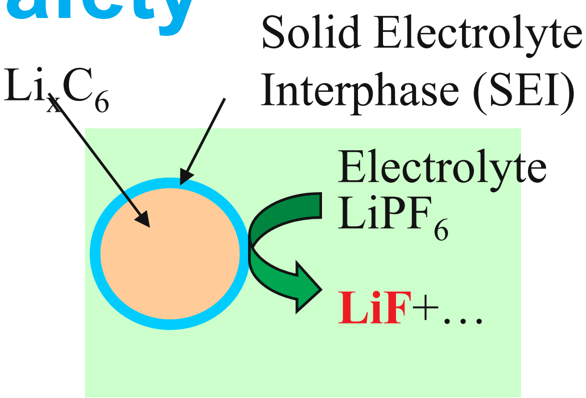
- The thermal heat generated by the continuous breakdown and formation of the SEI between 80°Cand 200°C could trigger the early thermal run away observed in the cell

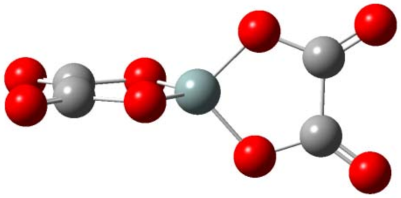
- This heat could be large enough to lead to the thermal runaway of the cell regardless of the nature of the cathode specially in large cells

Stable SEI film is critical for better safety.

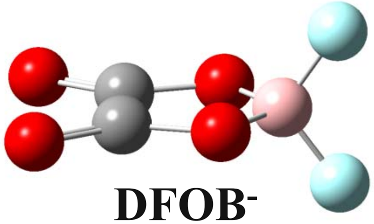
Use of Functional Additives can stabilize the SEI and improve safety







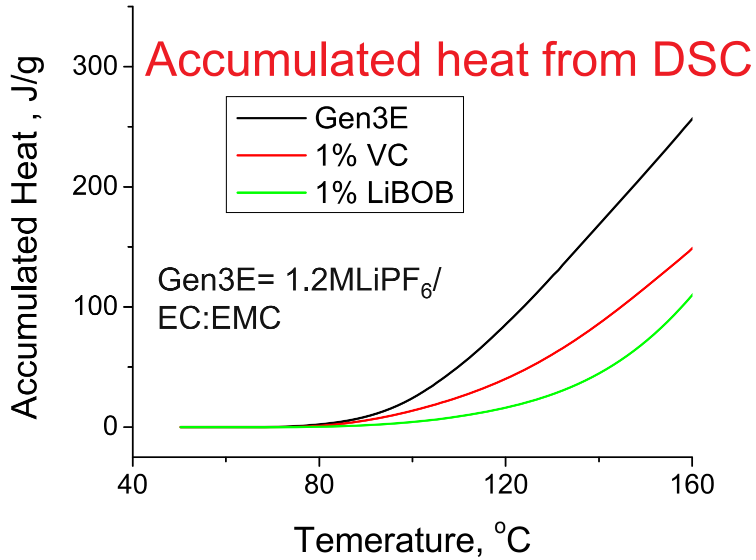
BOB$^-$
Lithium bis(oxalato)borate



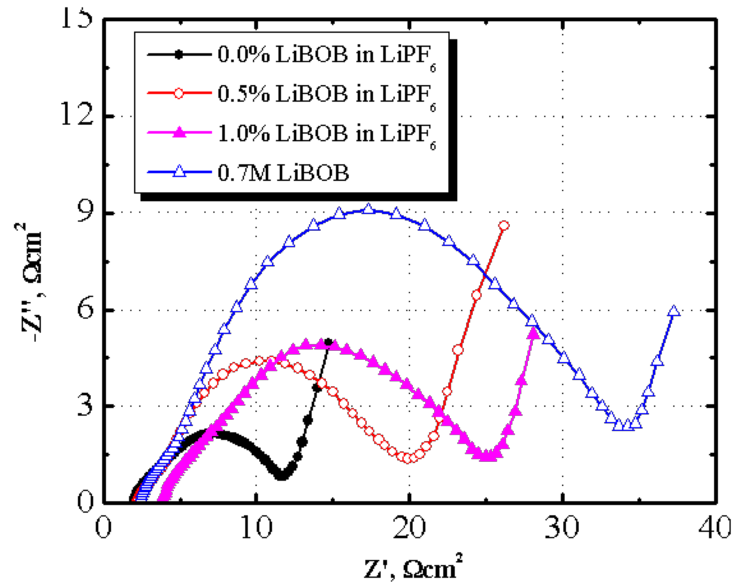
DFOB$^-$
Lithium difluoro(oxalato)borate

- Reduction occurs at 1.7 V (LiBOB) and 1.6 V (LiDFOB) and form a new SEI before the formation of conventional SEI layer at a potential lower than 1.0 V.

LiBoB additive is effective in reducing the heat caused by the secondary SEI breakdown but leads to high cell impedance

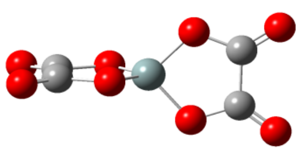


Electrolyte additive suppress the heat generation and onset temperature of SEI breakdown.

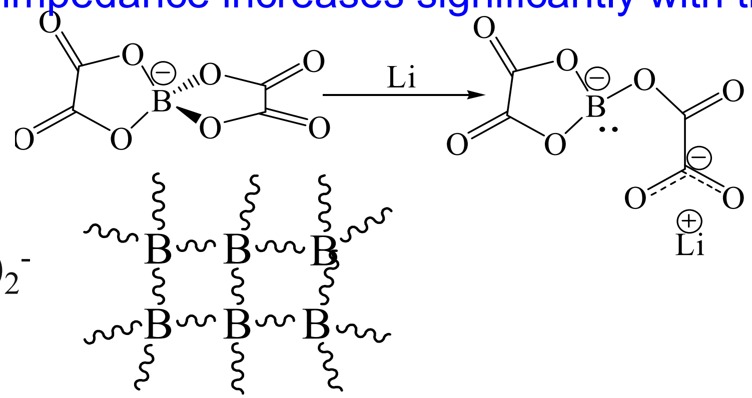


Addition of LiBOB significantly increase the interfacial impedance.

Why cell impedance increases significantly with the content of LiBOB added?



BOB^-, $B(C_2O_4)_2^-$

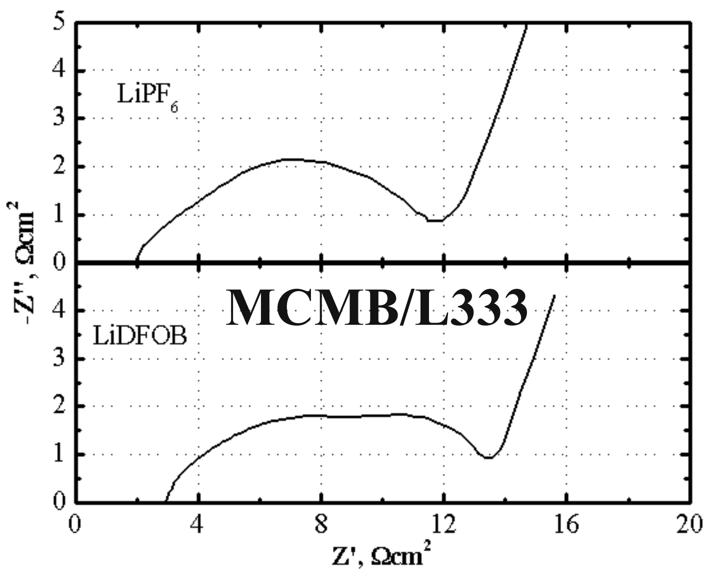


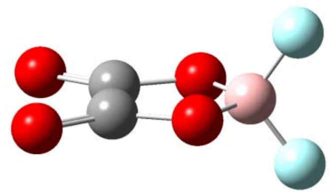
2-D network leads to dense and thick SEI layer that increases the interfacial impedance of the electrode.

Need additive that doesn't sacrifice the power capability.

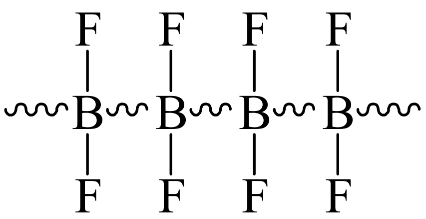
LiDFOB additive provide low impedance after SEI formation and improve safety

AC impedance @ 3.8V





DFOB$^-$, $BF_2C_2O_4^-$ as alternative additive



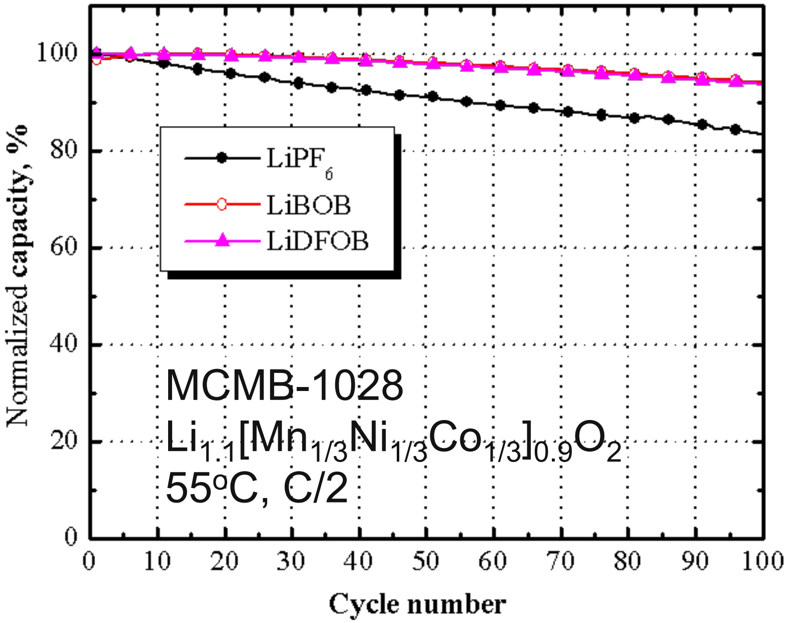
Linear polymer self-limits the growth of SEI layer.

