

Electrolytes - Advanced Electrolyte and Electrolyte Additives

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DOE merit review
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This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Timeline

- Start: April 1, 2009
- **Finish: Sept. 30 2014**
- **60%**

Budget

- Total project funding
 - DOE share: \$1200 K
 - Contractor share
- FY10: \$ 300 K
- FY11: \$ 300 K
- FY12: \$ 300K

Barriers

- Barriers addressed
 - Cycle life
 - Calendar life
 - Abuse tolerance

Partners

- Interactions/ collaborations
 - Dimitry Bedrov, University of Utah
 - Oleg Borodin, ARL
 - Daikin America

Objectives

- Integrated theoretical/experimental program to develop additives for increased cycle, calendar life, and safety
- Develop advanced quantum chemical models to understand and predict functional additives that form stable Solid Electrolyte Interface (SEI) on carbon anode and cathodes as well as shuttles for overcharge protection
- Synthesize suitable additives predicted by model, characterize them and carry out extensive cycle and calendar life test.



Approach/Strategies

- Search for new electrolyte materials that react in a preferential manner to prevent detrimental decomposition of other cell components
- Quantum chemical screening of potential additive candidates for electrolytes for SEI formation
 - Prediction of reduction potentials from first principles calculations
 - Prediction of decomposition pathways and stabilities
 - Understanding protective film formation
- Closely coupled theoretical/experimental studies

Approach: highly accurate quantum chemical modeling methods

- Reduction/oxidation/potentials
 - Accurate calculation of electron affinity (ionization potential) + inclusion of solvation effects using a continuum model/explicit solvent molecules
 - Density functional theory (B3LYP); very high accuracy Gn theories in some cases
- Energetics of reaction pathways
 - Same methods as above for reduction/oxidation potentials
 - Explicit inclusion of solvent and salt molecules
- SEI growth, characterization
 - Periodic DFT studies
- Scale bridging modeling
 - Provide accurate quantum chemical data for use in more approximate modeling that can handle many more molecules



Approach: experimental methods

Synthesis of new additive molecules

Additive testing

- Cathode: $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$
- Anode: MCMB, LTO
- Electrolyte-1: 1.2M LiPF_6 EC/EMC 3/7 with or without additive
- Electrolyte-2: fully or partially fluorinated electrolyte for high voltage
- Separator: Celgard[®] 2325
- Operating Voltage window: 2.7-4.9V
 - Charge and discharge current: 1C
- Temperature: RT and 55 °C.

Validation of theory: Cyclic voltammetry, AC impedance, cycling performance

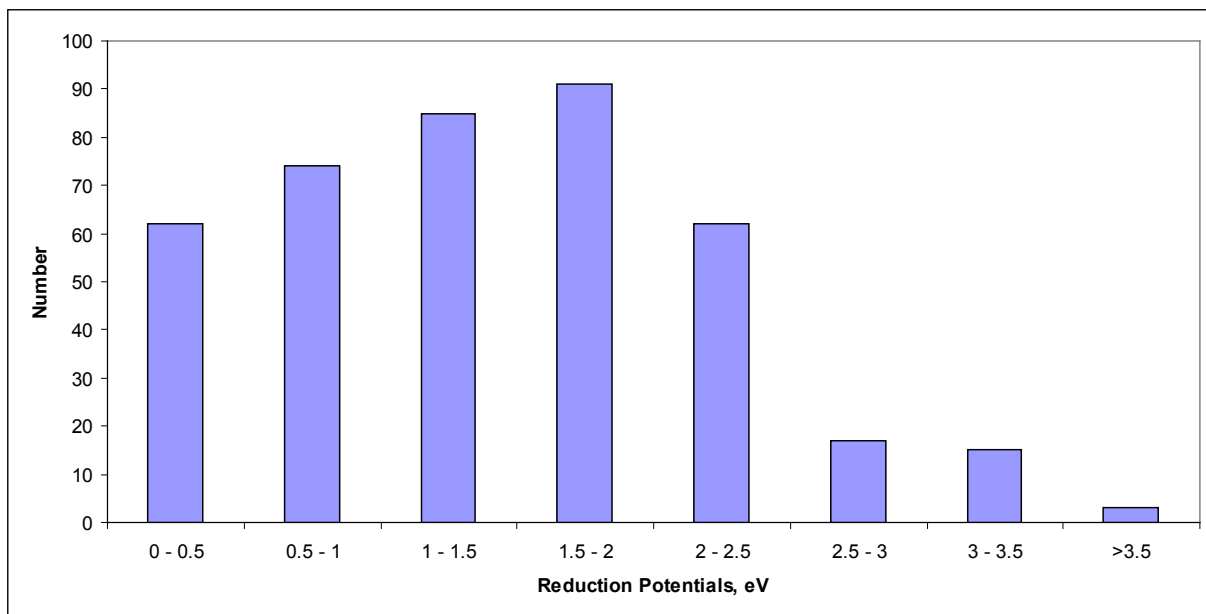


Accomplishments

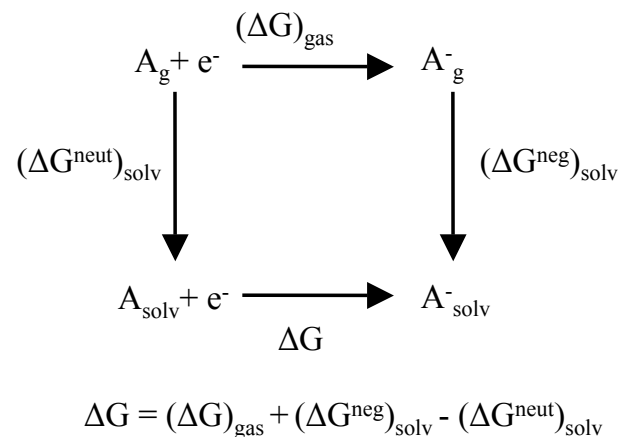
- Identification and Screening of candidate additives
- Three examples of additives for polymeric SEI formation
 - Citraconic anhydride
 - 3-oxabicyclohexane-2,4-dione
 - 2,4,6-Tris(2-propen-1-yloxy)-1,3,5-triazene
- New redox shuttle additives for overcharge protection and cell balancing
- Fluorinated high voltage electrolyte

Screening of reduction/oxidation potentials of over 400 additive candidates

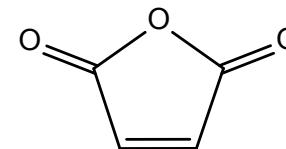
- Bar chart shows the distribution of the reduction potentials relative to Li electrode of more than 400 candidate additives
- Promising candidates selected for further investigation – decomposition pathways



Thermodynamic Cycle Used to Calculate Reduction Potentials



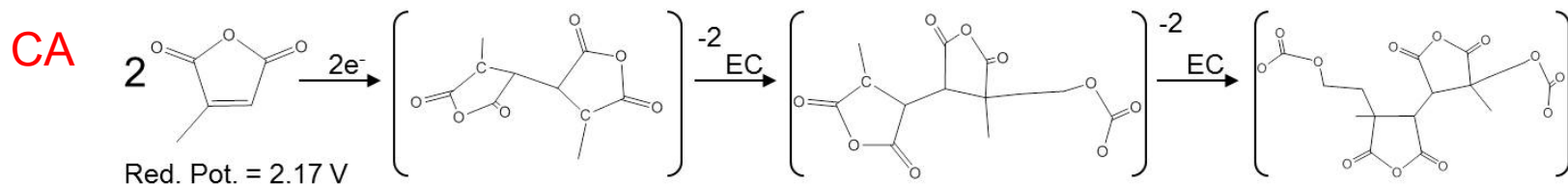
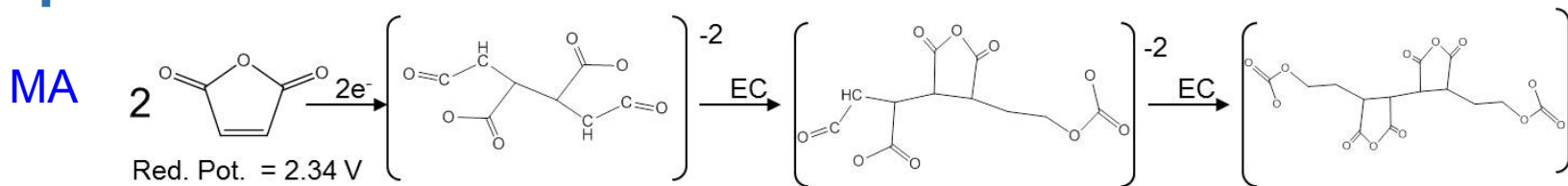
Anhydrides: SEI Formation through Polymerization



