Advanced Electrolyte Additives for PHEV/EV Lithium-ion Battery

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Argonne National Laboratory

Vehicle Technologies Program
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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 FY11: $300K
- Funding for FY12: $400K

Partners

- US Army Research Lab
- University of Utah
- Center of Nanoscale Materials (ANL)
- Industrial Partners: ConocoPhilips,Saft, EnerDel.
- Project Lead - Zhengcheng Zhang

Project 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.

- FY11's objective is to continue to evaluate and categorize the existing chemical compounds as possible SEI ADDITIVE to stabilize the carbonaceous anode/electrolyte interphase and to develop novel SEI additives using organic synthesis based on the knowledge gained in the screening.

Technical Approach

- Screen, identify and evaluate a large number of various functional compounds containing cyclic and double bond structures, including oxalic, carboxylic anhydride, vinyl, heterocyclic containing compounds based on the empirical rule of Degree of Unsaturation (DU) as potential electrolyte additives.

- Combine quantum chemical calculation (DFT and MD) and electrochemical experimental testing to select the compounds that can be reductively decomposed prior to the formation of conventional SEI layer at 0.5~0.8V *vs* Li/Li^+.

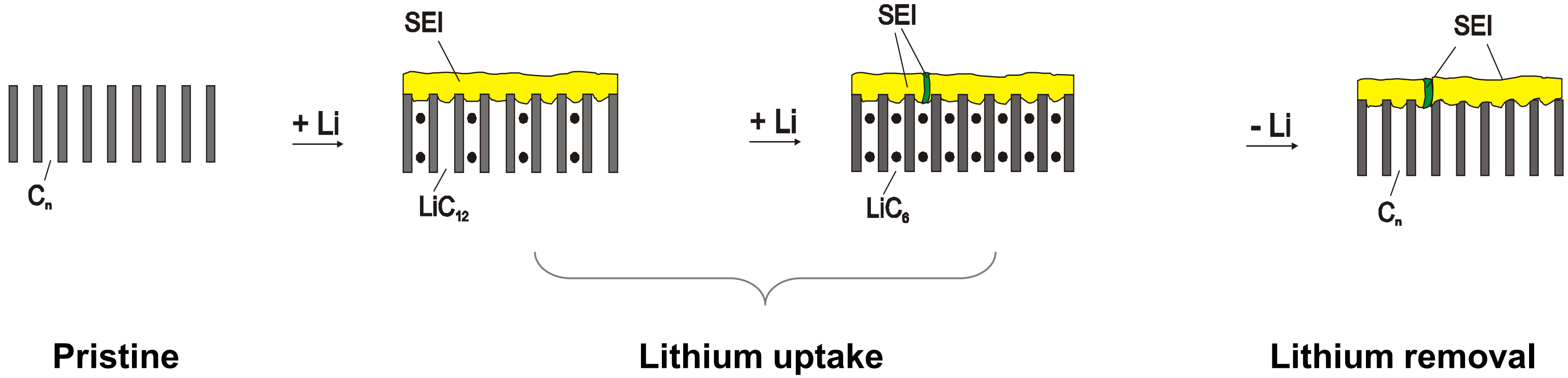
- Evaluate the battery performance of the best additive screened using $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/MCMB full cell testing vehicle: the capacity retention with cycling at various temperatures, storage property at elevated temperature, impedance growth with cycling, and cell power capability.

- Propose the mechanisms of the SEI formation by the new additive with the aid of theoretical calculation method and provide insights for the next step research of advanced additives.

Technical Accomplishments

- Lithium anodes - Instantaneous SEI formation in contact with electrolyte
- Carbonaceous anodes: Stepwise formation, potential dependent and co-intercalation of Li and electrolyte (1990s, Dahn's findings)
- 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.

SEI Formation Process of Graphite Based Anode

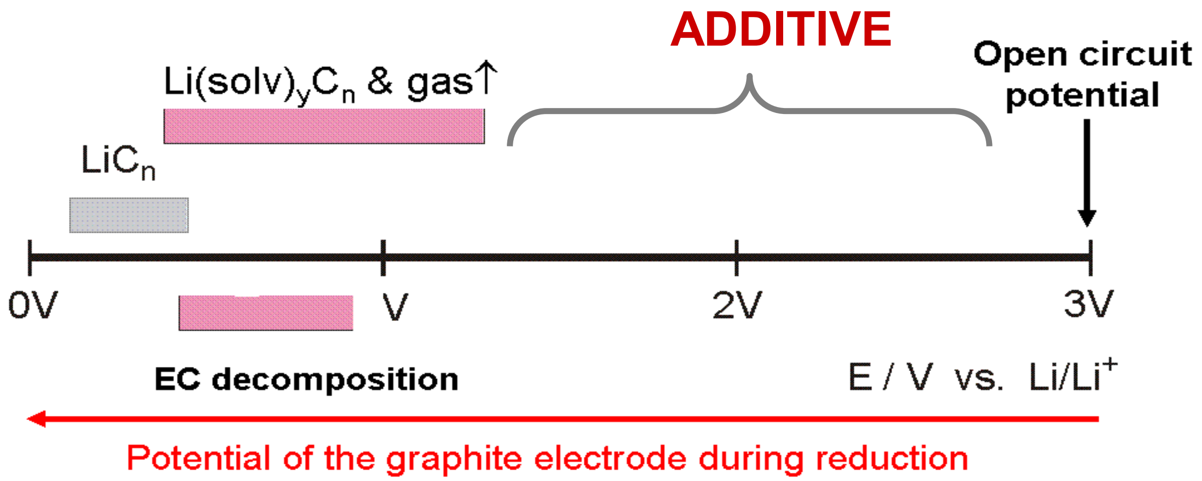


SEI Additive Category and Function

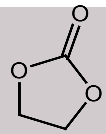
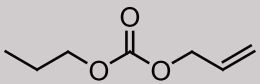
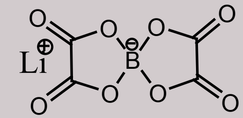
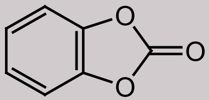
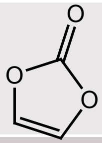
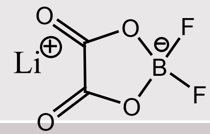
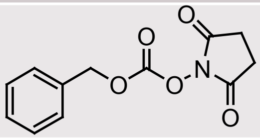
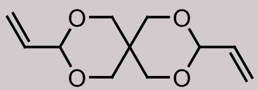
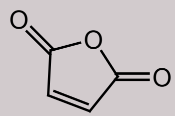
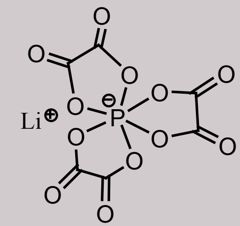
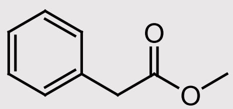
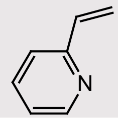
1. SEI Additive to <u>Enable</u> Li-ion Cell Operation:
For new electrolytes (i.e. PC based electrolyte), the SEI additive is mandatory and indispensible for cell performance. SEI is formed on graphite anode surface to prevent the electrolyte solvent co-intercalation and carbon exfoliation with gas evolution.

2. SEI Additive to <u>Improve</u> Li-ion Cell Performance:
For conventional electrolyte (for example 1.2M $LiPF_6$ EC/EMC 3/7), the SEI additive is the performance improver.

❑Artificial SEI forms prior the regular SEI and suppress the formation of the regular SEI. A brand new artificial SEI is formed (**A-SEI**)
❑New SEI forms in addition to the formation of regular SEI. A dual SEI is formed (**D-SEI**).



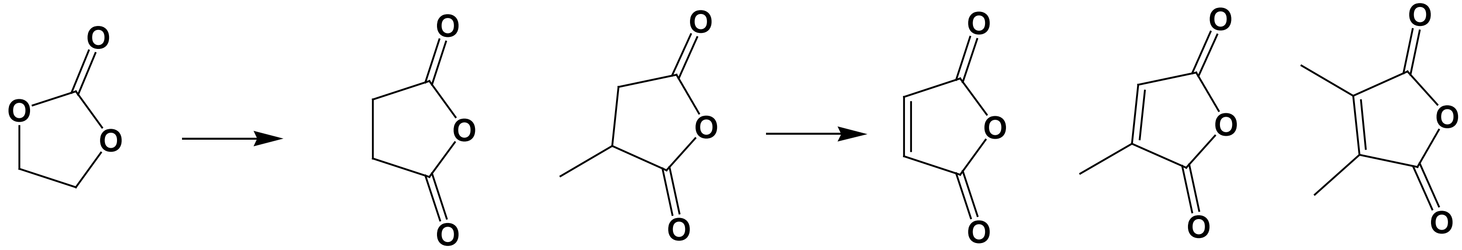
SEI Additive Selection Rule

Degree of Unsaturation	Chemical Formula	Degree of Unsaturation	Chemical Formula
2	 	6	 
3	 	7	
4	 	9	
5	 		

- ➢ Rings count as one degree of unsaturation.
- ➢ Double bonds count as one degree of unsaturation.
- ➢ Triple bonds count as two degrees of unsaturation.

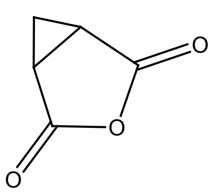
- ❑ Degree of unsaturation (DU) should be more than two.
- ❑ The higher the degree of unsaturation, the better the performance of additive?