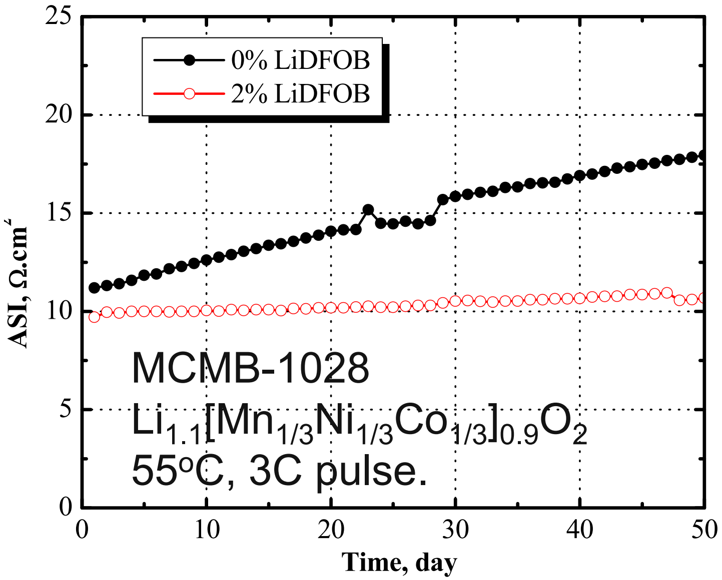
MCMB=mesocarbon microbeads,
L333=$Li_{1.1}[Mn_{1/3}Ni_{1/3}Co_{1/3}]_{0.9}O_2$

- Cell with LiDFOB additive has similar impedance to those with no additive

- LiDFOB can be added with any concentration to maximize the capacity retention, and stabilize the anode without hurting the power capability of the lithium-ion cell.

LiDFOB improves cell capacity retention and calendar life at 55^oC



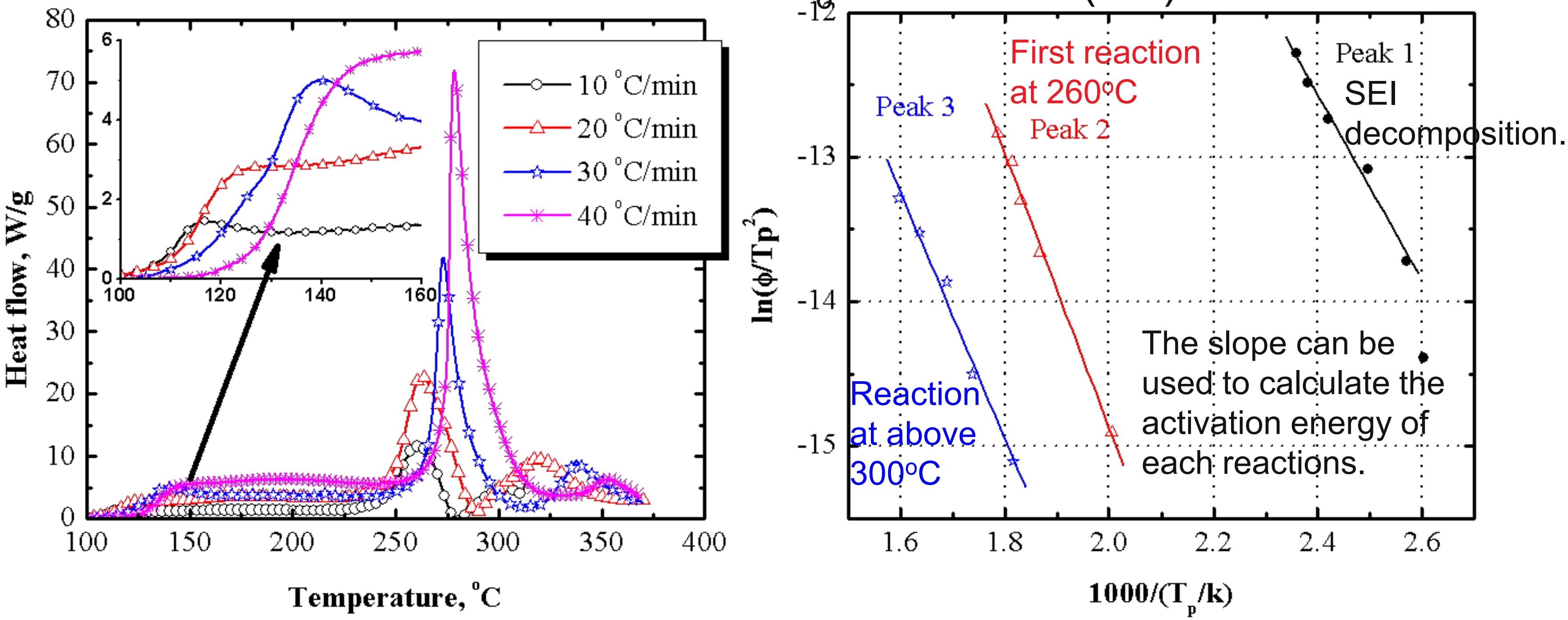


- •LiDFOB has the same protection capability as LiBOB does, but provide low cell impedance.

- •The ASI of cell without LiDFOB increase about 50% in 50-day storage at 60% SOC, while the cell with 2% LiDFOB showed stable ASI during the same period of testing time.

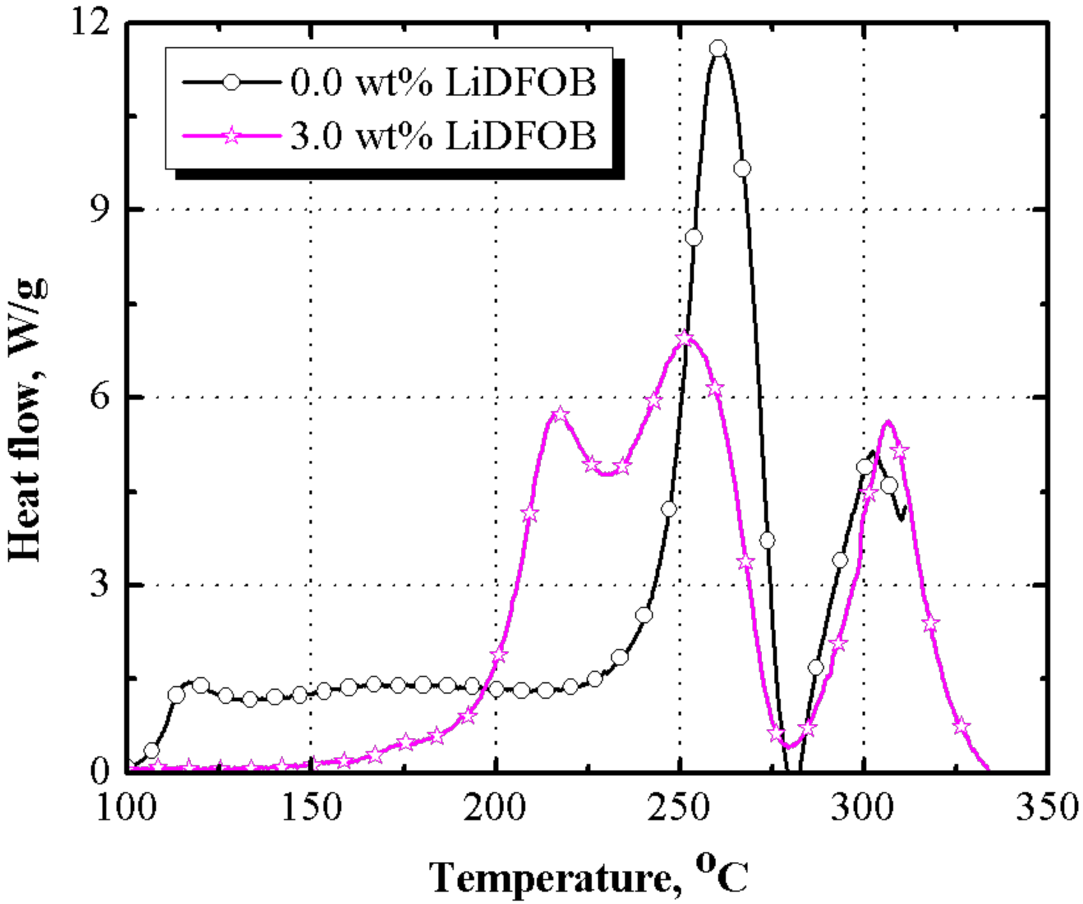
Effect of SEI on the thermal reactivity of lithiated MCMB graphite with electrolytes

Lithiated MCMB with 1.2 M Li PF_6 in EC/EMC(3:7)



- *Continuous SEI breakdown/formation is responsible for exothermal heat from 100°C to 200°C.*
- *Kinetics of the exothermal reaction can be determined using differential scanning calorimetry (DSC).*

Impact of LiDFOB on the thermal reactivity of lithiated MCMB graphite with electrolytes



DSC of charged MCMB graphite in the presence of 1.2 M Li PF_6 in EC/EMC(3:7) with different amount of LiDFOB additive.

