Novel Electrolytes and Additives

Project Id: ES023

D.P. Abraham

Gang Cheng

Vehicle Technologies Program Annual Merit Review

Washington DC, May 9-13, 2011

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: FY10
- End date: On-going
- Percent complete:
  - project on-going

Budget

- Total project funding
  - 100% DOE
- FY10: $300K
- FY11: $300K

Barriers

- Performance
- Calendar/Cycle Life
- Abuse tolerance

Partners

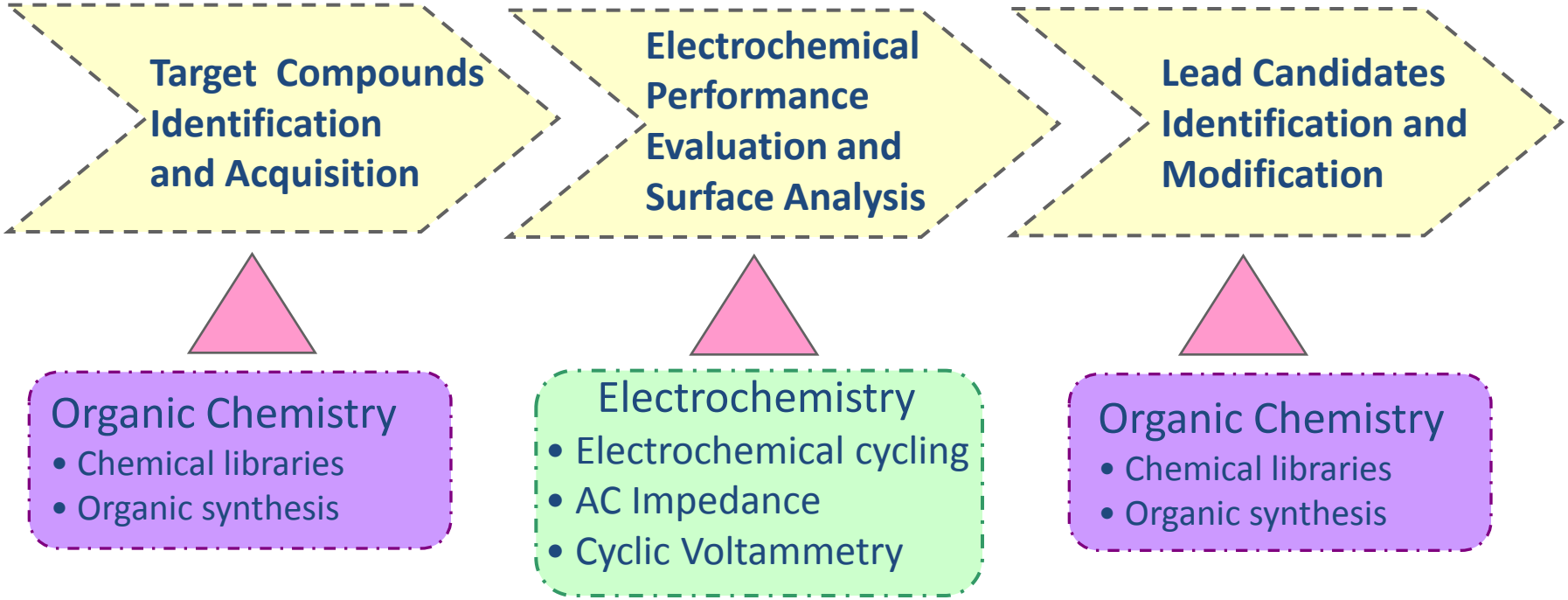
- Argonne colleagues
- Purdue University
- University of Rhode Island
- Kang Xu, ARL
- JPL colleagues
- Industrial collaborators

Project Objectives - Relevance

Performance, calendar-life, and safety characteristics of Li-ion cells are dictated by the nature and stability of the electrolyte and the electrode-electrolyte interfaces.

- To enable commercialization of safe, 40-mile range, Li-ion based PHEV batteries with calendar life that exceeds 10y
- To identify and synthesize electrolyte components (solvents, salts, additives) that are compatible with electrodes relevant to the ABR program
- To evaluate performance of these electrolyte components in ABR cells
- To identify electrolyte performance mechanisms – the knowledge can be used to design improved electrolyte systems for transportation applications

Approach

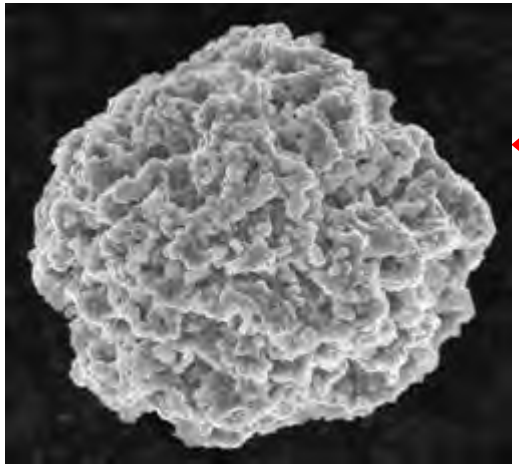


Analytical Chemistry
- X-Ray Photoelectron Spectroscopy
- FTIR & Raman Spectroscopy
- NMR Spectroscopy
- Mass Spectroscopy

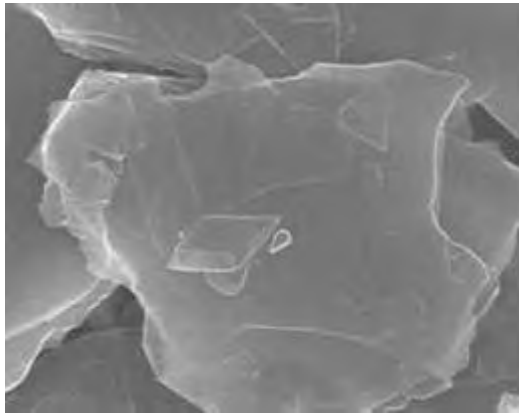
Technical Accomplishments and Progress

- **Identified new family of heteroaromatics substituted carboxylic ester-based compounds as electrolyte additives**
  - Determined effects on cell performance and calendar life
  - Argonne filed a USA Patent Application based on these compounds (ANL-376, Cheng, G.; Abraham, D.P., 2010, September 23)
  - Recommended list of electrolyte additive compounds for scale-up
- **Investigating the relationship of additive structure to characteristics of surface films at both positive and negative electrodes**
  - Currently examining the effect of SEI composition/morphology on interactions with Li-ion.
- **Designed and synthesized various GC-derivative compounds including alkyl ethers, carboxylic esters, and alkyl carbonates**
  - Examined performance/cycling behavior of these compounds, both as co-solvents and as electrolyte additives
  - Argonne filed a USA Patent Application (ANL-368, Serial No. 12/910,549) and is in the process of filing another non-provisional patent application (ANL-382, Argonne Invention No. ANL-10-093) based on data from these compounds

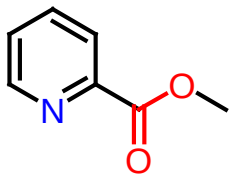
Baseline Chemistry used for electrolyte evaluation



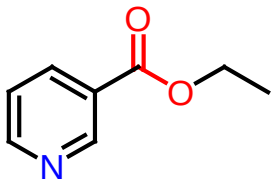
- Positive Electrode:
  - 84% Fuji CA1505 (NCA)
  - 4% SFG-6 + 4% carbon black
  - 8% PVDF binder (KF1100)
- Negative Electrode:
  - 92% Mag-10 Graphite (Gr)
  - 8% PVDF binder (Kureha#C)
- Baseline Electrolyte (Gen2):
  - 1.2 M $LiPF_6$ in EC/EMC (3:7)
- Typical cycling range:
  - Positive: 3 – 4.3V vs. Li
  - Negative: 2 – 0 vs. Li
  - Full Cell: 3 – 4.1V



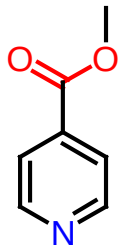
Examples of heteroaromatic compounds examined as electrolyte additives for Lithium Batteries



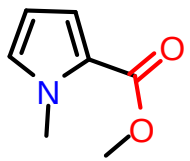
Methyl Picolinate (**MP**)



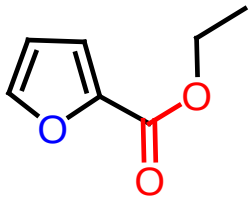
Ethyl Nicotinate (**EN**)



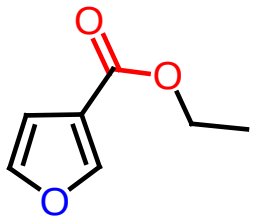
Methyl Isonicotinate (**MIN**)