Achievements and Progress

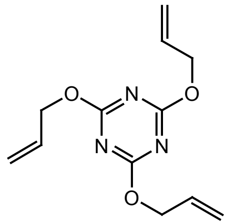


EC A1 A2 A5 A6 A7

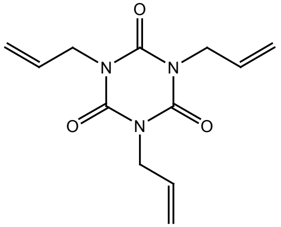
- Screening Results: Empirical rule was established to help generate the screening list of SEI additive candidates and an evaluation procedure using $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/MCMB chemistry was chosen. As a result, several promising SEI additive candidates (A1-A7) stand out with superior features in terms of improving cell cyclability and impedance.
- Mechanism Study: New SEI additives (ANL-SEI-1, 2, 3) were chosen to conduct further investigation due to their promising performance. Many surface characterization techniques, such as FT-IR, Raman, SEM, and XPS, were employed to understand the mechanism of the SEI formation process.
- Novel SEI Additive Development: Based on the knowledge gained during the first two phases, novel cyclic phosphate compounds were designed and synthesized as new SEI additives. Chemical structure of the phosphates was characterized by ^{1}H, ^{13}C and ^{31}P-NMR and GC-MS. Evaluation of lithium ion cell performance demonstrates promising results.



ANL-SEI-1



ANL-SEI-2

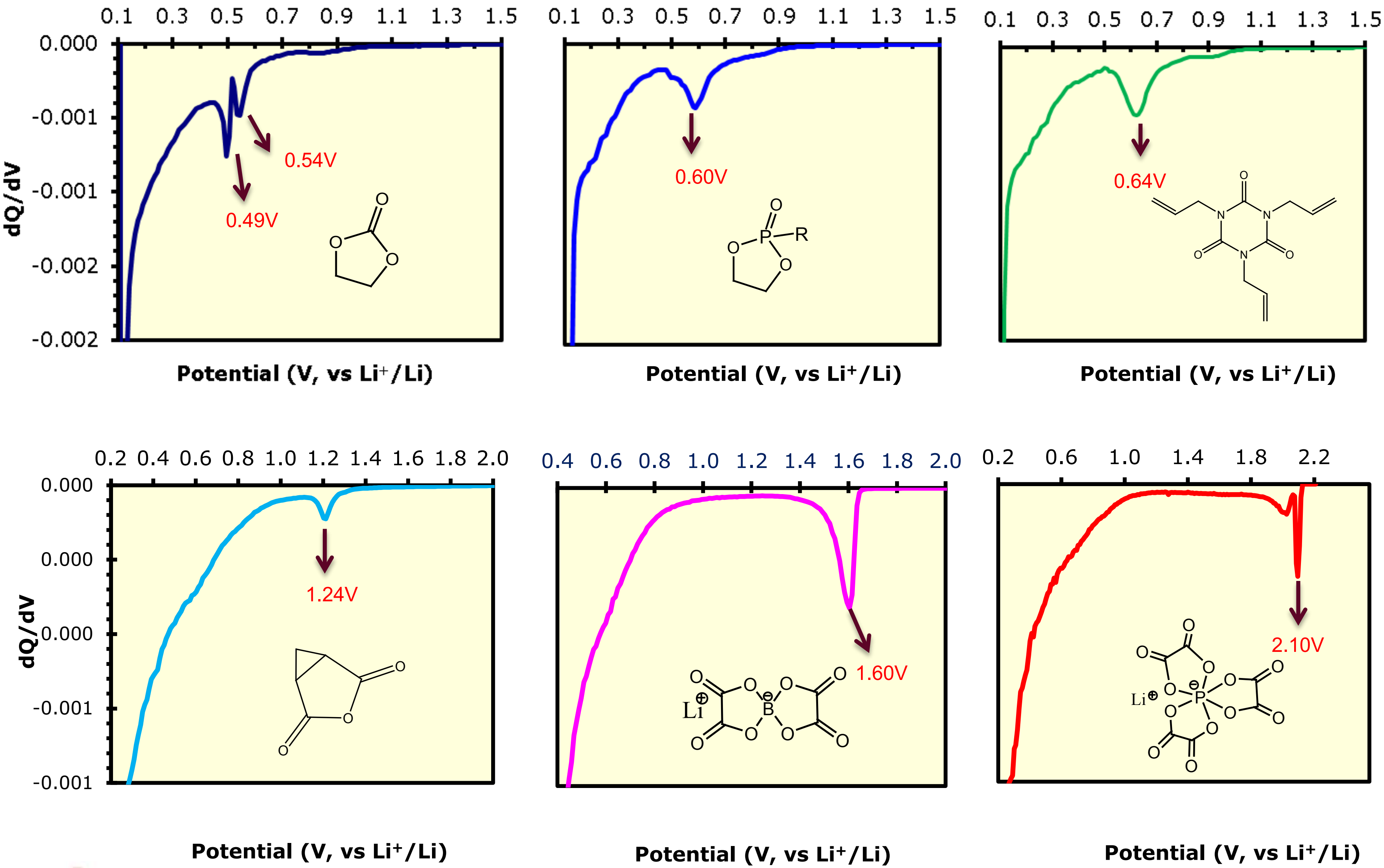


ANLSEI-3

Cyclic Phosphate Compounds

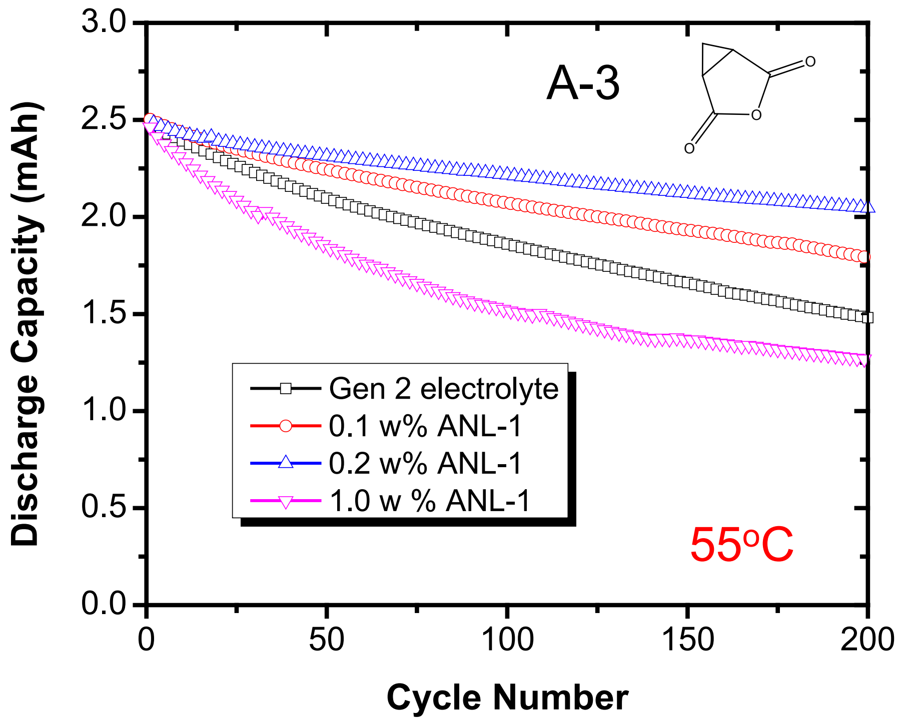
EMP

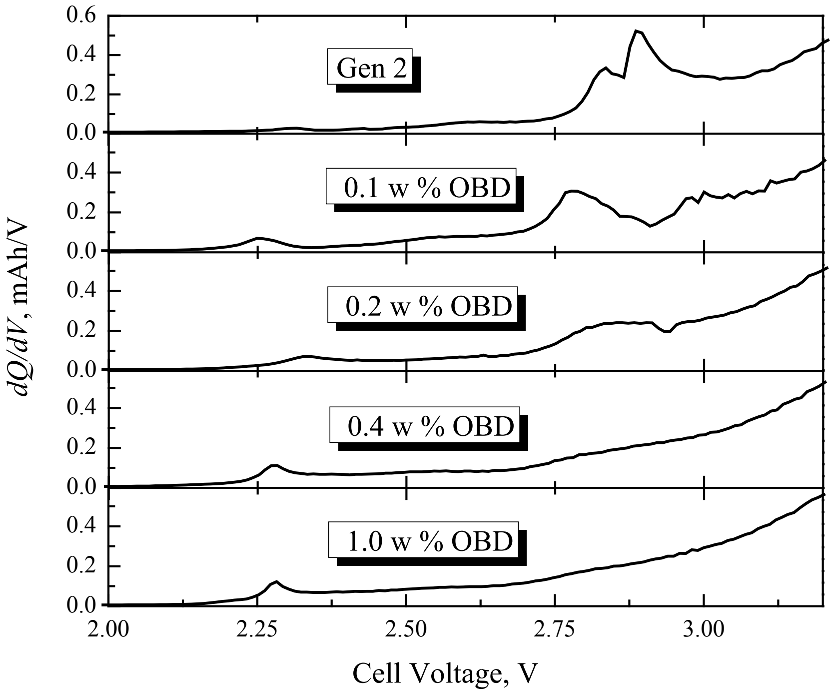
SEI Formations at Different Potentials (*vs* Li^+/Li)



Li/Graphite half cell 1st cycle differential capacity profiles: 1.2M $LiPF_6$ EC/EMC 3/7+1% Additive at RT using C/10 rate.

