Electrolytes - Advanced Electrolyte and Electrolyte Additives

P.I.: K. Amine
Presenter: L. A. Curtiss
Argonne National Laboratory

DOE merit review

May 15 , 2012

Project ID# ES-066-amine

Overview

Timeline

- Start: April 1, 2009
- Finish: Sept. 30 2014
- 40%

Barriers

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

Budget

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

Partners

- Interactions/ collaborations
  - Dimitry Bedrov, University of Utah
  - Kevin Gering, INEL
  - Oleg Borodin, ARL
  - Enerdel
  - J_Saft

Objectives

- Integrated theoretical/experimental program to develop additives for increased cycle and calendar life
- 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 stabilties
  - Understanding protective film formation
- Closely coupled theoretical/experimental studies

Approach: highly accurate quantum chemical modeling methods

- Reduction potentials
  - Accurate calculation of electron affinity + inclusion of solvation effects using a continuum model
  - Density functional theory (B3LYP); very high accuracy Gn theories in some cases
- Energetics of of reaction pathways
  - Same methods as above for reduction potentials
  - Explicit inclusion of solvent and salt molecules (AIMD)
- SEI growth, characterization
  - Periodic DFT studies
- Scale bridging modeling
  - Collaboration with Oleg Borodin (ARO), Dimitri Bedrov (Utah) Kevin Gering (INEL)
  - Provide accurate quantum chemical data for use in more approximate modeling that can handle many more molecules

Approach: experimental methods

Additive testing

- Cathode: LiNi1/3Mn1/3Co1/3O2
- Anode: MCMB
- Electrolyte: 1.2M LiPF6 EC/EMC 3/7 with or without additive
  - Separator: Celgard 2325
- Voltage for cycling: 2.7-4.2V
  - Charge and discharge current: 1C or 2mA
- Temperature: 55°C.

For AC impedance measurements

- The cells were charged to 3.8 V and then the impedance test was run at RT.
- The charge rate was 1C.