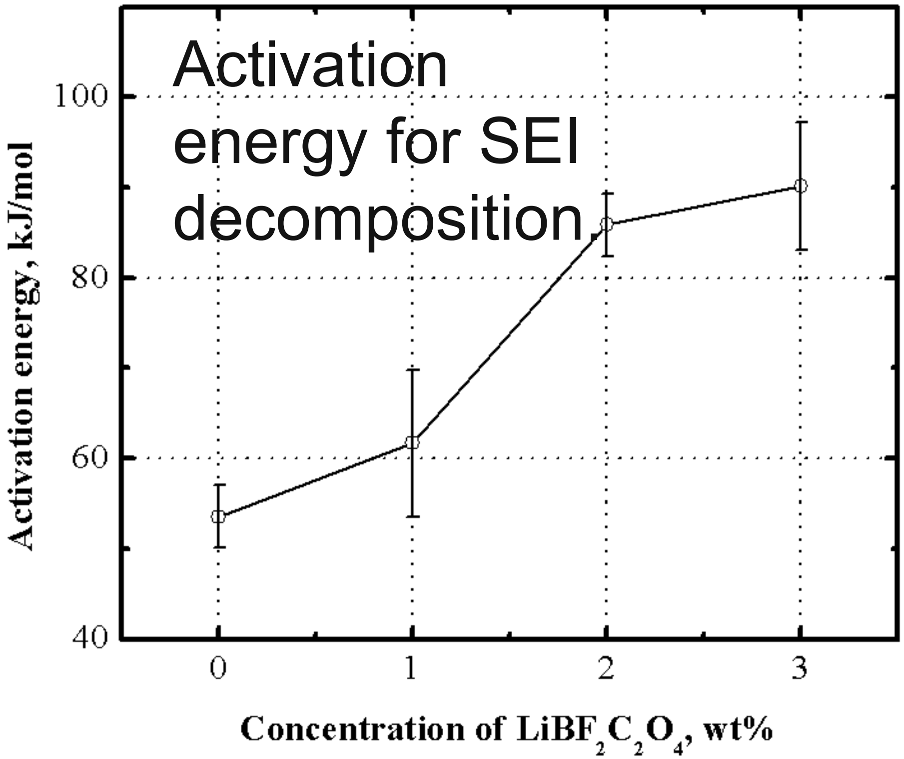
The addition of LiDFOB push the decomposition temperature of SEI to a higher value; meaning:

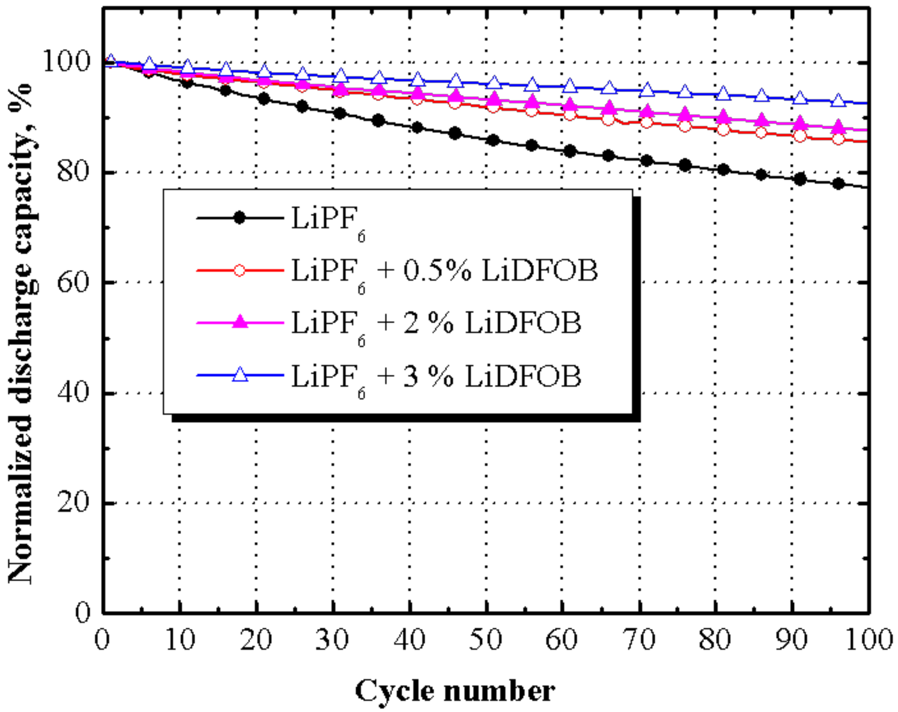
(1)Higher activation energy;

(2)Better thermal stability;

(3)Lower heat generated between 100^{o}C and 200^{o}C.

Correlation between concentration of additive, thermal stability and activation energy





Cells with 2 ~3wt% of LiDFOB show higher activation energy, better thermal stability and improved cycling performance because the additive effectively stabilize the carbon anode against electrolyte reactivity

Approaches for the investigation of cathode safety

- The reactions of cathodes are more complicated than anodes, both thermodynamics and kinetics will be used to evaluate the stability of cathodes.

- Investigated the impact electrolytes additive like TPFPB and LiDFOB.

  TPFPB was demonstrated to promote the SEI stability on anodes.

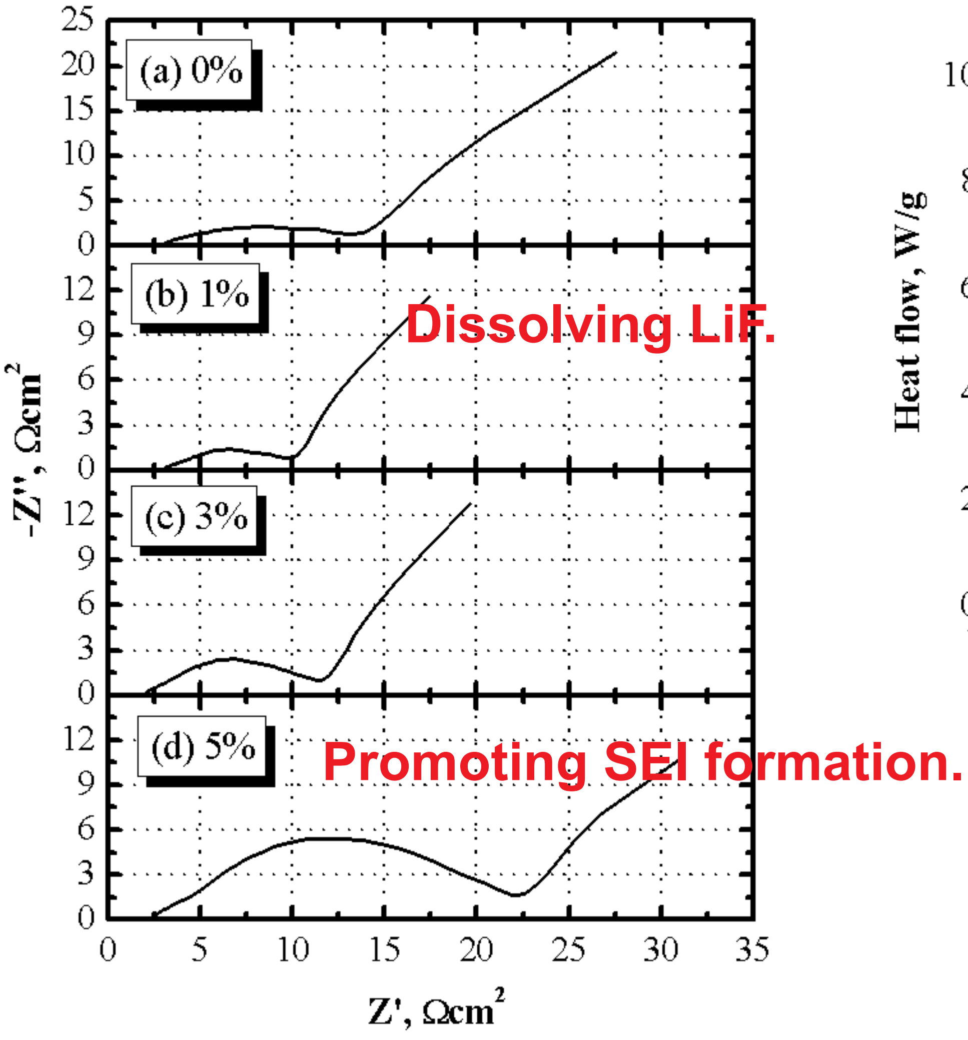
  What's the impact of TPFPB on cathodes?

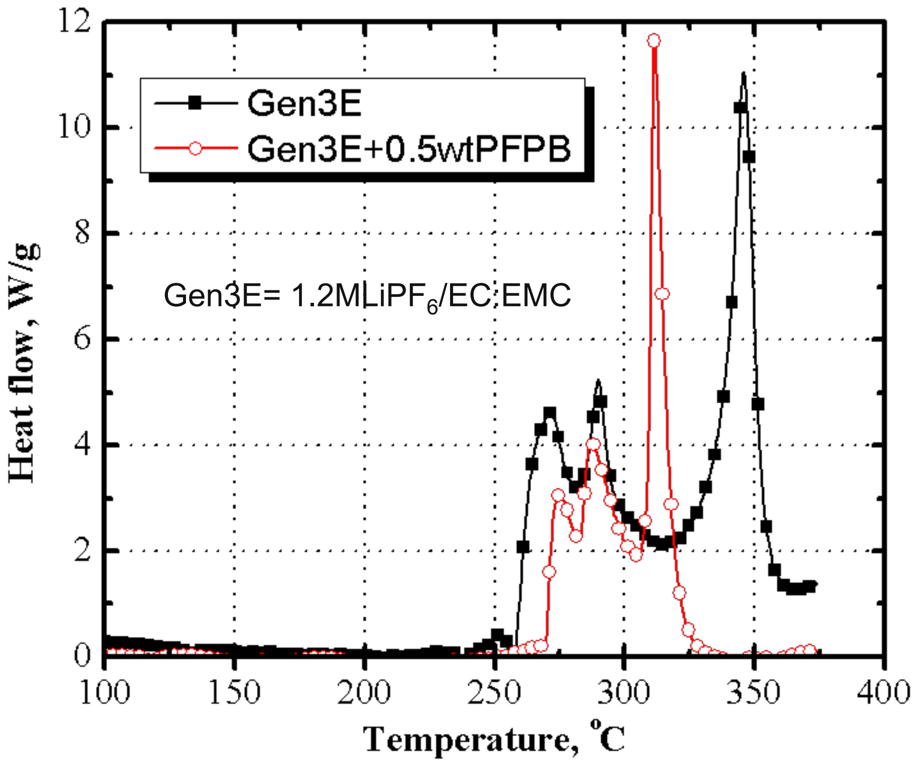
  How about LiDFOB?