Additive Concentration Effect on SEI Formation Process and Cell Cycling Performance



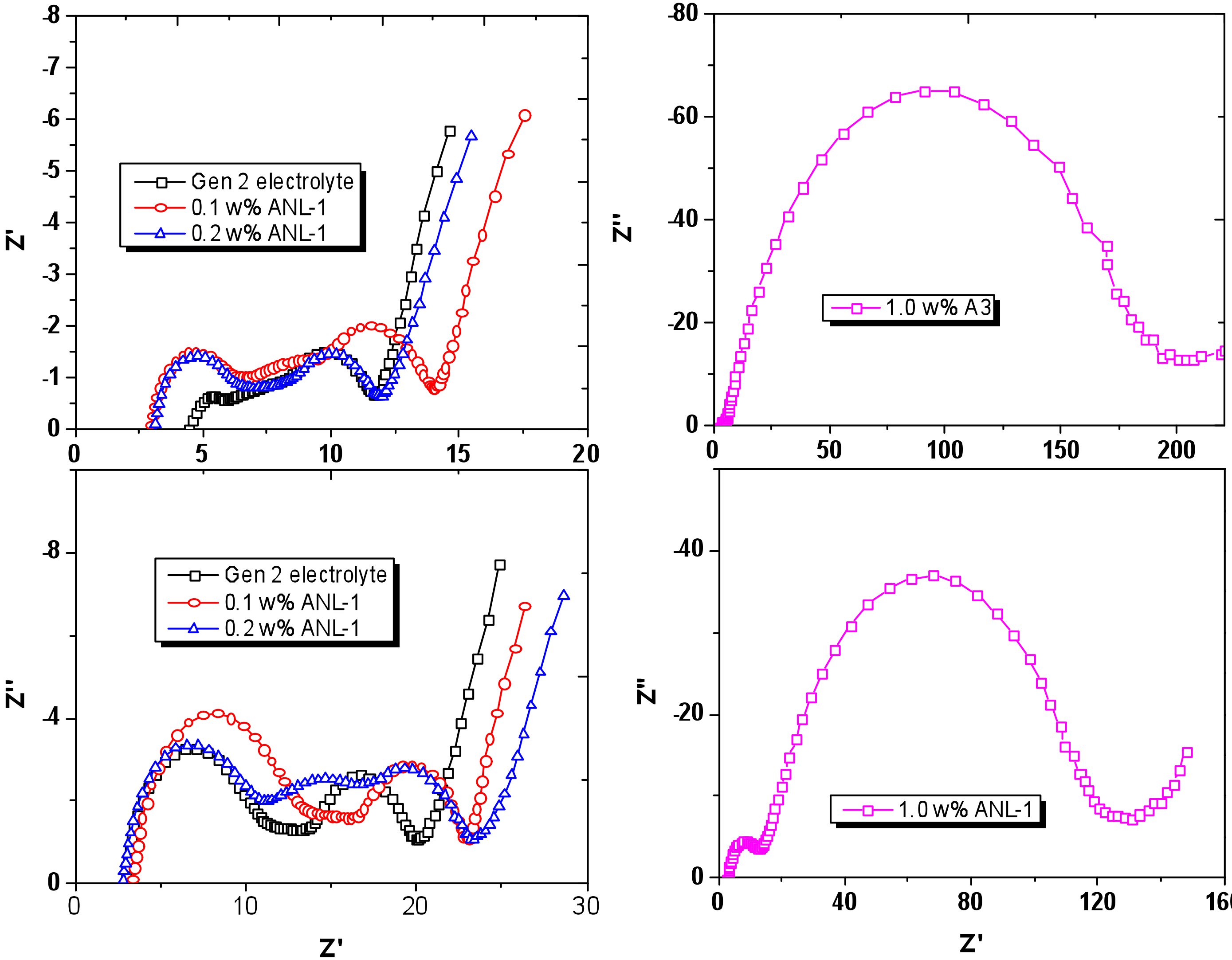


- Capacity retention of MCMB/NMC cells in Gen2 electrolyte with or without additive A3 (left). The cells were cycled at 55◦C with 1C rate, cut-off voltages: 2.7 ~ 4.2 V.
- At 55°C, low concentration of additive A3 showed much improved capacity retention with cycling.
- However, the high concentration of additive forms a thick SEI film leading to the high cell resistance.
- 1st Cycle differential capacity profiles (dQdV) of NMC/MCMB cells (right) indicated different SEI formation process with various additive concentrations.

Cell Impedance Variation with SEI Additive ANL-SEI-1

Before cycling

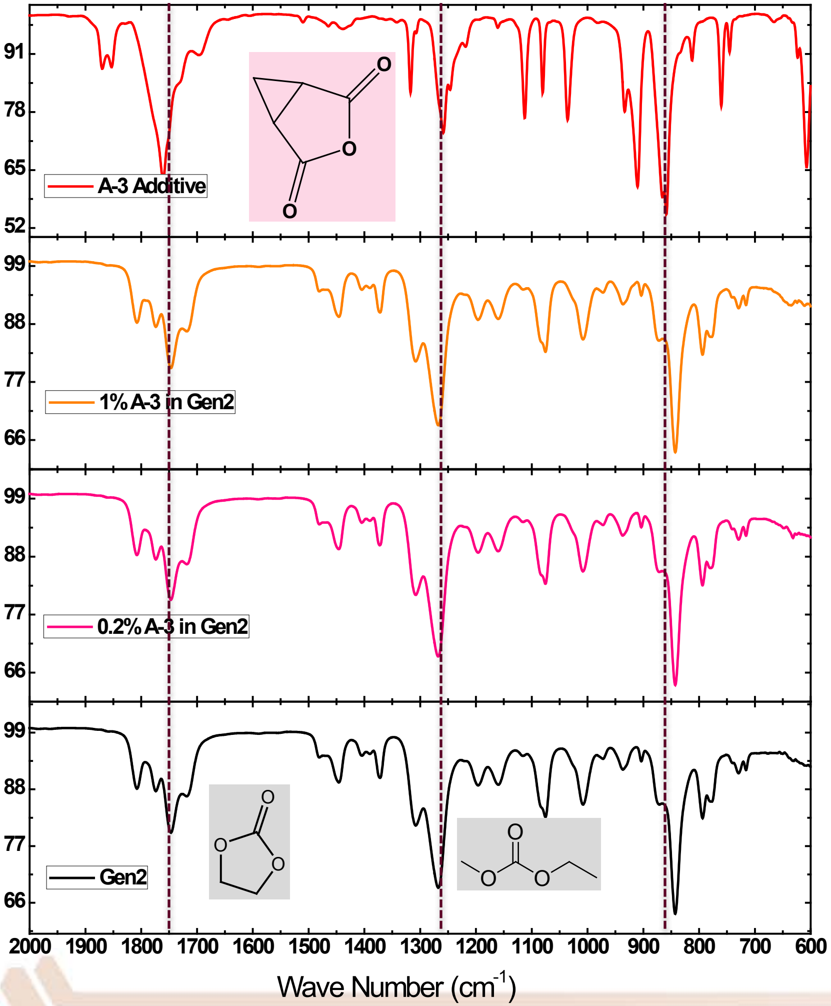
After cycling



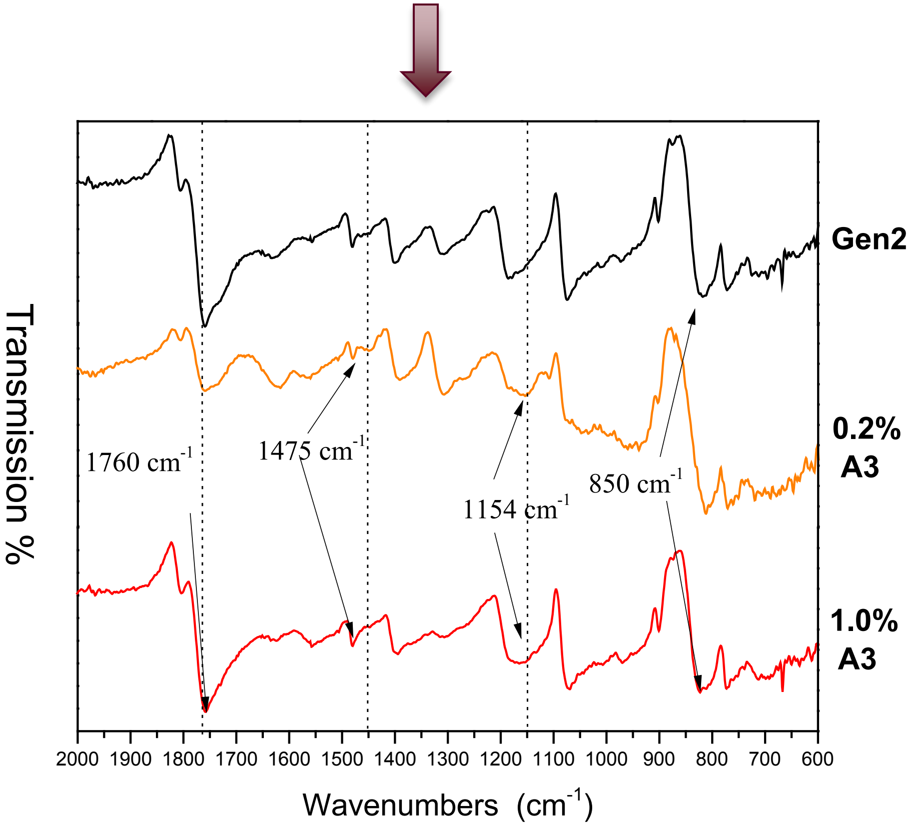
Impedance profiles of MCMB/NMC cell before cycling at 25°C; The Rb is smaller for the additive cell indicating the more conductive SEI layer formed compared to that of the pristine electrolyte. Unlike most of the existing commercial additives that show high initial interfacial impedance, ANL-Additive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

FT-IR Characterization of SEI Formed on Graphite Electrode Surface

Gen2 and Additive A3 IR spectrum as reference

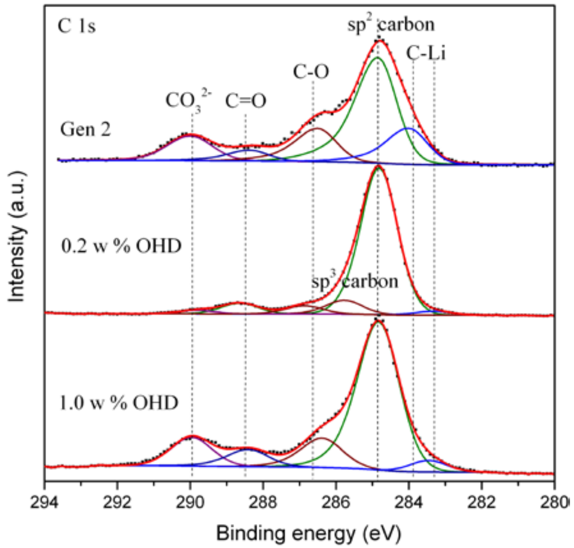


FT-IR spectra of graphite electrode surface after 2-cycle formation. Measurement was performed in an Ar glove box.