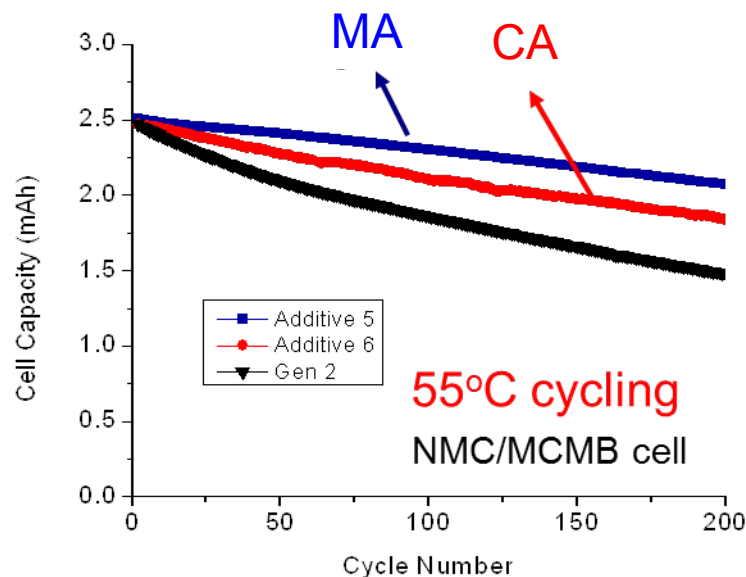
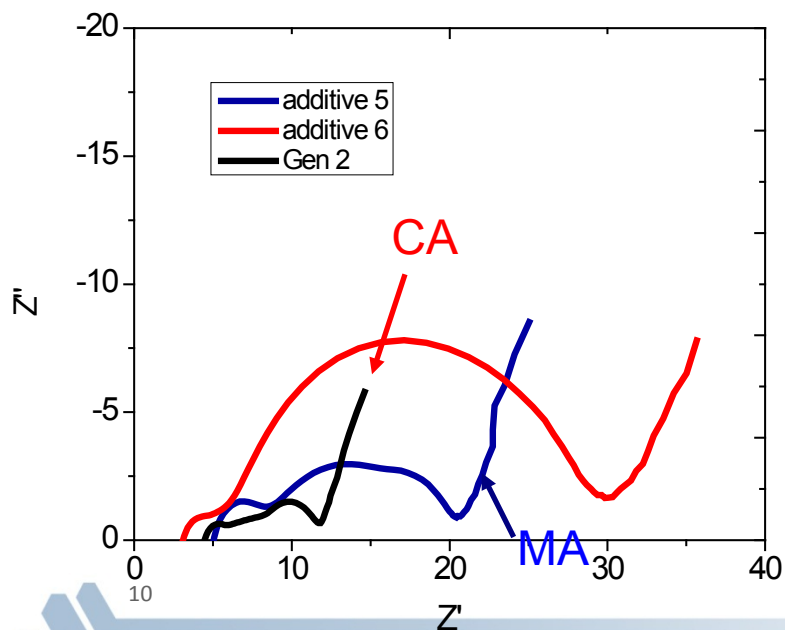
- Promising candidates: maleic, citraconic, and dimethylmaleic anhydride
 - Reduction potentials all $> 2V$ due to conjugation, decrease as more methyl groups attached
- Anionic polymerization via EC addition and ring opening
 - Thermodynamic stability order: maleic $>$ citraconic $>$ dimethylmaleic
- Potential additives for SEI formation due to favorable reduction potential and polymer reaction pathway



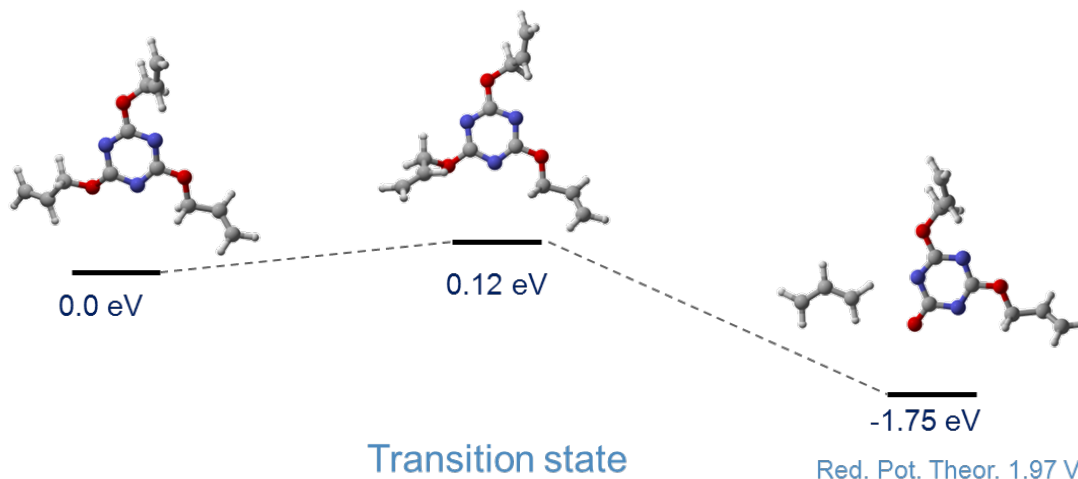
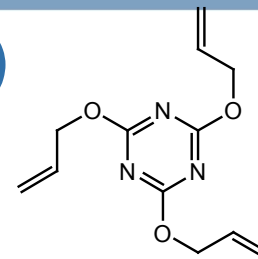
Maleic anhydride (MA) and citraconic acid (CA) as potential additives



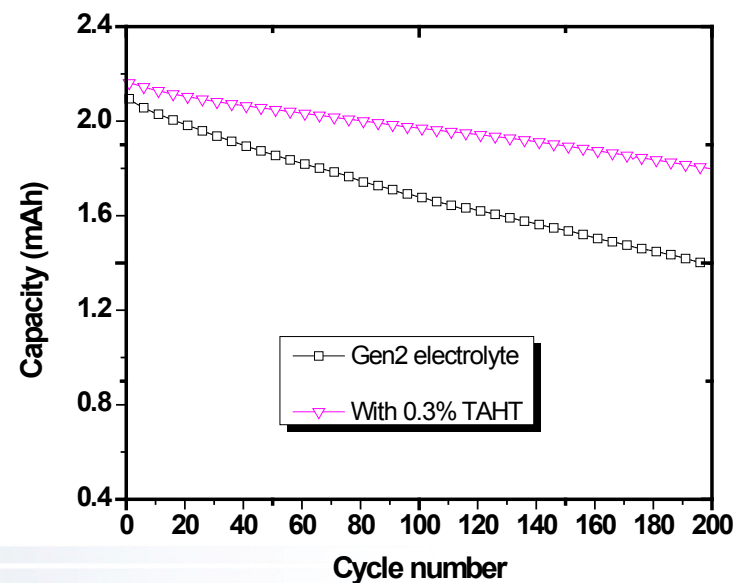
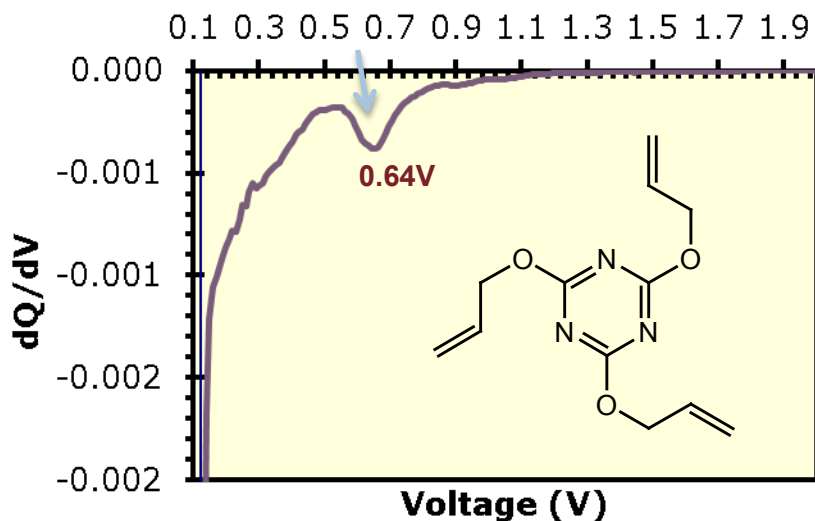
$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 // 1.2\text{M LiPF}_6 \text{ EC/EMC } 3/7 + 1\% \text{ Add.} // \text{MCMB}$



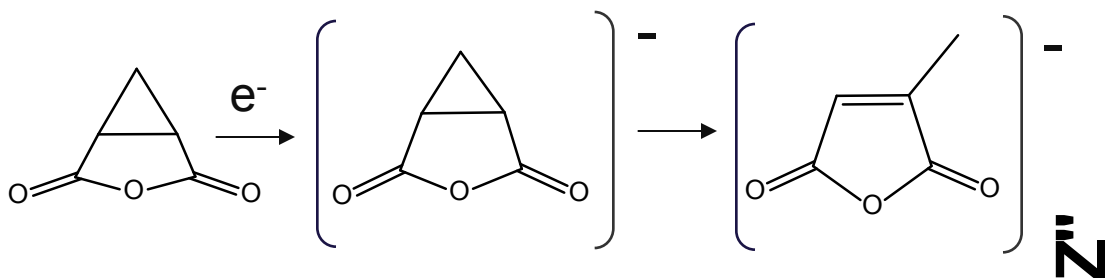
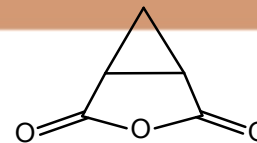
1,3,5-triacryloyloxyhexahydro-1,3,5-triazine (THAT) as a potential additive



Decomposition of TAHT after reduction can lead to further reaction with EC to form an effective SEI.