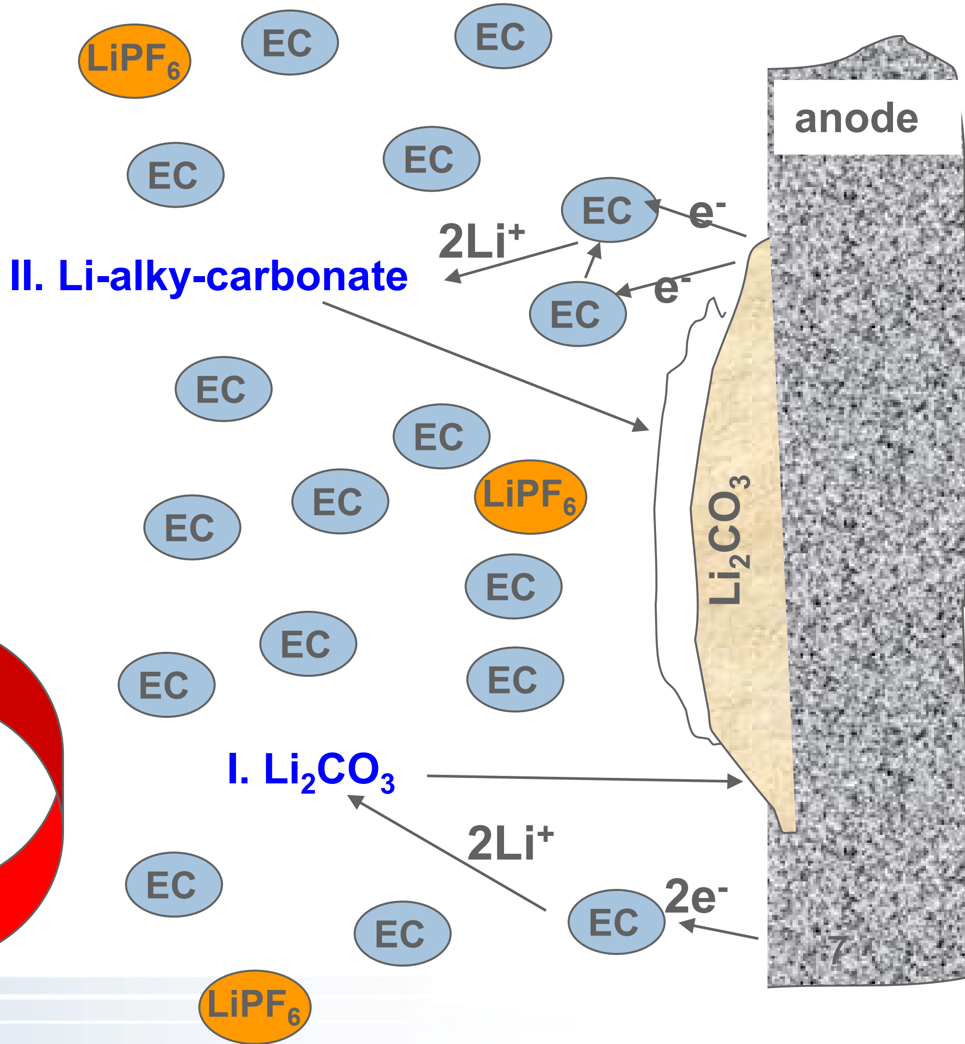
Synthesis of new additive molecules

Investigation of reaction pathways for ethylene carbonate (EC) reactions for lithium alkyl formation including reaction barriers

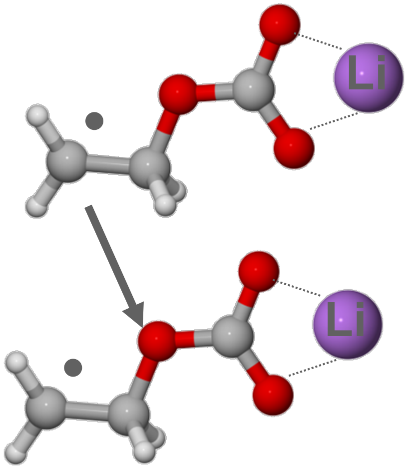
- Lithium carbonate formation 2-electron transfer mechanism (I) well-studied
- Lithium alkyl carbonate formation mechanism (II) is less understood

<u>Collaborative effort on multi-scale modeling of SEI formation</u>

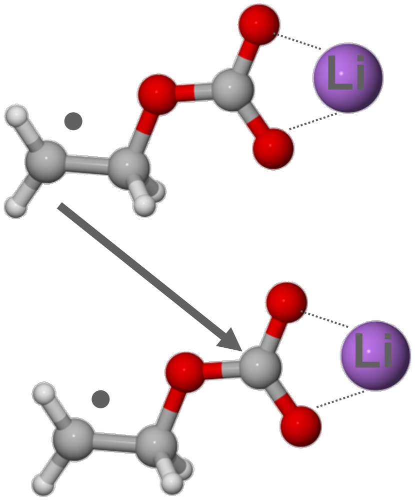
- Accurate quantum chemical calculations with continuum model for solvent (this project)
- DFT with explicit solvent molecules included, AIMD
- REAXX force fields (Bedrov, Utah)
- MD simulations (Bedrov, Utah)



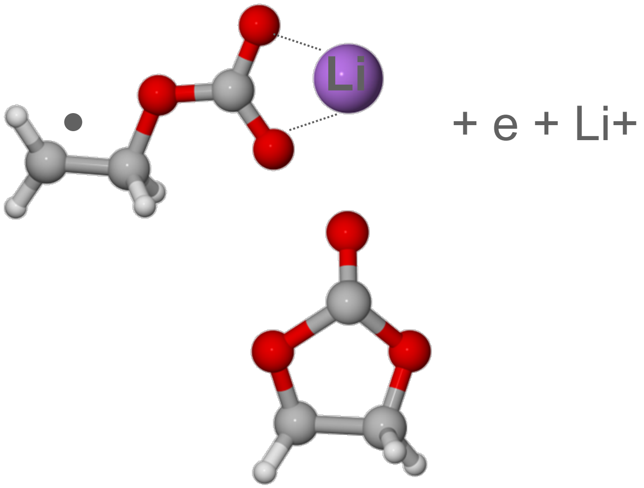
Investigation of reaction pathways for different possible EC reduced species



