Development of Advanced Electrolytes and Electrolyte Additives

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Argonne National Laboratory

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Project ID #: ES025

Overview

Timeline

- Start Date: FY09 (New project)
- End Date: September 2014
- Percent complete: 20%

Barriers

- Insufficient voltage stability
- High flammability, low safety
- Poor Cycle & calendar life
- Surface reactivity with electrodes

Budget

- Total project funding
  - 100% DOE
- FY10: $300K

Partners

- K. Amine, A. Abouimrane
  Y. Qin, Z. Chen, L. Zhang (CSE/ANL)
- L. Curtiss (MSD/CNM/ANL)
- H. Iddir (MSD/CNM/ANL)

Project Lead: Zhang & Amine

Objectives

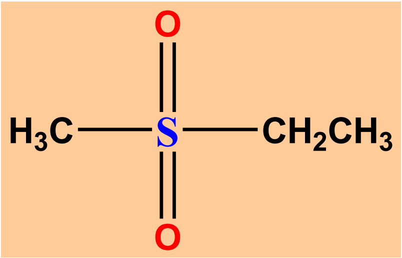
- Develop advanced electrolyte with high voltage stability, combined with high lithium ion conductivity, high thermal stability, non toxicity, non-flammability and enhanced safety.

- Identify functional electrolyte additives that provide stable solid electrolyte interface (SEI) and investigate their formation mechanism and their effects on improving the cell performance.

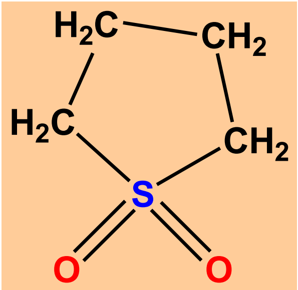
Approaches

- Develop novel electrolyte systems that include sulfone-based electrolytes, hybrid electrolytes of sulfone with other type of solvents, such as carbonate, ionic liquid to enable high power high energy lithium ion batteries with superior safety for PHEV applications.
- Investigate compatibility of new electrolytes with different battery electrode chemistries.
- Investigate electrolyte additives that stabilize the interface between the charged electrode and electrolyte and improve the cell performance. Electrolyte additives include compounds containing oxalic group, ester group, vinyl group et al..

Sulfones as High Voltage Electrolytes



EMS



TMS

ADVANTAGES:

- Large electrochemical windows
  - Can enable high voltage cathodes
- High to medium ionic conductivity
- Wide liquid-phase temperature
- Lower viscosity (*vs.* ionic-liquid)
- low cost (*byproduct in petroleum industry*)

Electrochemical Window stability

- **EMS-Ethyl methyl sulfone: 5.5V**
- **TMS-Tetramethylene sulfone: 5.0 V**
- **FS-1-Fluoro-2-(methylsulfonyl)benzene: 4.7 V**

- **BS-Butyl sulfone: 4.5 V**
- **EVS-Ethyl vinyl sulfone: 4.3 V**

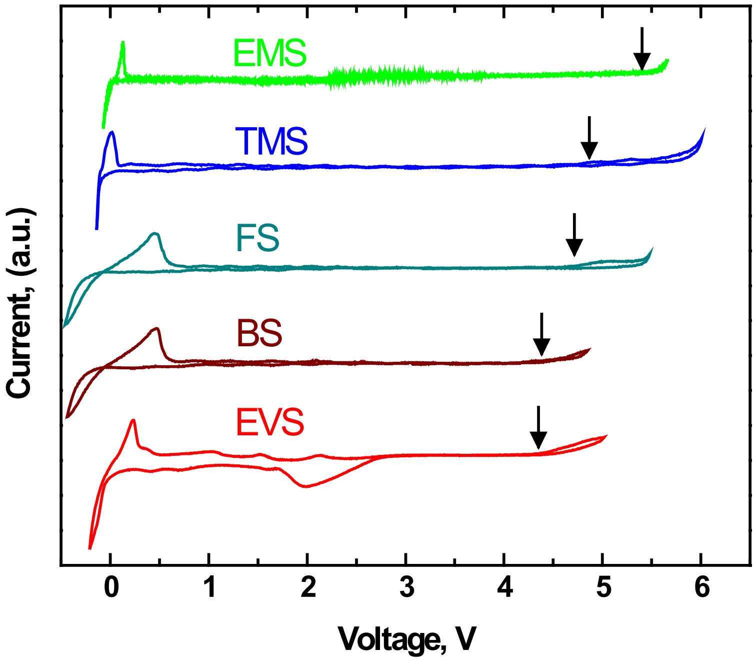
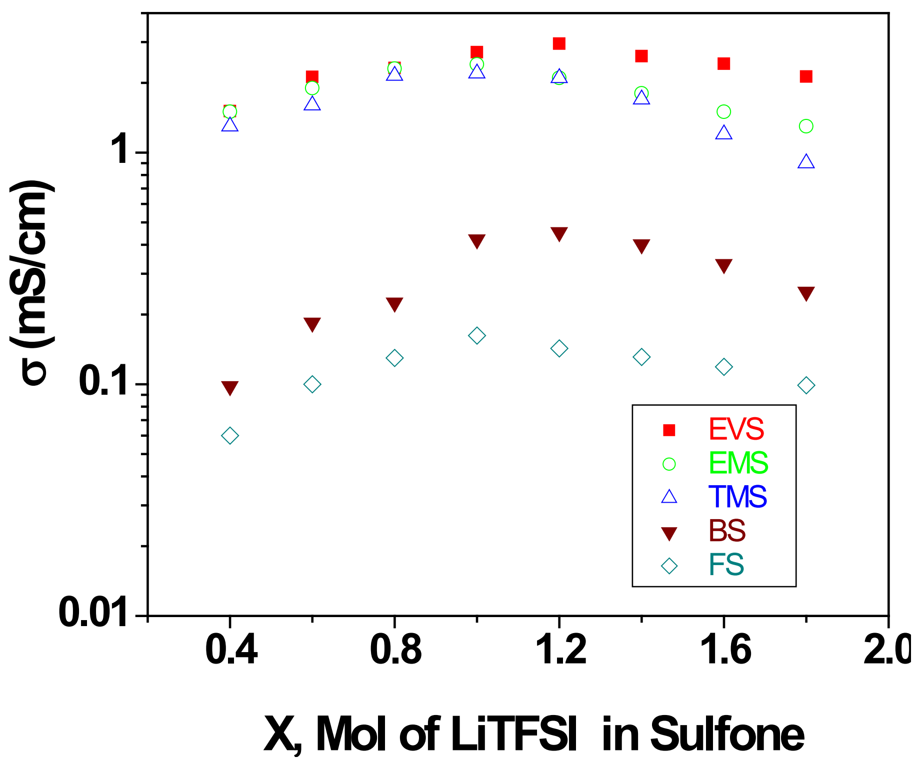


Fig.1 CV profiles of 1M LiTFSI in various sulfones.