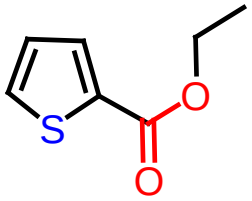
Methyl-1-methylpyrrole-2-carboxylate (**MMPC**)



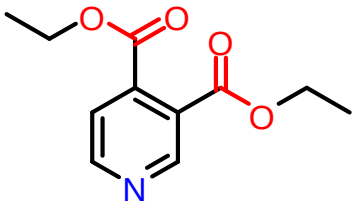
2-Ethyl furoate (**2-EF**)



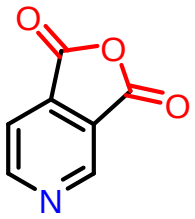
3-Ethyl furoate (**3-EF**)



2-Ethyl thiophenecarboxylate (**2-ETC**)



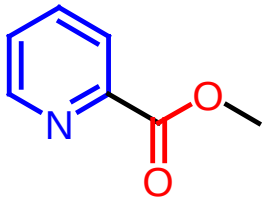
3,4-diethyl pyridine Carboxylate (**3,4-DEPC**)



3,4-pyridinedicarboxylic anhydride (**3,4-PyDCA**)

USA Patent Application, ANL-376, Cheng, G.; Abraham, D.P., **2010**

Merits of picolinates and their derivatives



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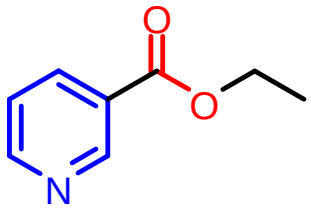
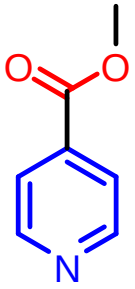


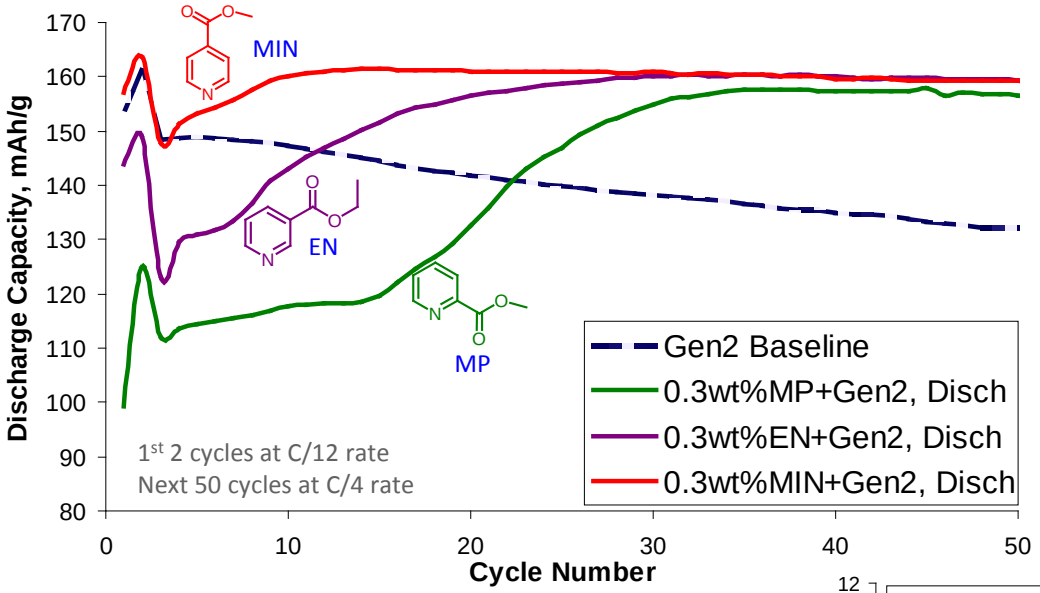
Ethyl Nicotinate (**EN**)



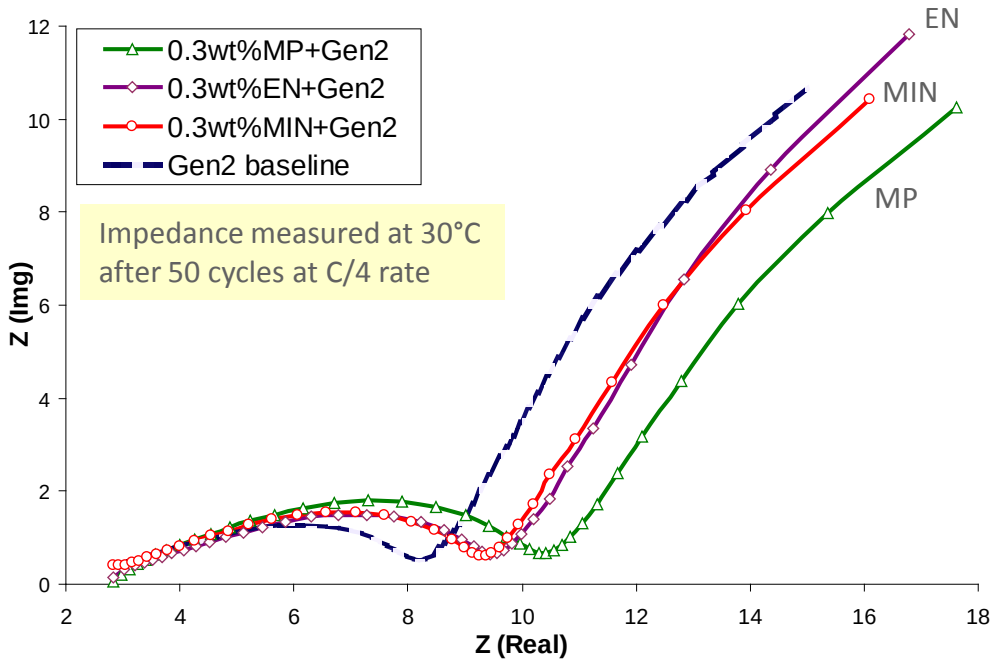
Methyl Isonicotinate (**MIN**)

- Compounds are relatively
  - ✓ low cost ($0.3 - $4/g)
  - ✓ non-toxic (Chromium piconlinate is used as a nutritional supplement, nicotinate is derived from tobacco)
  - ✓ flash points > 90 C

NCA+/Gr- cell – Effect of Additive Structure

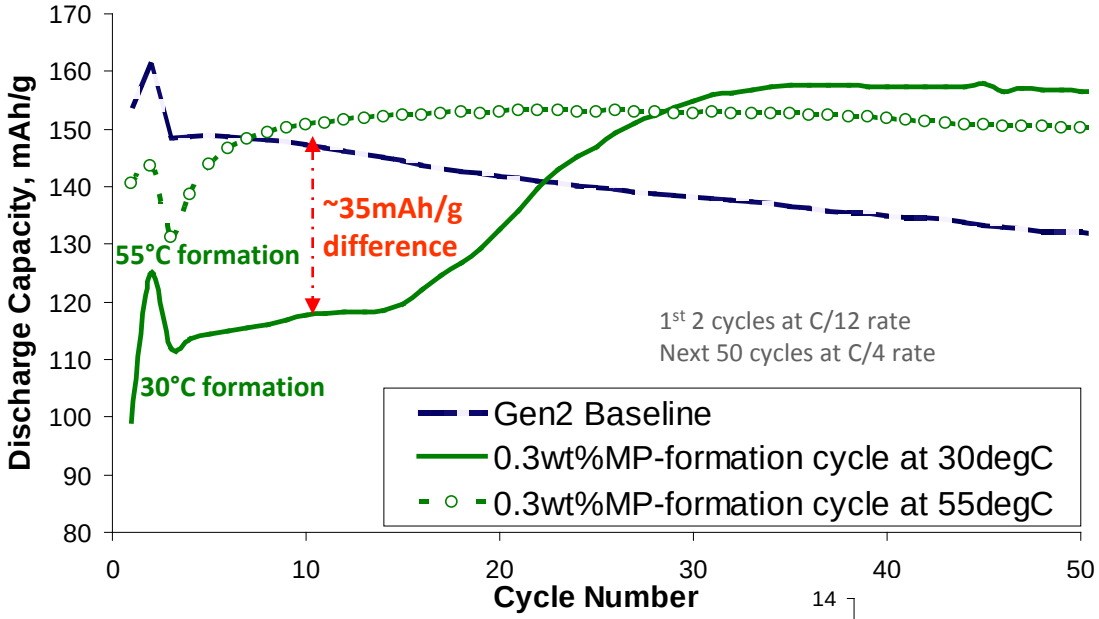


- Small amounts (0.3 wt%) of MP, EN and MIN addition to baseline electrolyte improves capacity retention. MIN appears to be the best performer based on initial capacity loss.
- Small structural changes cause significant impact on initial cycling behavior – further studies can provide information on the effect of molecular structure on SEI characteristics.