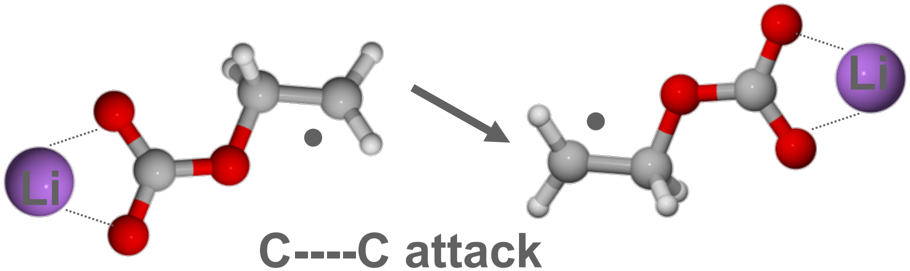
C----O attack



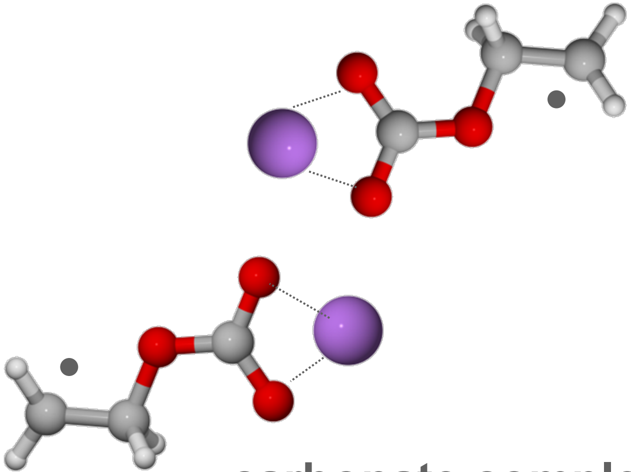
C- carboxyl attack



2-electron reduction

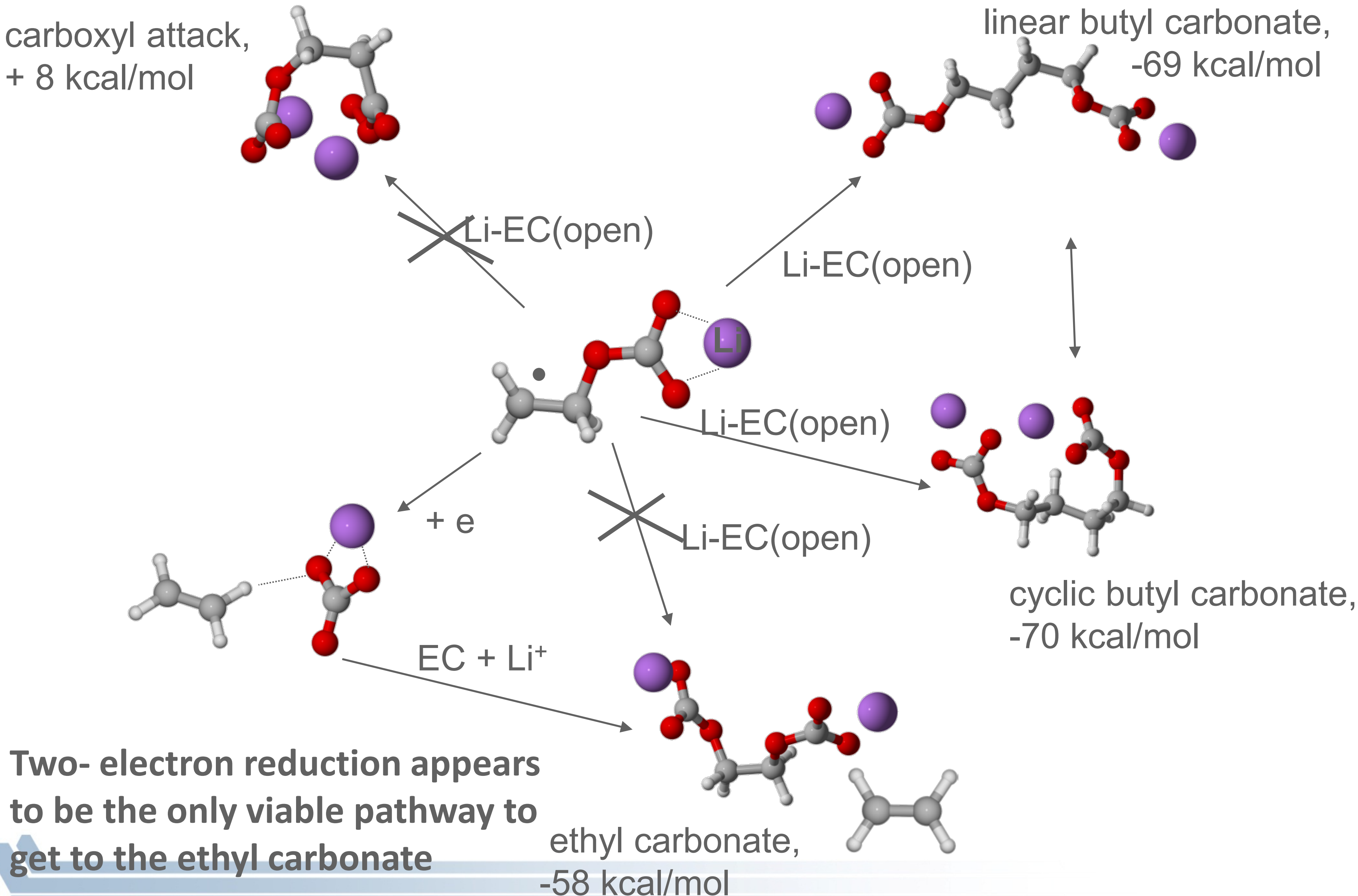


C----C attack



carbonate complex

Assessment of most favorable pathways to get to "ethyl" carbonate



carboxyl attack,
+ 8 kcal/mol

Li-EC(open)

linear butyl carbonate,
-69 kcal/mol

Li-EC(open)