Physical Properties of Sulfones

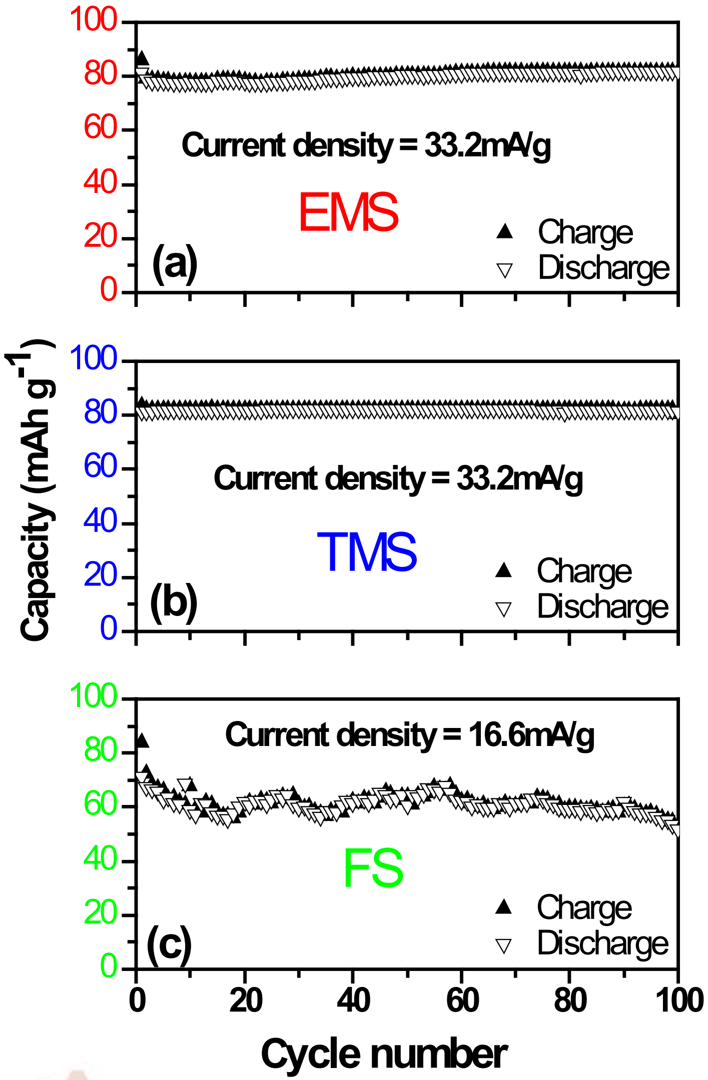
Solvent	Melting Point
EVS: ethyl vinyl sulfone [$C_2H_5SO_2CH{=}CH_2$]	<-50ºC
EMS: ethyl methyl sulfone [$C_2H_5SO_2CH_3$]	35ºC
TMS: tetramethylene sulfone [$C_4H_8O_2S$]	23ºC
BS: butyl sulfone {[$CH_3(CH_2)_3]_2SO_2$}	44ºC
FS: 1-fluoro-2-(methyl-sulfonyl)benzene [$C_7H_7FO_2S$]	50ºC

Ambient Ionic Conductivity of Various Sulfones



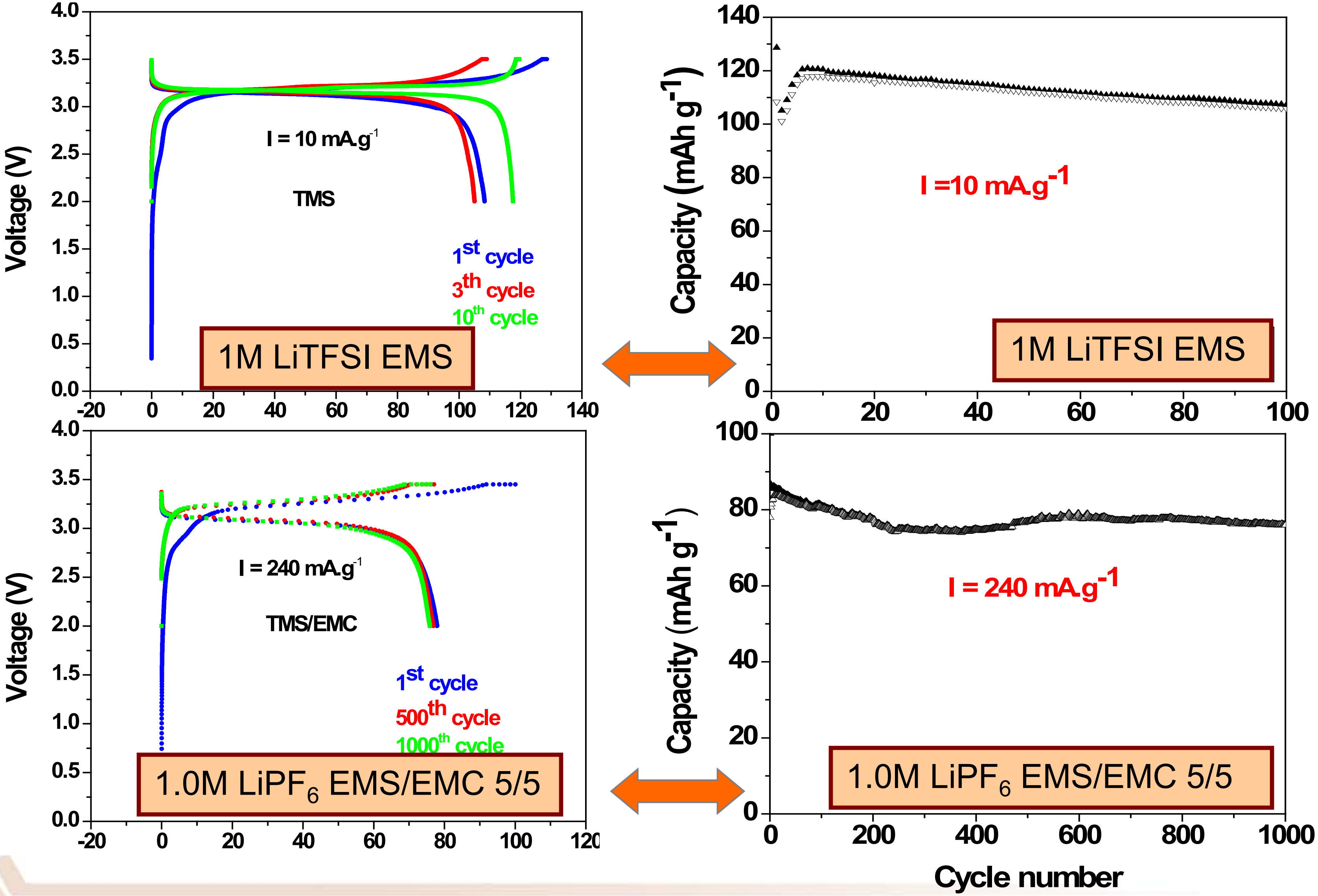
3 x 10^{-3} S/cm at 1.2M LiTFSI with EVS

Performance of Sulfone Based Electrolyte Using $Li_{1+x}Mn_{2-x}O_4$ Based System



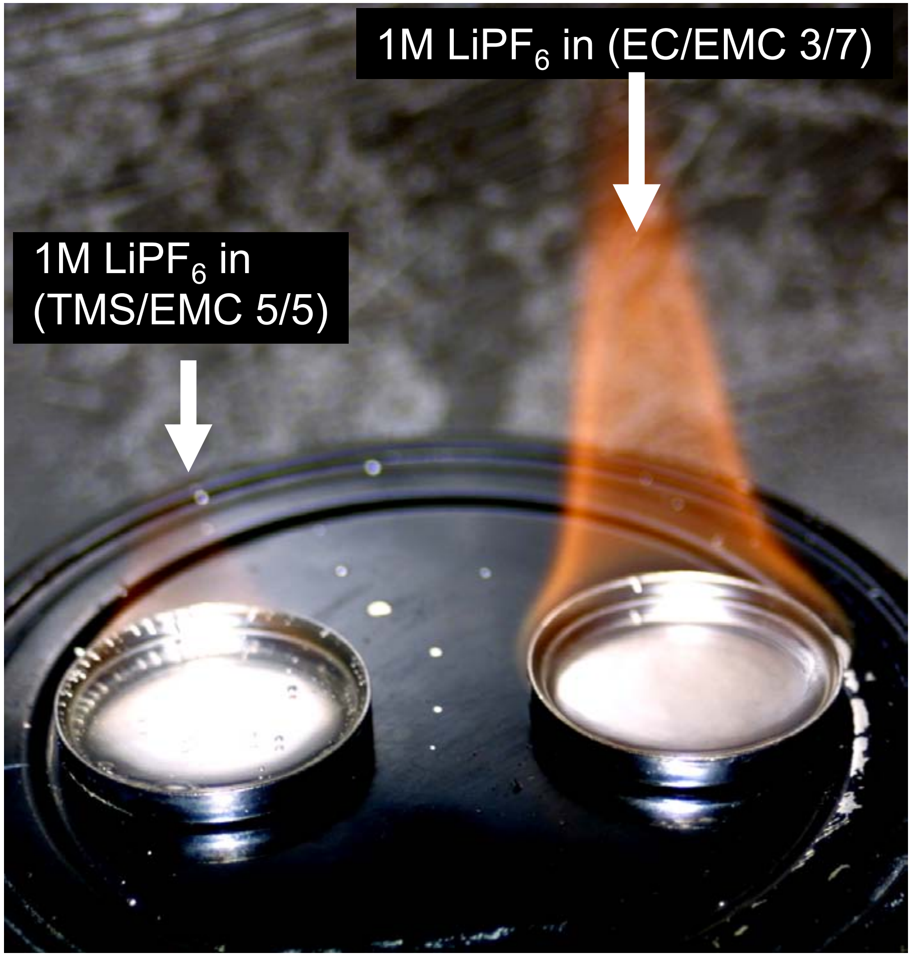
- Excellent cycling performance for cells using EMS or TMS as electrolyte solvents. No capacity fade for 100 cycles.
- Good performance was obtained using glass fiber separator (better wettability).
- Poor cycleability for cells using FS as electrolyte, even at low current density
  - Low ionic conductivity (10^{-4} S/cm)
  - High reactivity.
- Sulfone based electrolyte has an issue with wettability when using conventional separators. Ceramic coated separators will be preferable.