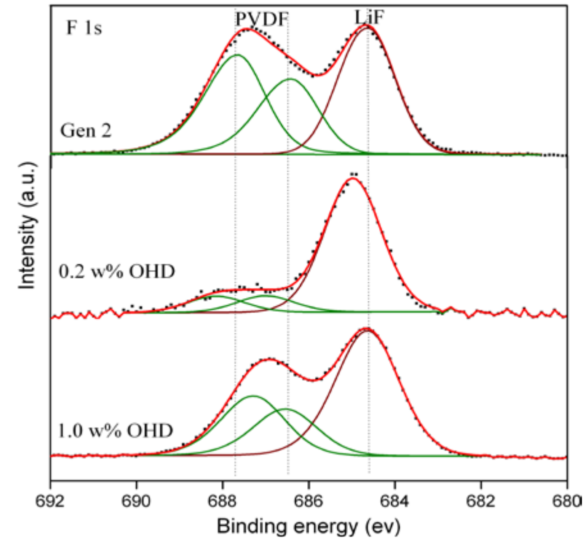


XPS Analysis of the New SEI Formed on Graphite

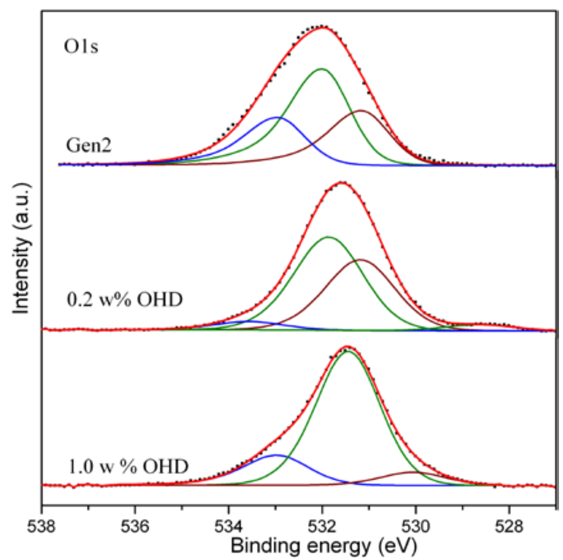
C1s



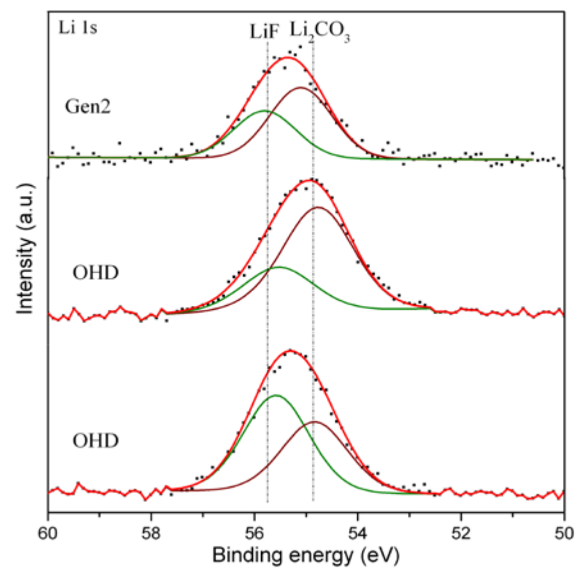
F1s



O1s

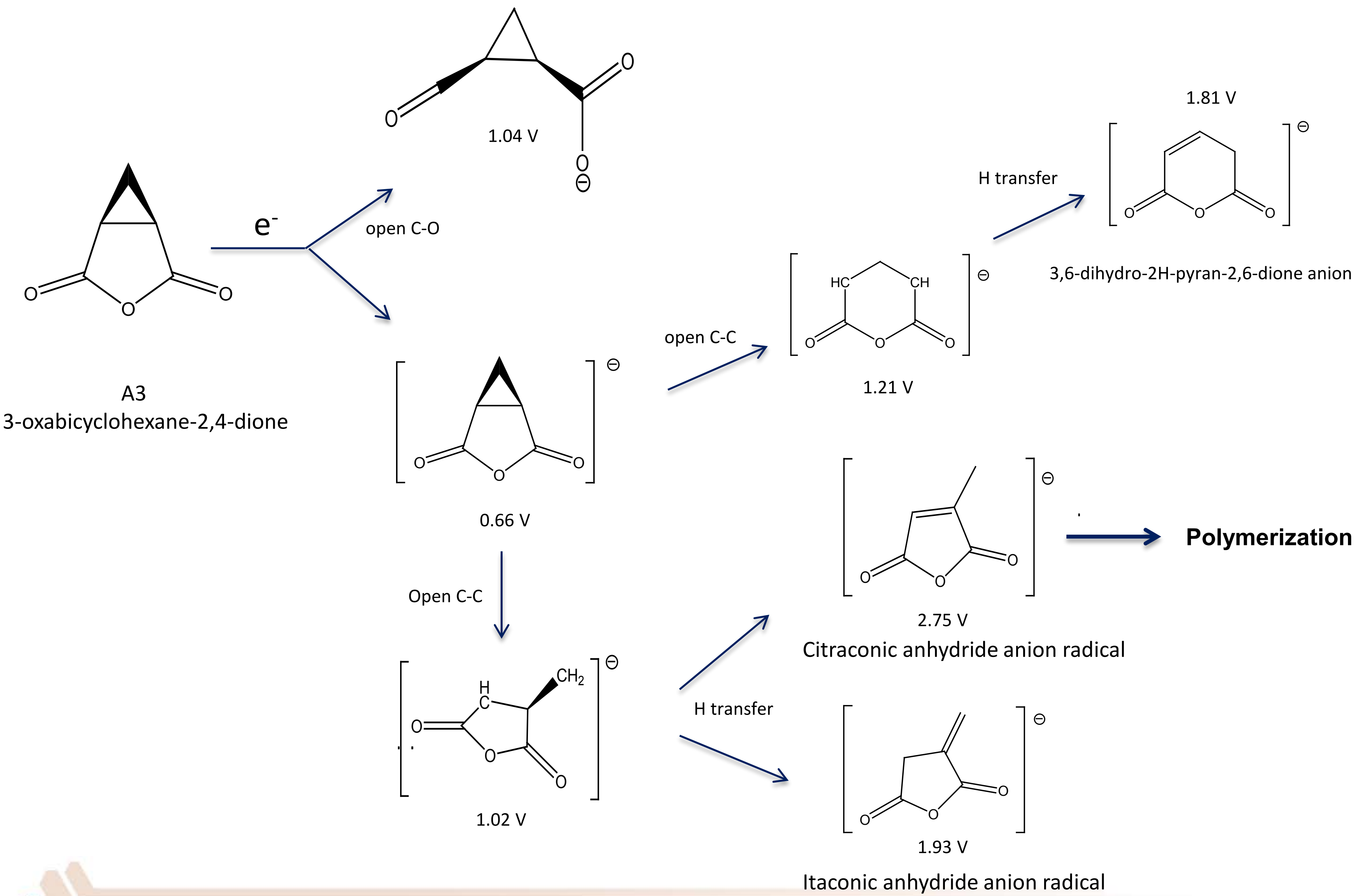


Li1s

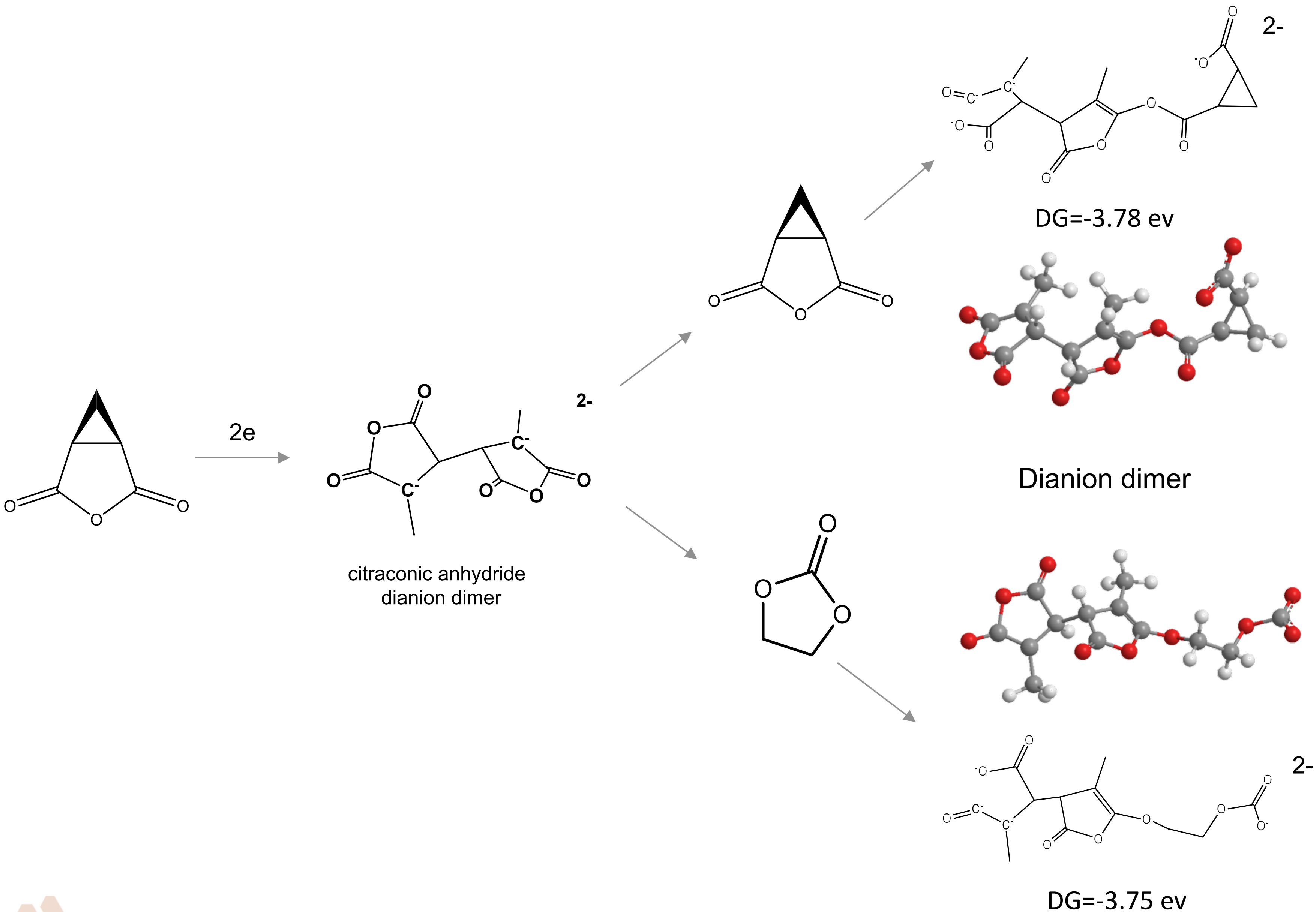


XPS spectra of C1s, O 1s, F 1s, and Li 1s core peaks of the MCMB electrodes from MCMB/NCM coin cells containing different amounts of A3 additive in the electrolyte of 1.2M $LiPF_6$ with ethylene carbonate/diethyl carbonate (3:7 weight ratio) after 2-cycle c/10 formation .

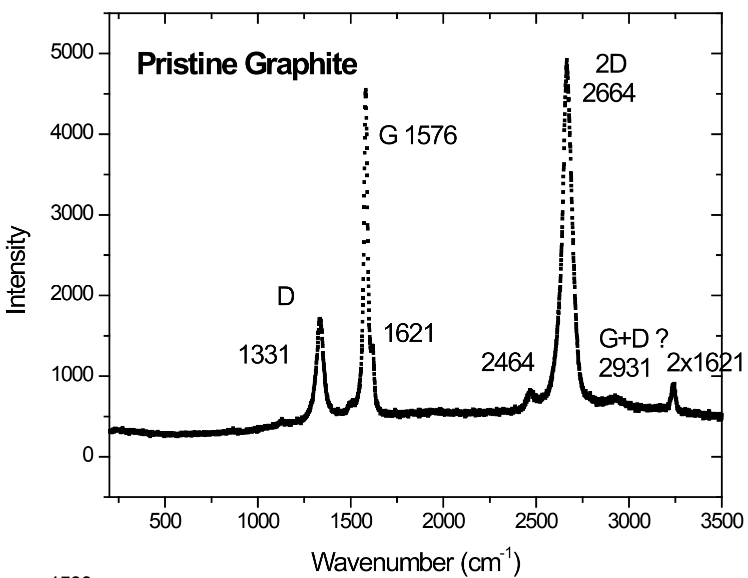
Proposed SEI Formation By Additive Reductive Decomposition

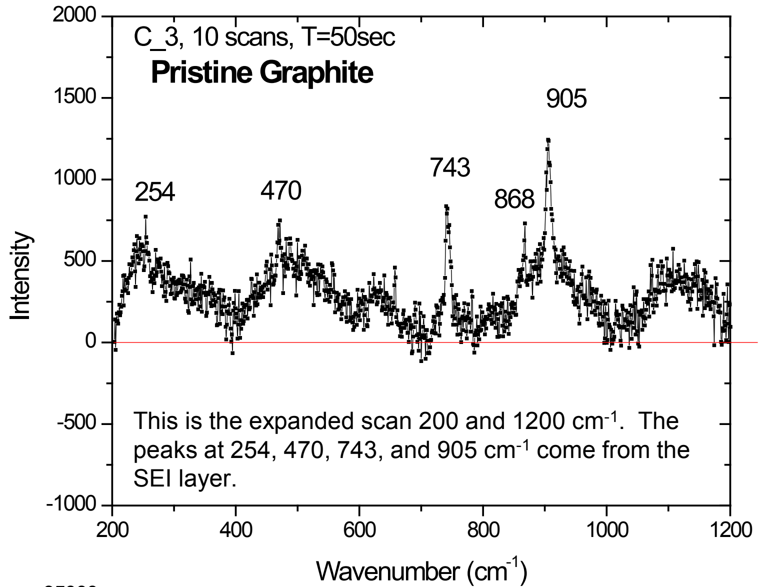


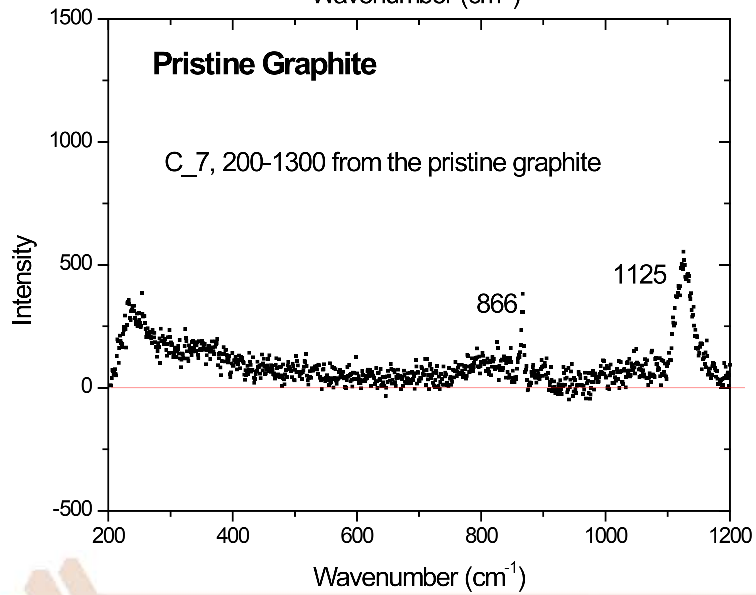
Two Favorable Polymerizations Pathways of ANL-SEI-1