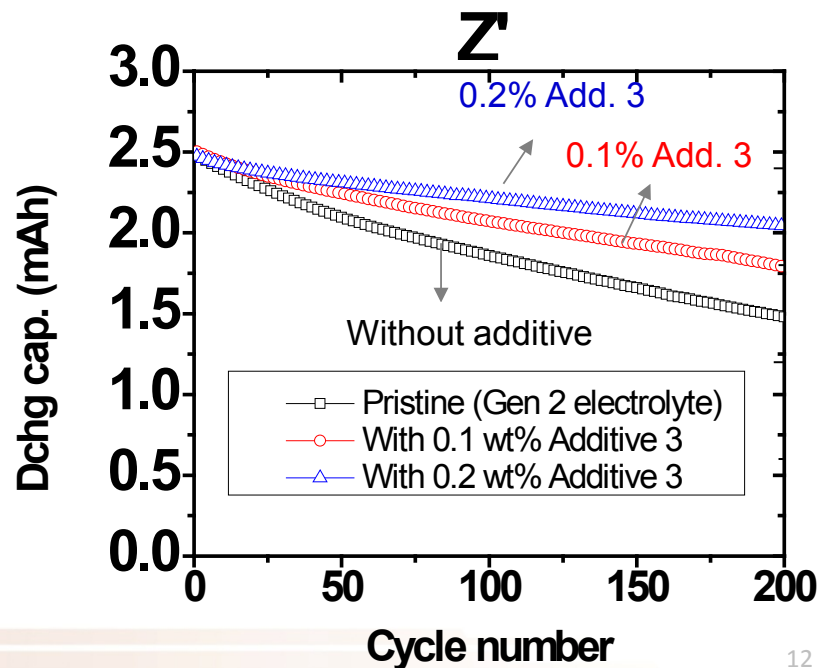
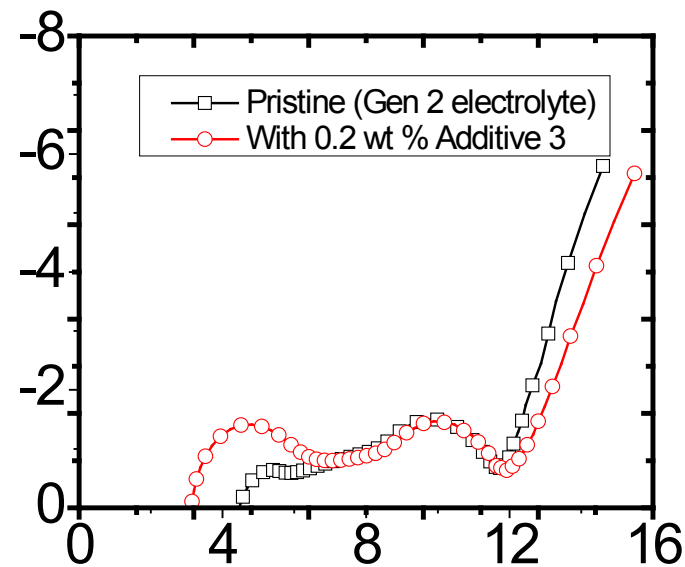
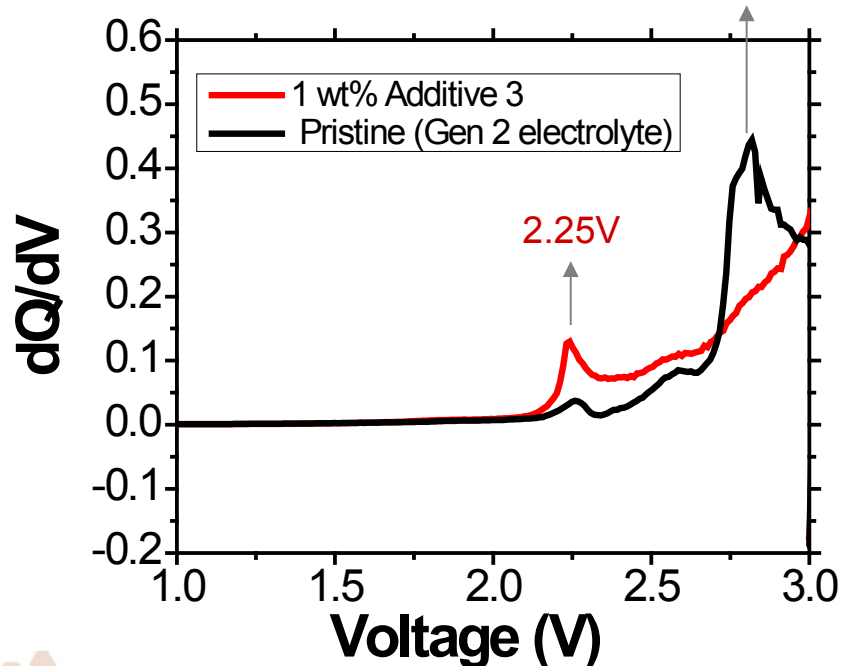


3-oxabicyclohexane-2,4-dione (A3) as potential additive



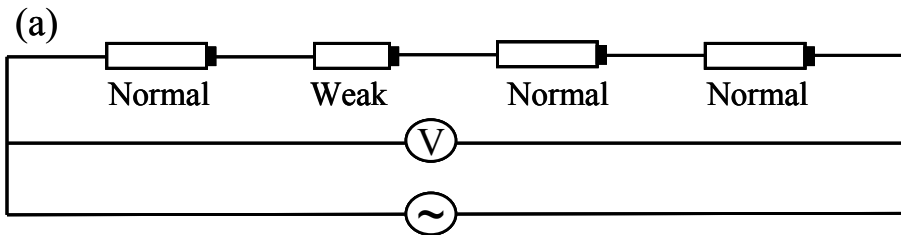
Ring expansion of A3 after reduction can lead reaction with EC to form an polymeric SEI component

Traditional SEI by EC

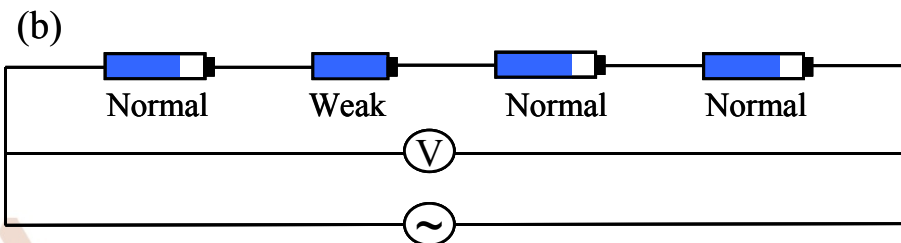


Redox shuttle for Overcharge abuse and capacity balancing in lithium ion cell

- Overcharge of a lithium ion cell can lead to:
 - (1) Decomposition of electrolyte;
 - (2) Lithium plating on negative electrode;
 - (3) Decomposition of positive electrode;
 - (4) Significant temperature elevation or even thermal runaway.
- Overcharge generally occurs in a battery pack with several cells connected in serial during charge operation.



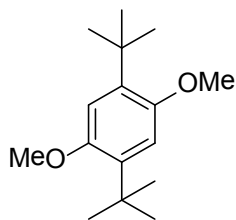
(a) Fully discharged battery pack.



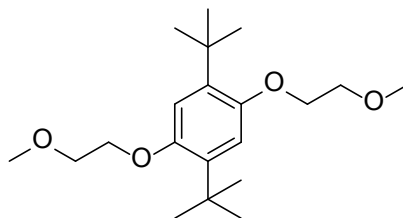
(b) Partially charged battery pack with the weak cell being fully charged.