Performance of Sulfone Based Electrolyte Using $LiMn_{1.5}Ni_{0.5}O_4$ (4.8V) Based System



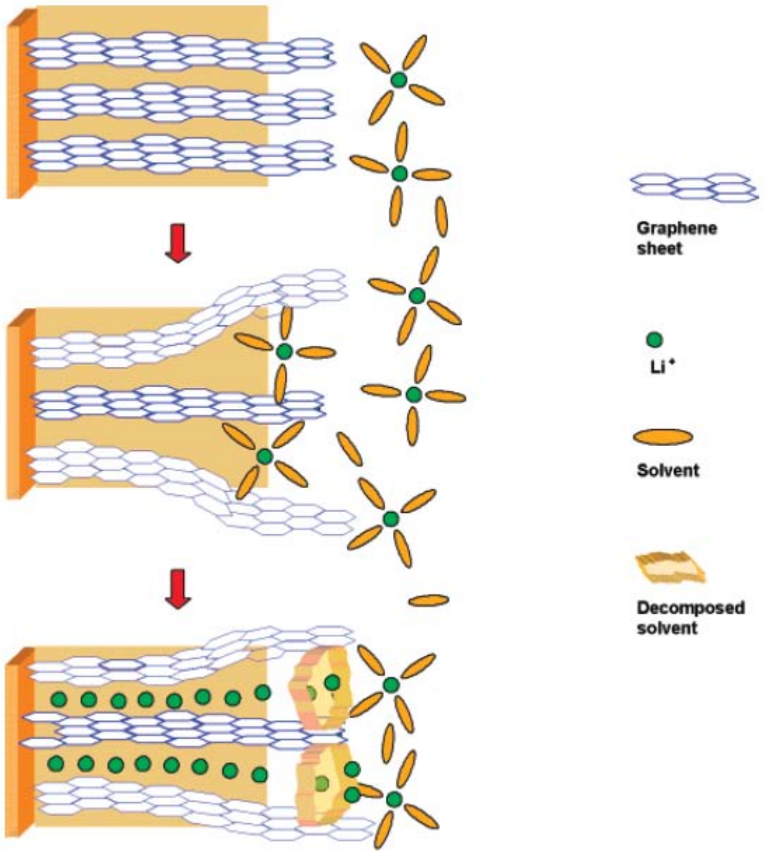
Flammability Test of Sulfone Based Electrolytes

- 1M $LiPF_6$ in (EC/EMC 3/7) need about 2 seconds to ignite.
- 1M $LiPF_6$ in (TMS/EMC 5/5) need about 45 seconds to ignite.
- Strong flame is observed for 1M $LiPF_6$ EC/EMC 3/7 electrolyte.
- Weak flame with self extinguished character is observed for 1M $LiPF_6$ TMS/EMC 5/5 electrolyte. Non-flammability is expected for pure sulfone electrolyte without EMC.

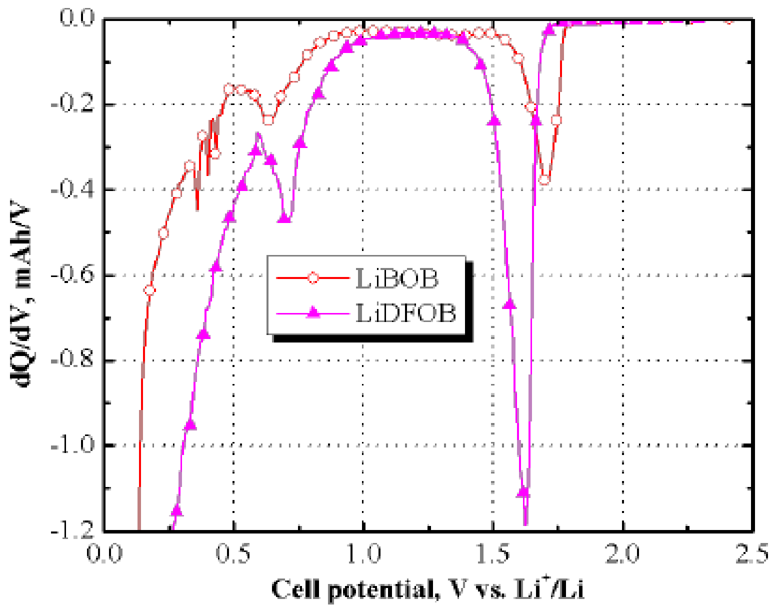


Background - *Electrolyte Additives*

Formation of Solid Electrolyte Interface (SEI)



Kang Xu, *Chem. Rev.* (2004)

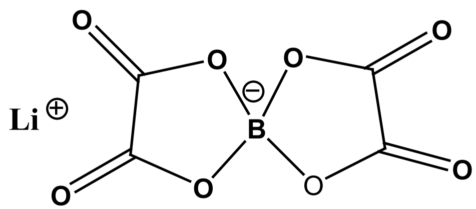


Reduction occurs at 1.7V (LiBOB) and 1.6V (LiDfOB) and form a new SEI before the formation of conventional SEI layer at a potential of 0.6~0.8V.

SEI Additives Candidates

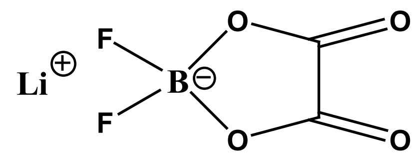
SEI Modification: *Additives to form polymerized artificial SEI film*