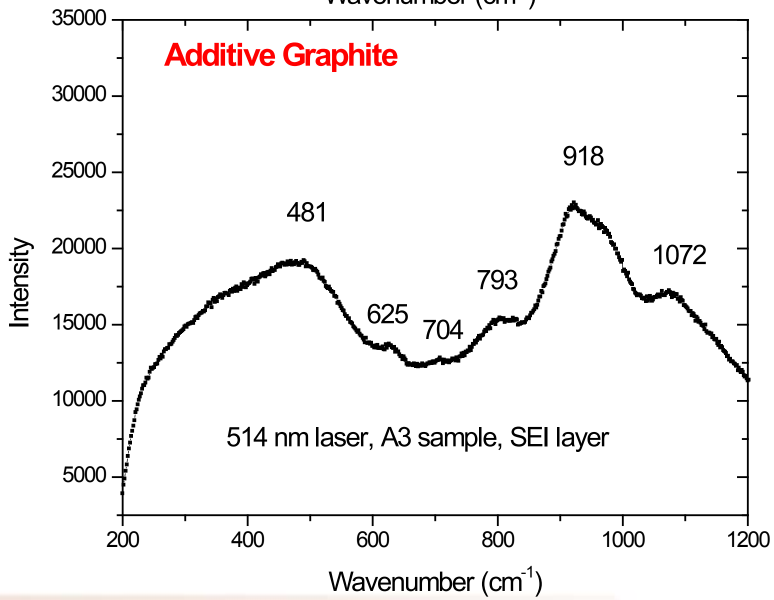


Raman Characterization of New SEI Formed on Graphite









Synthesis of New SEI Additives Which Can Improve the Cycle Life with Controlled Impedance

- Improve the cell cycle life is usually based on the sacrifice of impedance.
- Synthesize novel SEI additives that not only can improve the cell performance, but also control the impedance growth.
- "Efficient" additives should be able to help form stable SEI layer without a lot impedance increase.
- An "efficient" additive should have multiple cyclic or double bond structures so that it could easily form into a polymeric film on the electrode surface.
- An "efficient" additive should be reductively decomposed prior to the formation of the traditional SEI.