  How about nano coating of the materials?

- More additives and coating techniques will be investigated in the near future.

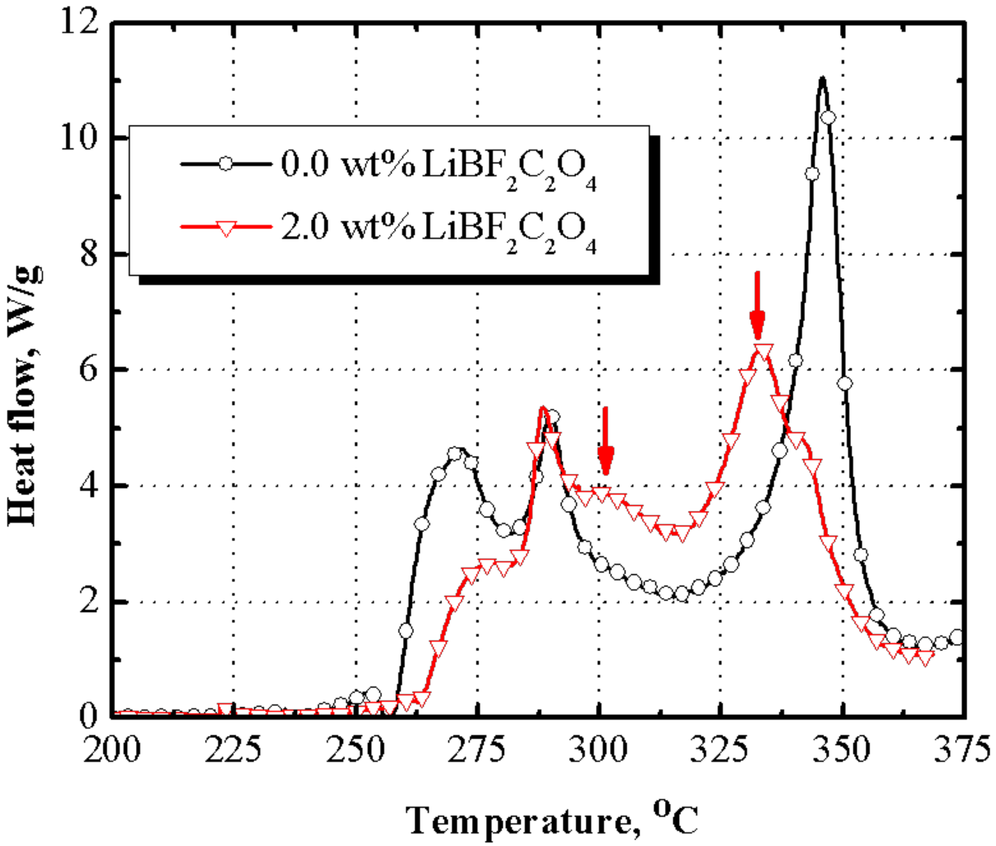
Use of TPFPB additive to improved passivation films at the cathode





- TPFPB can dissolve LiF and enhance the formation of SEI film.
- TPFPB also show positive impact of the onset temperature of delithiated cathode.
- Kinetic study will be carried out soon.

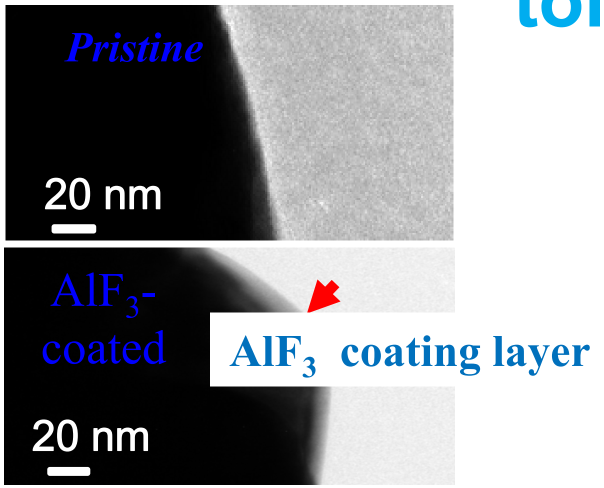
Impact of LiDFOB on the thermal reactivity of the cathode



DSC of charged $Li_{1-x}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$ graphite in the presence of 1.2 M Li PF_6 in EC/EMC(3:7) with different amount of LiDFOB additive.

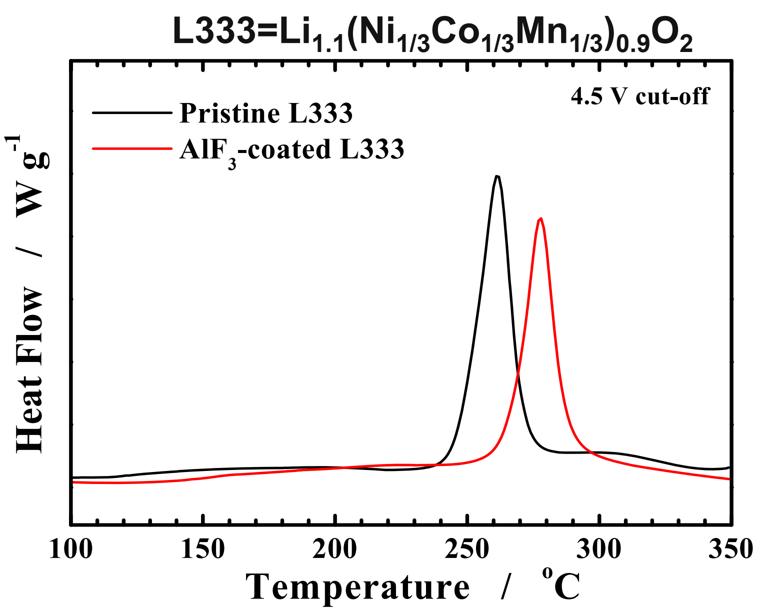
- The onset of the first exothermal peak was pushed up by about 10^{o}C.
- New reactions was observed at above 300^{o}C.
- The impact of LiDFOB on cathodes needs to be carefully verified in terms of kinetics and thermodynamics.

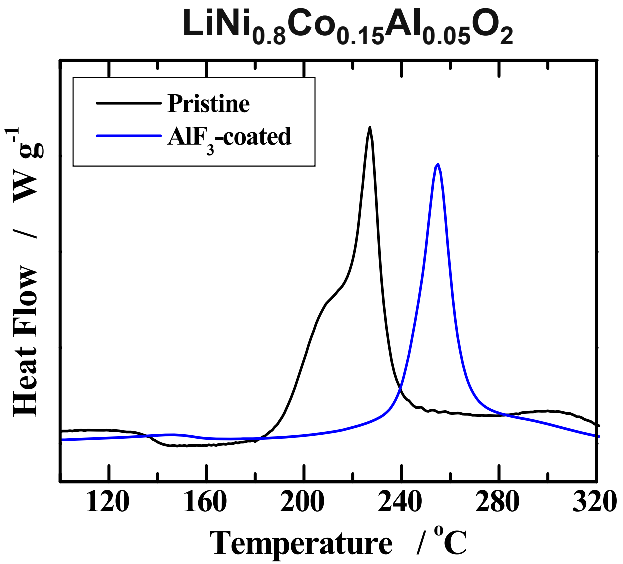
Increased cathode surface stability with AlF_3 nano-coating can significantly improve the abuse tolerance of the cathode



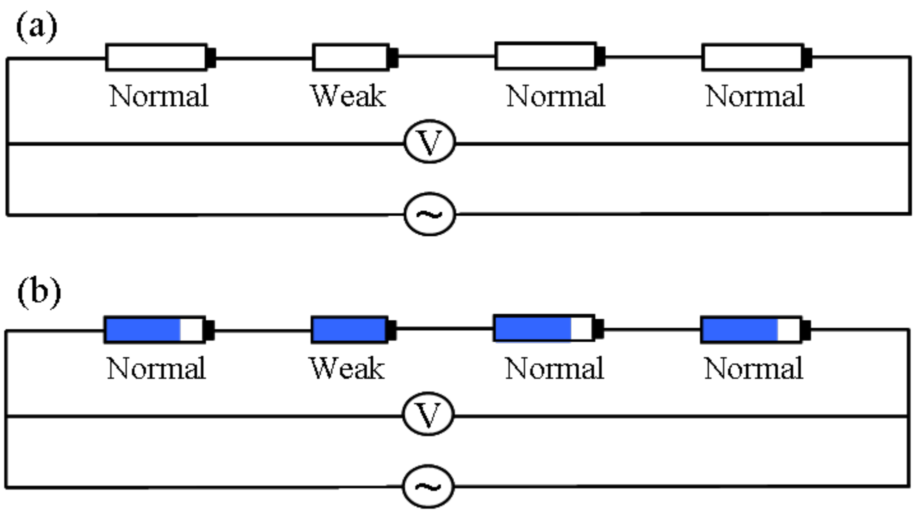
Coating cathode materials with nano-film of AlF_3 has resulted in a significant delay of the thermal reactivity with the electrolyte