LiBOB



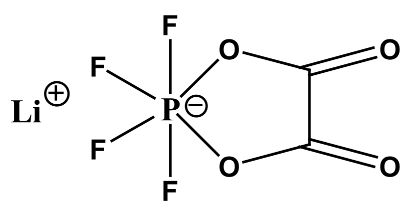
Lithium Bis(oxalato) Borate

LiDFOB



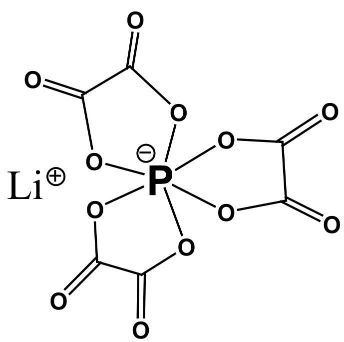
Lithium Difluoro(oxalato) Borate

LTFOP



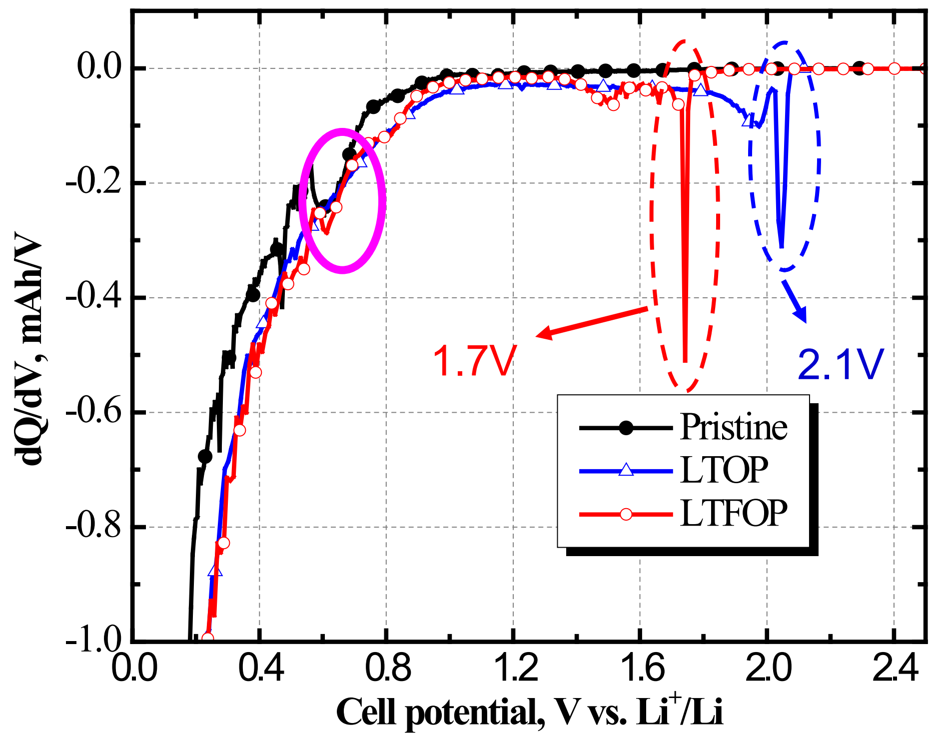
Lithium Tetrafluoro(oxalato) Phosphate

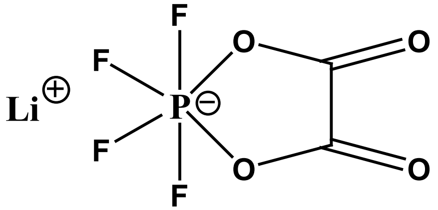
LTOP



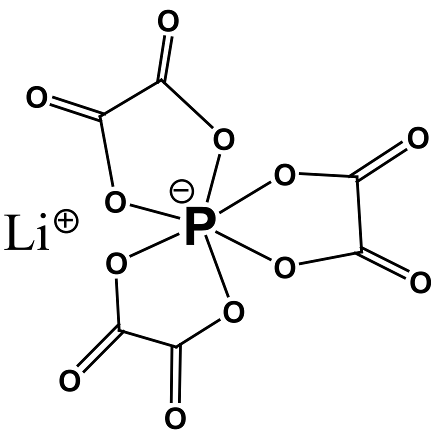
Lithium Tris(oxalato) Phosphate

Reduction Voltage of Different Additives





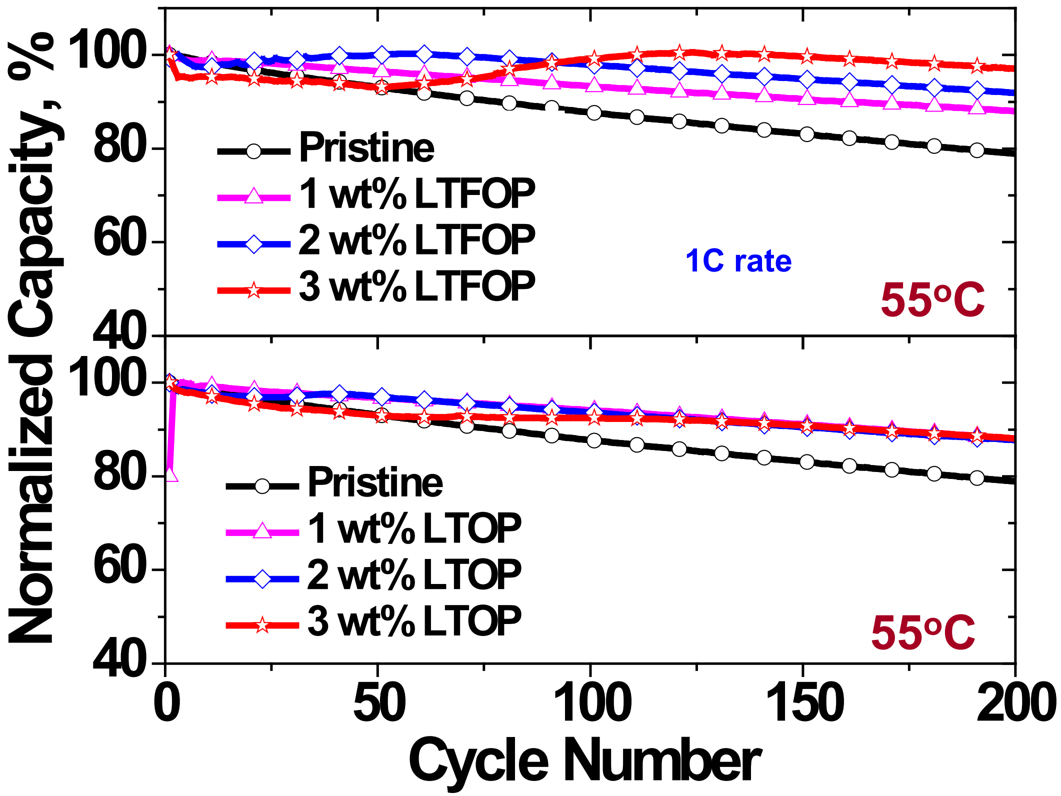
LTFOP (1.7V *vs* Li⁺/Li)

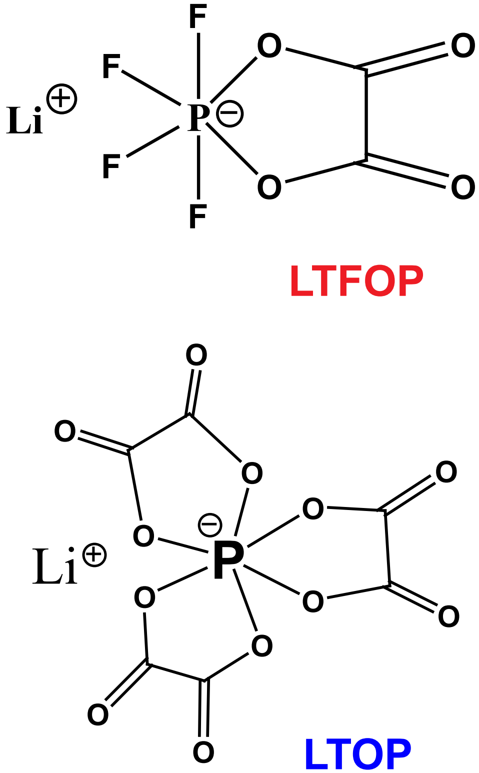


LTOP (2.1V *vs* Li⁺/Li)

Li/Graphite half cell differential capacity profiles
Electrolyte: 1.2M $LiPF_6$ EC/EMC 3/7+2% Additive