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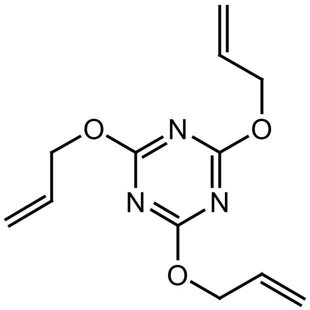
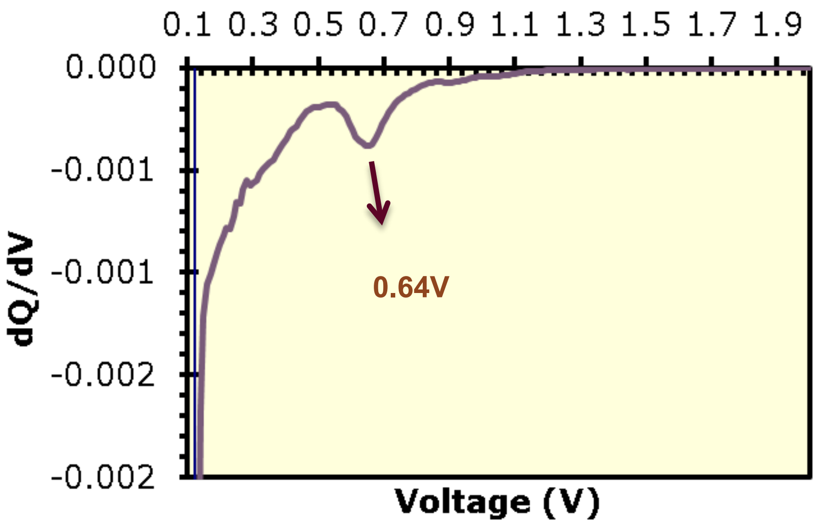
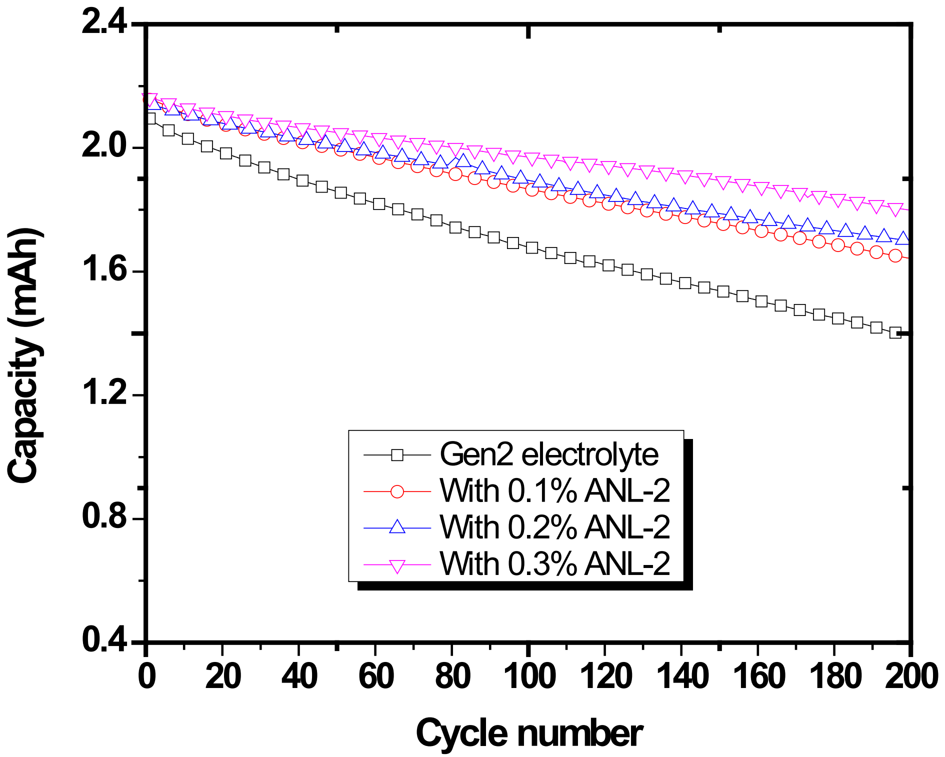
ANL-SEI-2 & ANL-SEI-3

Capacity Retention Profile of ANL-SEI-2 Compared with Gen 2 Electrolyte

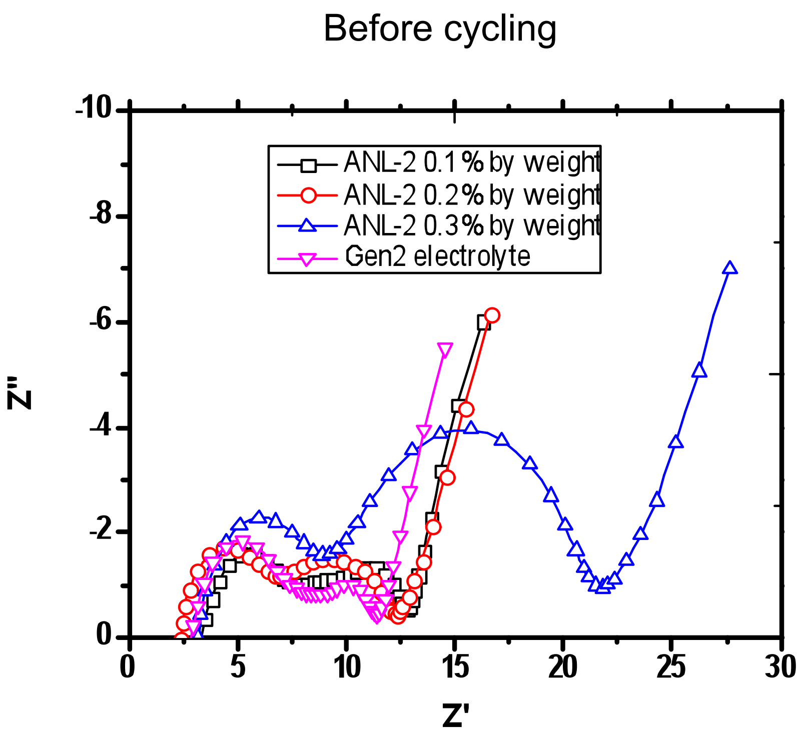


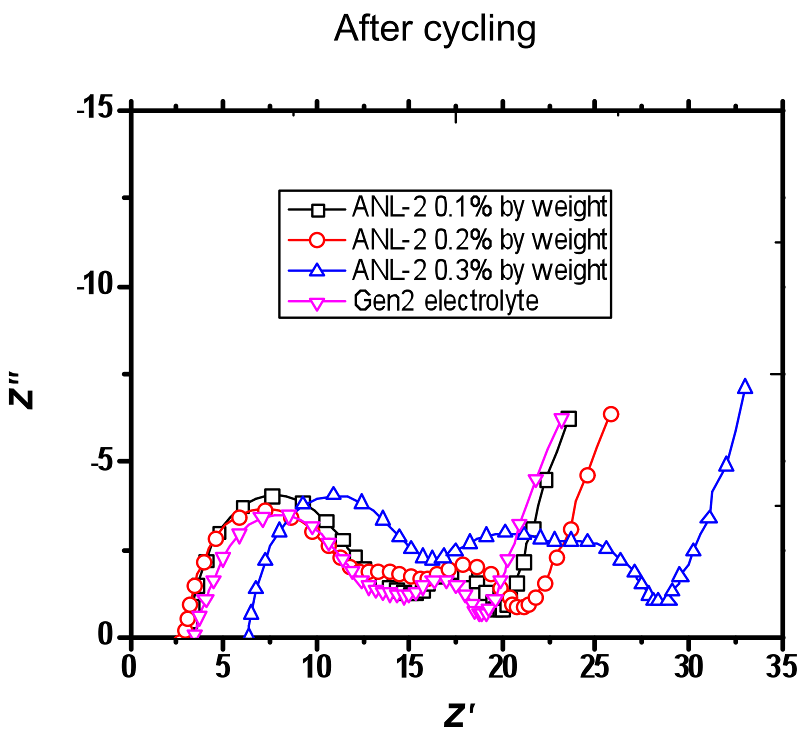
ANL-SEI-2: 1,3,5-triacryloylhexahydro-1,3,5-triazine





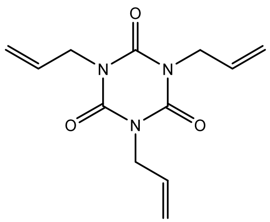
Impedance Profiles for Cells with ANL-SEI-2



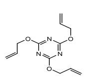


AC impedance profile of MCMB-1028/$Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O_2$ coin cells in 3E7EMC/PF12 with or without additives. The cells were charged to 3.8 V. The charge rate was 1C.

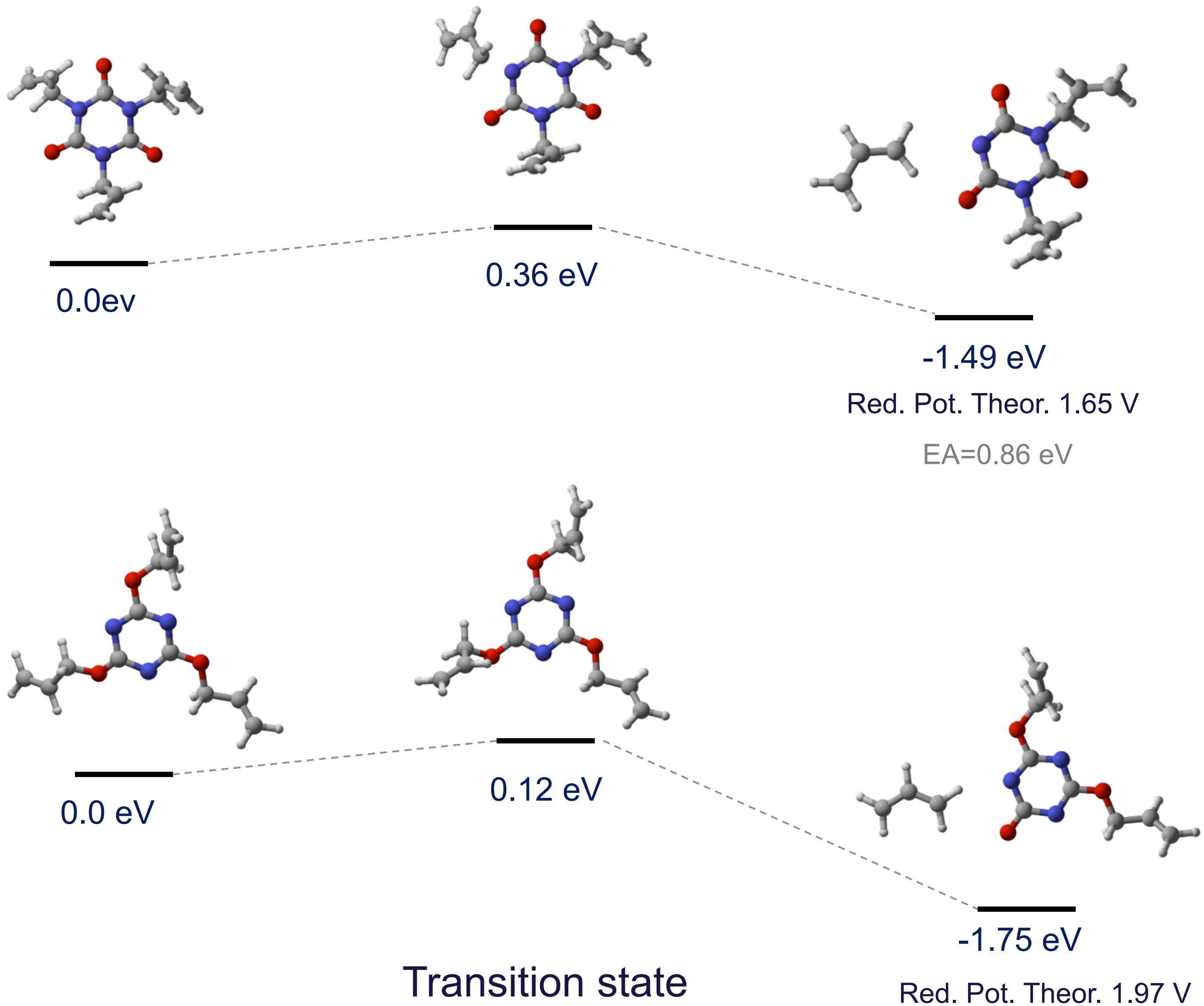
Energetics of ANL-SEI-2 Reductive Decomposition