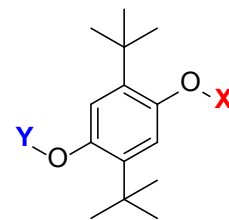
Previous redox shuttle work (from DDB to RS-2)



DDB (Jeff Dahn)

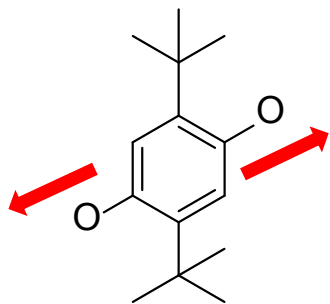


ANL-RS2 (Our group)



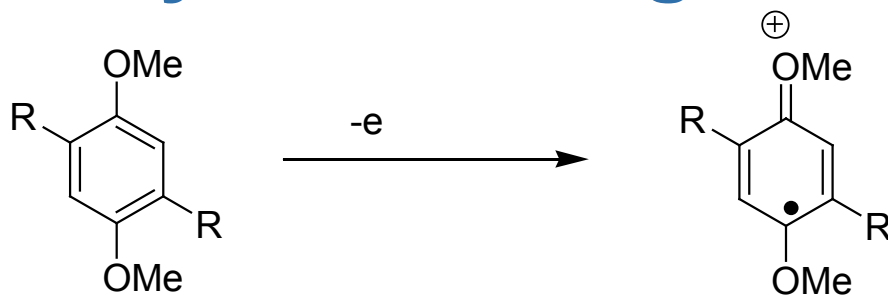
ANL-RS (1-8)

- ❑ DDB and ANL-RS2 are stable redox shuttle for LiFePO_4 system (200 cycles of 100% overcharge)
- ❑ By varying X, Y functional groups, we can adjust the redox potential according to applications
- ❑ They all share the same core structure (the redox reaction happens in center ring).



- ✓ DDB has limited solubility in EC/EMC solvent; Possible reason is symmetric distribution of polar C-O bond cancelling out to give a net low polarity
- ✓ Polar functional group has been introduced in RS1-RS8 to improve solubility

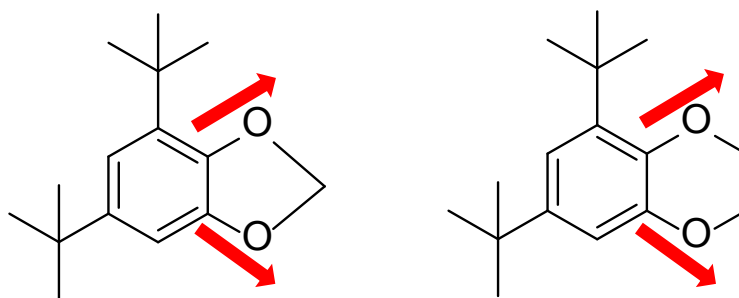
Why Fused Ring Structure



-OMe, Phenyl ring: **NOT coplanar**

Coplanar

- Coplanar means more conjugation to stabilize the radical cation
- Fused ring may force the coplanar geometry

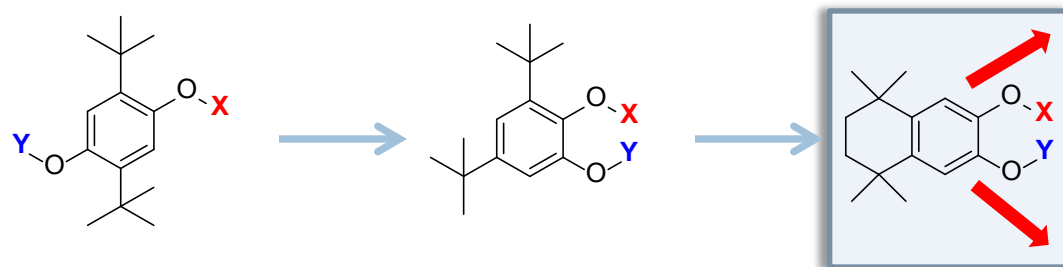


ANL shuttle

- Ortho-OMe makes the molecule polar
- Highly soluble in Carbonate solvent with high salt concentration