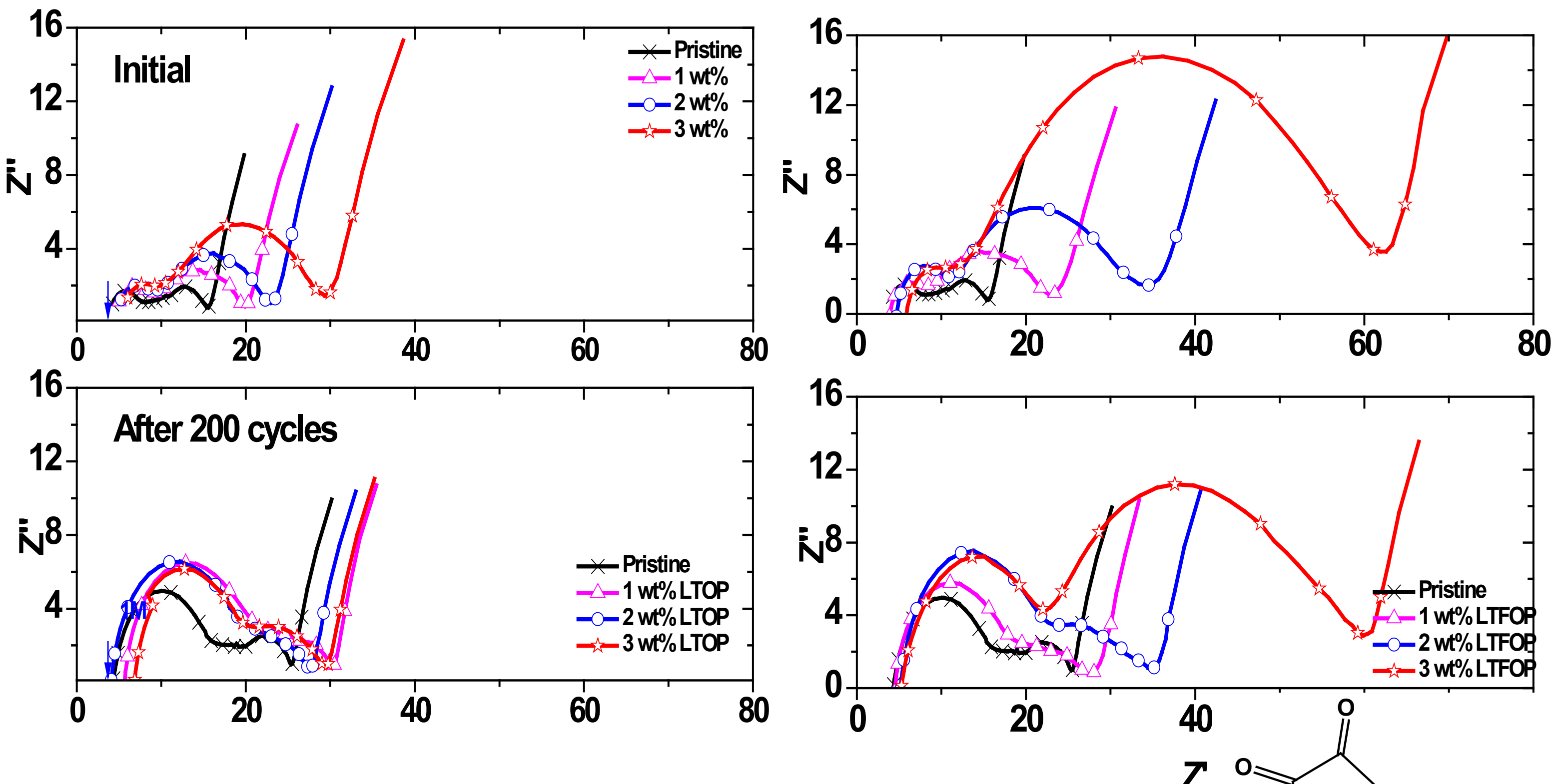
Cycling Performance at 55°C of NMC/MCMB W/O Additives

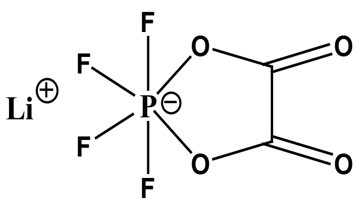


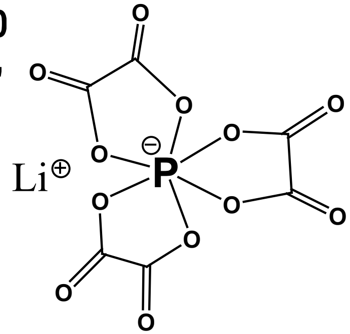


- Addition of 1~3 wt% LTFOP improves the cycle life, 3% shows the best result.
- More additive decreases the capacity due to thicker SEI layer formation.
- Addition of 1~3 wt% LTOP shows the similar improvement on the cycle life.

AC Impedance of NMC/MCMB Cells W/O Additives



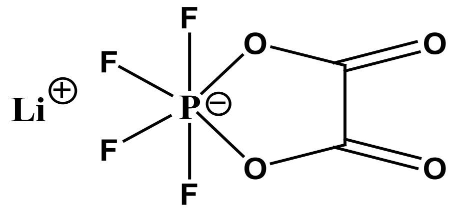




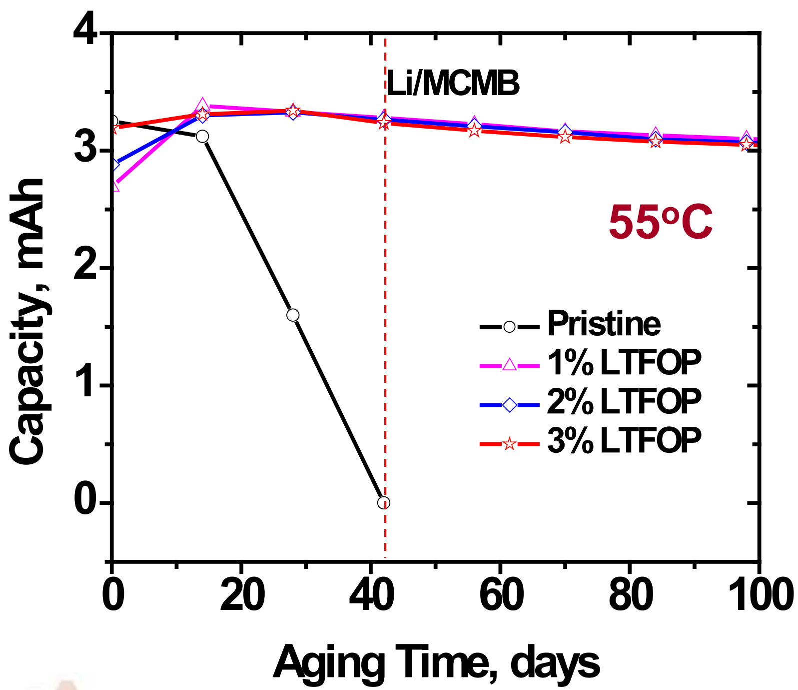
LTFOP
1 Oxalic group, Low Impedance

LTOP
3 Oxalic groups, High Impedance

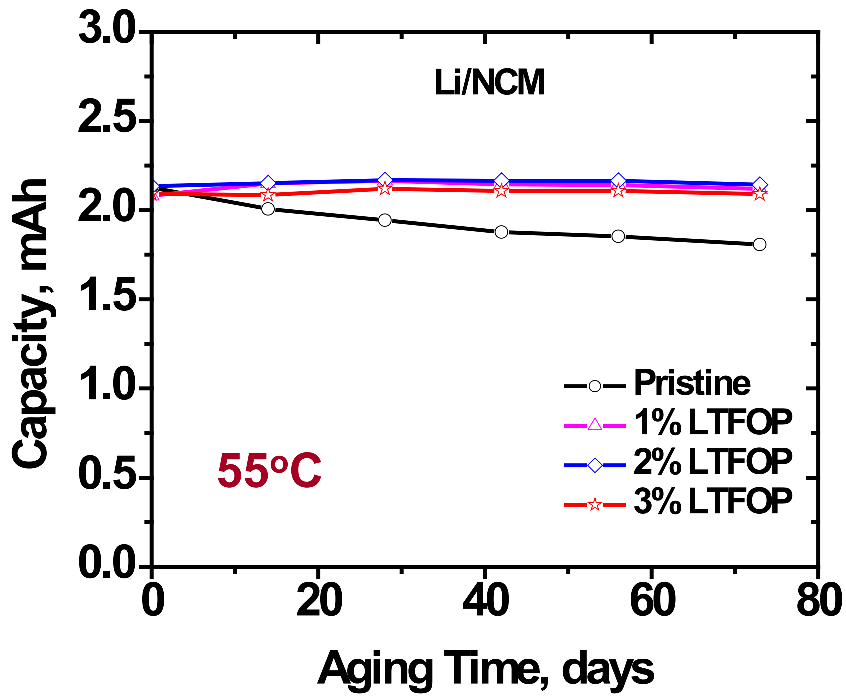
Effect of LTFOP Additive on NMC & MCMB Electrode During Aging at 55°C