DSC Scans



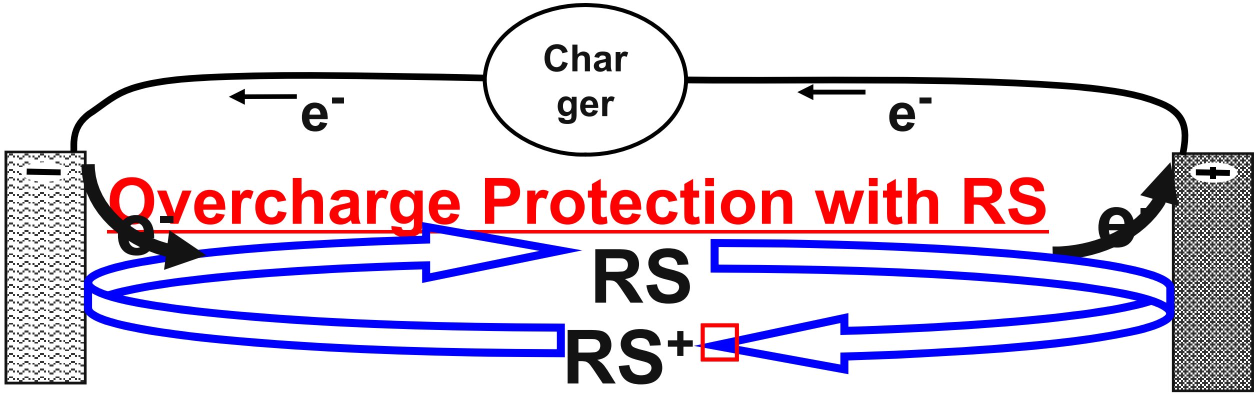


Overcharge protection for lithium ion batteries



(a) Fully discharged battery pack.

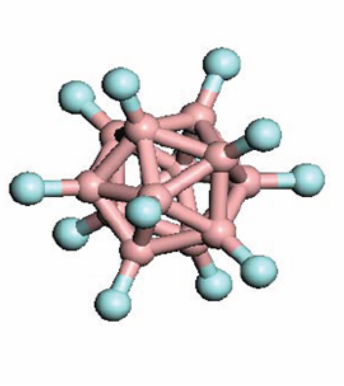
(b) Partially charged battery pack with the weak cell being fully charged.



Overcharge abuse can be mitigated by redox shuttle additives (RS).

Approaches for the investigation of overcharge tolerance (redox shuttles)

- 4V redox shuttles investigated

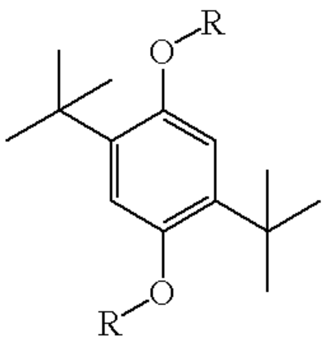


$B_{12}F_{12-x}H_x^{2-}$

APCI

4.2-4.7 V

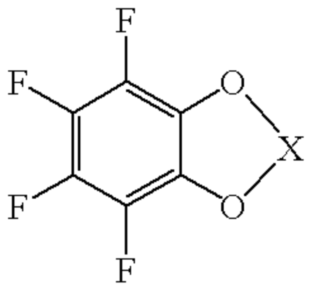
Secured $Li_2B_{12}F_{12}$



3M

4.2-4.4 V

Secured two samples



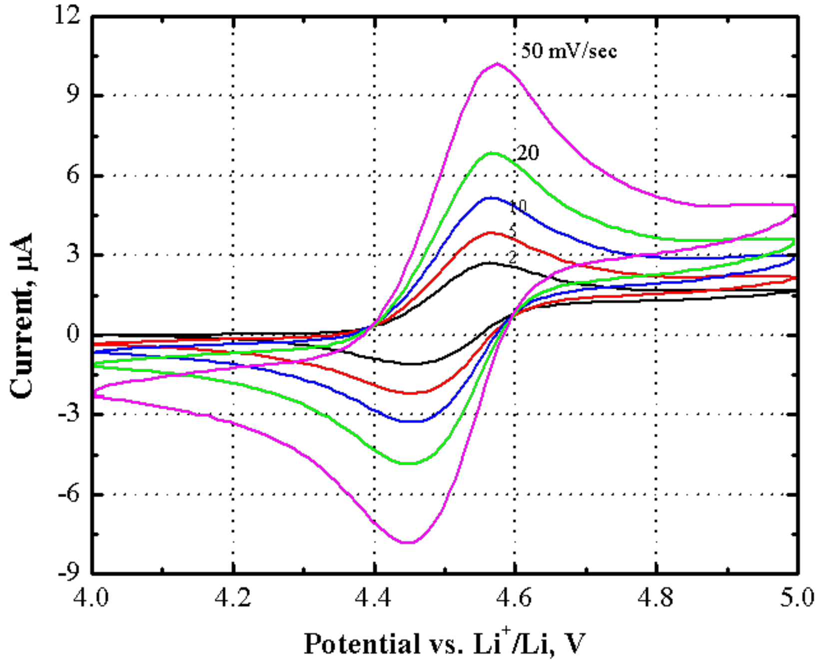
ANL

4.4 V

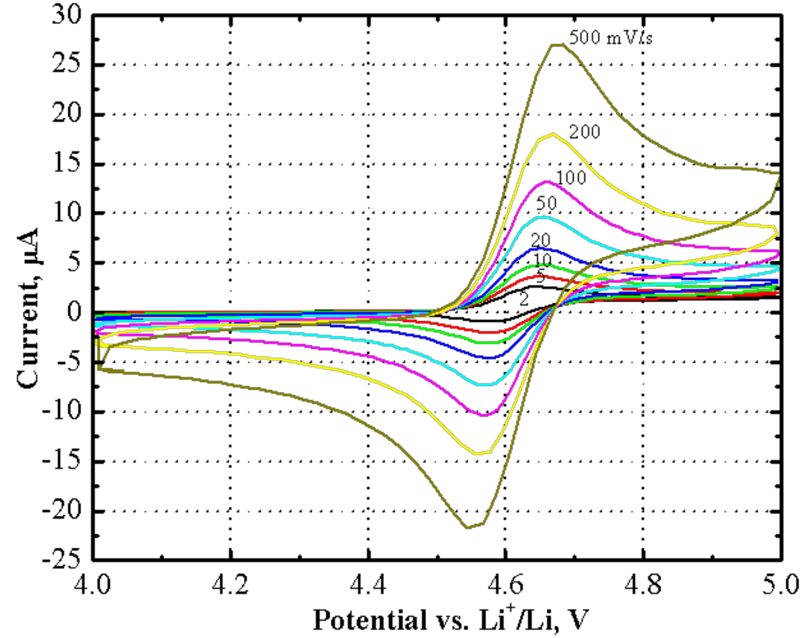
Synthesis of several new shuttles is in progress

