

Advanced Electrolyte Additives for PHEV/EV Lithium-ion Battery

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Argonne National Laboratory

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Project ID #: es025

Project Overview

Timeline

- Project start date: FY09
- Project end date: FY14
- Percent complete: 20%

Barriers

- Electrolyte/electrode surface reactivity
- Battery cycle life & calendar life
- Battery abuse tolerance

Budget

- Total project funding
 - 100% DOE funding
- Funding received in FY10: \$200K
- Funding for FY11: \$200K

Partners

- US Army Research Lab
- Northwestern University
- Center of Nanoscale Materials (ANL)
- Industrial Partners: EnerDel, Quallion, Central Glass Inc.
- Project Lead - Zhengcheng Zhang

Main Objectives

- ❑ To develop an efficient, inexpensive functional electrolyte ADDITIVE technology to address the barriers existing in the current lithium ion battery system such as poor cycle life, calendar life and battery abuse tolerance;
- ❑ To establish the ADDITIVE structure-property relationship by screening a variety of existing chemical compounds and develop (design, synthesize and evaluate) brand new electrolyte additives having superior performance with the aid of the theoretical modeling;
- ❑ FY10's objective is to evaluate and categorize the existing chemical compounds as possible SEI ADDITIVE to stabilize the carbonaceous anode/electrolyte interphase and improve battery performance.

Technical Approach

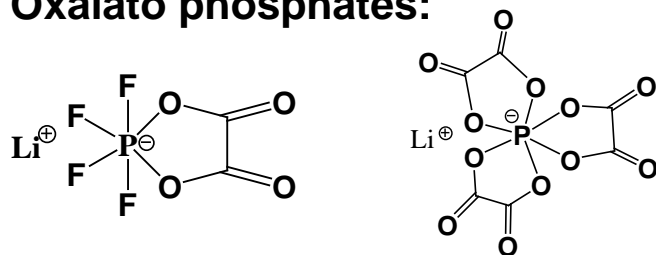
- Screen, identify various functional compounds including oxalic, carboxylic anhydride, vinyl, heterocyclic containing compounds based on the empirical rule of Degree of Unsaturation (DU) as potential electrolyte ADDITIVES;
- Evaluate the battery performance of the best ADDITIVE screened using $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ /MCMB full cell testing vehicle: the capacity retention with cycling at various temperatures, storage property at elevated temperature, impedance growth with cycling, and cell power capability;
- Propose the mechanisms of the SEI formation by the new ADDITIVE with aid of theoretical calculation method and provide insights for future research of advanced additives.

Achievements and Progress

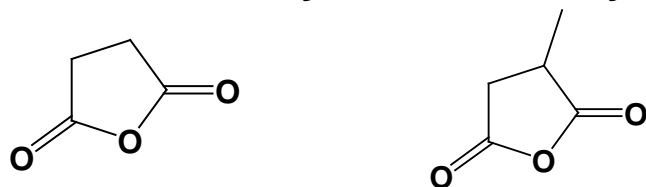
Previous Achievement (FY10)

Three categories of existing compounds were screened and tested as lithium ion battery electrolyte additives for prolonged cycle life and improved safety:

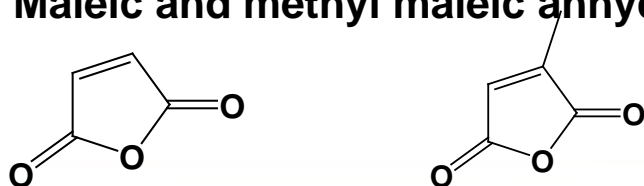
❑ Oxalato phosphates:



❑ Succinic, methyl succinic anhydride:



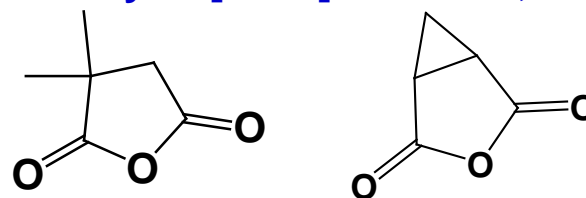
❑ Maleic and methyl maleic anhydride:



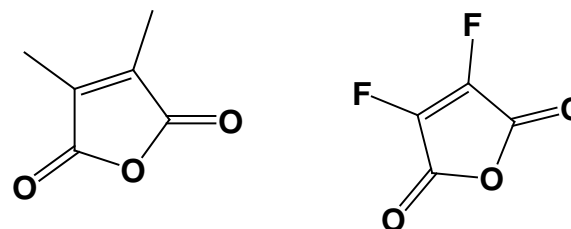
Current Work and Achievement (FY11)

As a continuation of FY10's work, this year we have investigated the following additives:

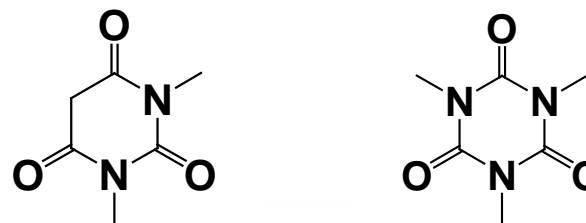
❖ 3-oxabicyclo[3.1.0]hexane-2,4-dione:



❖ Disubstituted maleic anhydride:



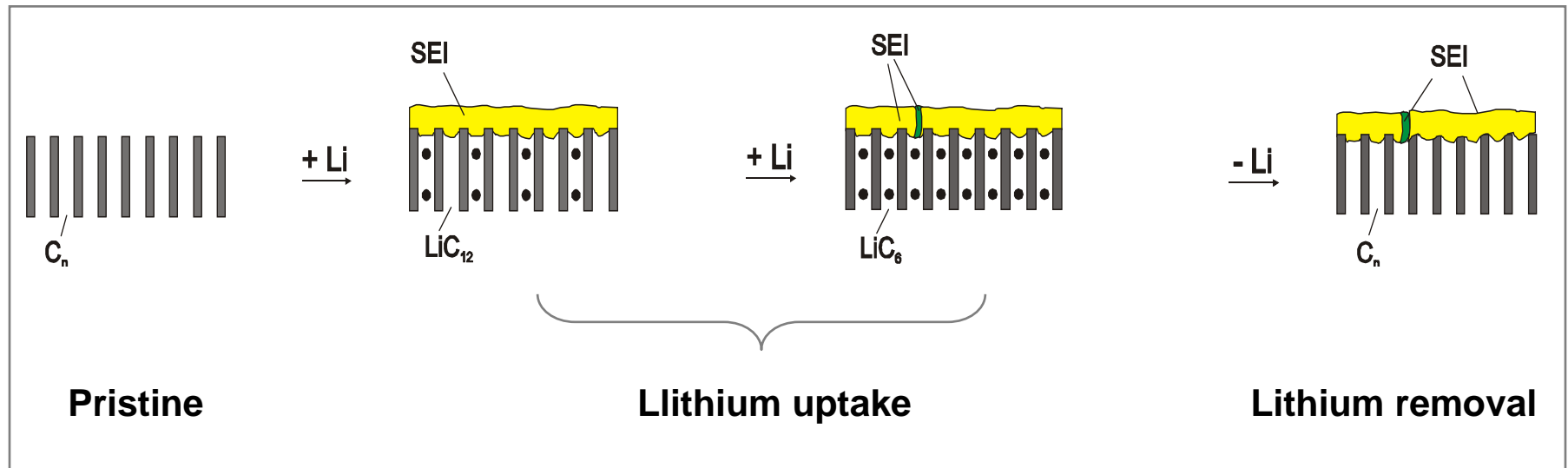
❖ Heterocyclic compounds:



Formation of Solid Electrolyte Interphase

- ✓ Lithiated graphite (LiC_6) is thermodynamically unstable in contact with the electrolyte component including electrolyte solvent, lithium salt, impurities...
- ✓ Lithiated graphite (LiC_6) is dynamically stable in contact with the electrolyte due to the existence of solid electrolyte interphase (SEI) layer formed at the electrolyte/electrode interphase during the first charging process.