Li/MCMB

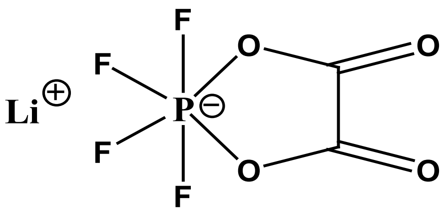


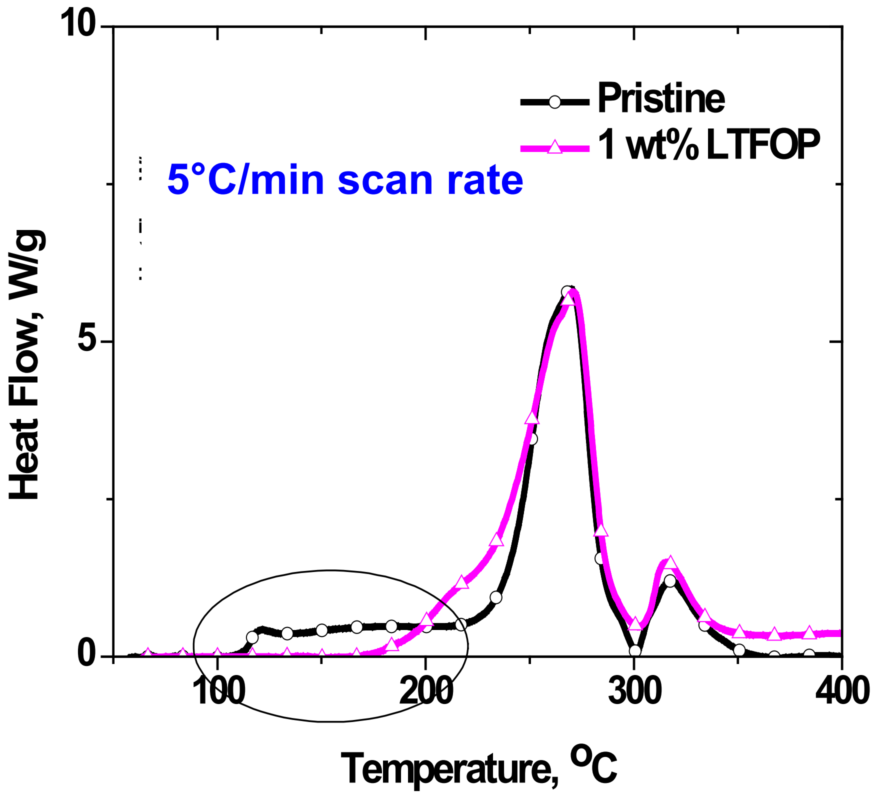
$Li/Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$

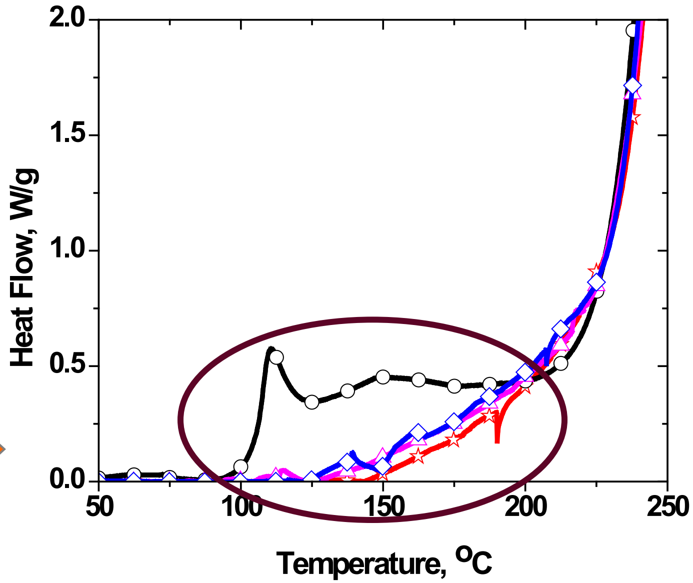


LTFOP improves the calendar life of both MCMB & NMC cathode at high temperature.

Effect of LTFOP Additive on Cell Safety

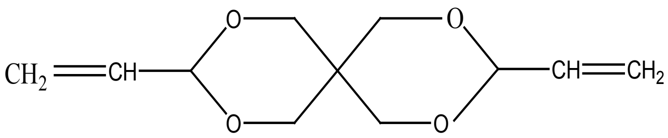




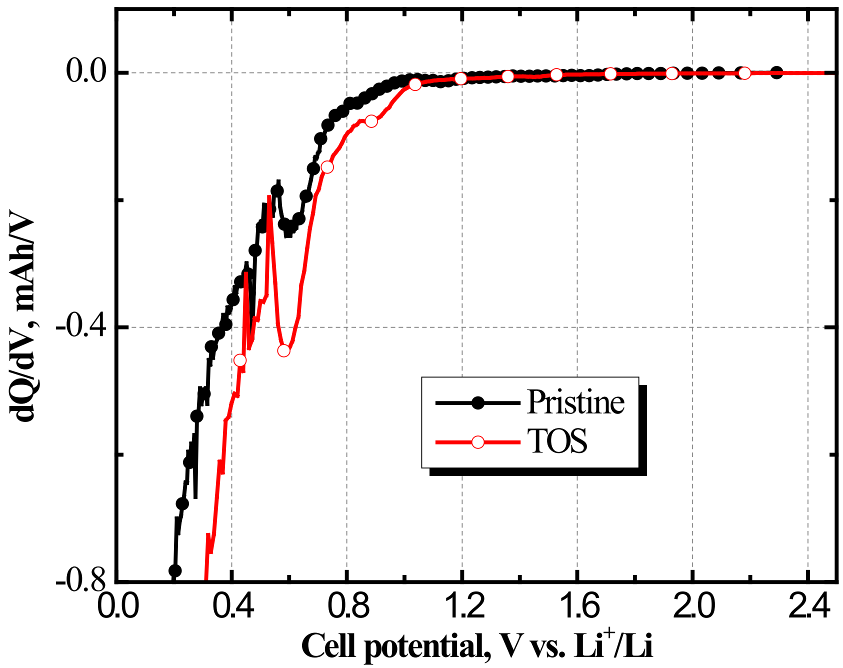


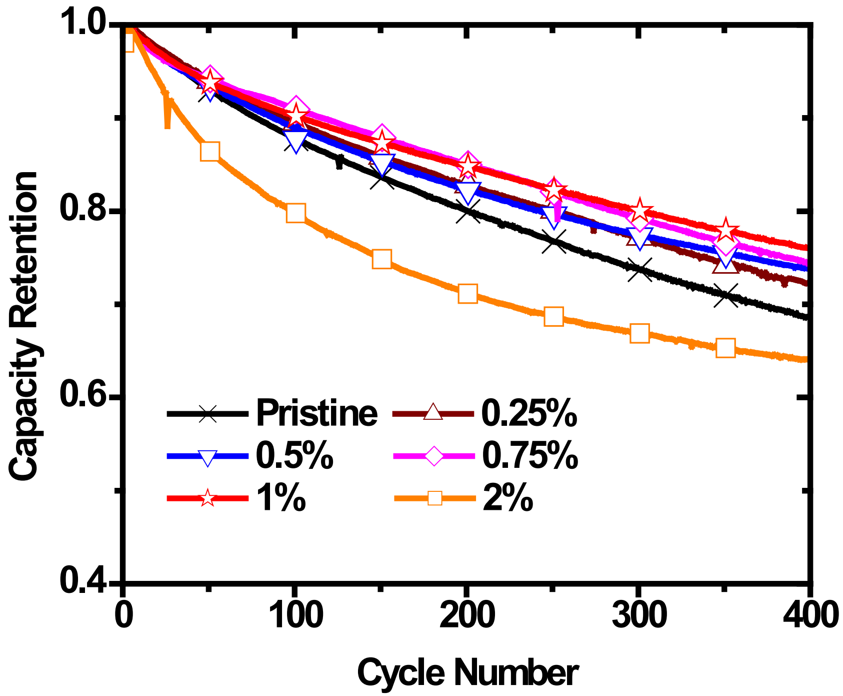
With addition of 1% LTFOP, the onset thermal decomposition temperature of SEI was pushed above 175°C (70°C increase compared with the conventional SEI).