Li

Li-EC(open)

+ e

Li-EC(open)

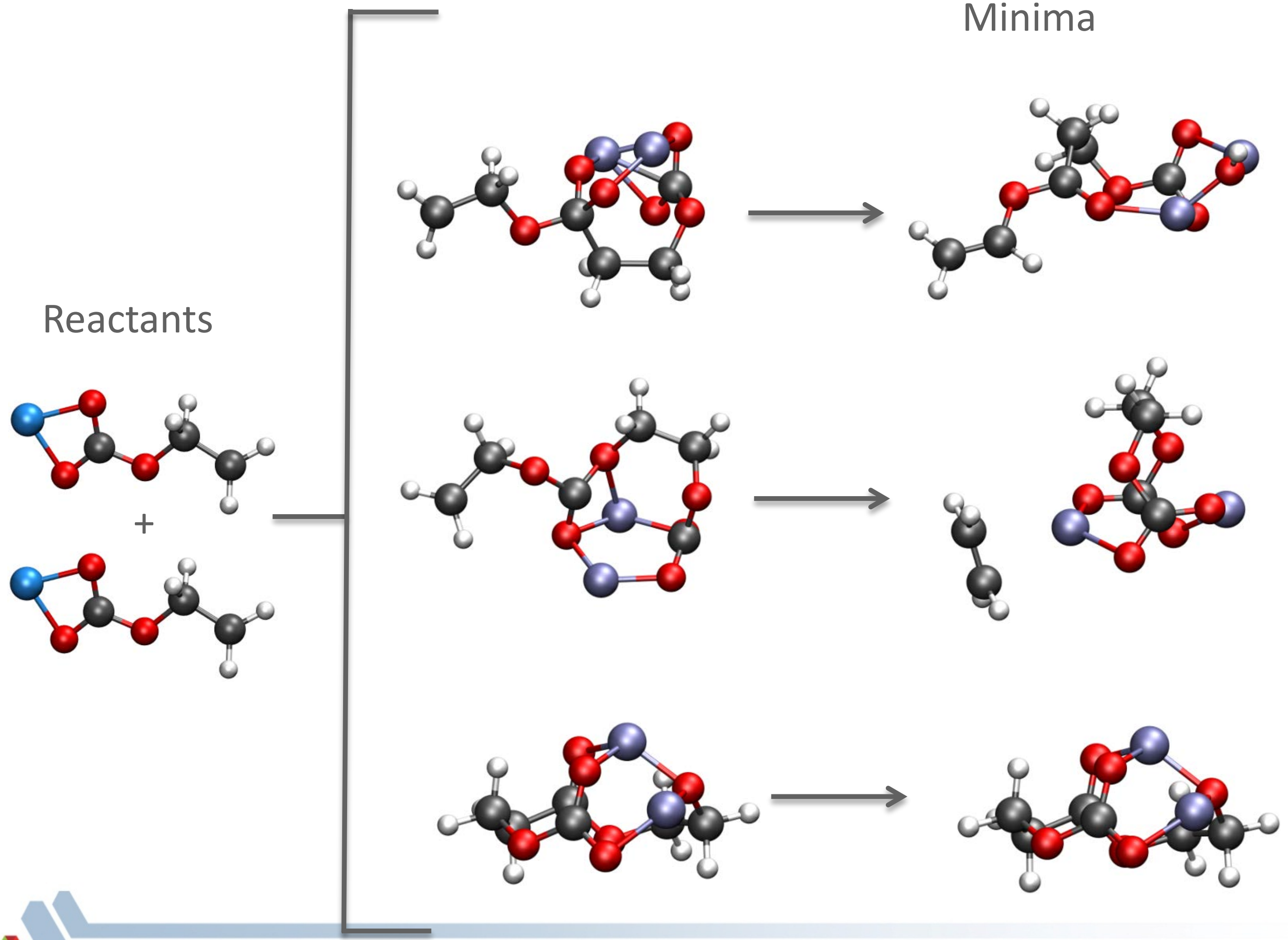
cyclic butyl carbonate,
-70 kcal/mol

EC + Li$^+$

ethyl carbonate,
-58 kcal/mol

- **Two- electron reduction appears to be the only viable pathway to get to the ethyl carbonate**