Electrochemical process of graphite based anode



SEI Additive Categories and Functions

1. SEI Additive to enable cell operation (cell enabler):

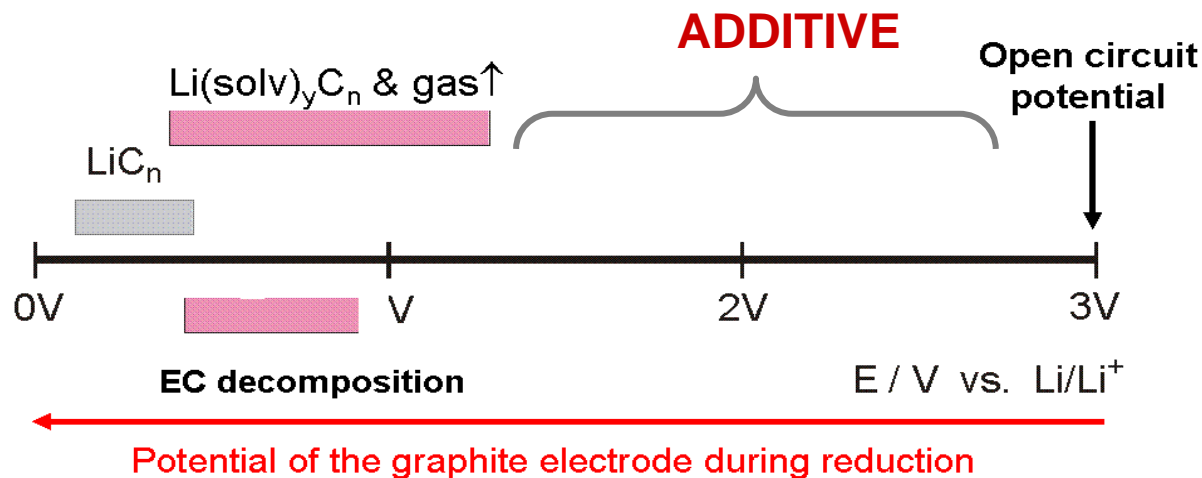
For new electrolytes (i.e. PC based electrolyte), the SEI additive is mandatory and indispensable for cell performance. SEI is formed on graphite anode surface to prevent the electrolyte solvent co-intercalation and carbon exfoliation with gas evolution.

2. SEI Additive to improve cell performance (cell improver):

For conventional electrolyte (for example 1.2M LiPF₆ EC/EMC), the SEI additive is the performance improver.

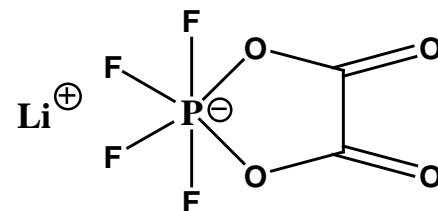
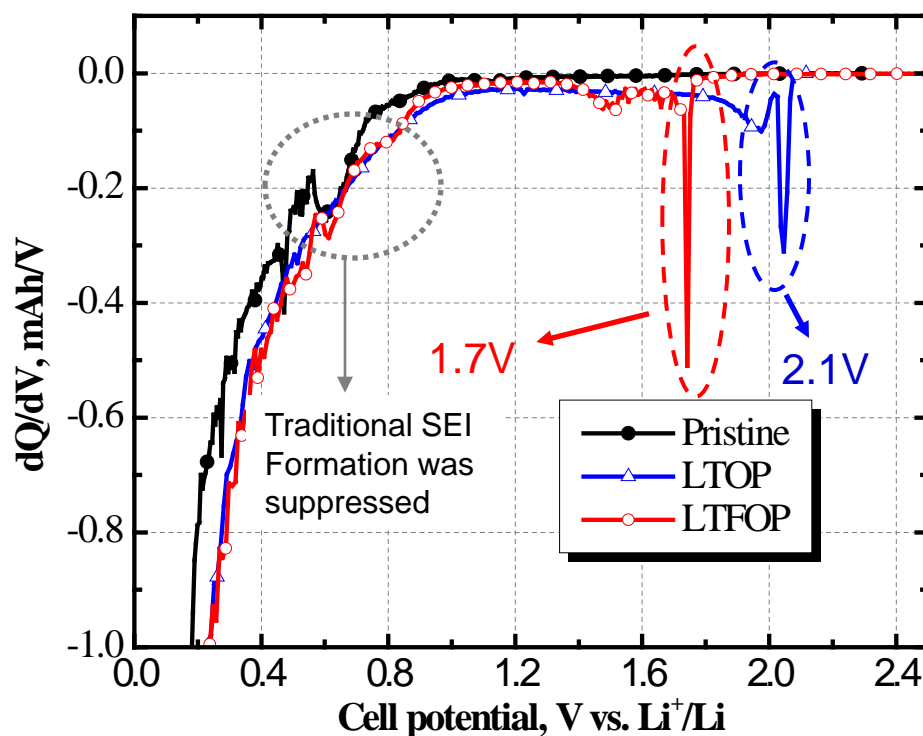
2-1. Artificial SEI forms prior the regular SEI and suppress the formation of the regular SEI.
A brand new artificial SEI is formed: (**A-SEI**)

2-2. New SEI forms in addition to the formation of regular SEI by EC decomposition:
A dual SEI is formed: (**D-SEI**)

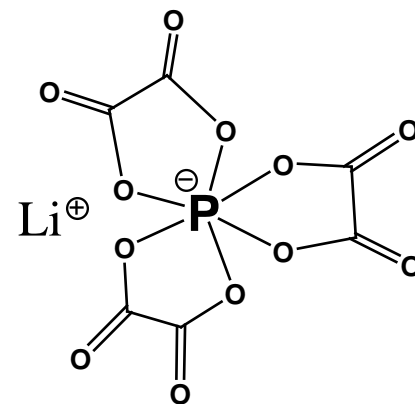


Artificial SEI Formation

(SEI additive suppresses the regular SEI formation)



LTFOP (1.7V vs Li^+/Li)

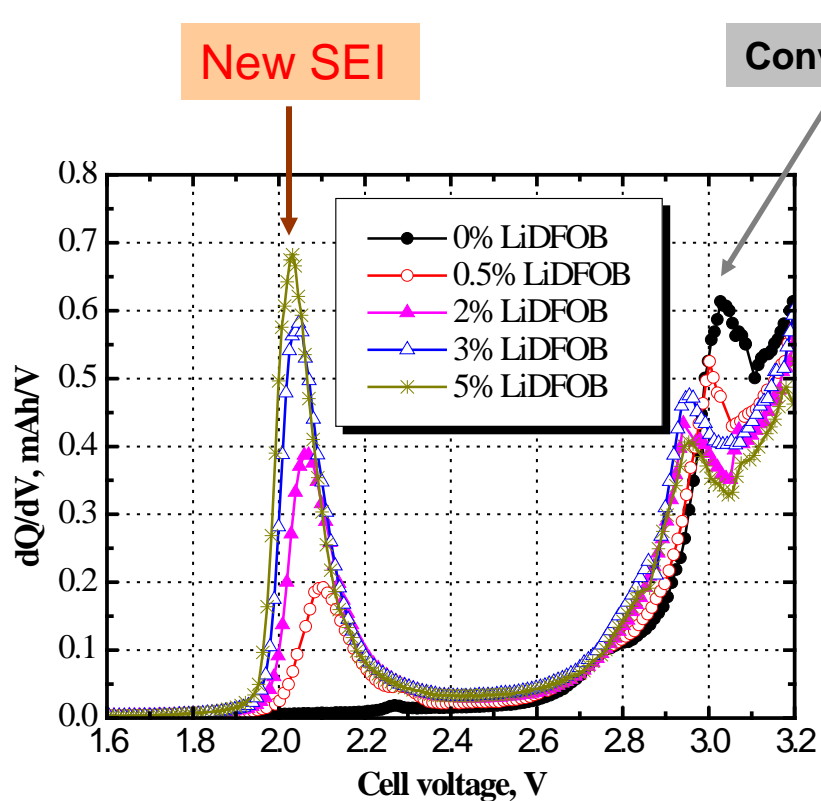


LTOP (2.1V vs Li^+/Li)