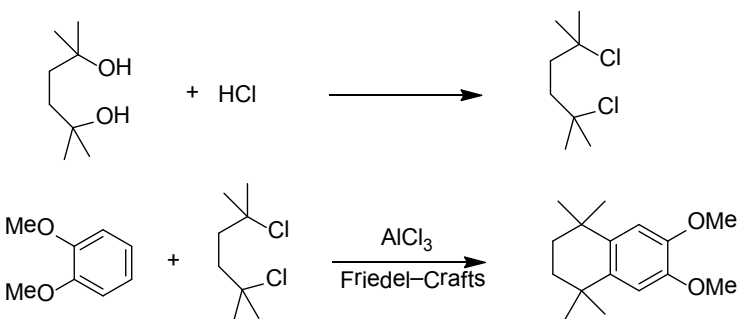


New Platform to Build Stable Redox Shuttle

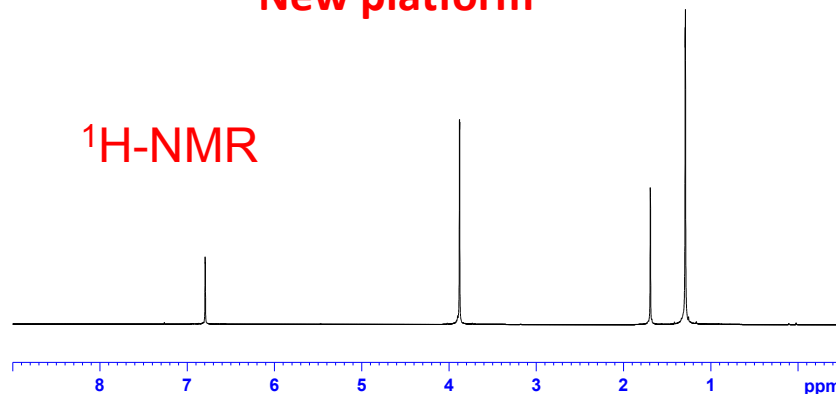


New platform

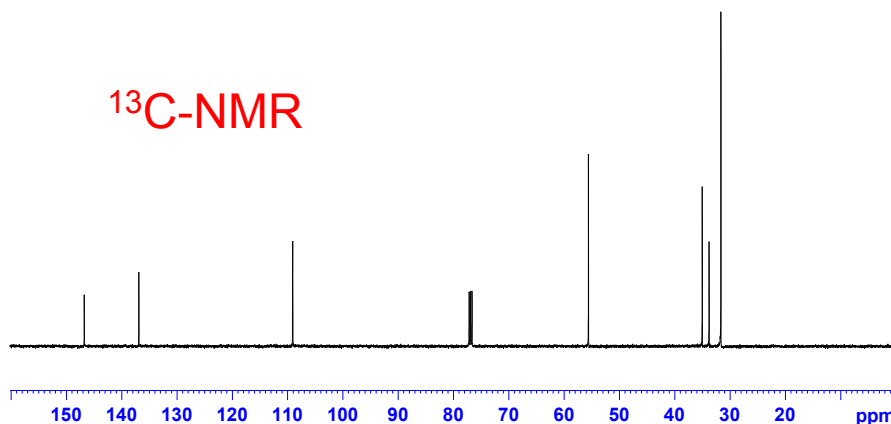
Example Synthesis



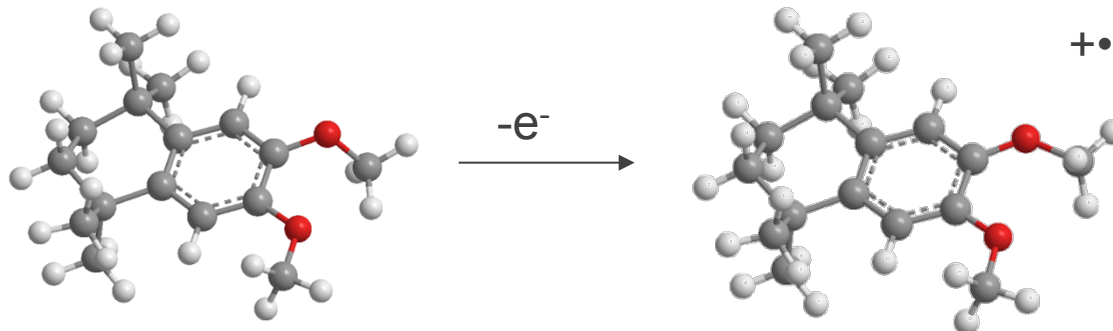
¹H-NMR



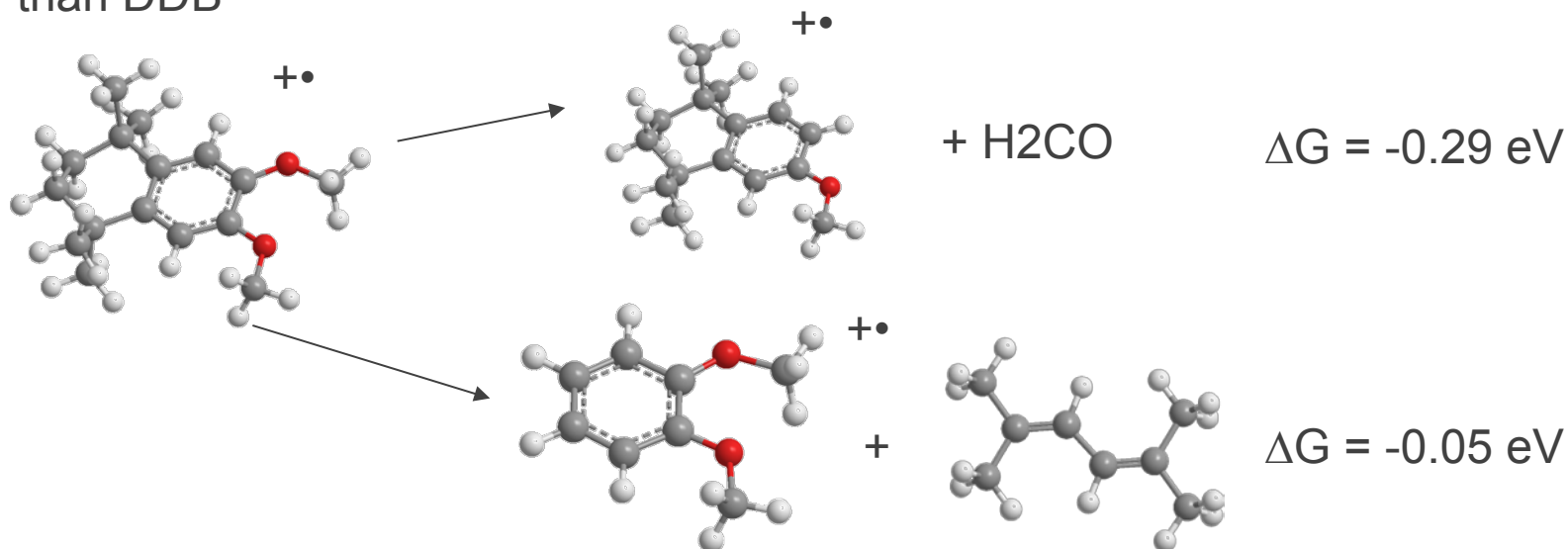
¹³C-NMR



Fused Ring Structure - Calculations



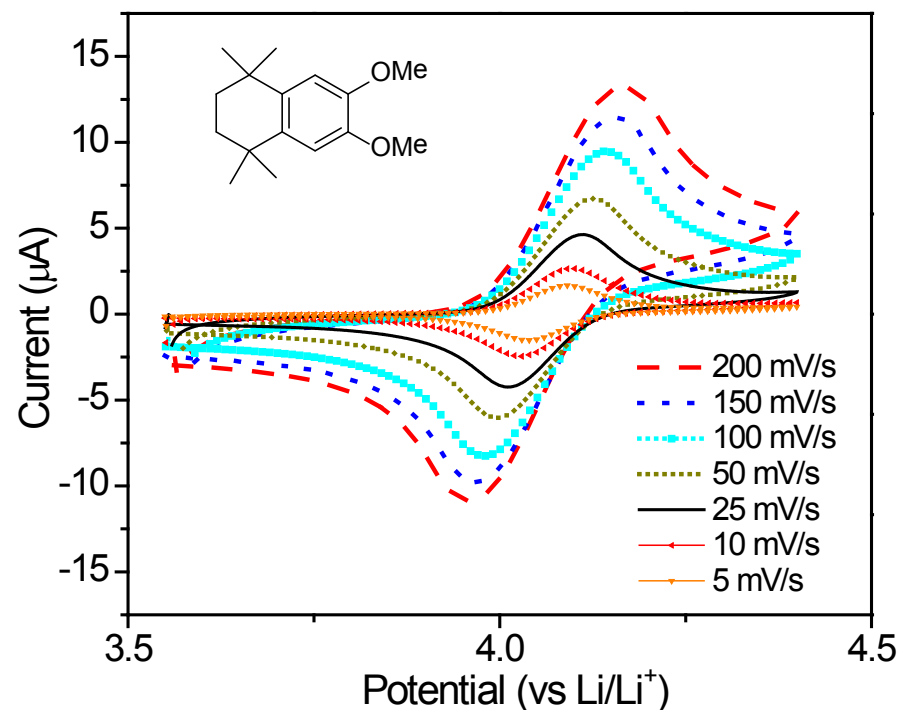
- Calculated oxidation potential = 4.06 V
- Steric repulsion between methoxy groups causes higher oxidation potential than DDB



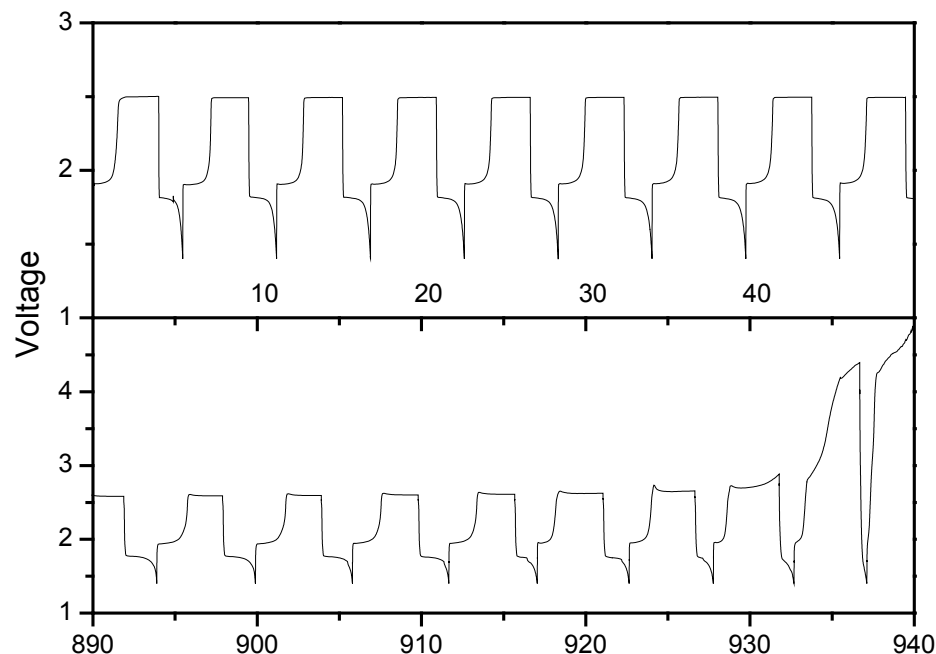
- Likely to be stable with respect to decomposition because of barriers to hydrogen transfer



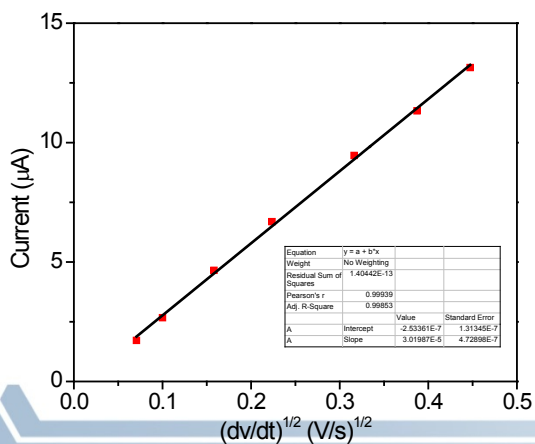
Overcharge Performance of New Redox Shuttle



$$E^{\circ'} = (E_p^a + E_p^c)/2 = 4.06 \text{ V vs Li/Li}^+$$



Good stability, can survive >150 overcharge cycles



Randles-Sevcik equation

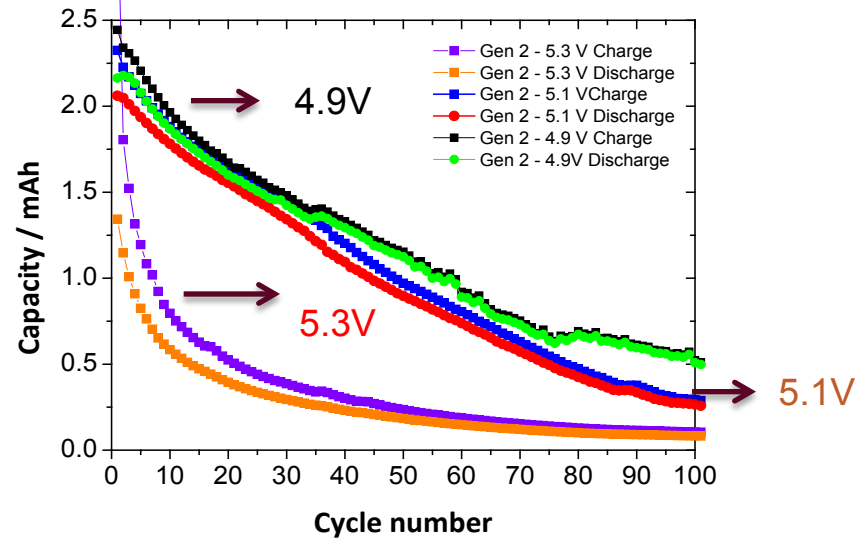
$$D = 1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

$$i_p = (269,000)n^{3/2}AD^{1/2}Cv^{1/2}$$

Highly soluble in EC/EMC solution (>0.4 M solution can be prepared)