Investigation of APCI's redox shuttles

$Li_2B_{12}F_9H_3$



$Li_2B_{12}F_{12}$

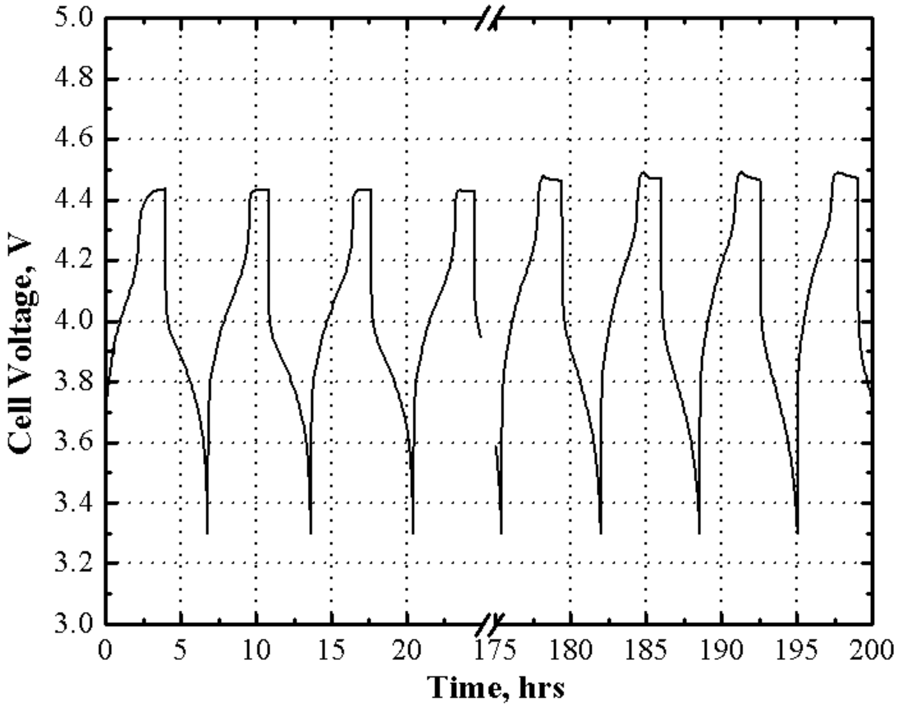


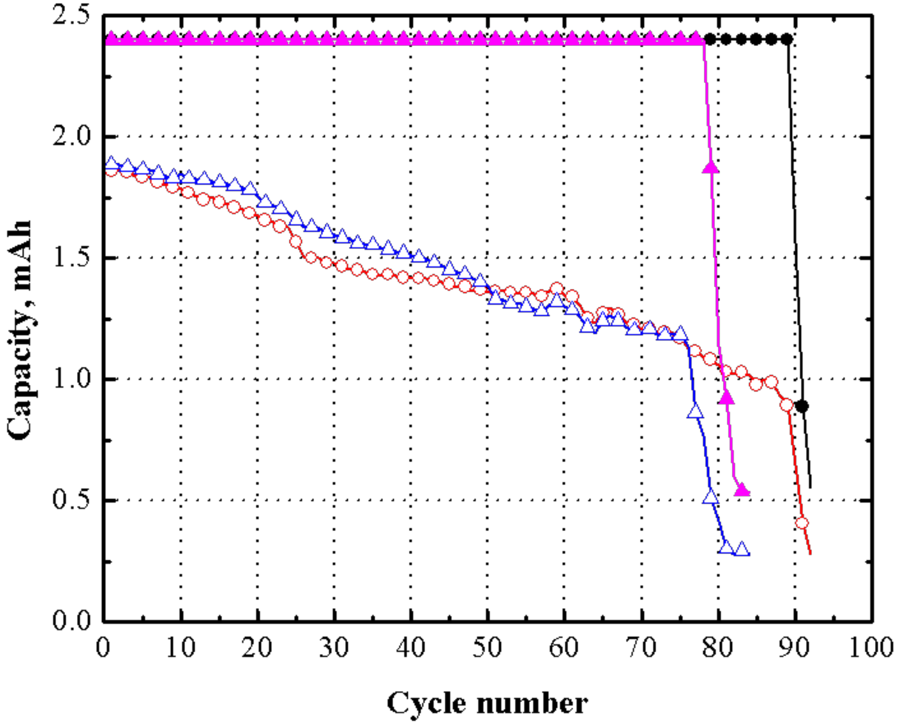
Reversible redox @ 4.5 V

Reversible redox @ 4.6 V

- These salts are promising for 4 V class lithium ion batteries.
- Tunable redox potential upon the degree of fluorination.
- These are also promising for high voltage materials for PHEV.

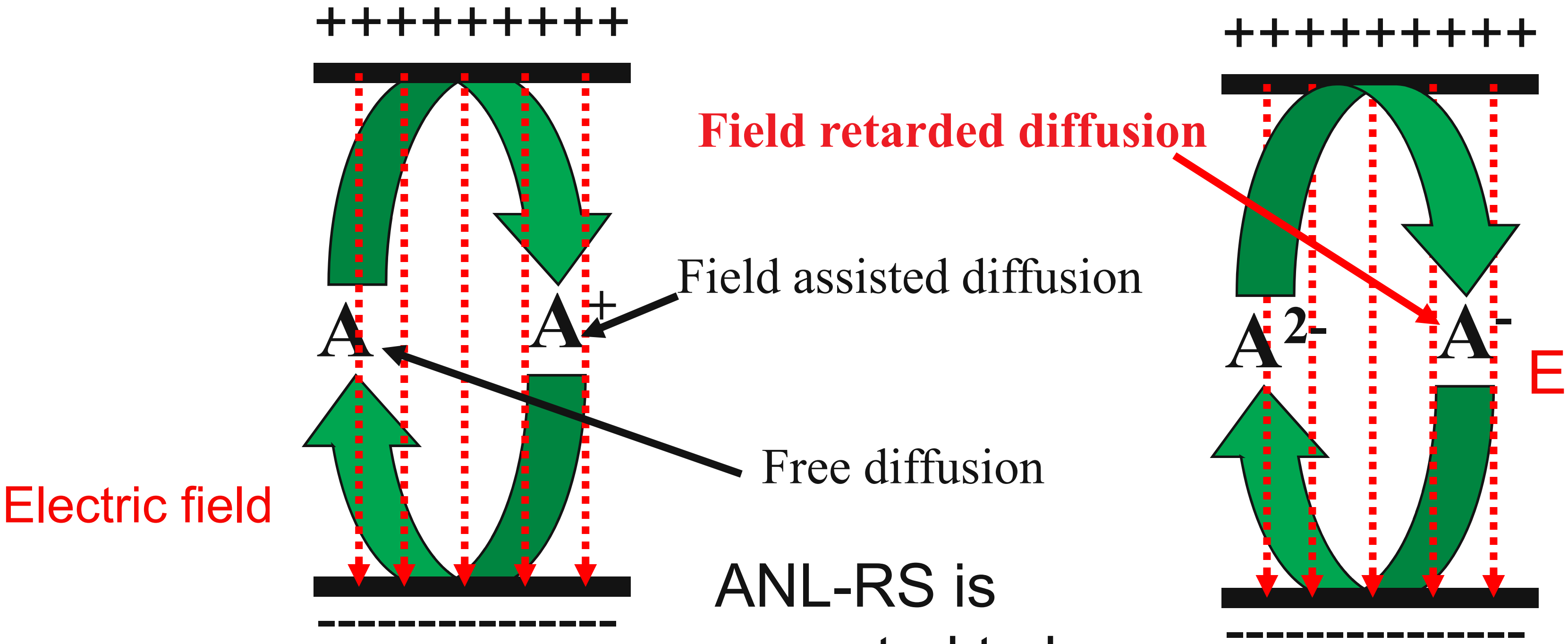
Overcharge protection for MCMB/ $Li_{1.1}[Ni_{1/3}Mn_{1/3}Co_{1/3}]_{0.9}O_2$



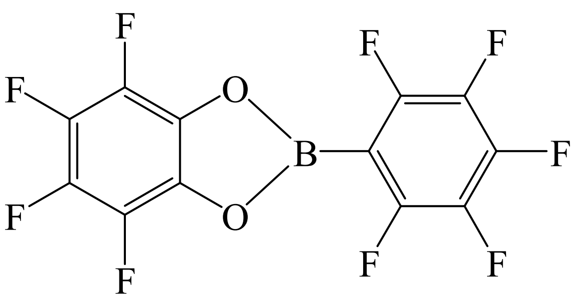


- Good solubility in non-aqueous electrolytes/solvents.
- Long term overcharge protection.
- Potential for high rate overcharge.

Interaction of redox shuttle molecule and internal electric field



ANL-RS is expected to have higher shuttle efficiency.

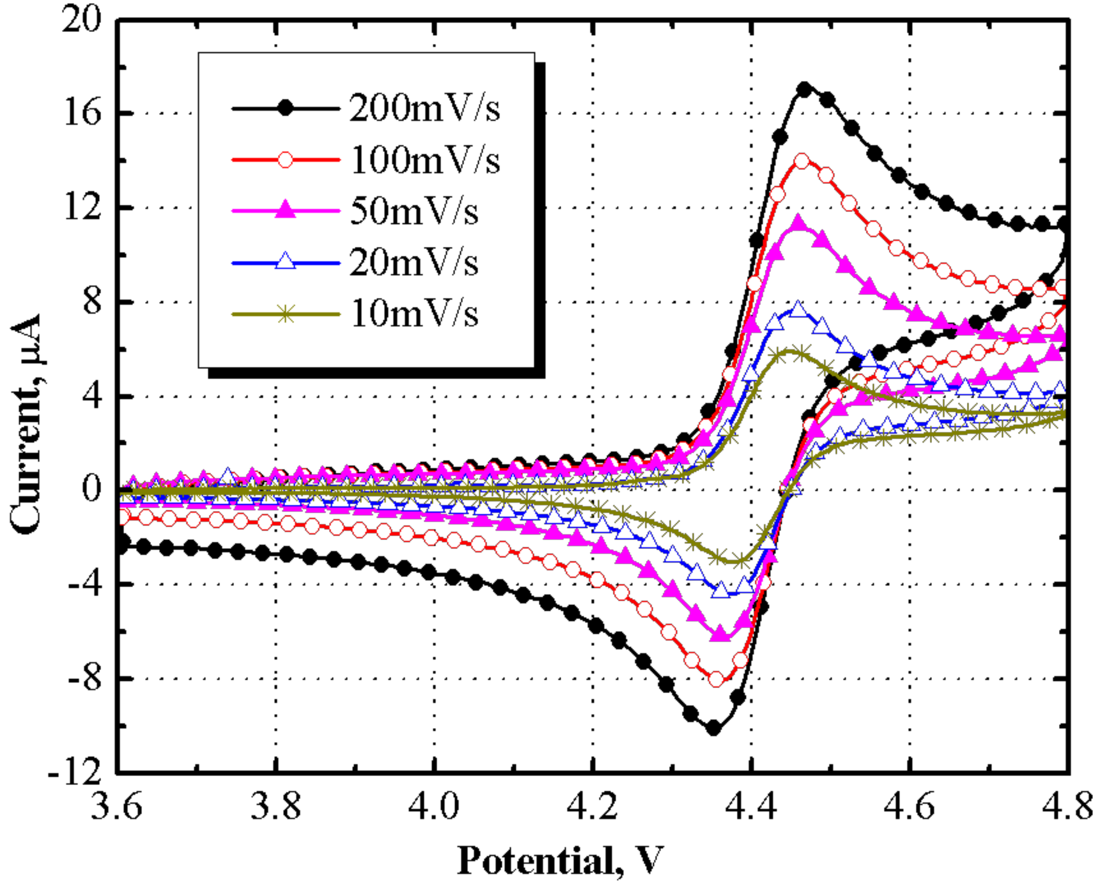


$Li_2B_{12}F_{12-x}H_x$

4.4V
ANL-RS

4.5-4.75 V

Cyclic voltamograms of 5 mM ANL-RS in 1.2mLiPF$_6$/EC:EMC (3:7 wt%)