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

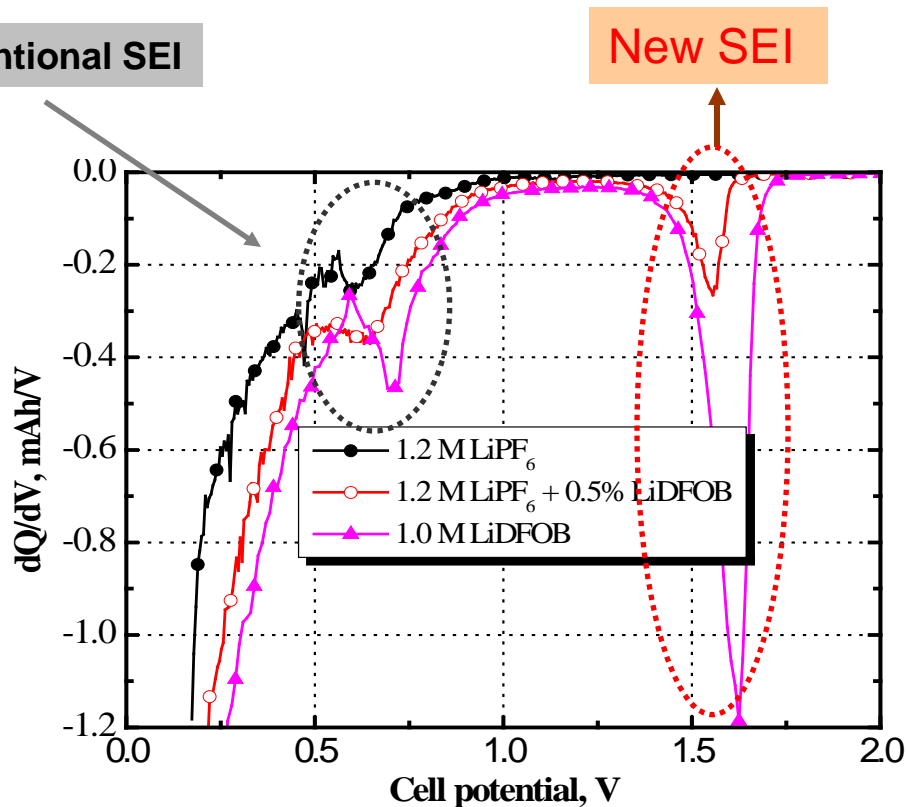
Dual SEI Formation

(SEI additive reduced prior the conventional SEI formation on Graphite)



NMC/MCMB Full Cell

In full cell, the peak at 2.1V is proportional to the concentration of additive, indicating the new SEI formation by the additive prior to the formation of conventional SEI at a potential $\sim 3.0V$.

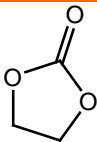
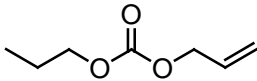
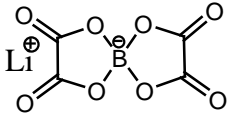
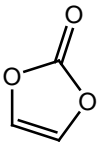
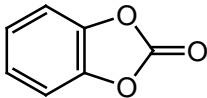
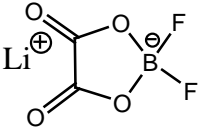
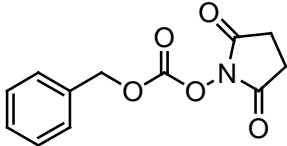

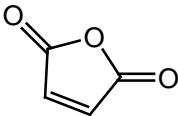
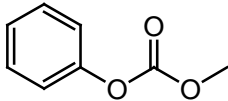
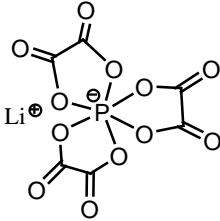
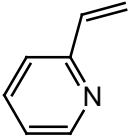


MCMB/Li Half Cell

In MCMB/Li half cell, additive reduction occurs at 1.6V, prior to the conventional SEI formation Which take place at a potential between 0.6~0.8V vs Li⁺/Li
Electrolyte: 1.2M LiPF₆ EC/EMC 3/7 +2% LiDfOB

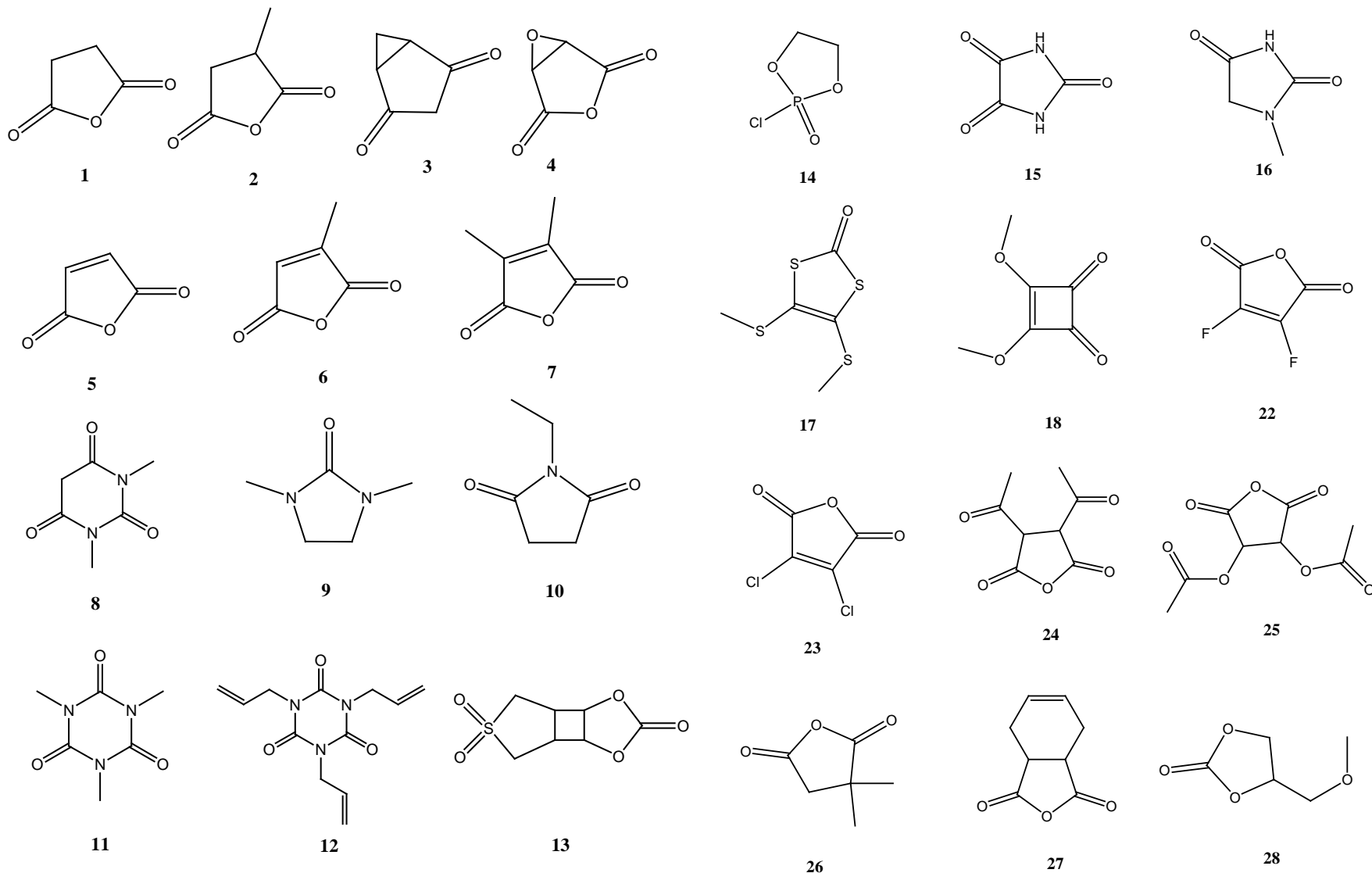
Empirical Rules for SEI Additive Screening

- * ➤ Rings count as one degree of unsaturation;
- Double bonds count as one degree of unsaturation;
- Triple bonds count as two degrees of unsaturation.