Poor stability of Carbonate Based Electrolyte at High Voltage Cells

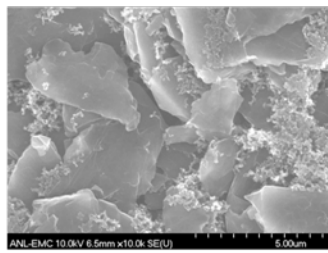
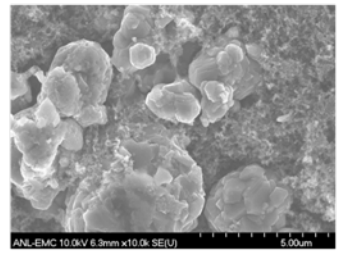
LiNi_{0.5}Mn_{1.5}O₄ / Graphite Couple



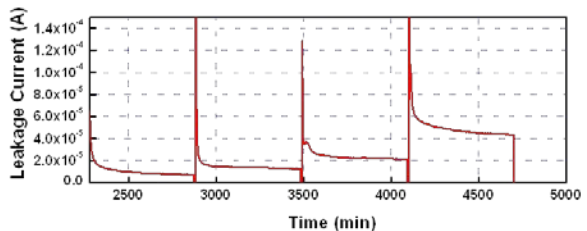
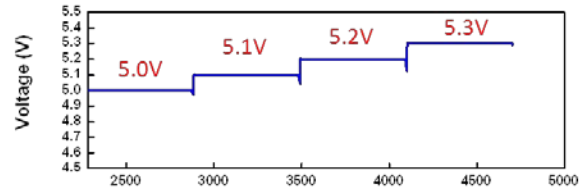
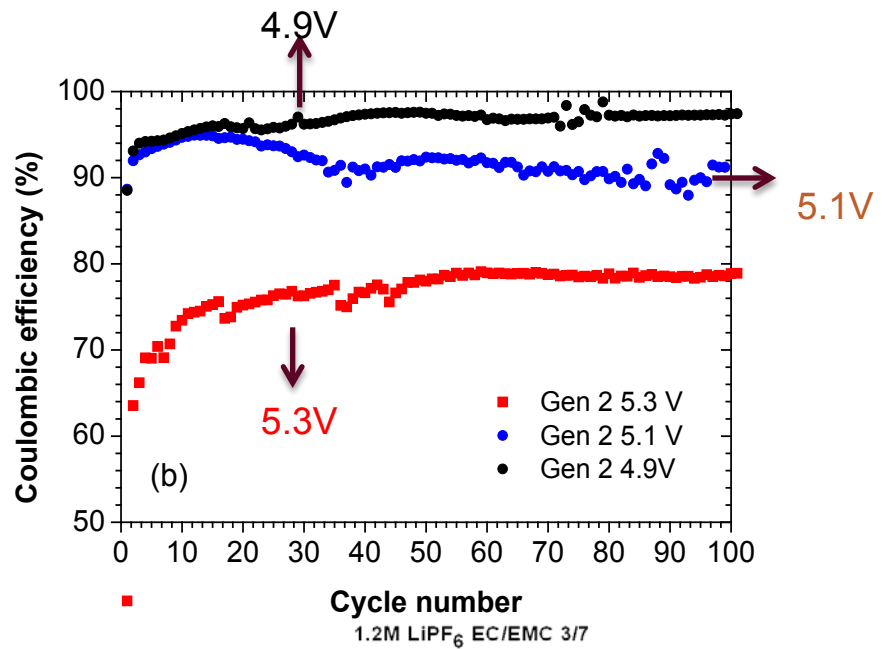
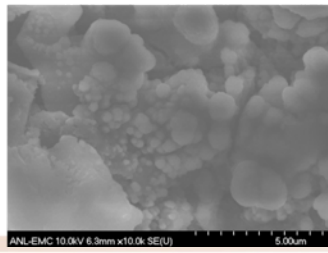
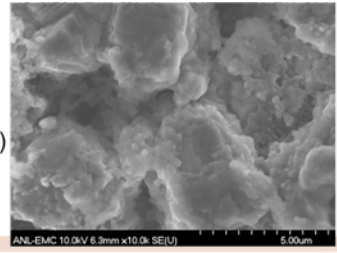
LiNi_{0.5}Mn_{1.5}O₄

Graphite (A12)

Pristine



Cycled (4.9V 55°C)

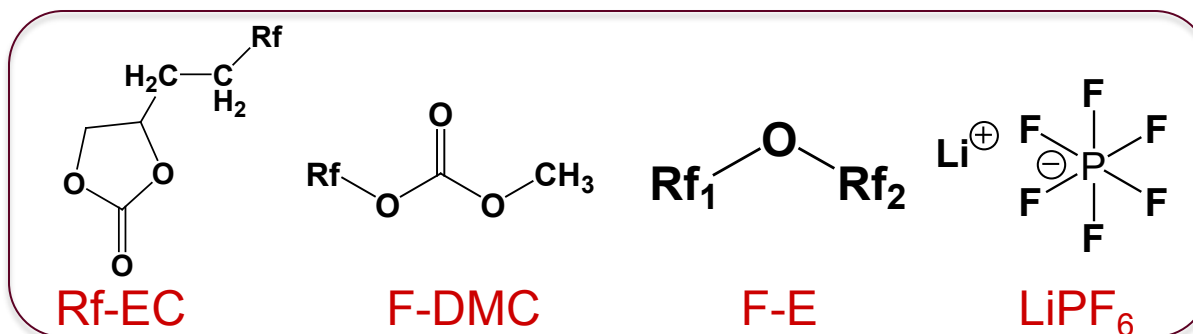
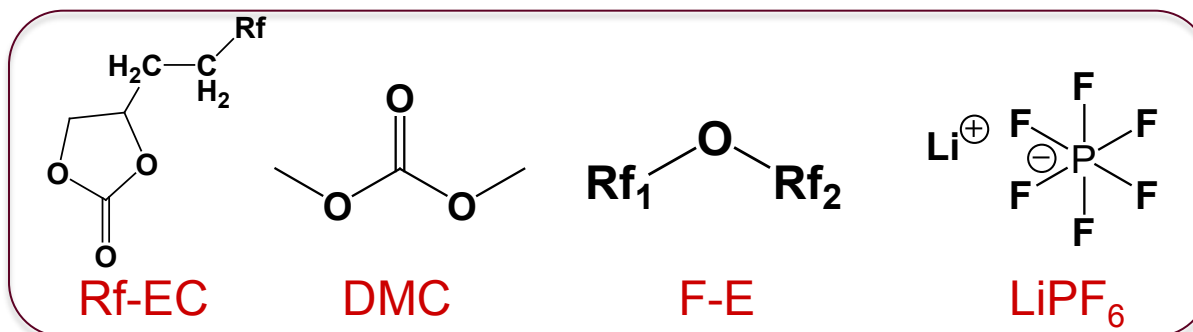
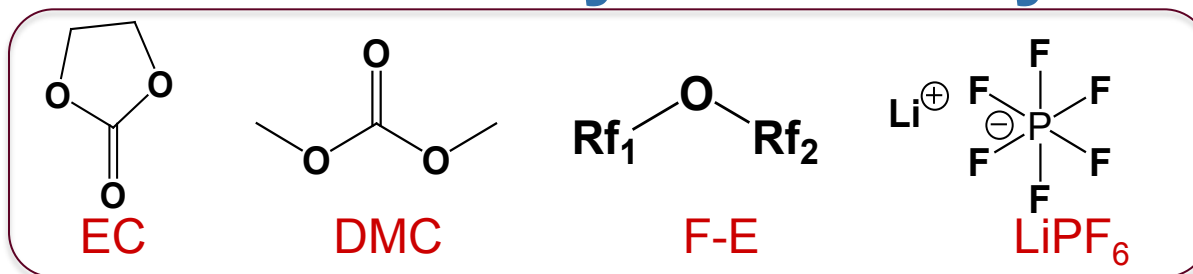