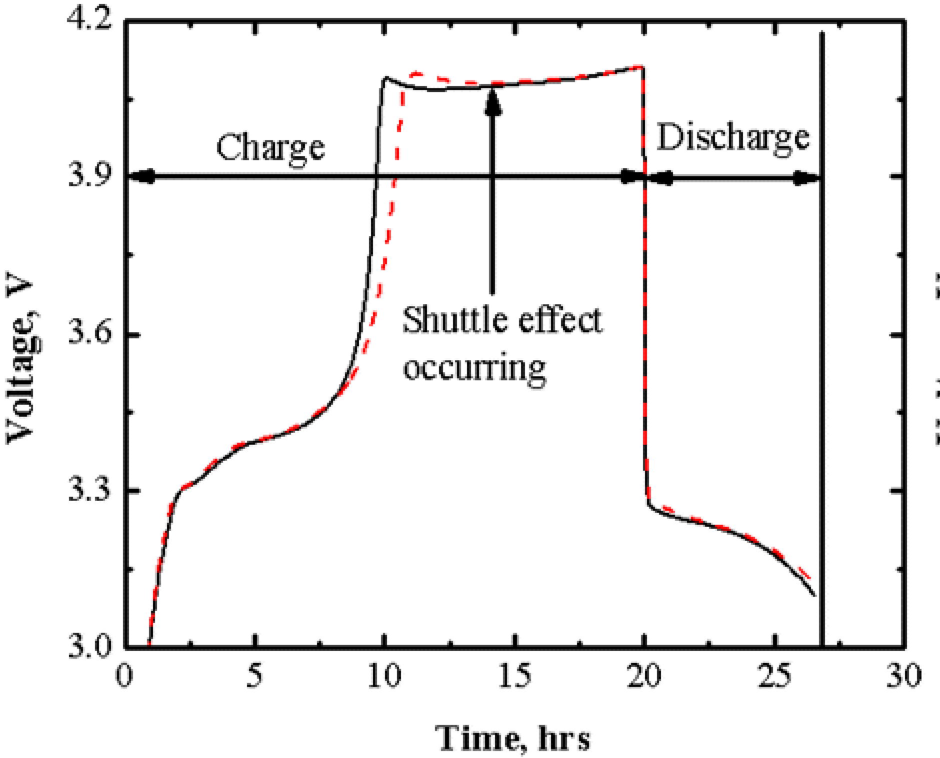
Redox potential: 4.3 V

- High enough to provide overcharge protection for 4 V materials.
- Lower then the oxidation potential solvents (~4.7 V).

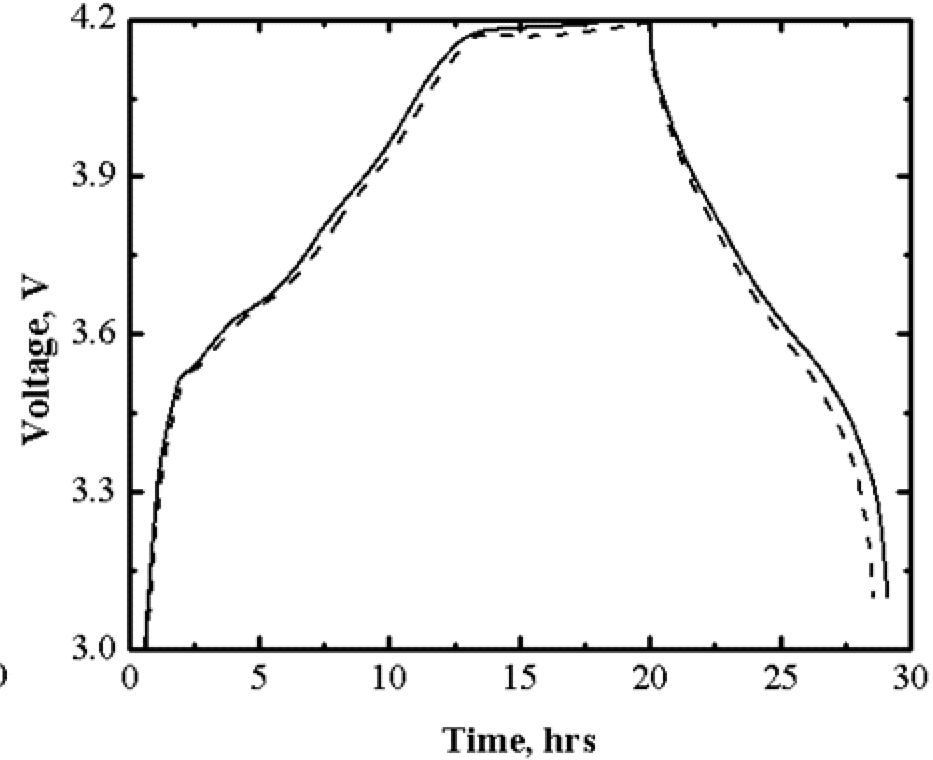
Boron based electron deficient center is also an anion receptor to promote the formation of SEI layer.

Gen3E= 1.2 M LiPF$_6$ in EC/EMC (3:7 by weight).

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

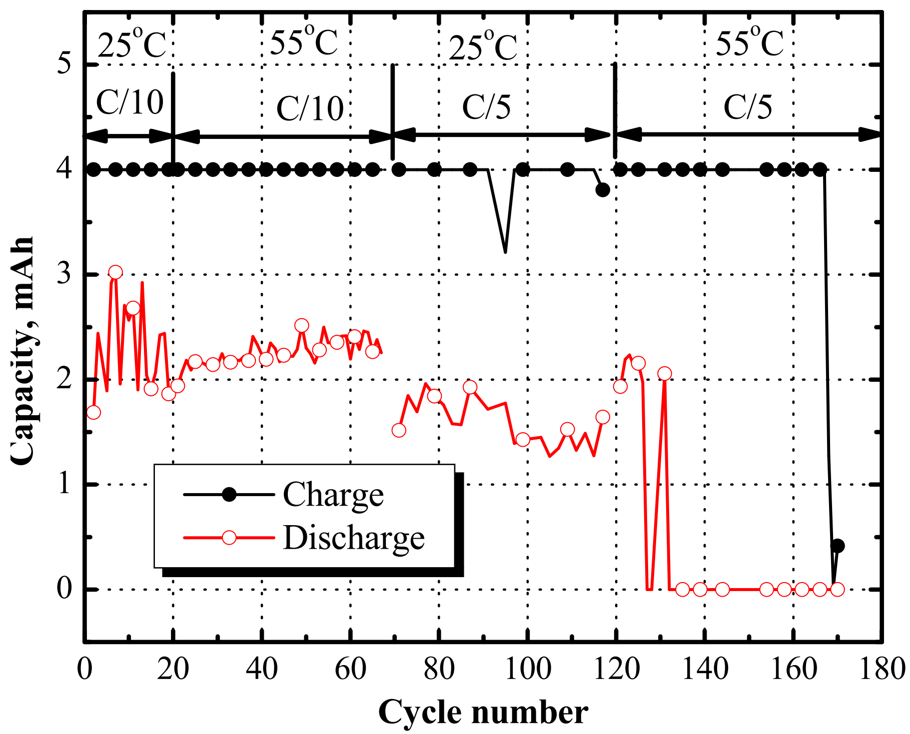


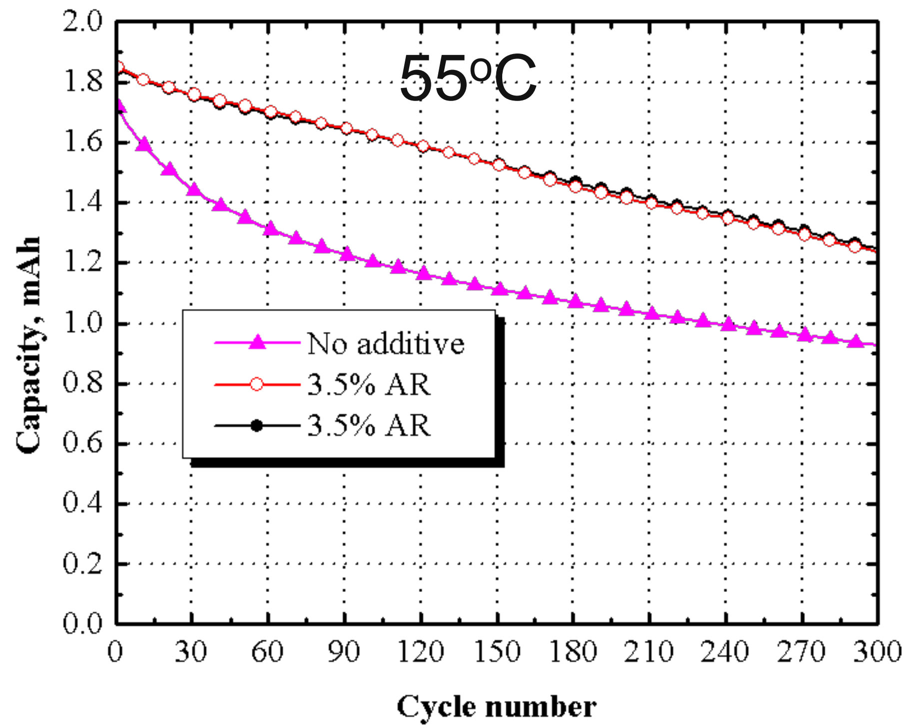
MCMB/$LiFePO_4$ with ANL-RS



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

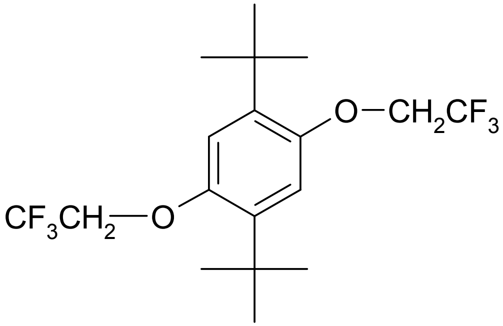
Repeated overcharge and cycling of $MCMB/LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ with ANL-RS





- ANL-RS provides overcharge protection even at high temperature (55°C).
- ANL-RS improves the capacity retention of the cell under normal cycling. (Functionality of anion receptor.)