DU*	Formula	DU*	Formula
2			
		6	
			
3		7	
4			
		9	
5			

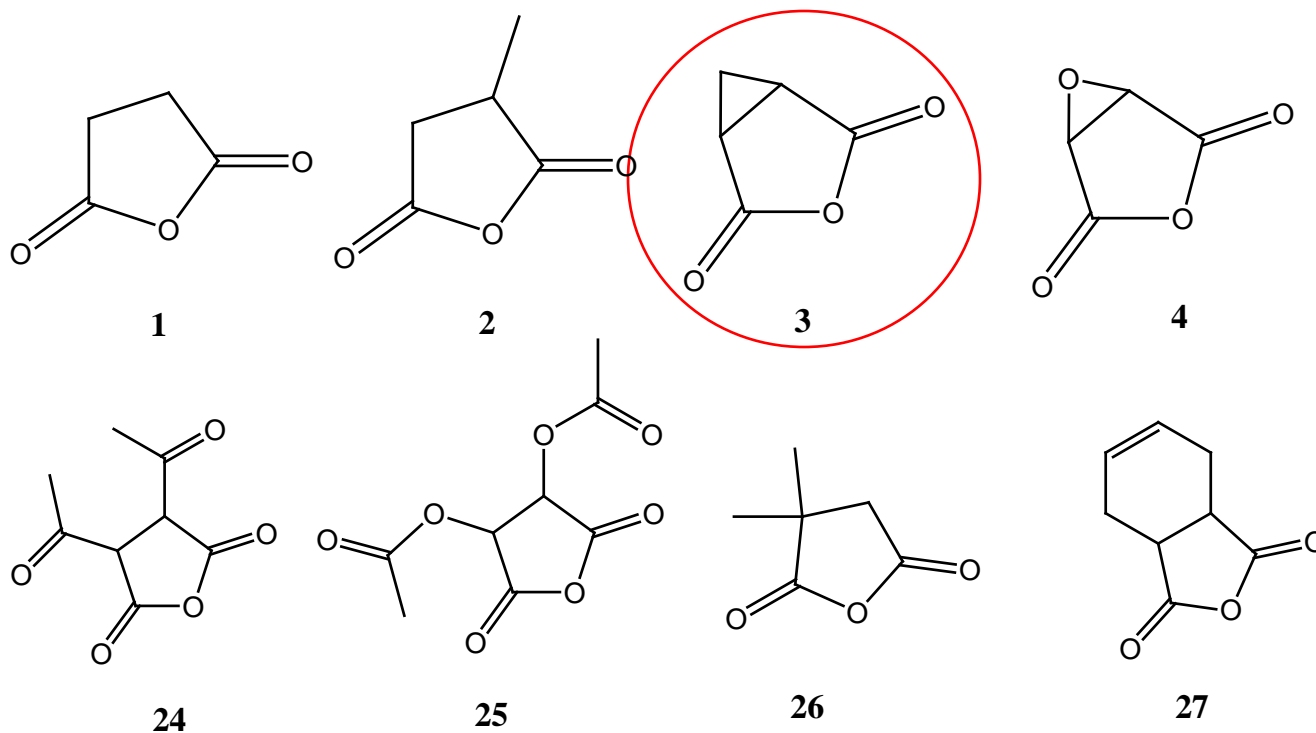
- ☐ Degree of unsaturation (DU) should be more than two;
- ☐ The higher degree of unsaturation, the better SEI additive?

Proposed SEI Formation Additive Candidates



Potential Compounds with multiple unsaturation degrees as Electrolyte Additives

1st Group: Succinic Anhydride (SA) and Its Derivatives

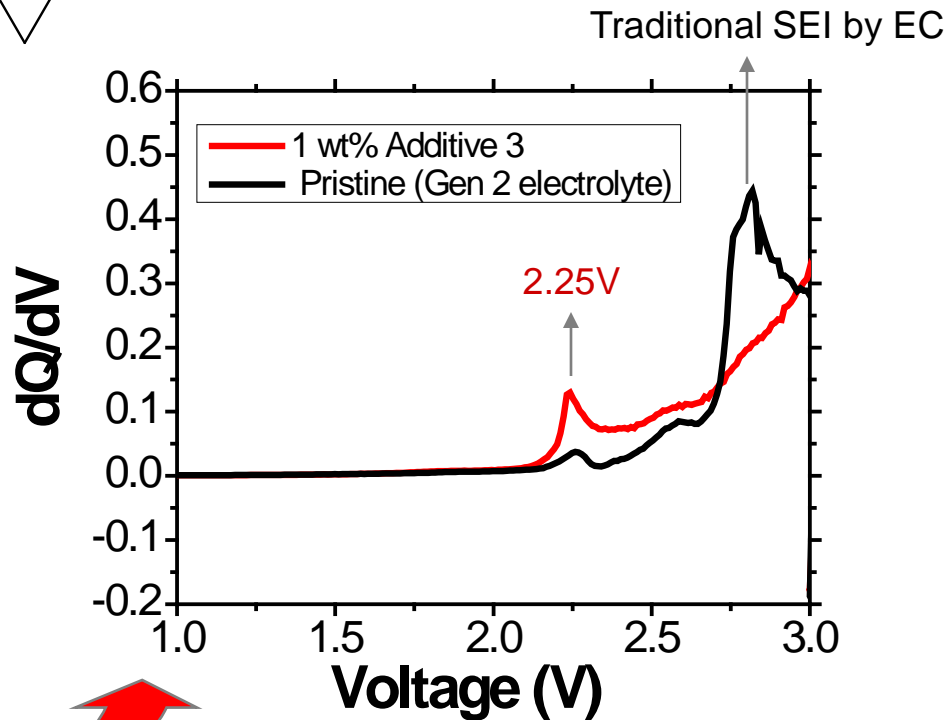
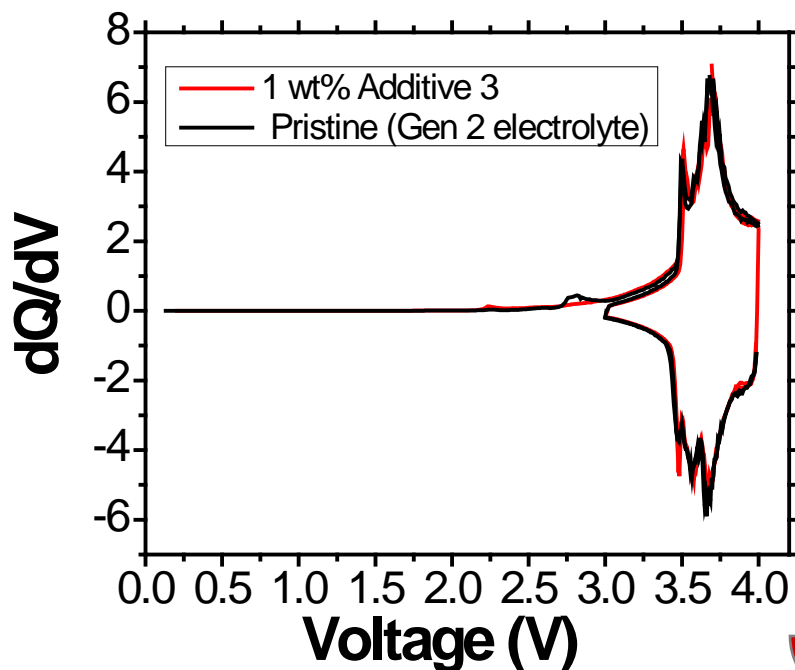
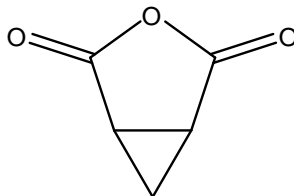


SA as basic additive structure:

Evaluate how the electronic structure and stereo hindrance affects the performance