Additional pathways explored



ReaxFF Minima

Quantum Minima

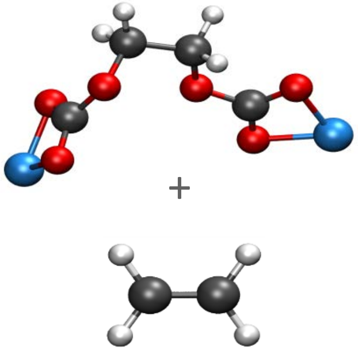
Reactants

+

Not a minima

High energy minima

Stable minima



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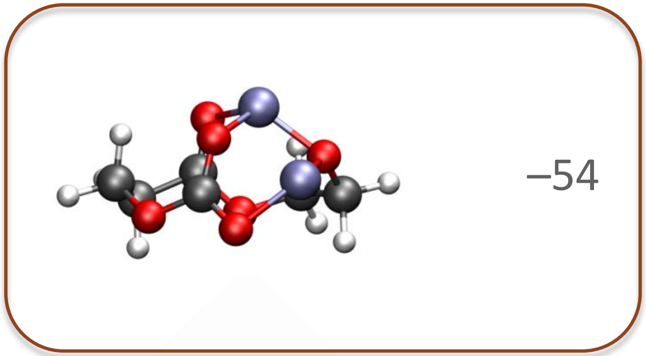

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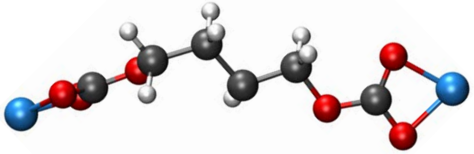


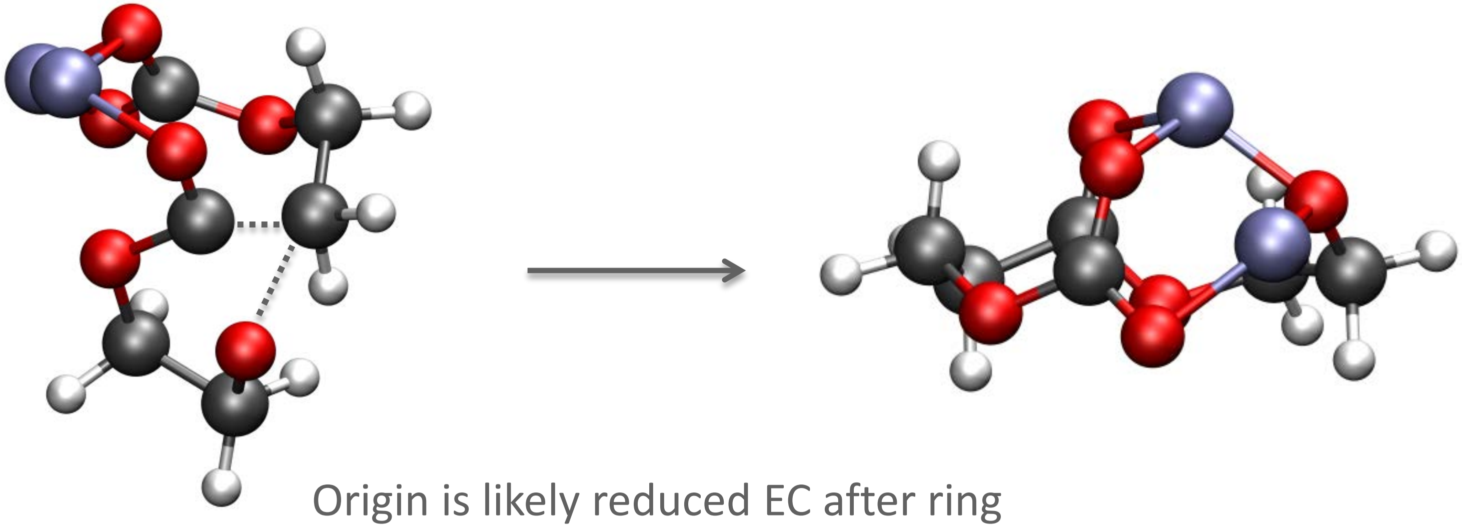
–70

Ester Carbonate is a possible minima

Energy is in between the butyl species and the ethyl species

Have not yet found a transition state

Origin of the Ester Carbonate



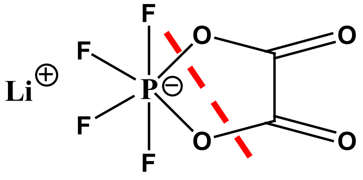
Origin is likely reduced EC after ring opening reacting with reduced EC that has not undergone ring opening

If the barrier is reasonable this species should be more strongly considered as a component of the outer SEI