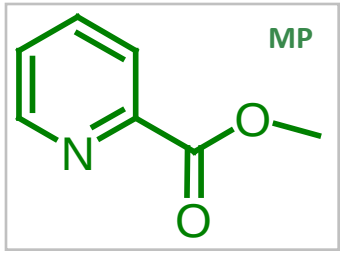


- Small amounts (0.3 wt%) of MP, EN and MIN addition to baseline electrolyte does not significantly alter cell impedance.
- The graphite SEI generated by MP may have the strongest interaction with the Li-ion, which may explain why the compound displays the widest mid-frequency arc.

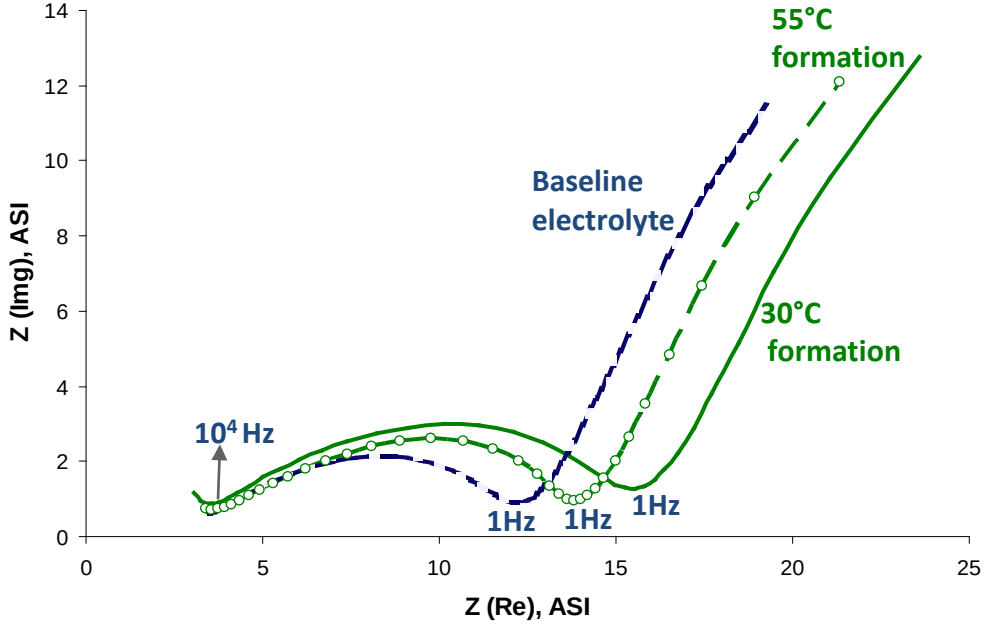
Initial Cycling Behavior of NCA+/Gr- cell: Effect of Formation Cycle (0.3wt% MP in baseline electrolyte)



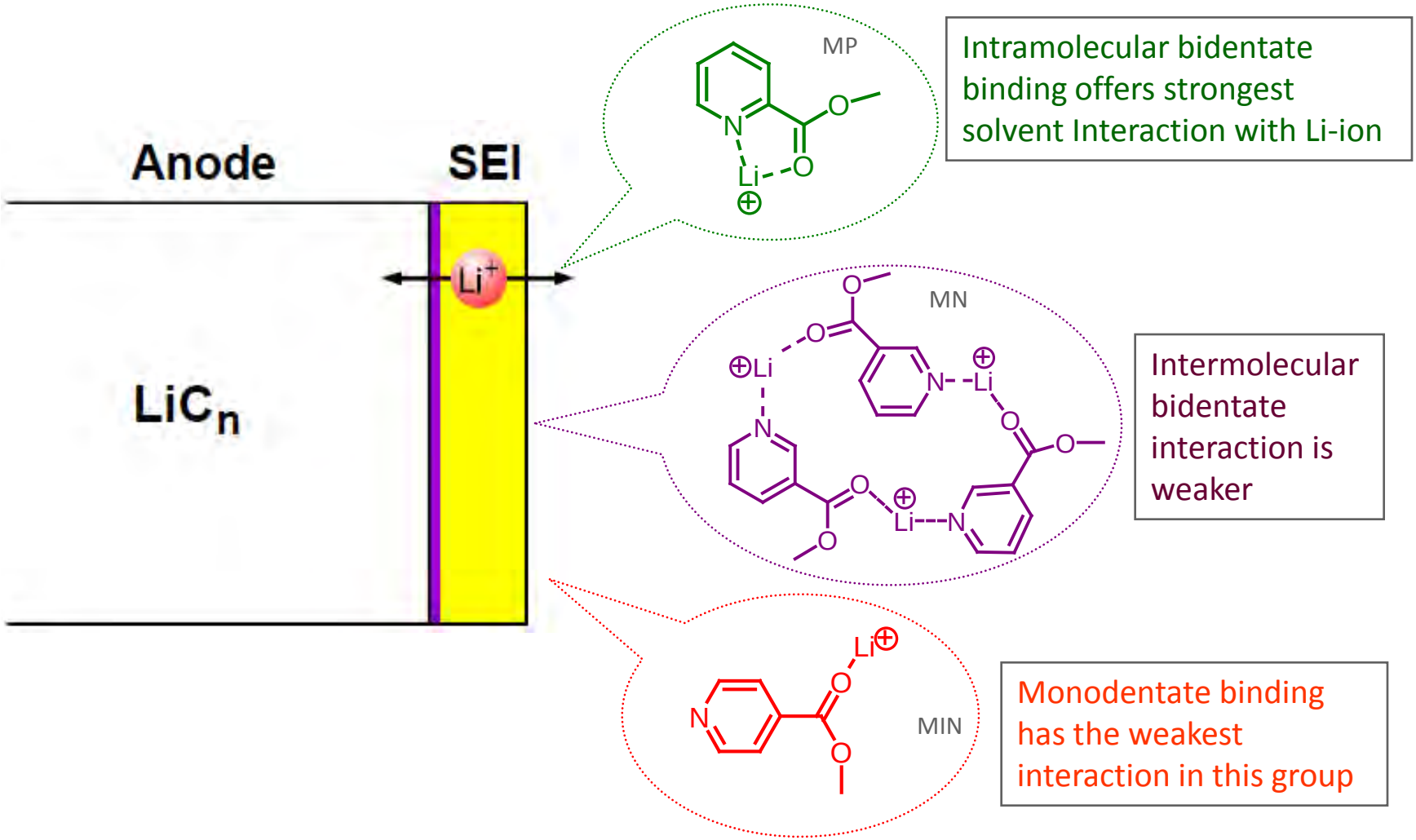
Cells with 0.3 wt% MP in baseline electrolyte show relatively lower initial capacity when formation is conducted at 30 C. The initial capacity is significantly higher when formation is conducted at 55°C.



For cells with the MP electrolyte additive, the one formed at 55°C shows a lower impedance than the one formed at 30°C.