Differential Capacity Profiles of Additive 3

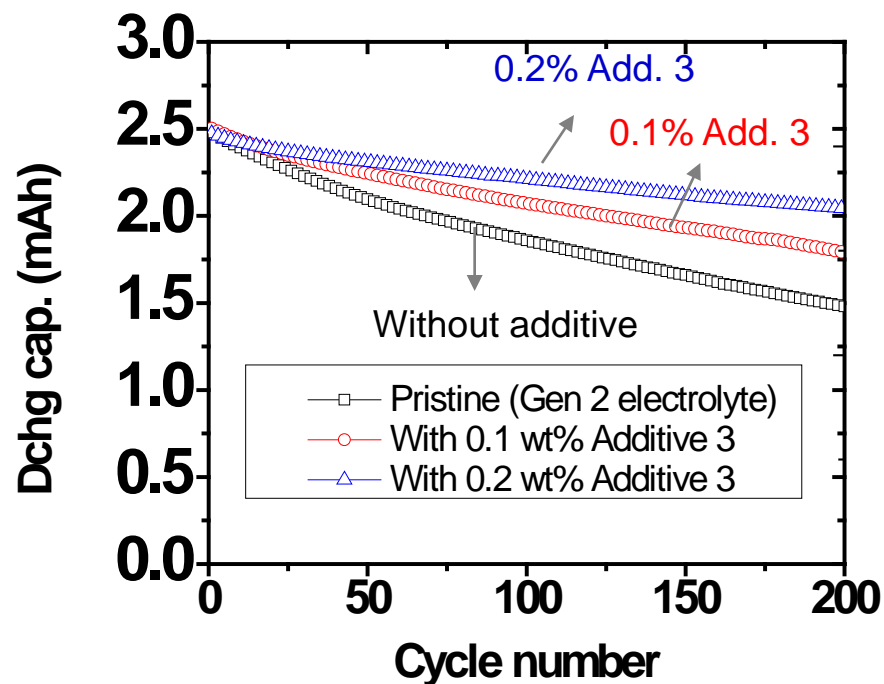
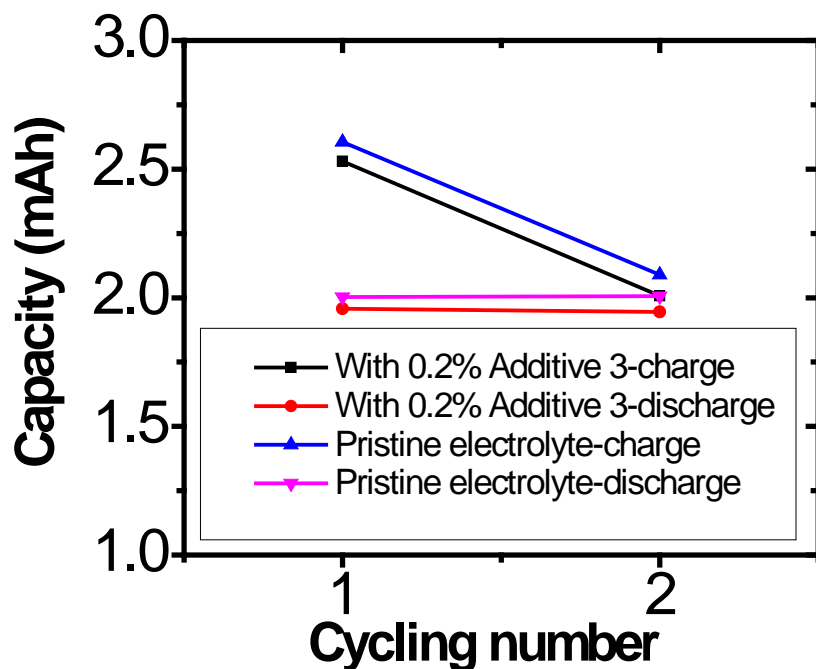
3-oxabicyclohexane-2,4-dione



□ Diff. capacity vs voltage of MCMB-1028/ $\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$ coin cells in 3E7EMC/PF12 with or without 1 wt% Additive 3. The charge and discharge rate was C/10 with cut-off voltage 3 ~ 4 V.

□ Peak at 2.25V is due to the new SEI formation through the decomposition of Additive 3, and the traditional SEI is not formed, indicating a brand new artificial SEI.

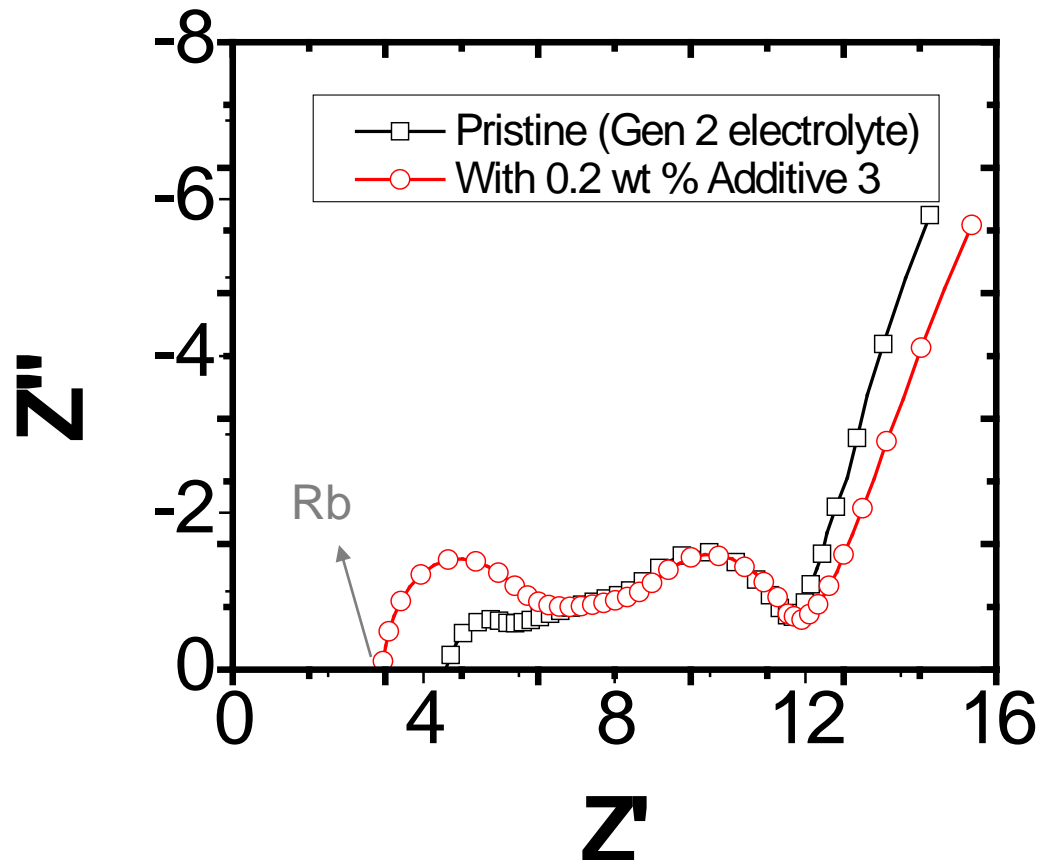
Cycling Performance of Additive 3



✓Fig. (Left): Two cycle capacity retention of MCMB/NMC cell at 25°C; The first and second cycle charge and discharge capacities are comparable to that of the pristine electrolyte.

✓Fig. (Right): Capacity improvement for cells in 3E7EMC/PF12 with Additive 3. 0.2% Additive 3 addition to the pristine electrolyte showed the most improvement. (cycled at 55 °C with 1C rate; cut-off voltage is 2.7 ~ 4.2 V).

AC Impedance of Cells with Additive 3

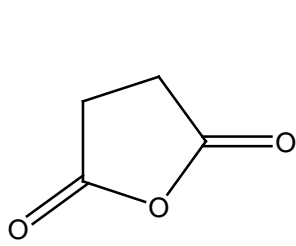


After formation (before cycling)

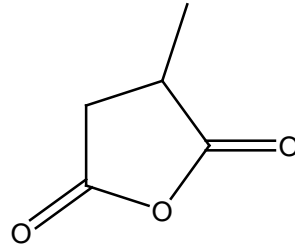
AC impedance profile of MCMB/NMC cells in 3E7EMC/PF12 with or without 0.2 wt% additive 3. The cells were charged to 3.8 V with a charge rate of 1C.

➤ Fig. Impedance profiles of MCMB/NMC cell before cycling at 25°C; The R_b is smaller for the additive cell indicating the more conductive SEI layer formed compared to that of the pristine electrolyte. Unlike most of the existing commercial additives that show high initial interfacial impedance, ANL-Additive 3 shows similar initial interfacial impedance as the one without additive (stable and thin SEI).