New Additive Candidate TOS



3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (TOS)

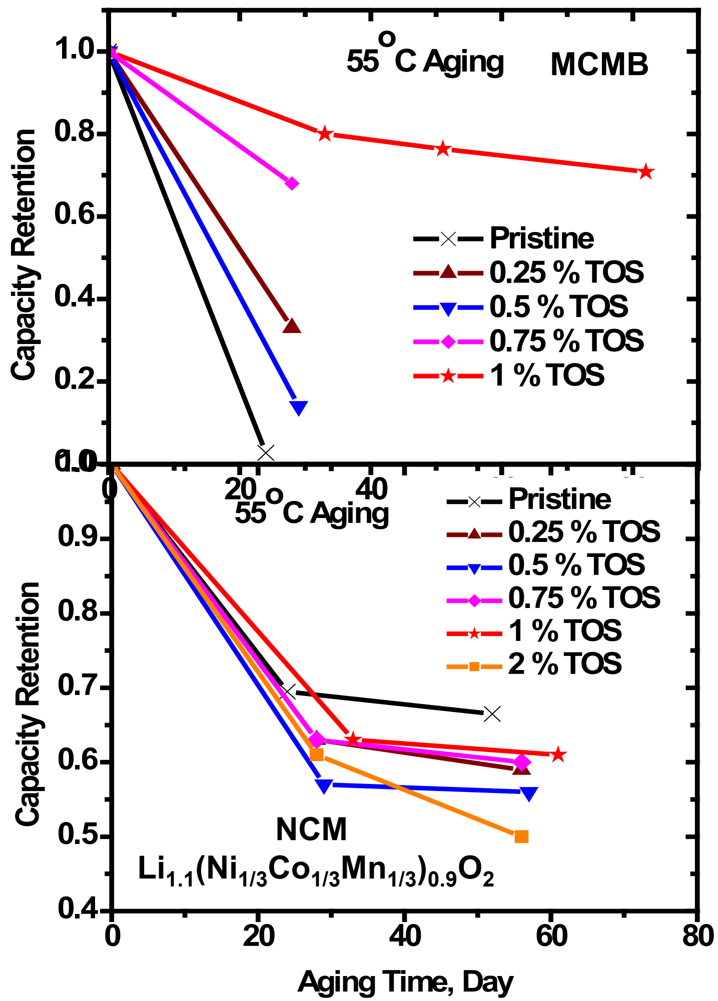


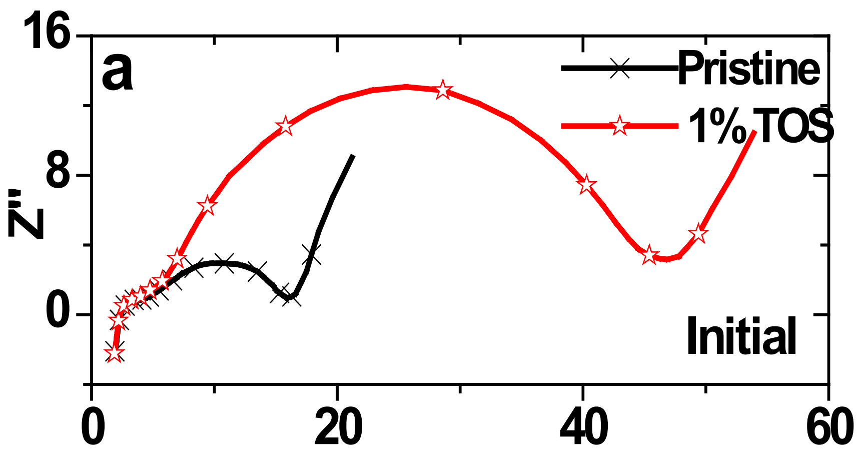


Reduction Peak is not observed, the reaction could be radical triggered instead of electrochemically induced.

TOS improves the cycle life of the lithium ion cell. 1 wt% can provide maximum improvement.

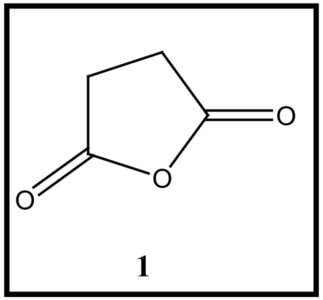
Effect of TOS on Performance of MCMB & NMC Electrode During Aging at 55°C

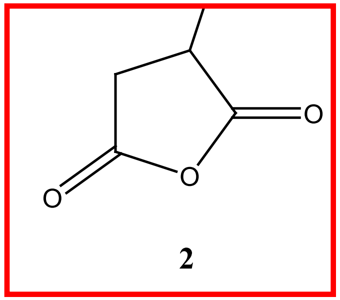


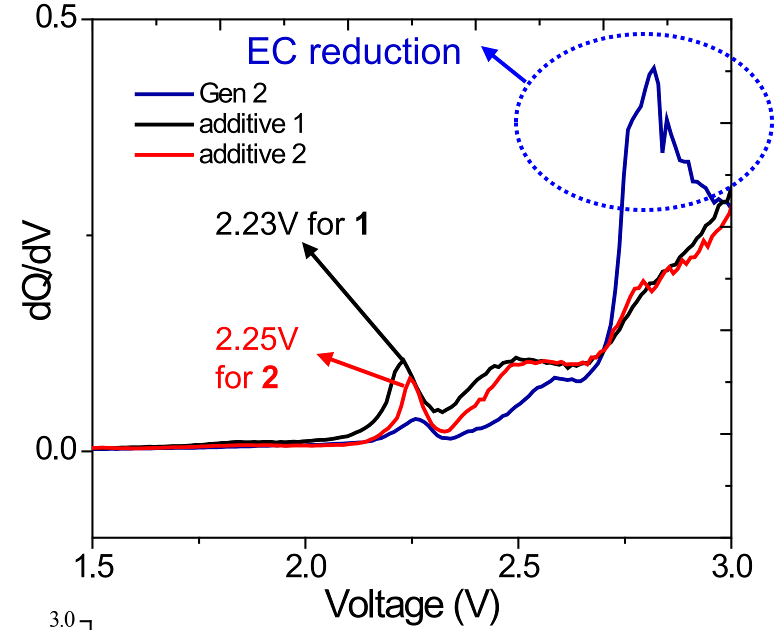


- TOS only provides very good protection for MCMB anode. No effect on cathode.
- Impedance of cell with 1% TOS additive is initially very high.

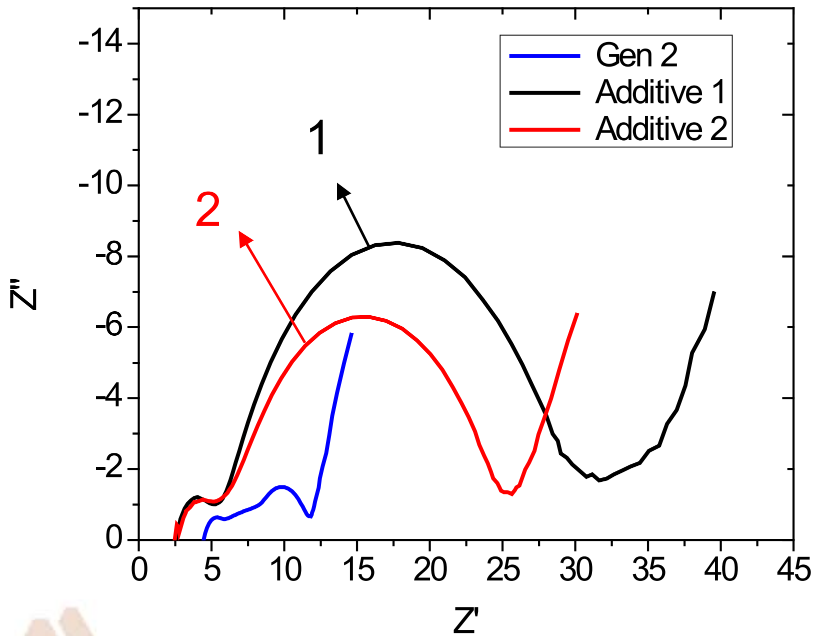
Succinic Anhydride as Potential Additive