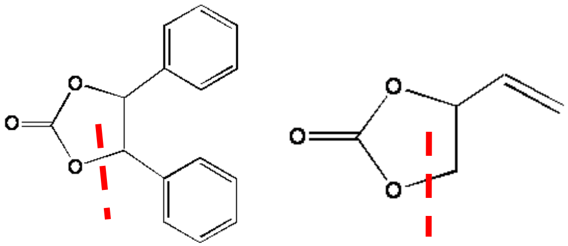
Other reactions of this type are still being investigated

Screening of reduction potentials of over 370 additive candidates

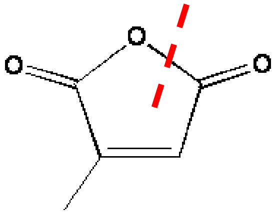
- **Some subsets of candidate molecules**



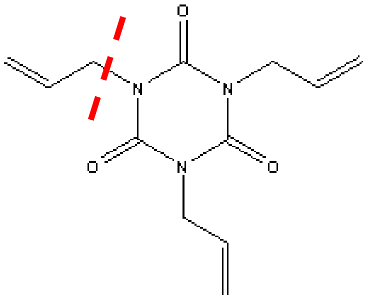
Oxalates (4)



Carbonates (52)



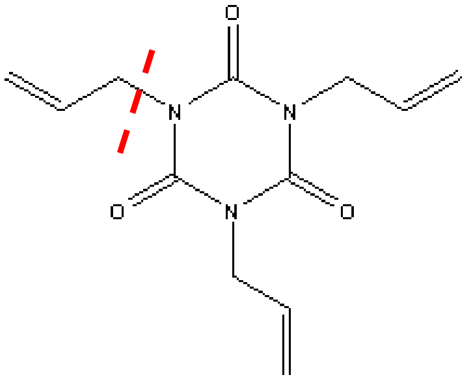
Anhydrides (19)

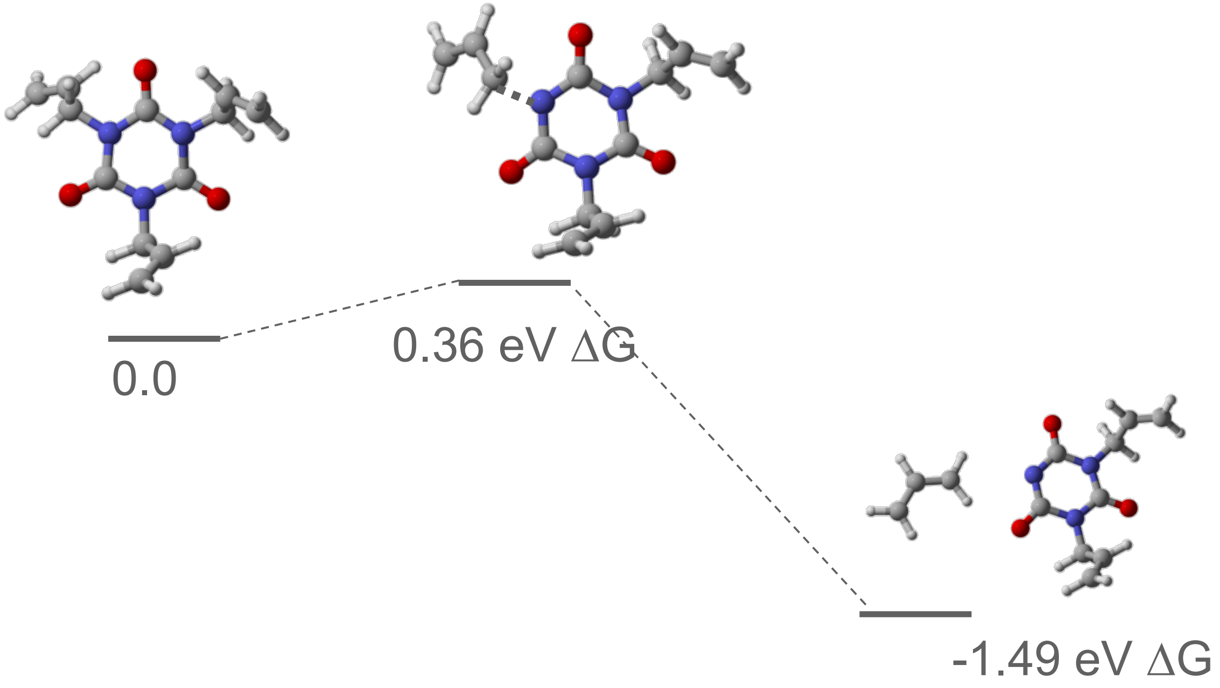


Allyl-substituted rings (2)

Allyl-substituted rings: Reduction of TTT (3,5-triallyl-[1,3,5]triazinane-2,4,6-trione) leads to decomposition that may lead to good SEI