Floating test results

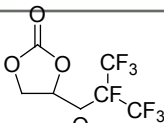
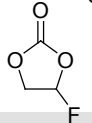
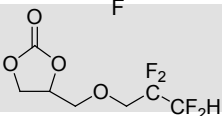
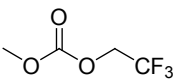
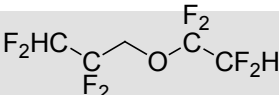


Fluorinated Solvent to Improve the Electrolyte Stability

To increase the voltage endurance



DFT Calculation to Predict the Oxidation Stability of Fluorinated Carbonate Compounds

Code Name	Chemical Structure	P_{ox}^a / V	P_{red} / V
FCC-1		6.97	1.69
FEC		7.16	1.63
FCC-3		6.93	1.50
FLC-1		7.10	1.58
FE-1		7.29	1.82

Use of fluorinated solvent as Co-Solvent with organic Electrolyte

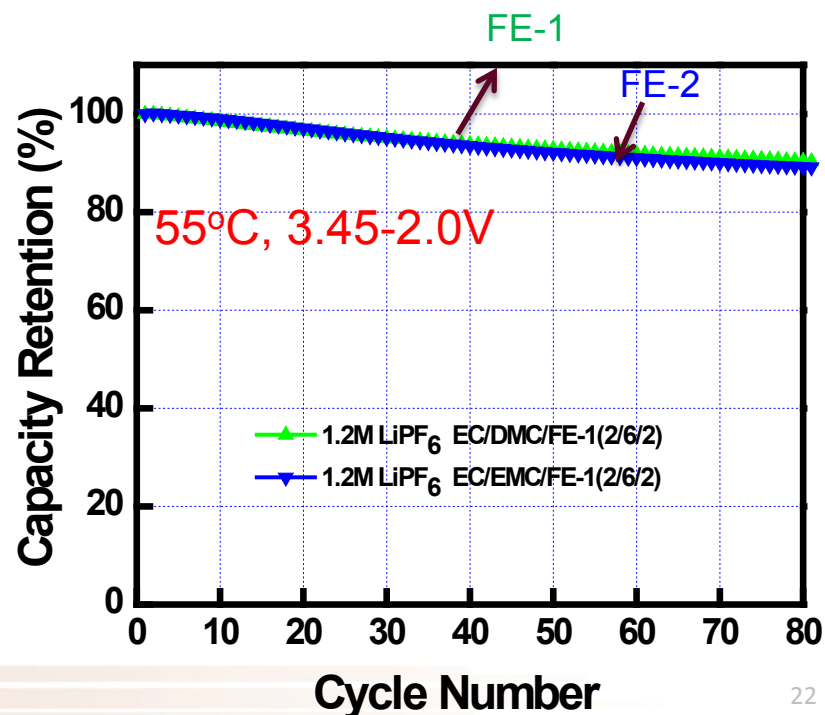
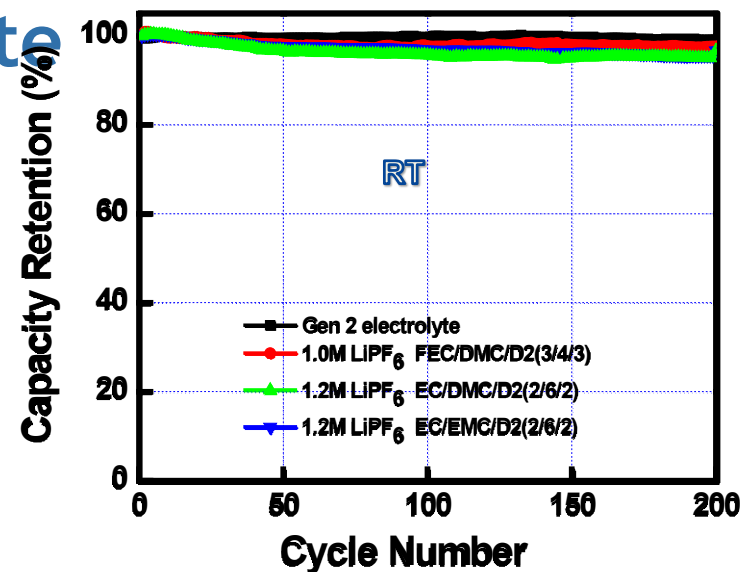
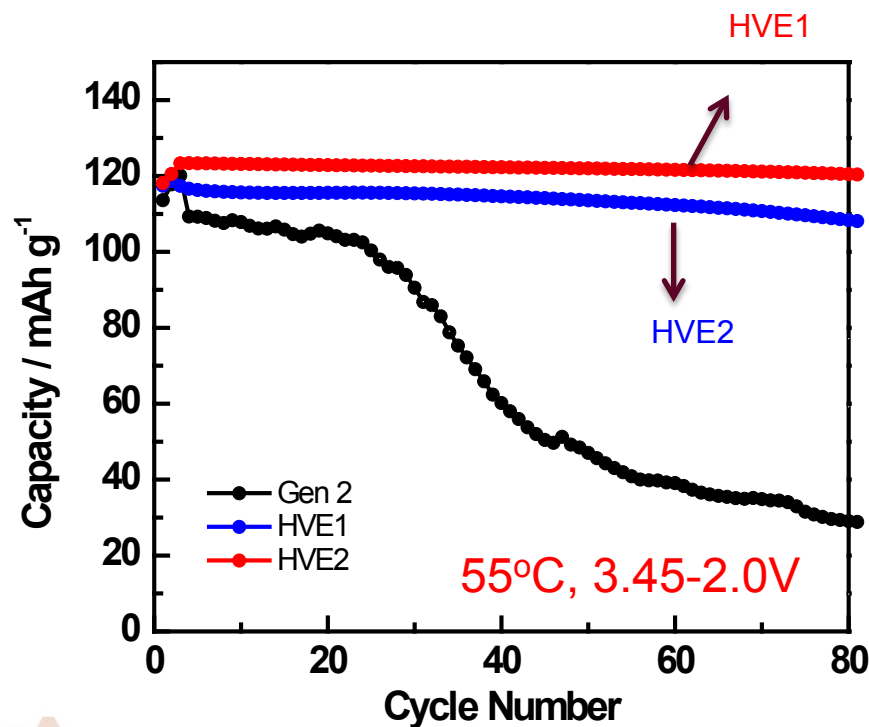
Gen 2 electrolyte (1.2 M LiPF_6 EC/EMC (3/7))

1.0M LiPF_6 FCC-1/FLC-1/FE-1 (3/4/3) – HVE1

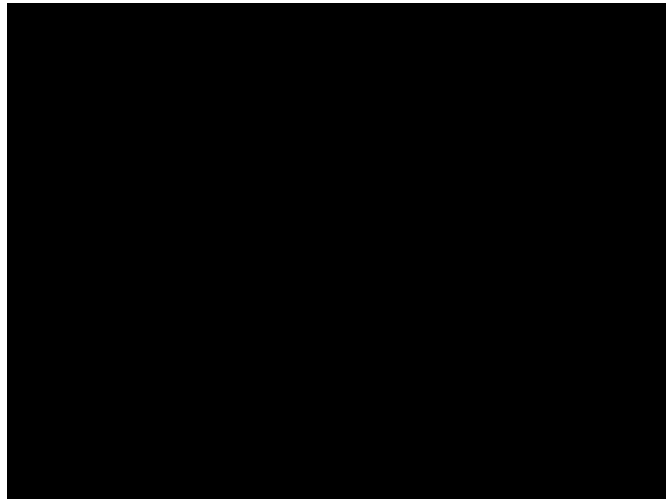
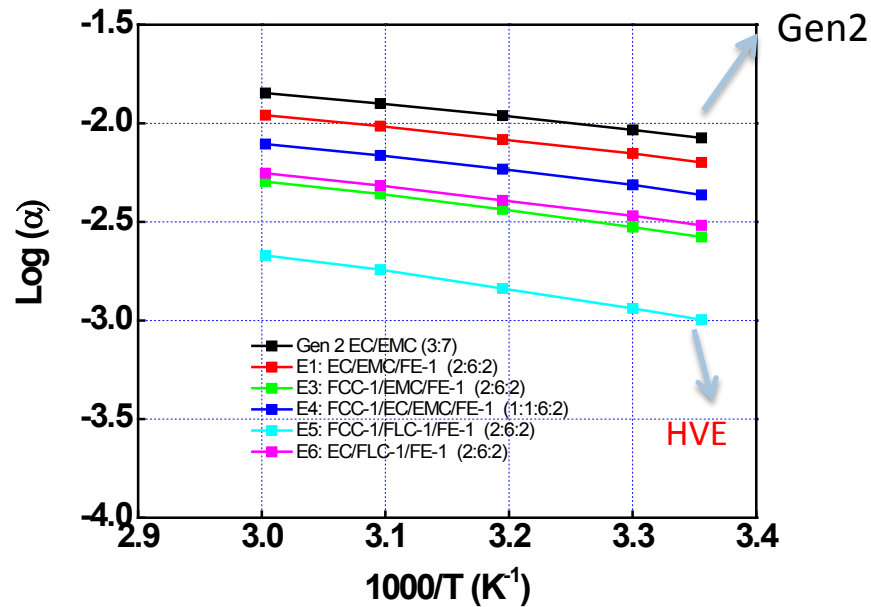
1.2M LiPF_6 FCC-1/EC/FLC-1/FE-1 (2/6/2) – HVE2