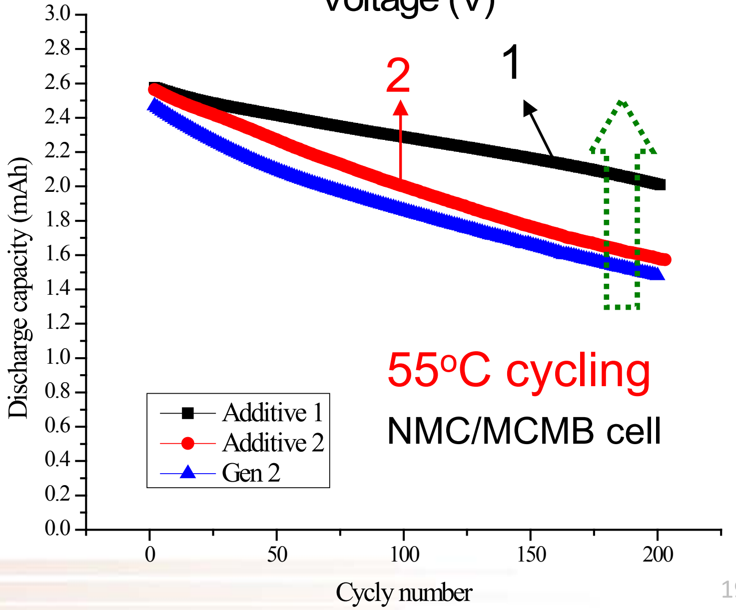




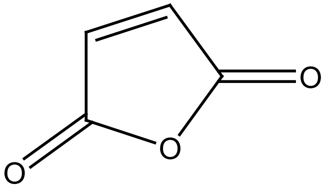


$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ //1.2M $LiPF_6$ EC/EMC 3/7+1% Add//MCMB





Maleic Anhydride as Potential Additive



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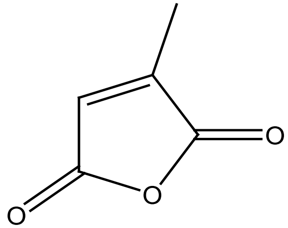

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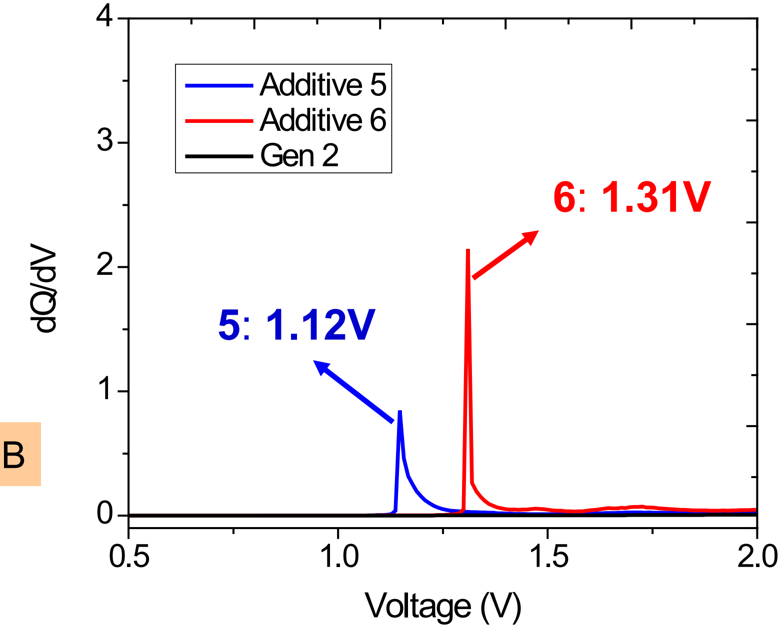
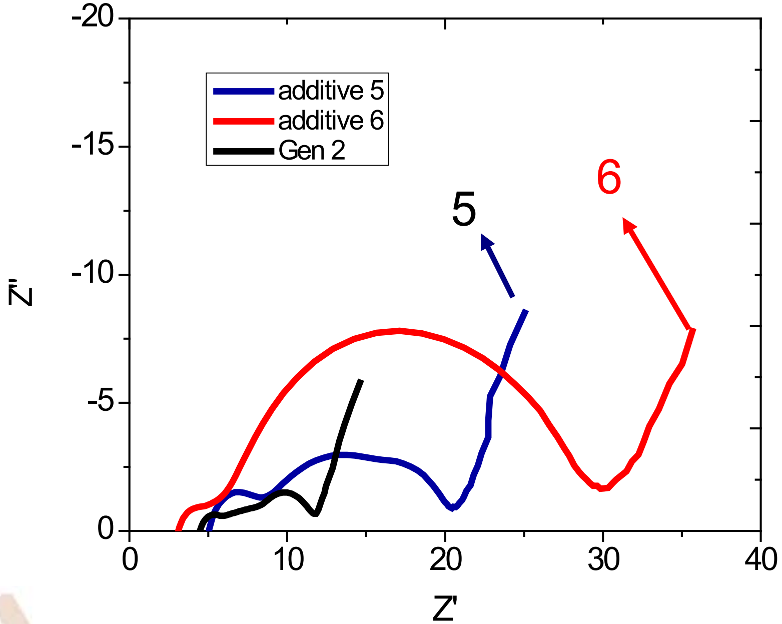
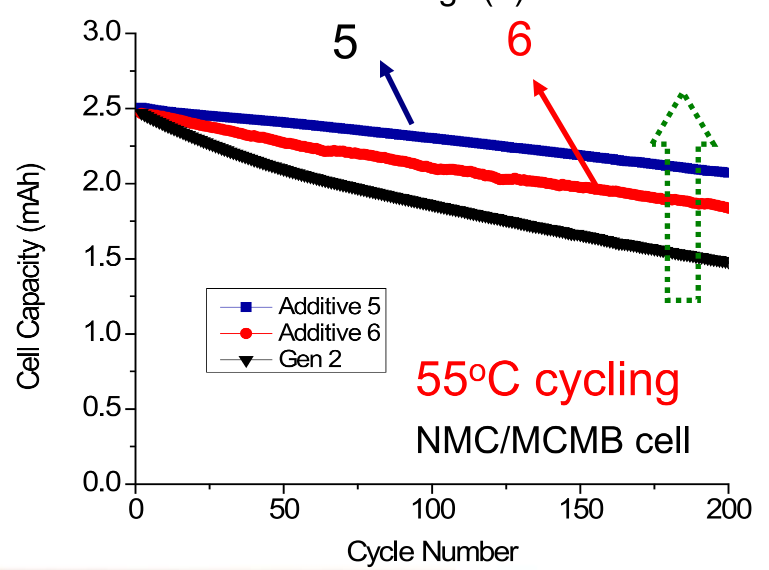
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ //1.2M $LiPF_6$ EC/EMC 3/7+1% Add.//MCMB







Summary

- EMS and TMS were identified as solvents with high voltage stability (around 5.5V)
- Wettability issues were identified when using sulfone based electrolytes. Need ceramic or ceramic coated separators for maximum performance.
- Both TMS/ LiTFSI and EMS/LiTFSI electrolytes showed stable cycling using both $Li_{1+x}Mn_{2-x}O_4$ and $LiMn_{1.5}Ni_{0.5}O_4$ systems (1000 cycles was achieved for the 4.8V spinel).
- New compounds with oxalic group were identified as excellent SEI formation additives.
- Using Lithium tetrafluoro(oxalato) phosphate (LTFOP) and lithium tris(oxalato) phosphate (LTOP) as additives has led to a significant improvement in cycling and aging performance of both NMC cathode and MCMB anode at 55°C.
- Additives with unsaturated bonds (TOS) also exhibit positive effect on cell performance, however, initial impedance is large.
- Succinic anhydride (SA) and maleic anhydride (MA) are reduced prior the decomposition of EC forming a unique SEI layer. This new SEI (without EC participation) provides excellent cycling stability and low impedance, which benefit both high power and high energy applications.

Work Plan for FY 11

- Continue investigating sulfone-based electrolytes.
  - Examine how sulfone-based electrolyte performs in graphite system
  - Attempt enabling graphite cell by co-solvent approach
  - Develop new additives to enable graphite system with these solvents

- Investigate ionic liquids as new electrolyte solvents.
  - Screen existing ionic liquids and evaluate potential candidates
  - Develop new ionic liquids with good compatibility with cell components
  - Synthesize new additives to enable ionic liquids for Li-ion cells

- Continue the development of electrolyte additives.
  - Examine other performance of succinic/maleic anhydride additives including SEI thermal stability, cell self-discharge, and storage property
  - Initiate the SEI morphology and SEI component study by SEM, TEM, XPS, FT-IR, Raman et al.