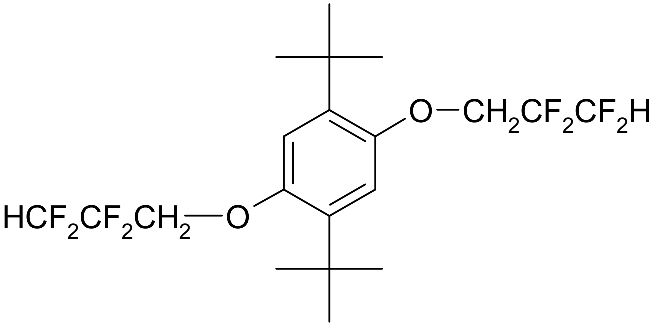
Investigation of 3M's redox shuttles



L-20487

E_{ox} = 4.25V

Preliminary test!

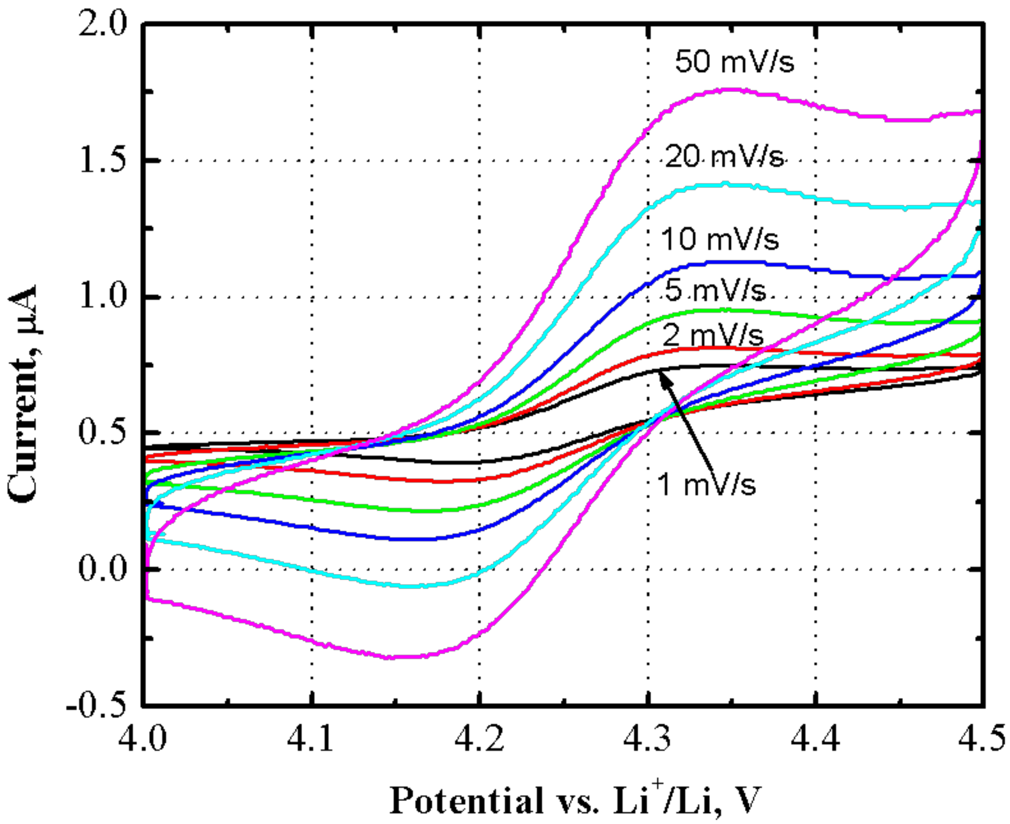


L-20538

E_{ox} = 4.13V

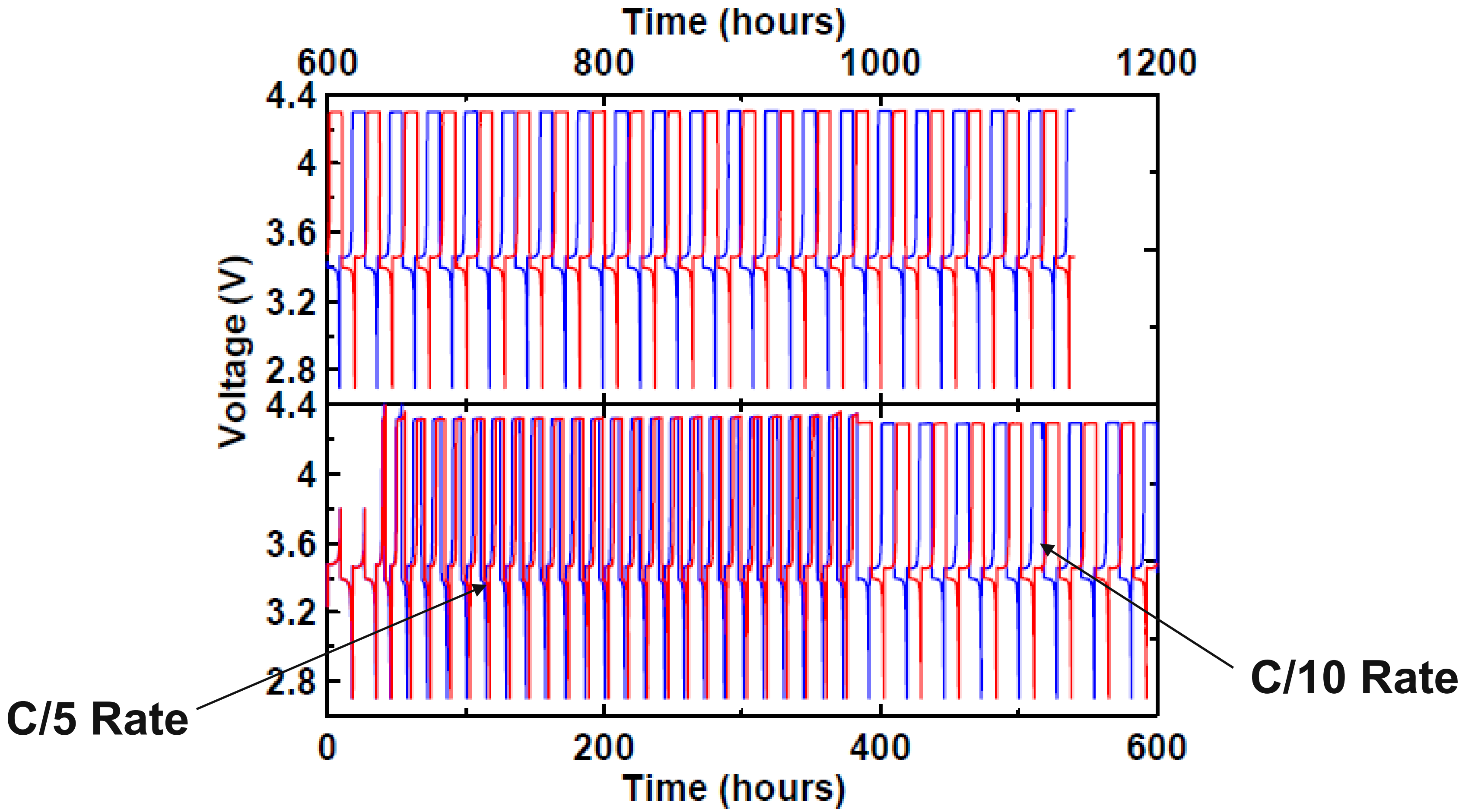
Low solubility in1.2 M $LiPF_6$ in EC/EMC (3:7)
Need to test in alternative electrolyte.

3M's redox shutlle (L20487)



- Confirmed that the redox potential is about 4.25 V, which is suitable for NMC cells.
- Long term stability needs to be confirmed in real cells.

Performance of 3M's L20487 in Li/$LiFePO_4$



- Data confirms the redox potential and stability of L 20487.
- Performance of L20487 in MNC cells will be validated and reported soon.

Summary

•Lithiated anodes are thermodynamically unstable in non-aqueous electrolyte. Slow kinetics of SEI decomposition are the key for long life and good safety characteristics.

•Kinetics of SEI breakdown are critical indicator for life and safety of the cell.

•LiDFOB is an effective electrolyte additive that: (1) improve the safety of anode and (2) improve the life of the cell without sacrificing the power capability.

•The kinetic investigation will also be applied to safety characteristics of the cathode side.

•Redox shuttles are intrinsic overcharge protection mechanism for lithium ion cells.

•Investigation of 4V redox shuttles for NMC-based cells is the focus of the near future. These shuttles include $Li_2B_{12}F_{12}$(APCI), L20487 (3M) , L20538 (3M) and new shuttles discovered recently at Argonne National Laboratory.

Future work

- Investigate the effect of more additives on the safety of lithium batteries
- Investigate the effect of varying concentration of AIF3 on the safety of the coated cathodes
- Investigate the effect of using the atomic layer deposition (ALD) on the safety of the coated cathodes
- Further exploring 3M's redox shuttles potential on preventing overcharge
- Investigate the effect fluorinated carbonates on the safety of lithium batteries
- Investigate the effect of Ionic liquid as co-solvents on the safety of high energy lithium ion

- Investigate the Impact of carbons surface area on the sfaety at the 18650 level
- Investigate the effect of carbon morphology on the safety of lithium battery at the 18650 level