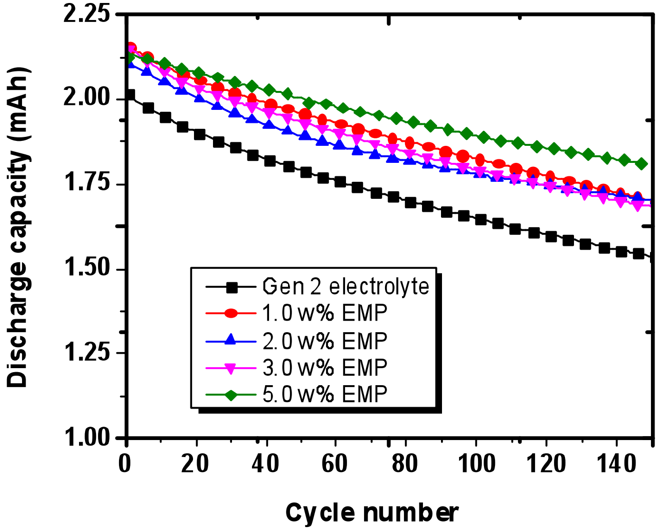
ANL-SEI-3



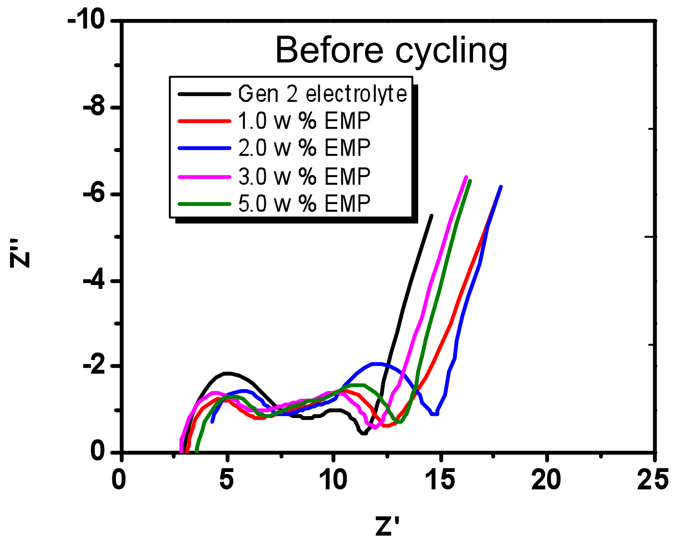
ANL-SEI-2

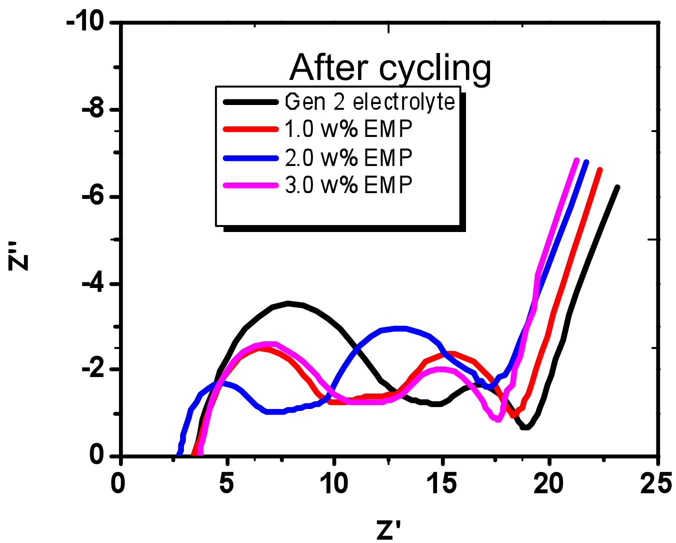


Cell Performance of Synthesized Additive Cyclic Phosphate (in progress)



Capacity retention of MCMB/NMC cells in 3E7EMC/PF12 with or without various amount of EMP additives. The cells were cycled at 55 °C. The charge rate was 1C.





AC impedance profile of MCMB-1028/$Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O_2$ coin cells in 3E7EMC/PF12 with or without additives. The cells were charged to 3.8 V. The charge rate was 1C.

Collaborations and Interactions with Other Institutions

- **Center of Nano-Materials at Argonne (DOE Lab)**
  - Dr. Larry Curtiss and Dr. Paul Redfurn for DFT calculation of reduction potentials of additives and SEI formation mechanism.
  - Dr. Hsien-Hau Wang for the Raman and AFM measurement.

- **University of Utah**
  - Professor Fang for SEI characterization by XPS.

- **US Army Research Laboratory (DOD Lab)**
  - Dr. Richard Jow and Dr. Kang Xu for technical and information exchanges.

- **ConocoPhilips, Saft and EnerDel**
  - Electrode supply.

Proposed Future Work

For the rest of this fiscal year and FY13, we are proposing the following research work:

- Continue to develop additives with the aid of the quantum chemical models and the electrochemical screening of the list of selected compounds and expand the SEI additive database.
- Design and synthesize suitable SEI additives.
- Conduct extensive electrochemical performance evaluation using selected lithium ion battery chemistry.
- Extend electrolyte additive research into other areas including overcharge protection additive (redox shuttle) and cathode additive.

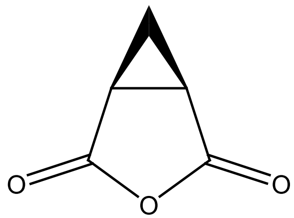
Summary

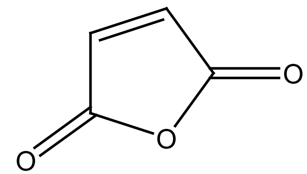
PHEV and EV batteries face many challenges including energy density, calendar life, cost, and abuse tolerance. The approach of this project to overcome the above barriers is to develop advanced electrolyte additive that can stabilize the electrode/electrolyte surface and significantly improve the cell cycle life and calendar life without sacrificing the safety to enable large-scale, cost competitive production of the next generation of electric-drive vehicles.

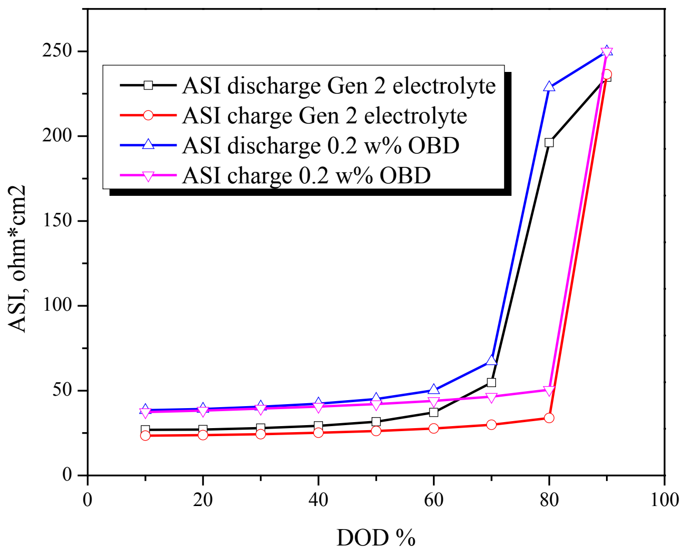
- Argonne has discovered many classes of the SEI additives based on the empirical selection rule and the quantum chemical calculations.
- Electrochemical properties of new SEI additives were thoroughly investigated in graphite based lithium ion batteries.
- SEI formation were fully characterized by electrochemical method and FT-IR, Raman, XPS instrumental measurements. The lithium ion cells containing ANL-SEI -1, ANL-SEI-2 and ANL-SEI-3 showed no or less impedance growth after cycling and excellent capacity retention even at elevated temperature (55^{o}C).
- Novel SEI additive based on cyclic phosphate compounds were designed and synthesized. Initial electrochemical study has shown promising results. We will continue to explore this additive and its derivatives in FY13.