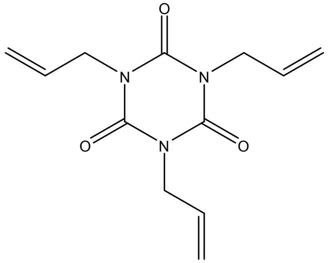
TTT ,3,5-triallyl-[1,3,5]triazinane-2,4,6-trione

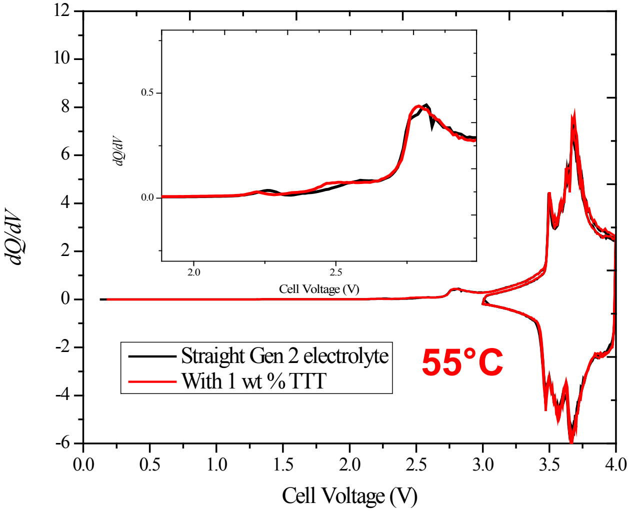




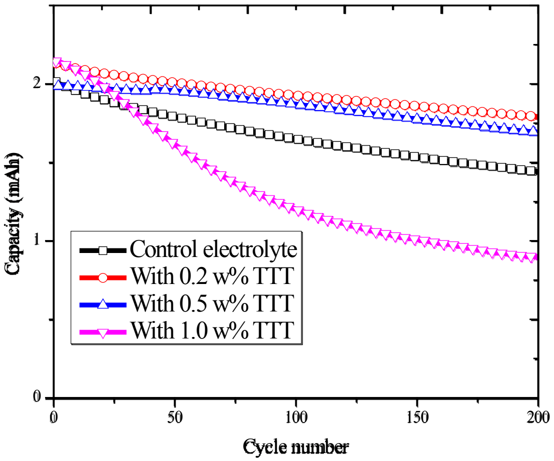
Upon reduction, the allyl radical detaches from TTT.
This allyl radical probably can react with other species in solution to form an SEI layer.
The pores of this SEI layer are likely to be large enough to allow Li^+ tranport.

Differential capacity profiles of TTT and Gen 2 electrolyte





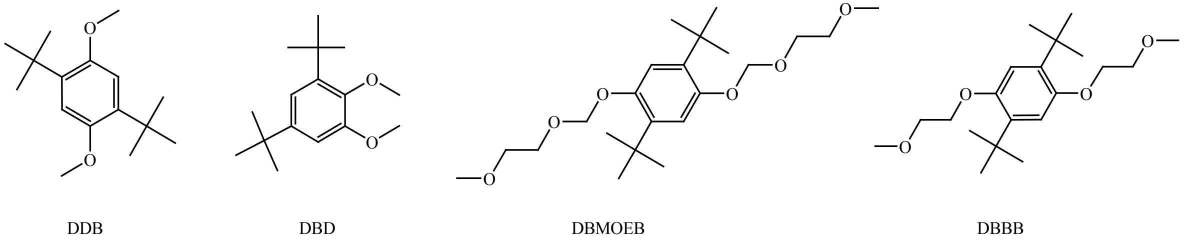
Diff. Capacity vs voltage of MCMB 1028/$Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]0.9O_2$ coin cells in 3E7EMC/PF12 with or without 1 wt% additives. The cells were cycled at 55 °C. The charge rate was C/10. The cut-off voltages were 3 ~ 4 V.



Capacity retention 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 1 wt% additives. The cells were cycled at 55 °C. The charge rate was 1C. The cut-off voltages were 3~4 V.