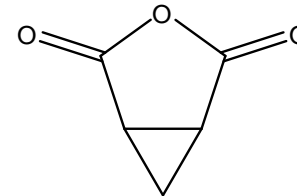
Chemical Structure Effect on AC Impedance



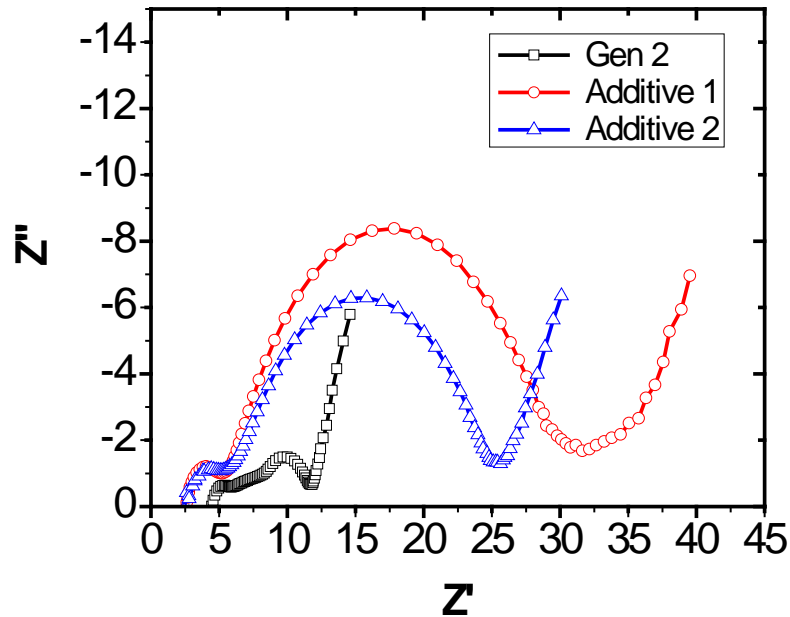
1



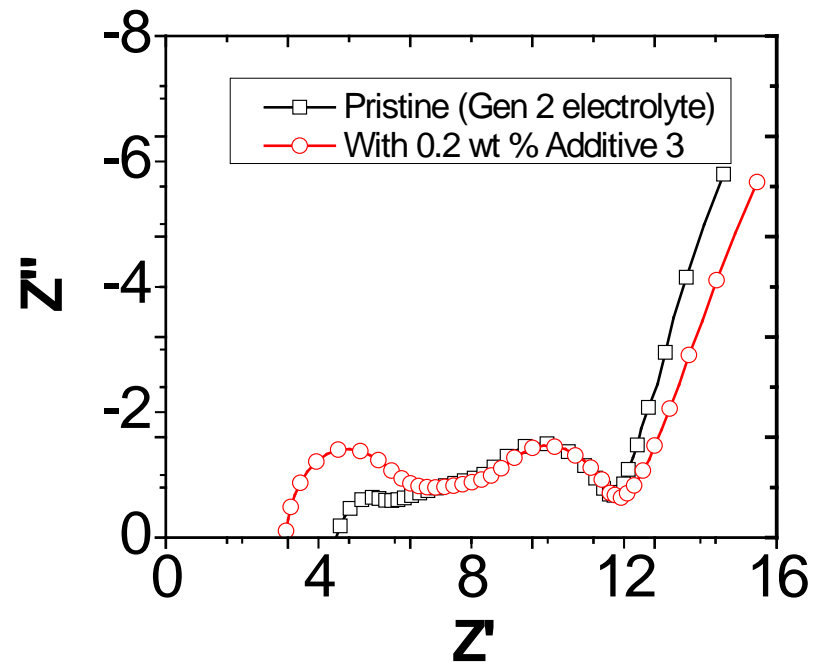
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3



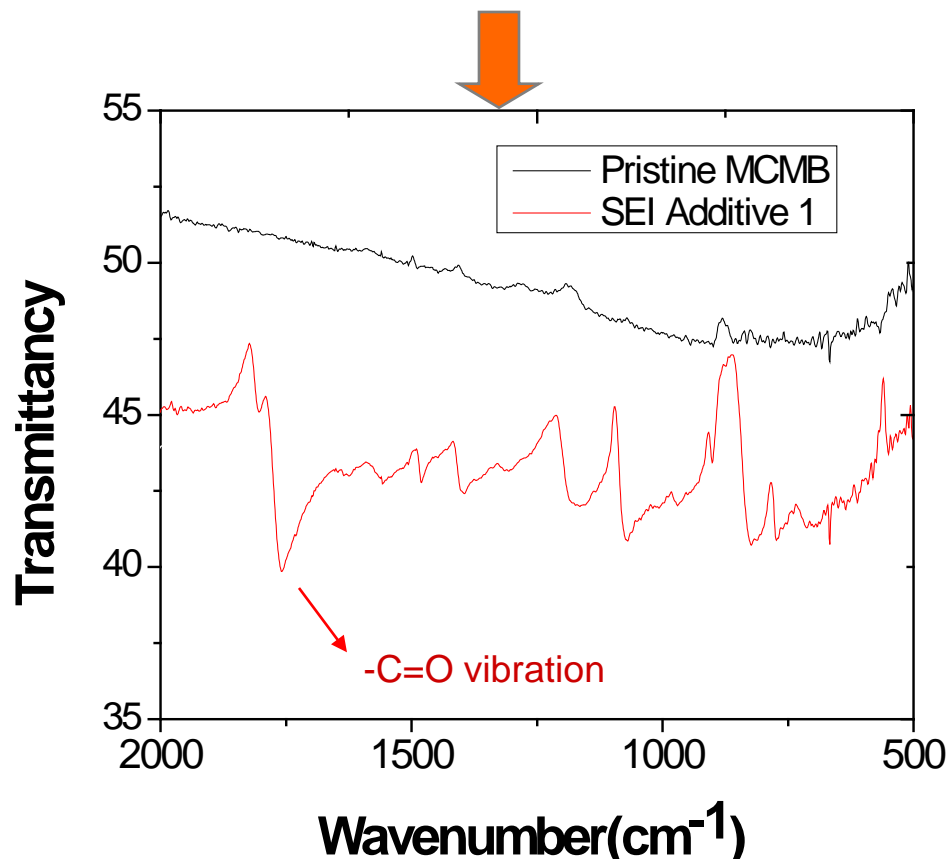
After Formation



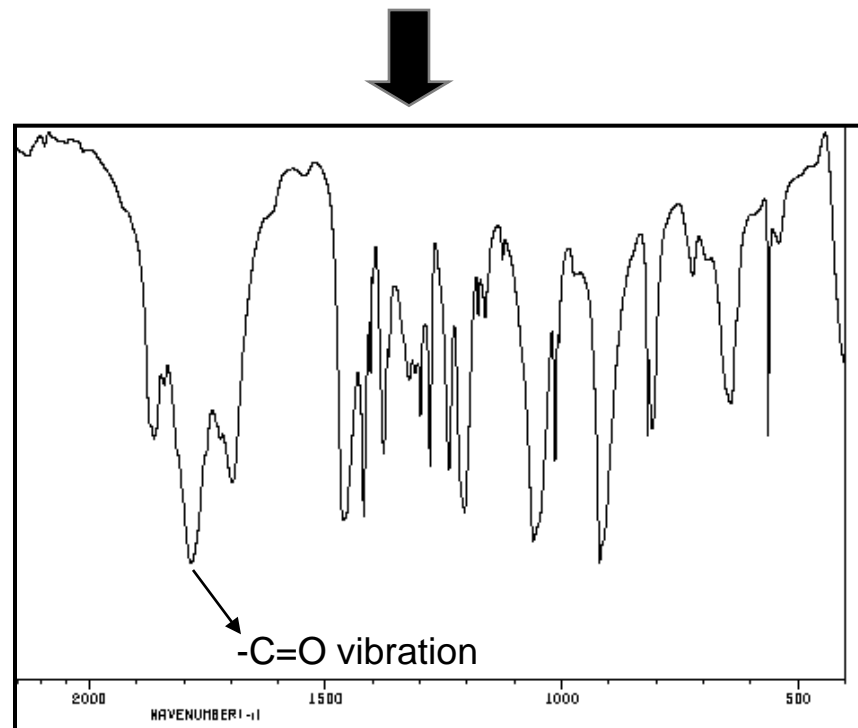
Additive 3 showed very low initial impedance, however Additives 1, 2 showed a much larger initial impedance than the electrolyte without additive. Although good capacity retention was achieved with Additive 1 & 2, the power of the cell based on these additives is jeopardized.