Mechanistic Hypothesis



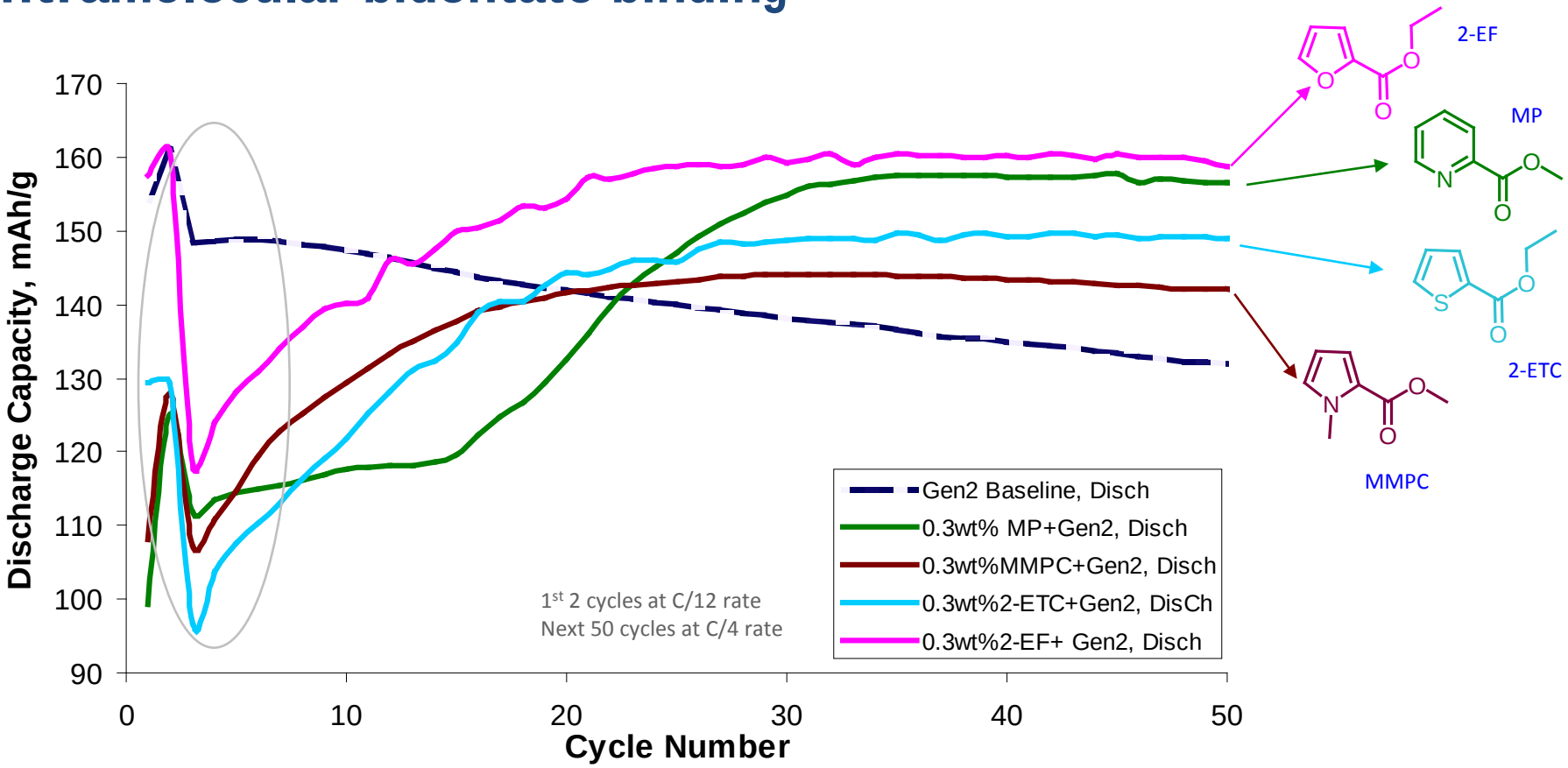
Intramolecular bidentate binding offers strongest solvent Interaction with Li-ion

Intermolecular bidentate interaction is weaker

Monodentate binding has the weakest interaction in this group

The SEI generated by the various additives is expected to bear signatures of the corresponding lithium-additive complexes. Stronger SEI/Li^+ interaction may cause higher impedance.
The "initial induction period" reflects changes in SEI characteristics during cycling.

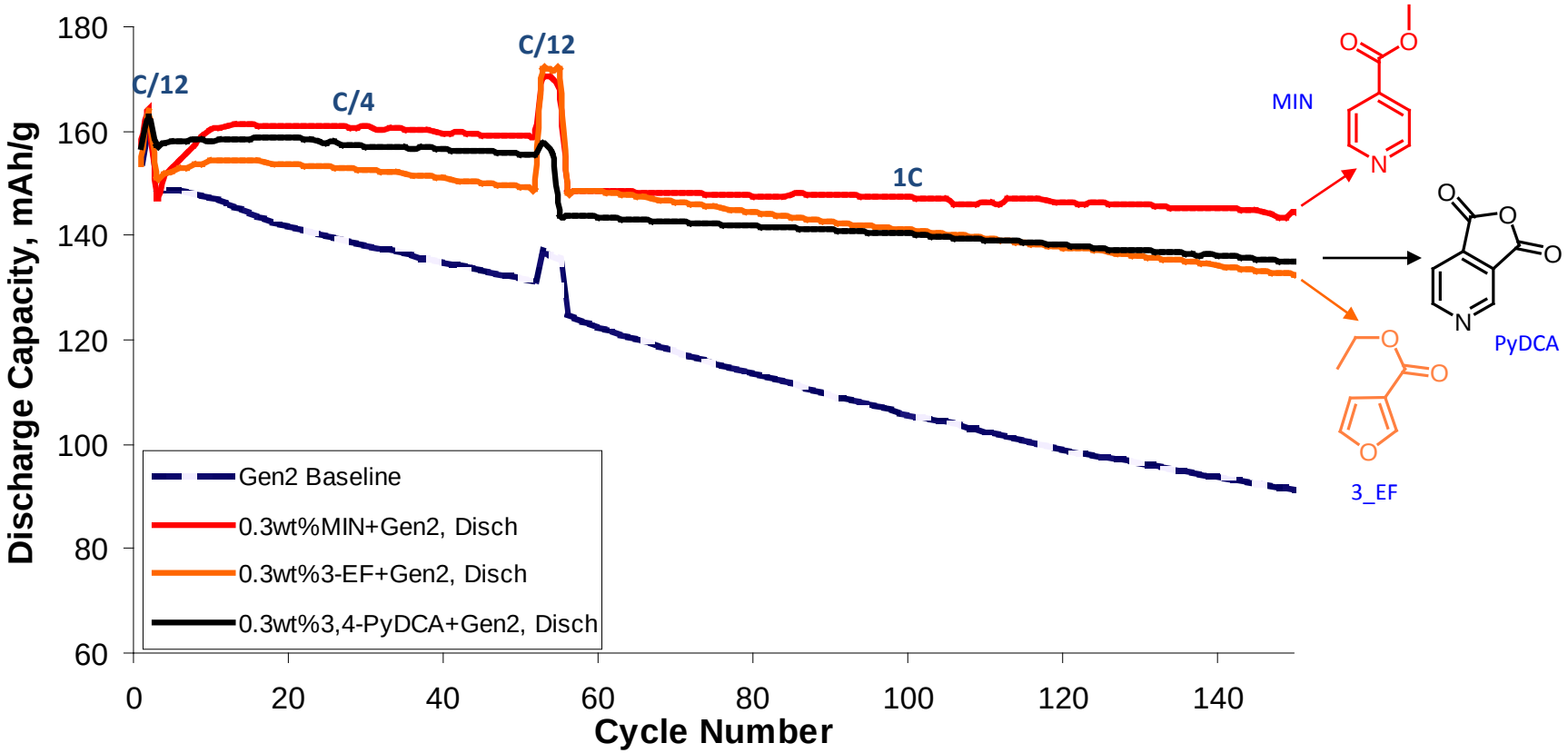
Initial Cycling behavior of NCA+/Gr- cells - Effects of Intramolecular bidentate binding



All additives with possible intramolecular bidentate binding site for Li-ion exhibit a long "initial induction period" during cycling

Different heteroatoms have different binding affinities to the Li-ion; N and S binding to the Li-ion appears stronger than O

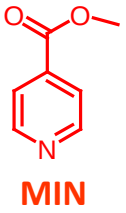
NCA+/Gr- cells capacity - Longer Term Cycling Performance