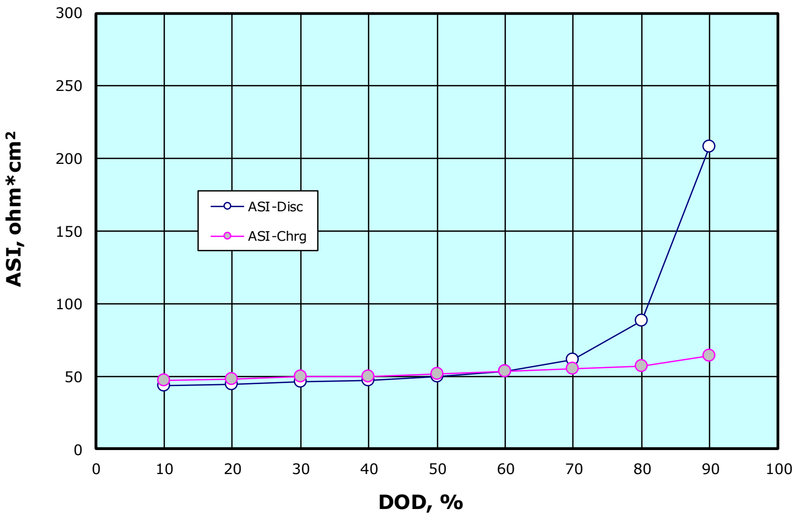
Technical Back-Up Slides

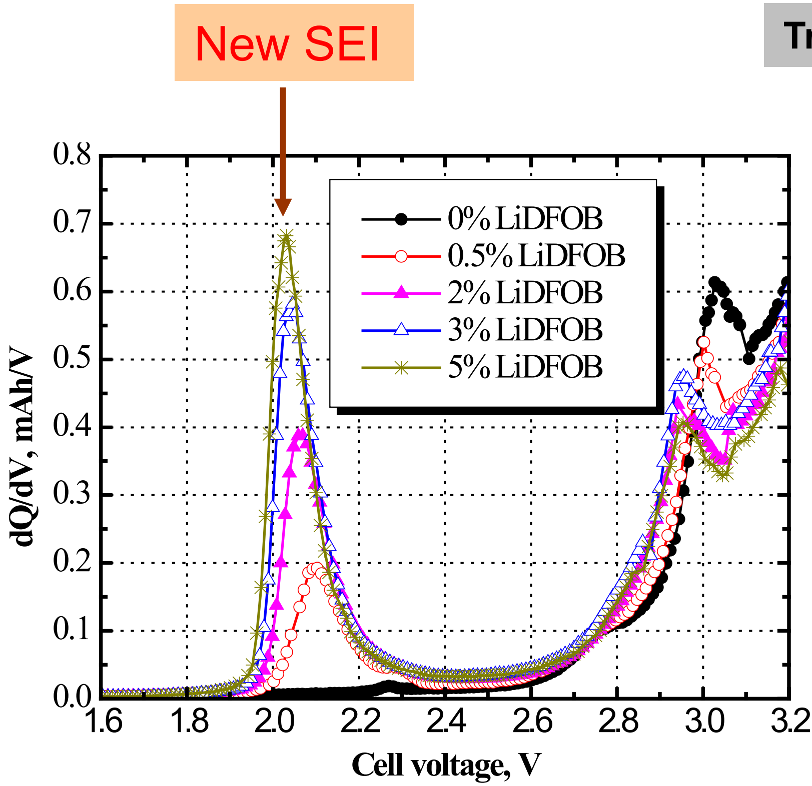
Power Evaluation of ANL-SEI-1: HPPC Data



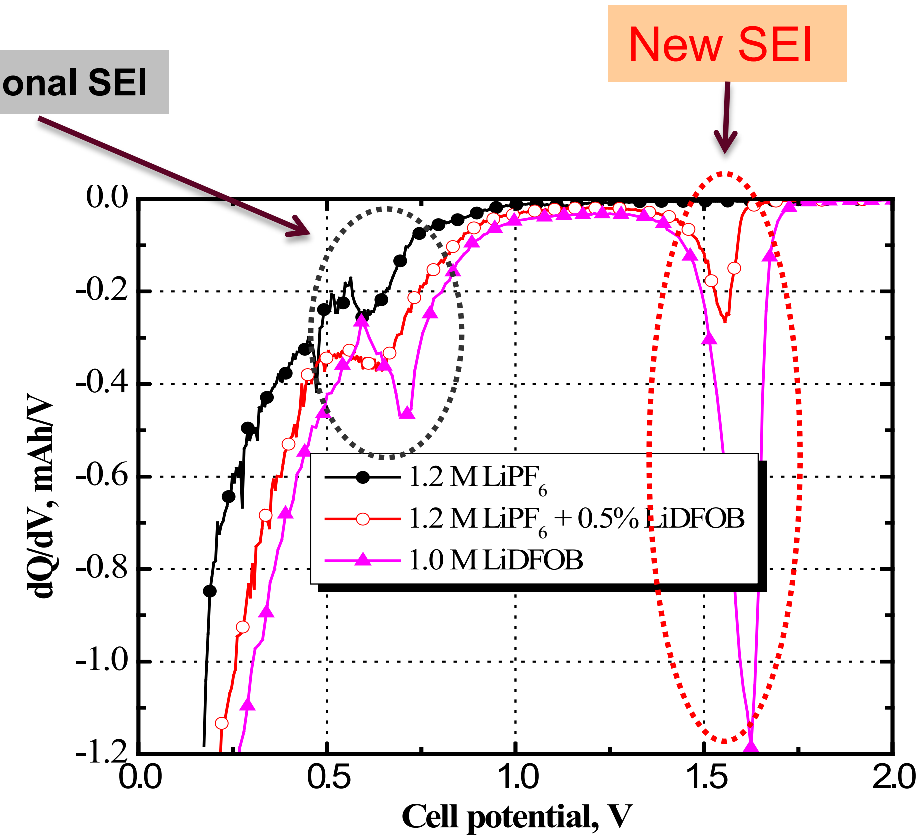








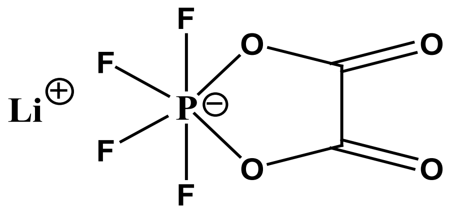
NMC/MCMB Cell



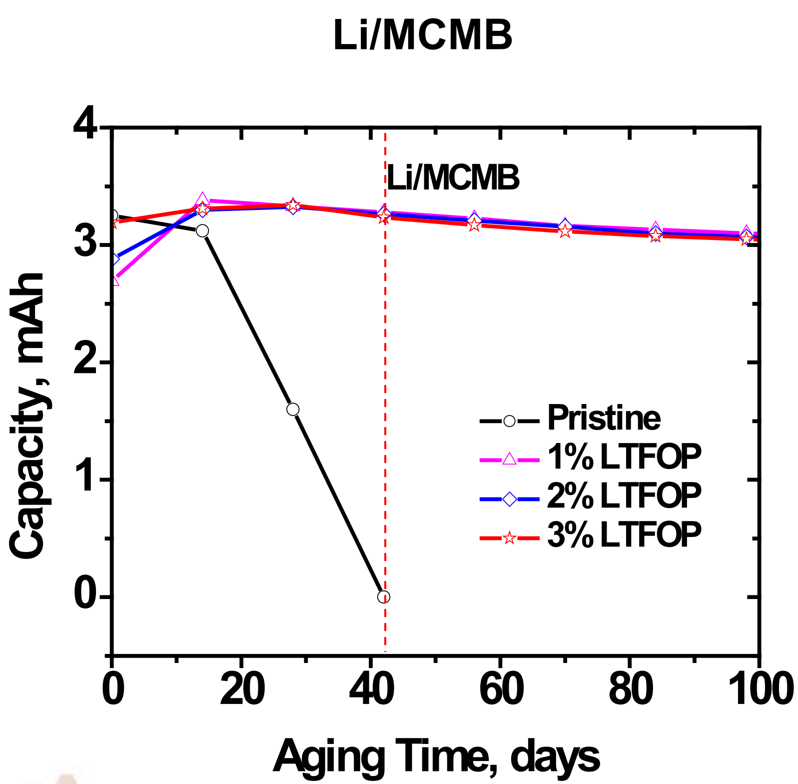
MCMB/Li Cell

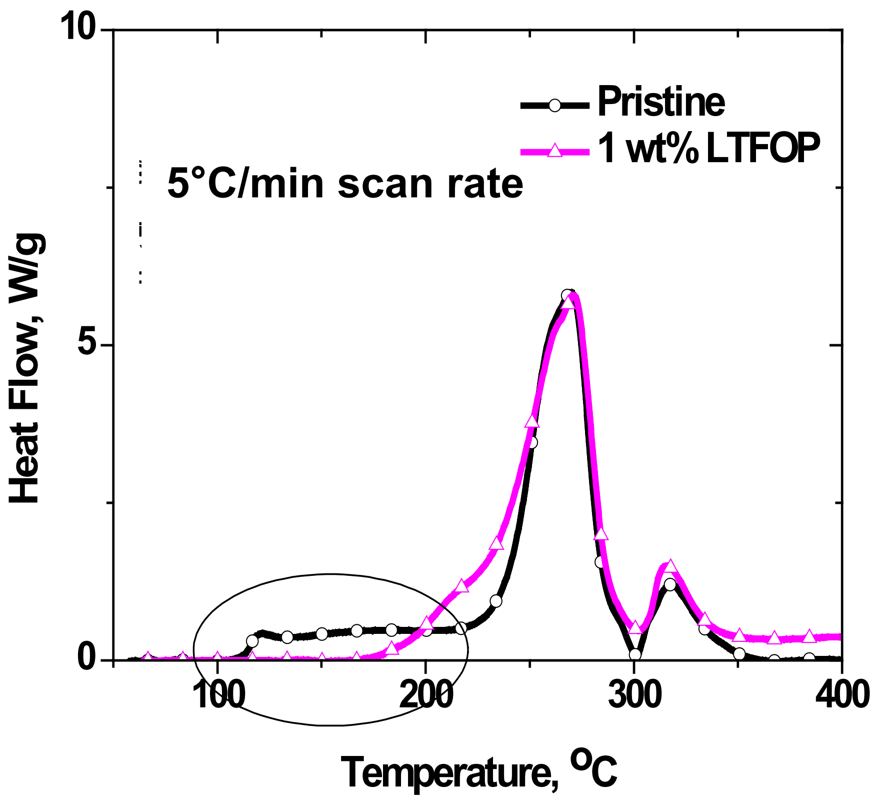
In MCMB/Li half cell, additive reduction occurs at 1.6V, prior to the SOA SEI formation at a potential between 0.6~0.8V vs Li^+/Li.

The peak intensity is proportional to the concentration of the additive.



LTFOP improves the calendar life of both MCMB anode at high temperature.





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).