FT-IR Identification of SEI Formed by Additive 1

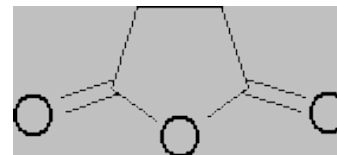
IR spectrum of new SEI
(MCMB anode after formation)



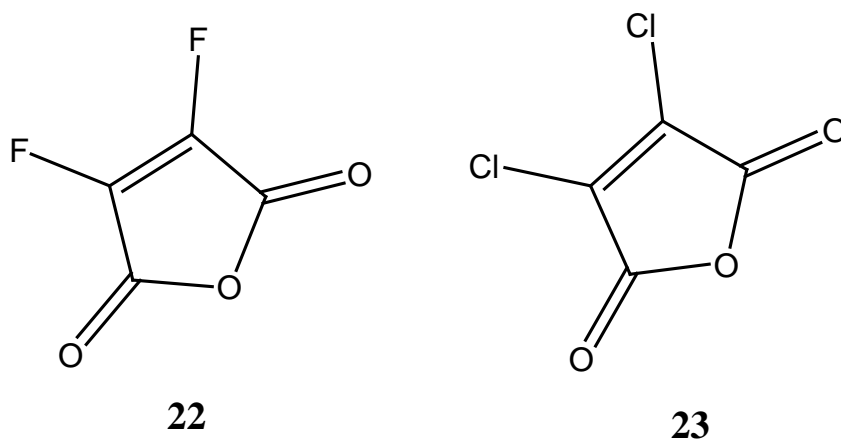
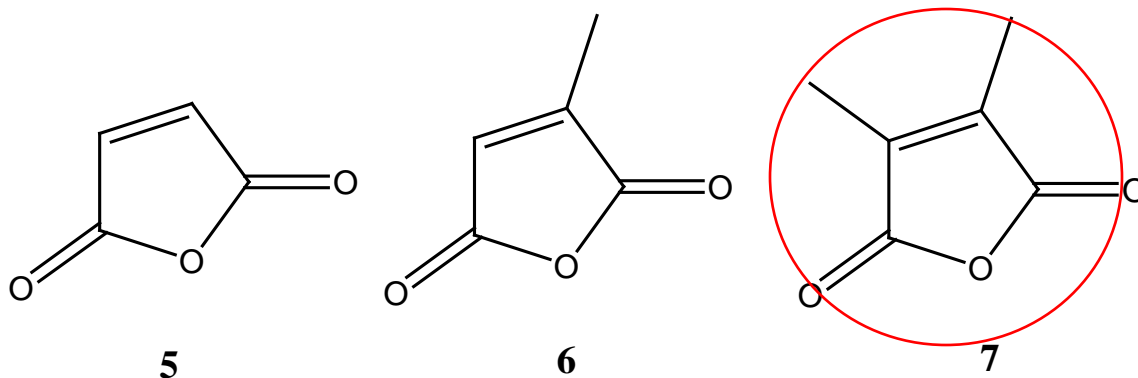
IR spectrum of Additive 1



Wavenumber (cm⁻¹)

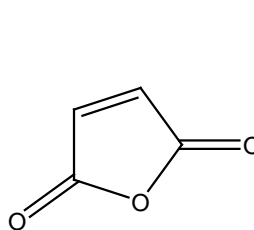
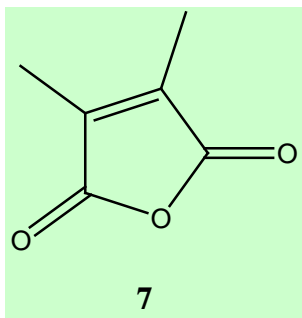


2nd Group: Maleic Anhydride (MA) and Its Derivatives

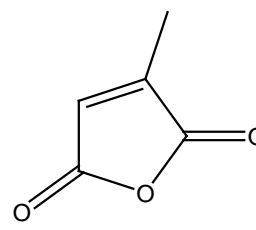


Evaluate how the electronic structure and the effect of stereo substitution group on MA basic additive on the cell performance

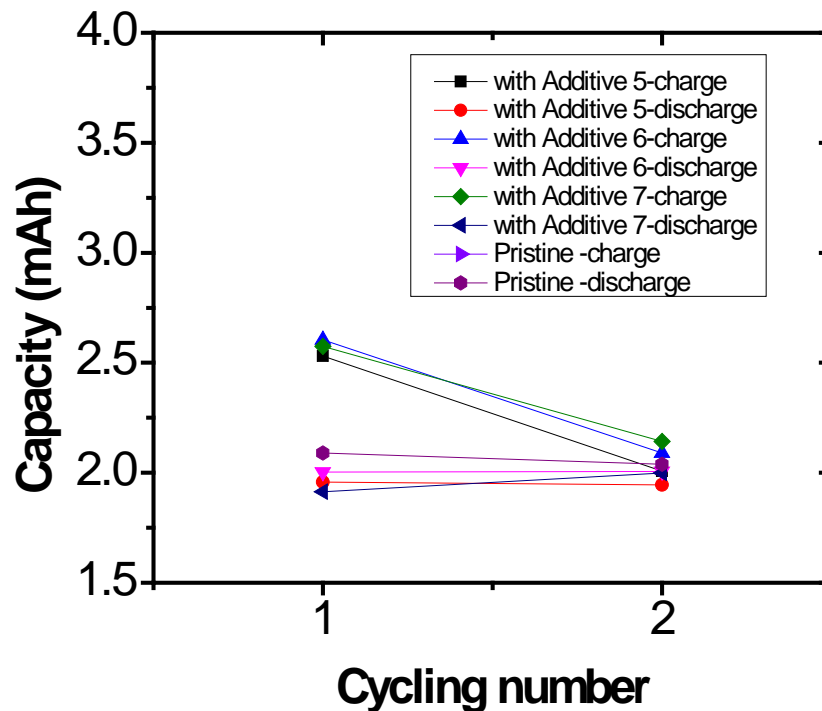
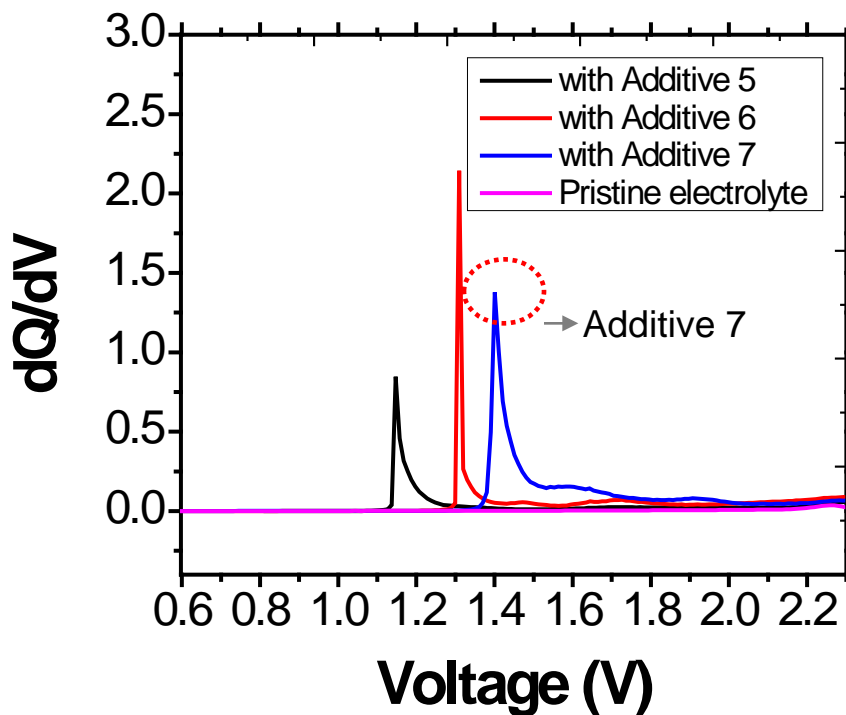
Differential Capacity and Initial Capacity of Additive 7