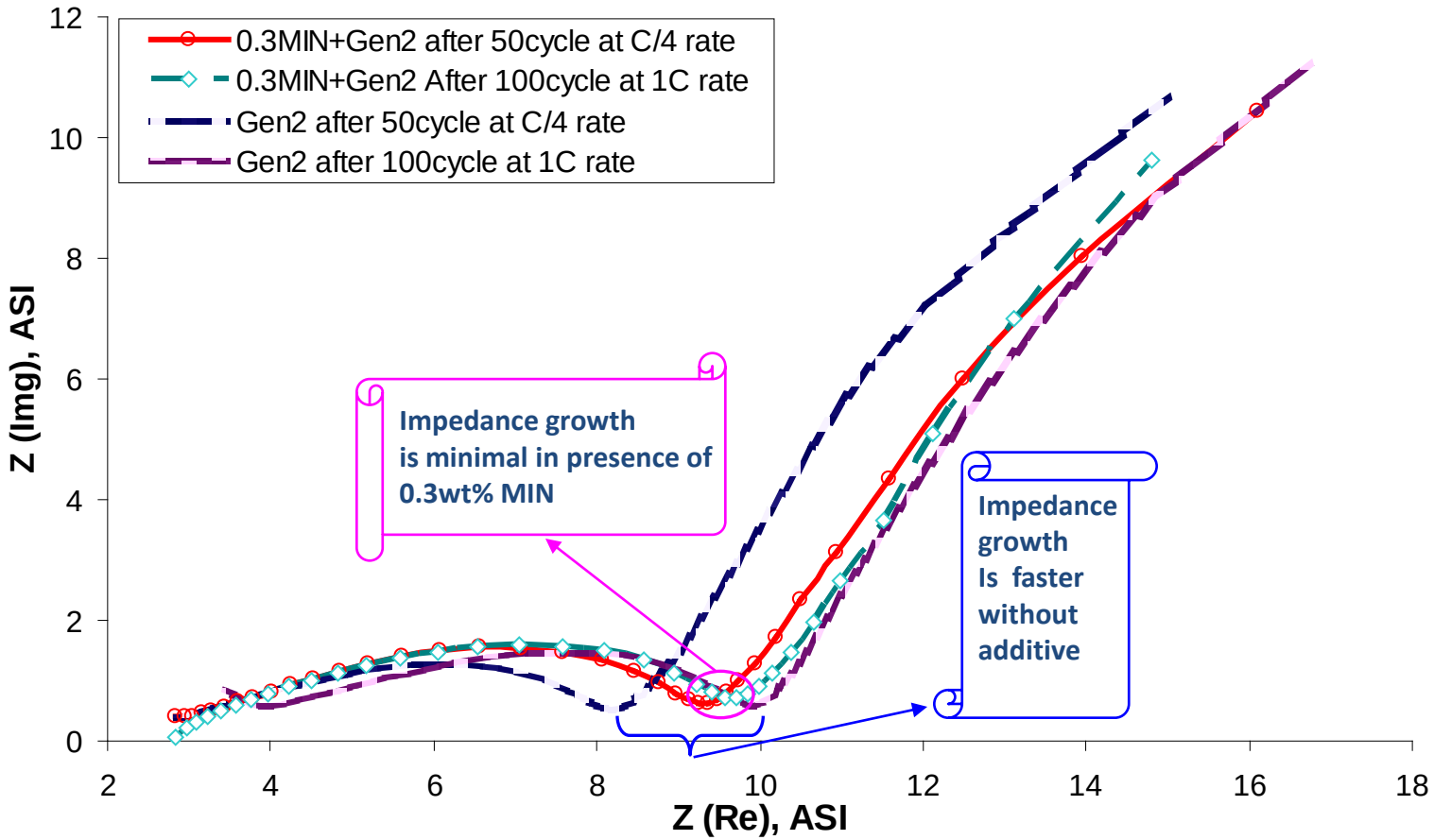


Specific capacity during the initial cycles improves significantly when the two possible binding sites for the Li-ion are moved away from each other, avoiding the stronger intramolecular interaction with the Li ion.

Small additions of MIN, PyDCA, and 3-EF (0.3wt%) to the baseline electrolyte improve cell capacity retention compared to the baseline electrolyte in the first 150 cycles.

NCA+/Gr- cells – AC impedance - Longer Term Cycling Performance — 0.3wt% MIN in baseline electrolyte





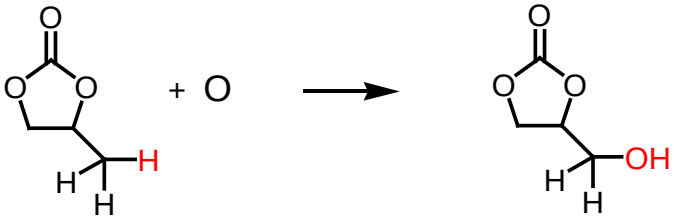
Cells with 0.3wt% MIN additive show lower impedance increase after 100 cycles at 1C rate than cells with the baseline electrolyte

Philosophy Behind Study of GC derivatives

- A Good System to Explore Novel Electrolytes

- What is Glycerol Carbonate (GC)?

Glycerol Carbonate is just an oxygen-substituted Propylene Carbonate!



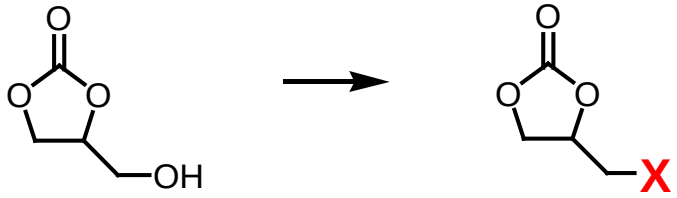
Propylene Carbonate

Glycerol Carbonate

Note: PC cannot be cycled with graphite anode but GC can.

- What makes GC a good system to study?

GC can be easily derivatized/modified. Therefore, it provides an excellent platform to study bi-/multi-functional electrolytes.

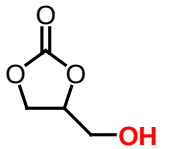


Note: X can be any functional group thanks to modern organic synthesis techniques

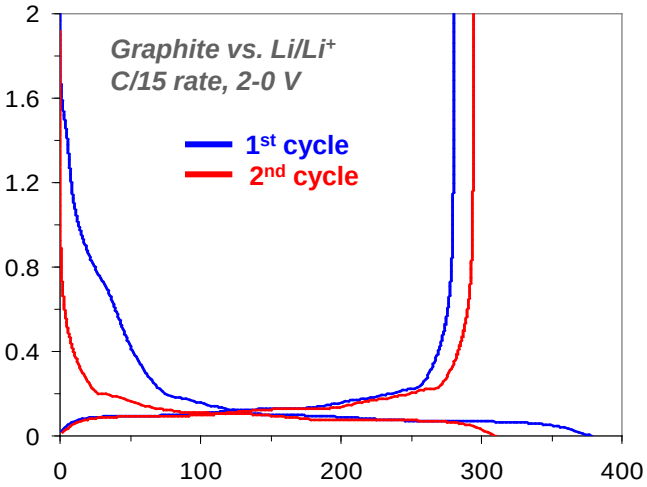
- Why its important to study bi-/multi-functional electrolyte systems?

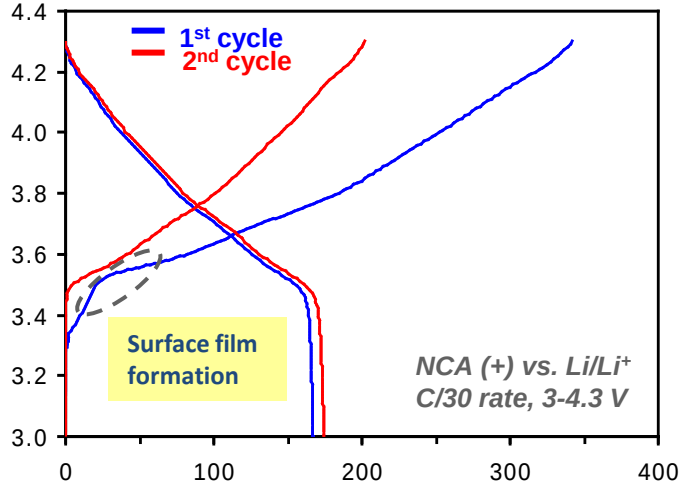
SEI formed by EC is good but not perfect, therefore electrolyte additives are often required. It is reasonable to believe that a better SEI can be achieved by introducing extra functionalities into the molecule.

Previously reported - GC and GCME data

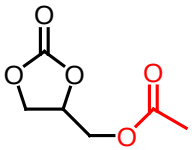


Glycerol Carbonate

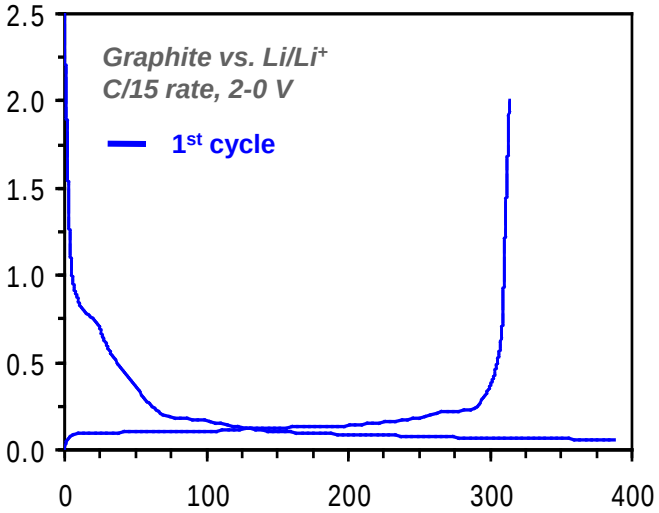


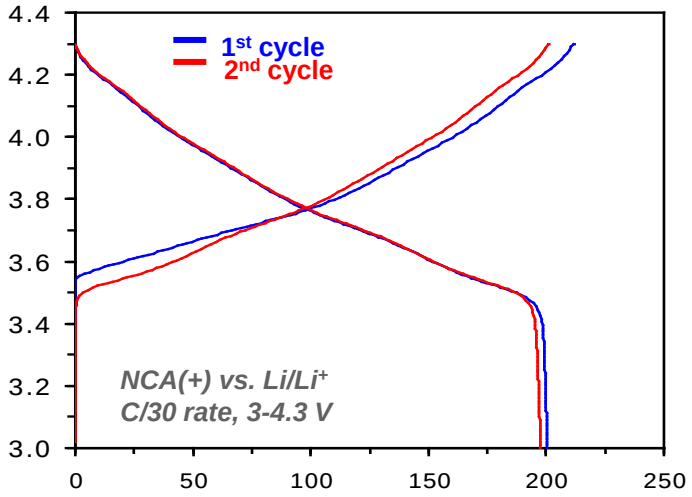


- Cell containing 1.2M $LiPF_6$ in GC:DMC=2:8 can be cycled with graphite anode.
- Surface film formation at the first cycle on oxide electrode indicates oxidation of GC.