1.2M LiPF_6 EC/DMC/FE-1(2/6/2) – FE-1

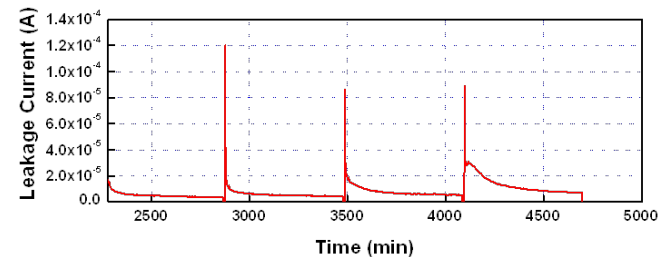
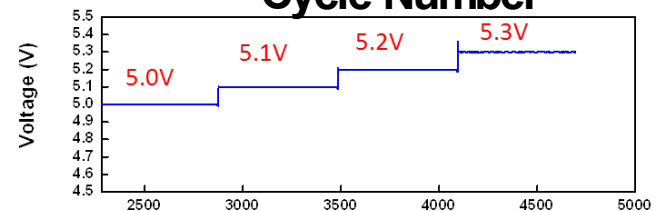
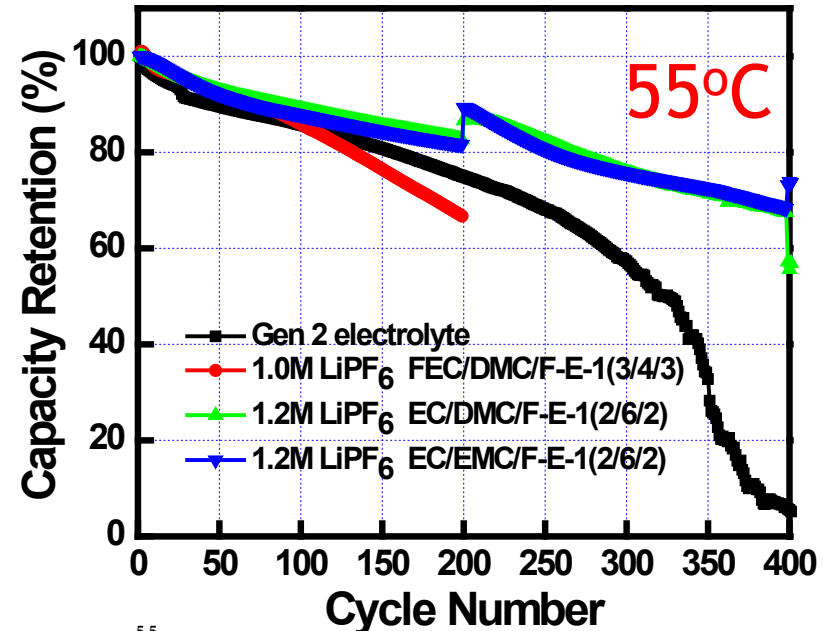
1.2M LiPF_6 EC/EMC/FE-1(2/6/2) – FE-2



Performance of Fully Fluorinated Electrolyte

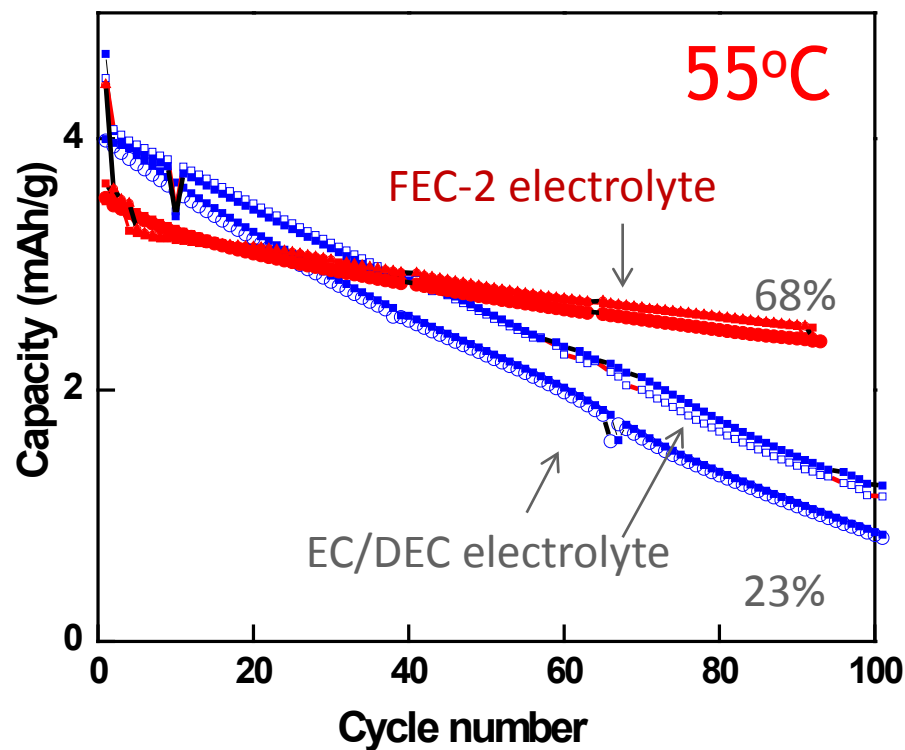
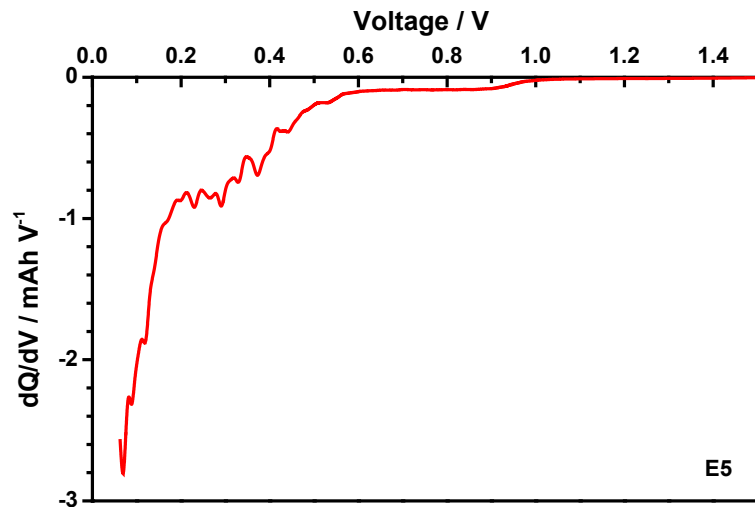


Flame propagation test



1.2 M LiPF₆ in FCC-1/FLC-1/FE-1

Cycling performance of fluorinated Electrolyte in the presence of Graphite at 55 °C



No apparent SEI formation peaks so the decomposition continues until lithiation happens.

FEC-2: 1.2 M LiPF₆ in FCC-1/FLC-1/FE1



Summary

- Exploration of new additives for SEI formation
 - Screening of over 400 candidate materials
 - Many new candidates identified from high level quantum chemical screening
 - Experimental testing
 - Example: **Maleic anhydride** has confirmed its value as an additive
- Use of fluorinated solvent as co-solvent with organic for high voltage electrolytes shows non flammability, high voltage capability and improved performance
- New fused ring redox shuttles shows good overcharge protection performance and good stability

Proposed Future Work

- Redox shuttles
 - Combined experimental theoretical studies to find new shuttles with redox potential around 4.3 V
- Additives for SEI formation
 - Combined experimental theoretical studies to find new SEI additives based on our extensive database. Expand the work to cover cathode SEI and silicon anode SEI
- Improved modeling of decomposition reaction pathways leading to SEI formation
 - Integrate high level quantum chemical studies with larger scale methods for modeling SEI formation mechanisms