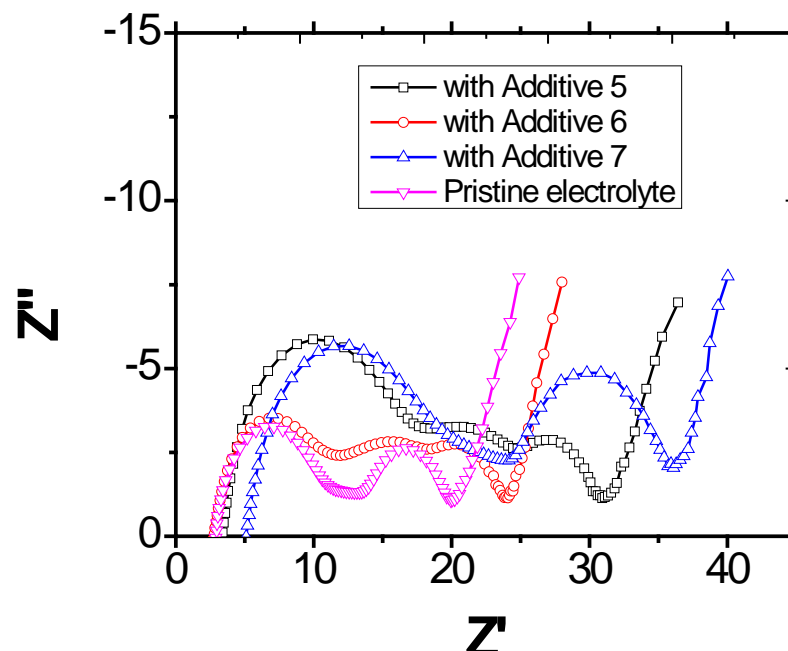
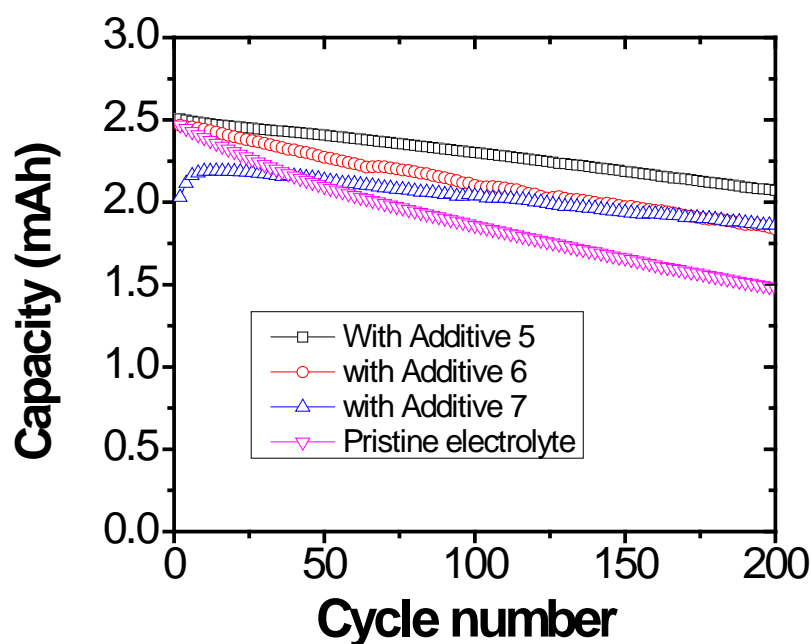
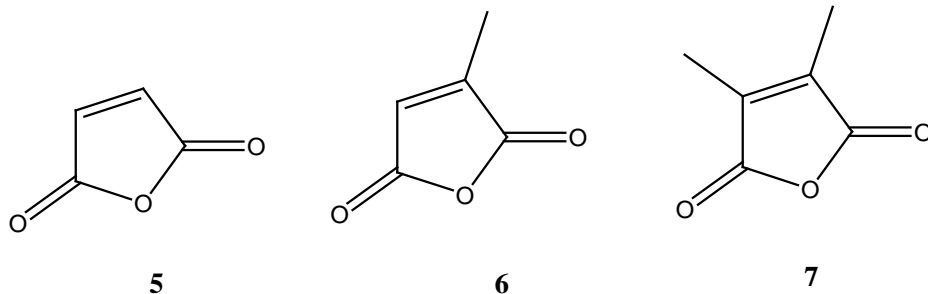
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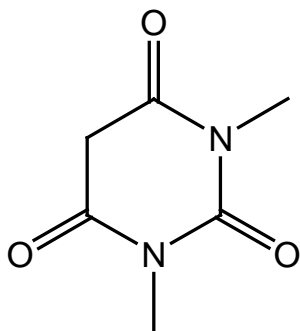
Capacity Retention, Impedance Profiles of Additive 5-7



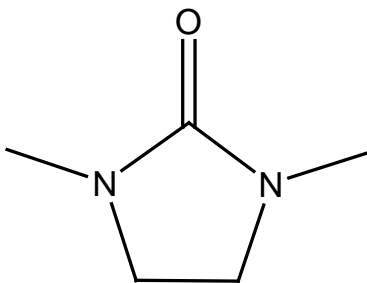
The cells were cycled at 55 °C with and without 1wt% of Additives. The charge rate was 1C. The cut-off voltages were 2.7 ~ 4.2 V.

AC impedance profile of MCMB/NMC cells in 3E7EMC/PF12 with or without 1 wt% additives. The cells were charged to 3.8 V with a charge current of 1C.

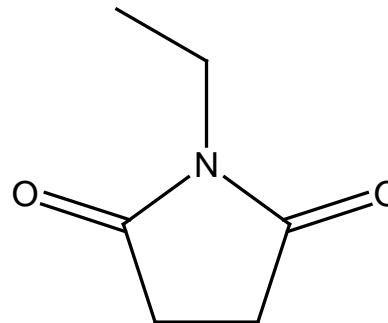
3rd Group: Heterocyclic Compounds (Ongoing)



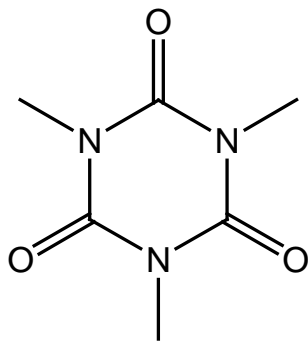
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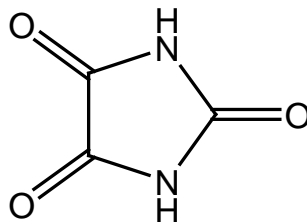
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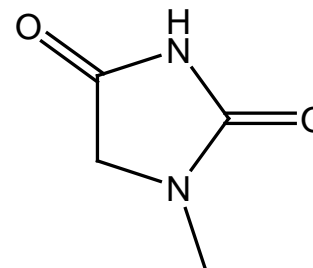
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11



15



16

Collaborations/Interactions

- **US Army Research Laboratory**

- Dr. Richard Jow and Dr. Kang Xu for technical and information exchanges;

- **Argonne National Laboratory**

- Dr. Larry Curtiss for calculation of reduction/oxidation potentials of additives by quantum chemical methods;

- **Northwest University**

- Professor Harold Kung for SEI characterization XPS and SEM;

- **EnerDel**

- Dr. Yumoto for the electrode and technical discussions.

Proposed Future Work

For the rest of this fiscal year of 2011 and FY12, we are proposing the following research work:

- ❑ Continue the quantum chemical and electrochemical screening of the remaining compounds in the 1st, 2nd and 3rd groups outlined in the slides 12, 18 and 21 and expand the potential additive database;
- ❑ Perform a study on the thermal stability of SEI formed by the best additives using differential scanning calorimetric and ARC method;
- ❑ Investigate the lithium-ion cell self-discharge property at elevated temperature and evaluate the effect of new SEI additives on the cell power capability using HPPC test profile;
- ❑ Characterize SEI morphology by SEM, TEM, XPS, IR, Raman et al. analytical methods;
- ❑ Initiate the design and synthesis of the new advanced electrolyte additives.

Summary

- ❑ New organic compounds containing oxalic, carboxylic anhydride, vinyl, heterocyclic groups were proposed and identified based on the empirical rule of Degree of Unsaturation (DU) as potential electrolyte ADDITIVES;
- ❑ Electrochemical experiments (Li/graphite half cell) were performed and the succinic anhydride based additives, maleic anhydride based additives can be reductively decomposed forming a brand new SEI on surface of the graphite surface prior to the formation of conventional SEI layer at 0.5~0.8V vs Li/Li⁺;
- ❑ The cell containing 3-oxabicyclohexane-2,4-dione (ANL-Additive 3) as an additive shows very low initial impedance and excellent capacity retention at both room temperature and at 55°C. This additive is very promising for extending the cycle and calendar life of lithium battery for automotive applications;
- ❑ New additives with heterocyclic groups were proposed and will be investigated further in FY12.