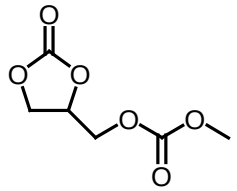
Glycerine carbonate methyl ester

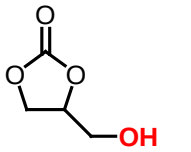




- Cell containing 1.2M $LiPF_6$ in GCME:DMC=2:8 can be cycled with both graphite and oxide electrodes.

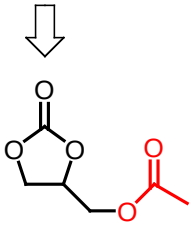
Evolution towards Glycerine Carbonate Methyl Carbonate (GCMC)





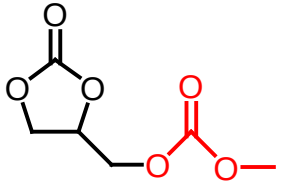
Glycerol Carbonate

- GC can be cycled with graphite anode without exfoliation!
- However, oxidation potential of GC is low due to the free hydroxyl group.

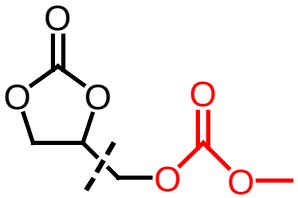


Glycerine carbonate methyl ester

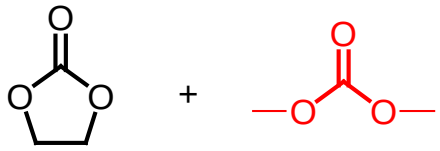
- Protection of free hydroxyl group in GC improves the cathodic stability significantly.



Glycerine carbonate methyl carbonate (GCMC)



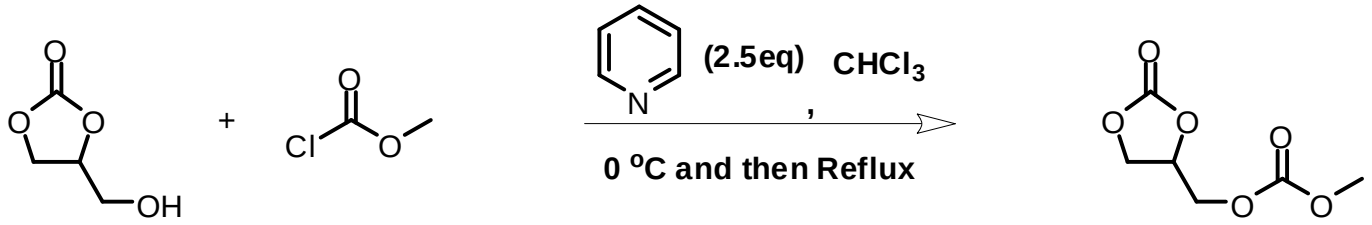
GCMC



Ethylene carbonate (EC)

Dimethyl carbonate (DMC)

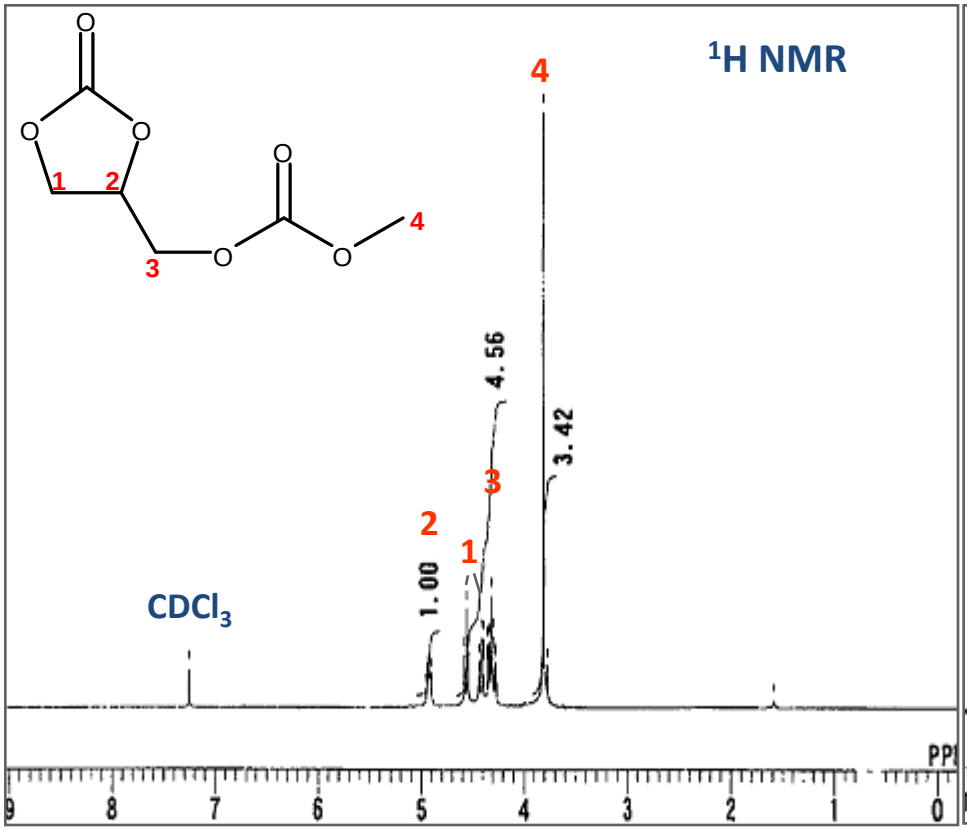
Synthesis and NMR Characterization of GCMC

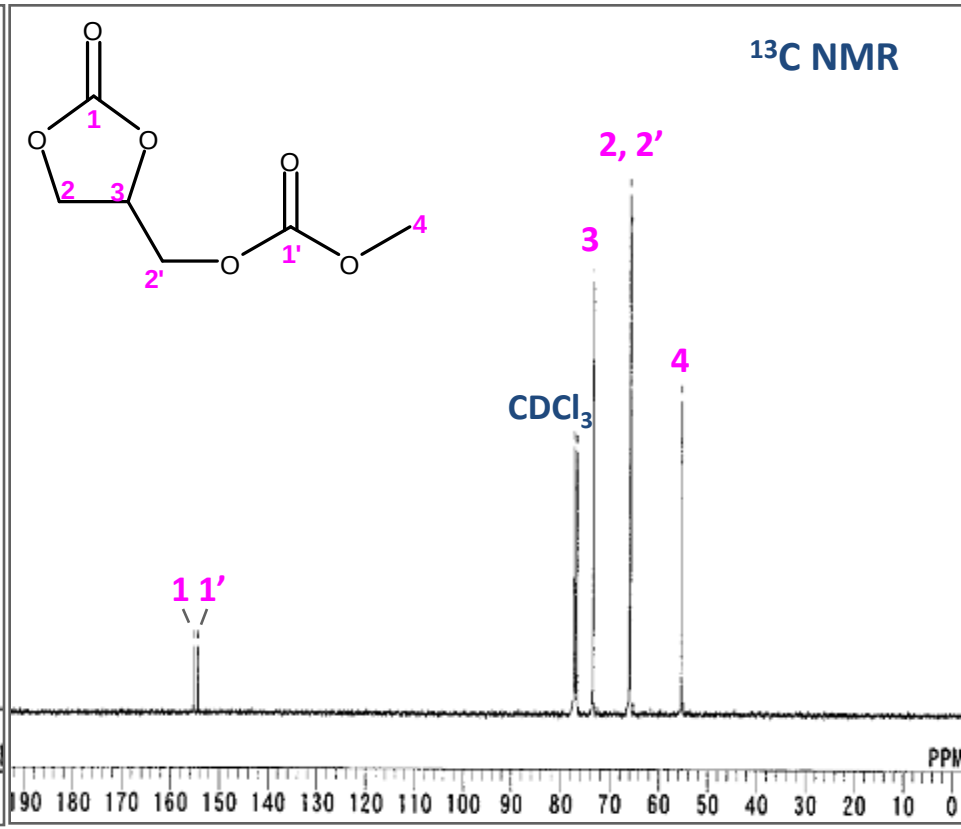


Glycerol Carbonate (1eq)

Methyl Chloroformate (1.25eq)

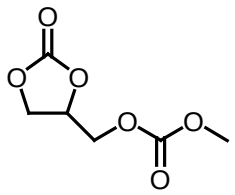
Glycerine carbonate methyl carbonate (GCMC)



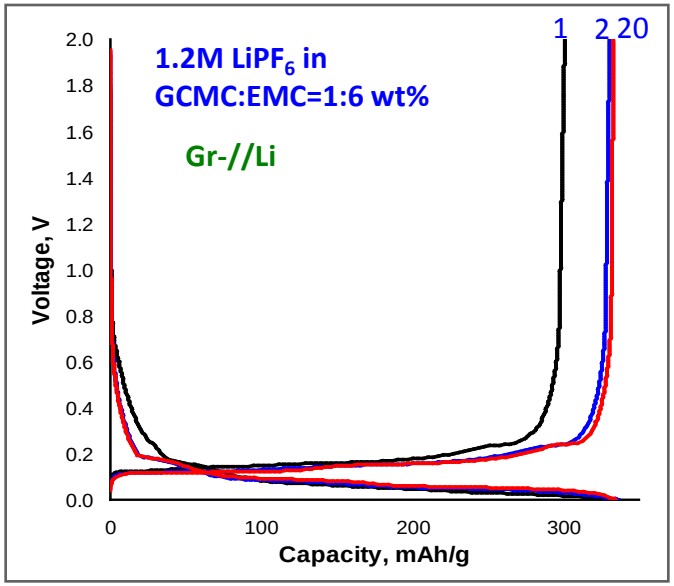


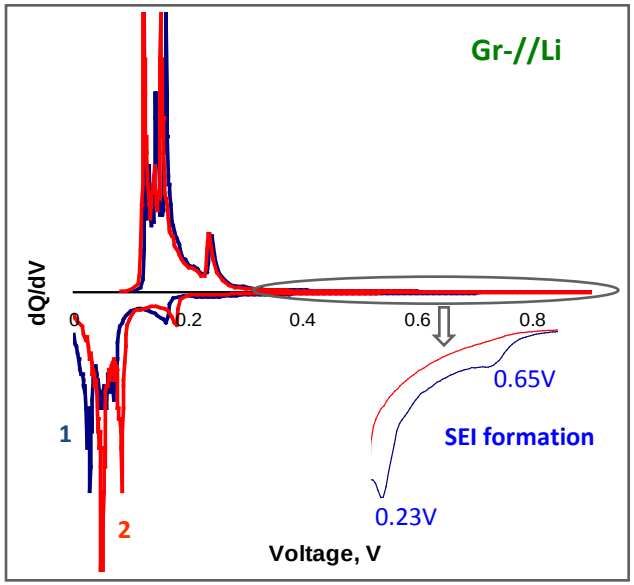
Collaboration with Dr. Kang Xu, ARL

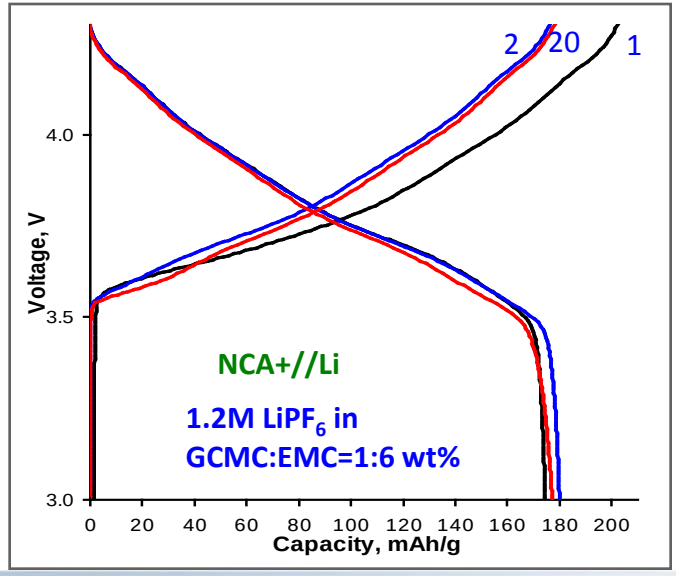
GCMC can be used as a co-solvent – data shown below is from cells that do not contain EC

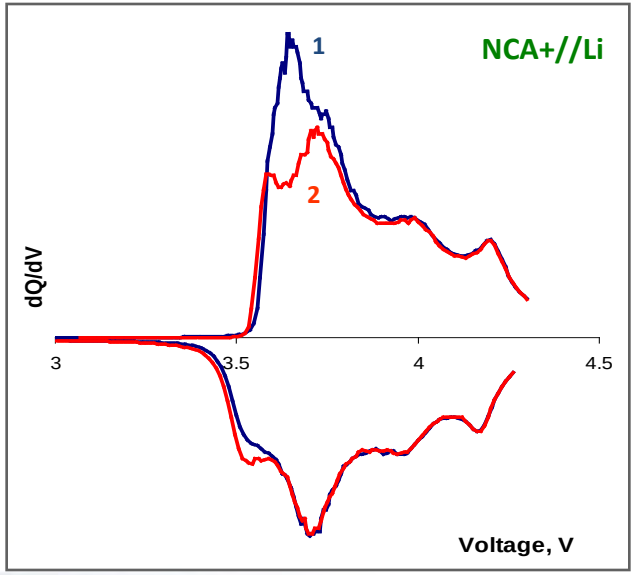


GCMC



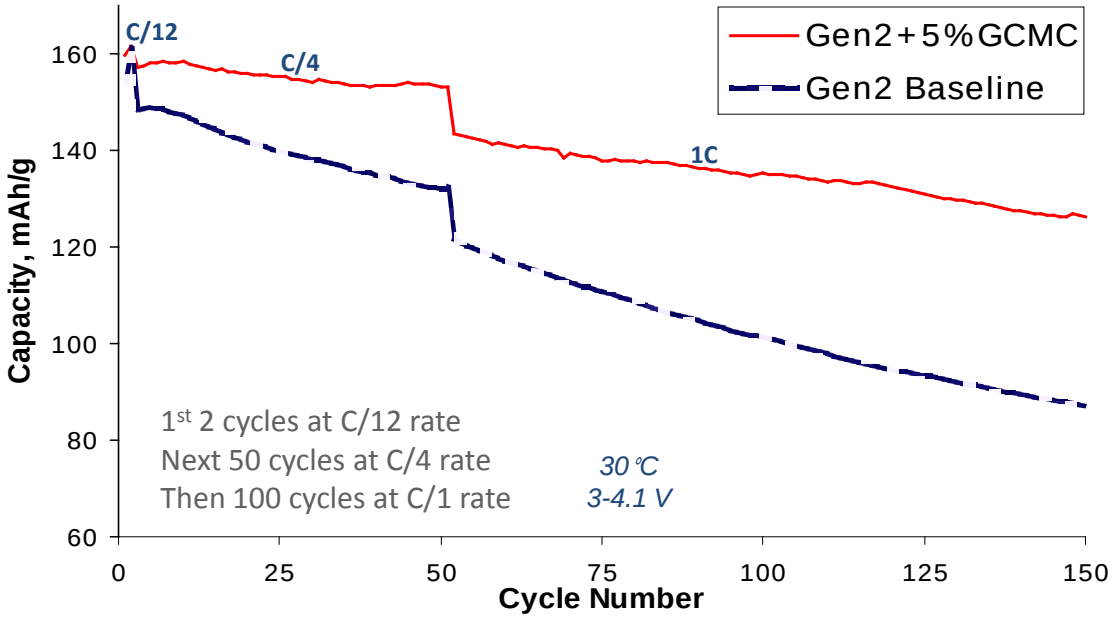


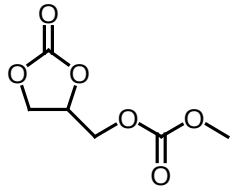




Collaboration with Dr. Kang Xu, ARL

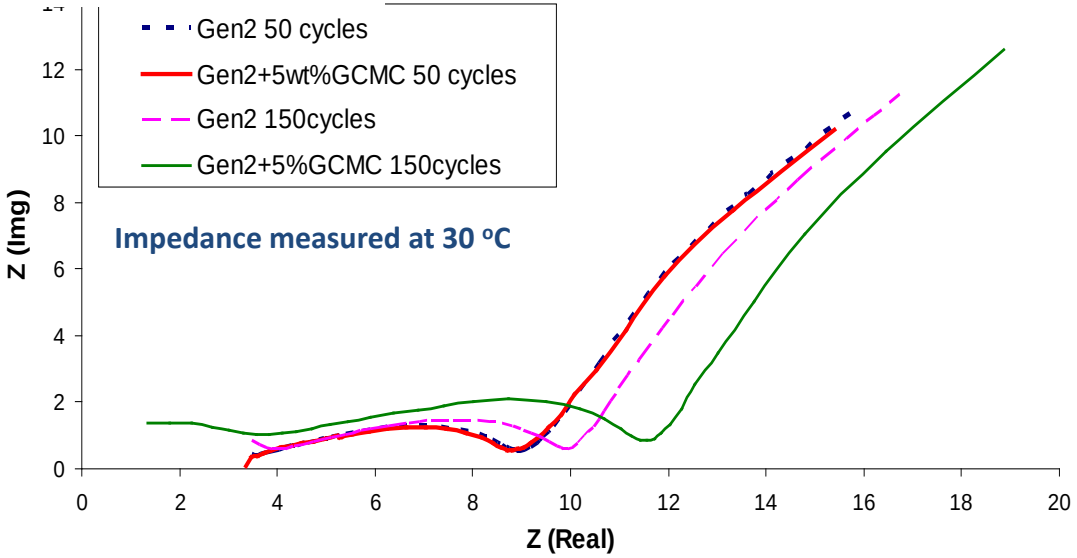
GCMC can also be used as an electrolyte additive - data below is from NCA+/Gr- cells with 5wt% GCMC in baseline electrolyte



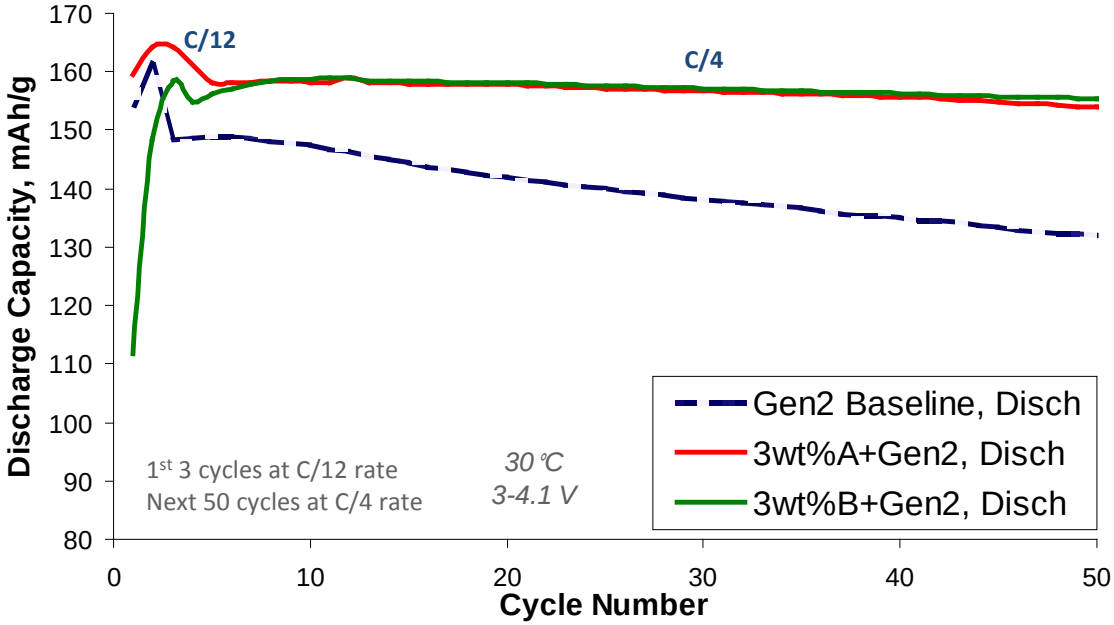


Cells with GCMC additive show improved capacity retention

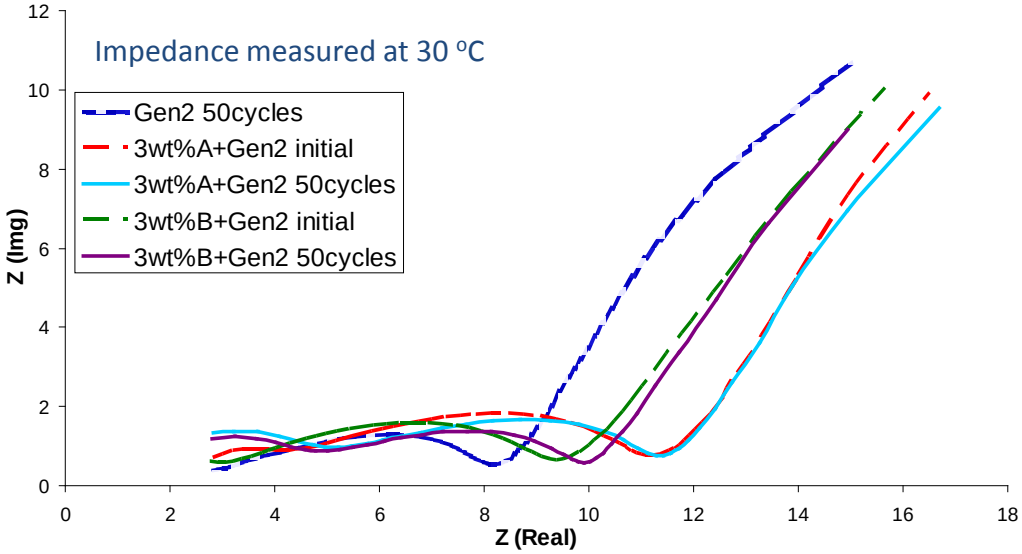
AC impedance data show that impedance of GCMC-bearing cells is similar to that of cells with baseline electrolyte during the first 50 cycles – the impedance is higher after longer term cycling (150 cycles)



Other promising GC derivatives are also being examined as electrolyte additives – data below is from NCA+/Gr- cells



Cells containing 3wt% of additives A and B showed almost no capacity loss after 50 cycles at C/4 rate. Long-term cycling is in progress.



The additive-containing cells have a slightly higher impedance than the baseline cells. However, cell impedance is unchanged after 50 cycles at C/4 rate.

Collaborations

- **Partners**
  - Purdue University (A. Wei et al.)
    - Collaboration to synthesize derivatives of glycerol carbonate and other promising electrolyte additive compounds
  - University of Rhode Island (B. Lucht et al.)
    - Collaboration to determine changes at the electrode-electrolyte interface using surface analysis techniques.
  - Colleagues at Labs (ARL, JPL)
    - Collaboration to evaluate electrolyte additives or solvents to facilitate/accelerate the development process.
  - Industry Colleagues
    - Collaborations to evaluate novel compounds in ABR cells
- **Technology Transfer**
  - Knowledge generated during the course of our studies is shared with colleagues in US battery industry through presentations, articles, and reports

Work in Progress/Future Work

- Continue exploration of novel electrolyte additives based on our approach: screening, testing, analyzing and optimizing. Our next experiments will be on electrodes identified for the next set of ABR PHEV cells. These experiments will include
  - ✓ Electrolyte stability studies at voltages >4.5V using high-energy NMC layered electrodes
  - ✓ Electrolyte stability studies at voltages >4.8V using $LiNi_{1/2}Mn_{3/2}O_4$ spinel electrodes
- Conduct surface characterization of formed and cycled electrodes to
  - ✓ Understand composition/constitution of “stable” electrode passivation layers
  - ✓ Determine oxidation/reduction pathways that lead to “stable” passivation layers
  - ✓ Optimize and design better candidates to meet cost, calendar life and safety requirements of batteries for PHEV applications.
- Continue investigations of glycerol carbonate (GC) derivatives
  - ✓ Systematically changing functional group on GC results to effect changes in electrochemical behavior. Charting the structure – activity relationships will yield the mechanistic understanding required to design better electrolyte systems
- Develop criteria to identify new electrolyte additives that can enhance cell life by protecting electrode surfaces from reactions with the electrolyte
  - ✓ Examine multifunctional additives that can simultaneously affect both positive and negative electrodes

Summary

- The objective of this study is to identify and develop novel electrolyte additives and electrolyte solvents to improve the electrochemical performance and calendar life of lithium-ion cells for PHEV applications
- Our approach is to conduct systematic investigation of promising candidates, such as heteroaromatic compounds and derivatives of glycerol carbonates, by employing synthetic organic chemistry, electrochemical testing, and surface analysis techniques
- We have identified a new family of heteroaromatics-substituted carboxylic ester-based electrolyte additives/co-solvents. Small additions (~0.3 wt%) of these compounds, which include methyl picolinate (MP), methyl isonicotinate (MIN), 3,4-diethyl pyridinecarboxylate (3,4-DEPC), 2,3-pyrazinedicarboxylic anhydride (2,3-PzDCA), etc. to the baseline electrolyte (1.2M $LiPF_6$ in 3EC:7EMC) improves capacity retention of NCA(+)//graphite(-) cells.
- We have conducted extensive investigations on compounds derived from glycerol carbonate (GC). Our data show that cells with 5wt% GCMC (Glycerol Carbonate Methyl Carbonate) as an additive to the baseline electrolyte exhibit improved long-term cycling performance. Noted that GCMC can be used as a replacement for Ethylene Carbonate (EC) in the electrolyte. Alkyl ether derivatives of GC have also been evaluated as electrolyte solvents or co-solvents. Noted that the secondary functional group on the molecules has a significant effect on electrochemical performance.