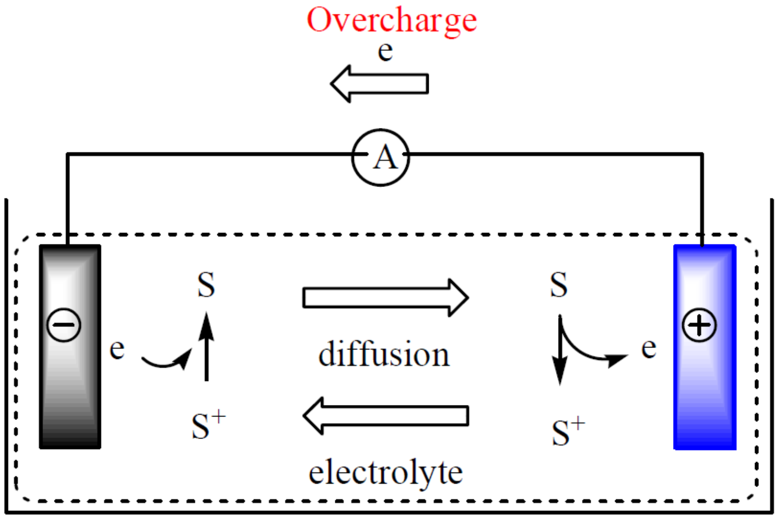
Dramatic improvements in capacity retention with 0.2 w% TTT.
Does not significantly increase the impedance of the cell system.
Favorable for high power applications of lithium-ion batteries.

2,5-di-*tert*-butyl-1,4-bis(2-methoxyethoxy)benzene (DBBB): a highly stable and compatible redox shuttle for overcharge protection



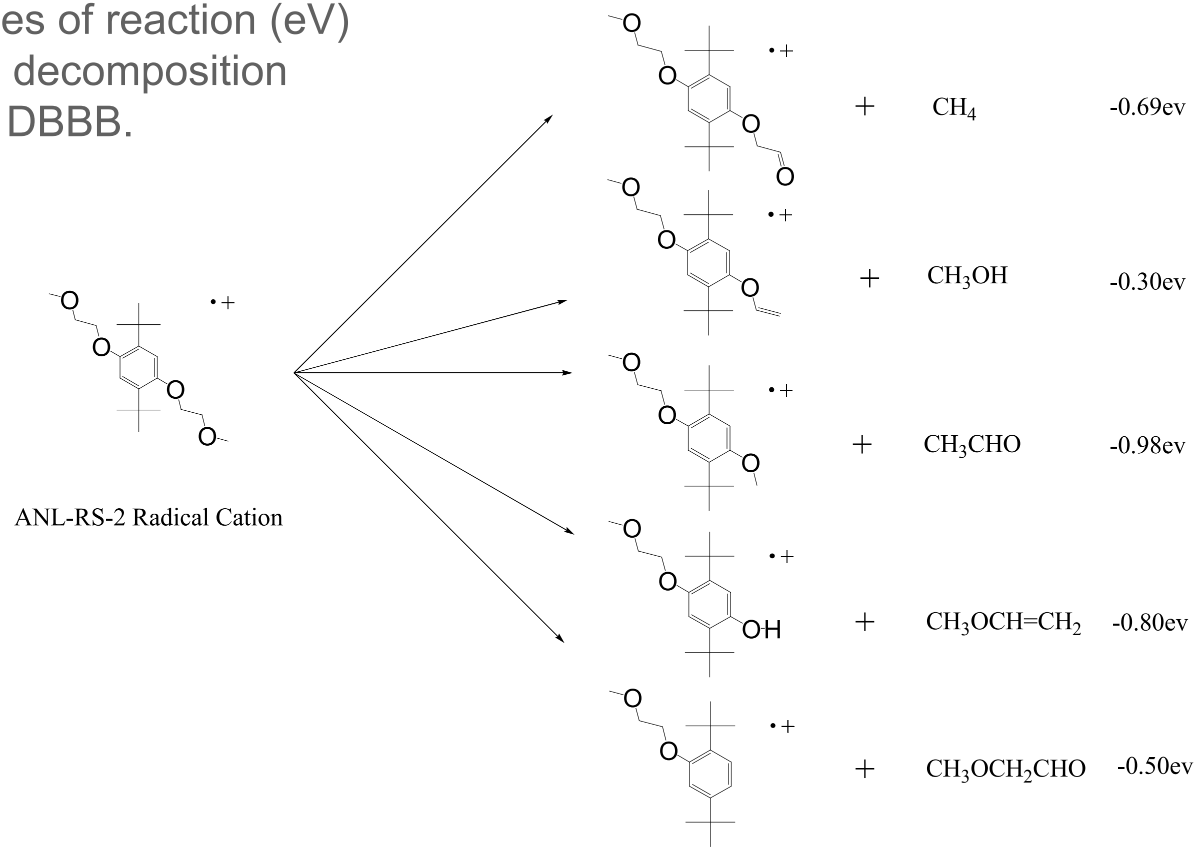
Chemical structures of some dimethoxybenzene based redox shuttles.

- **Density functional calculations were used to understand the properties of the DBBB as a redox shuttle**
  - **redox potential = 3.924 V**
  - **stability (next slide)**



DBBB – Decomposition pathways from theory

Free energies of reaction (eV) for possible decomposition products of DBBB.



ANL-RS-2 Radical Cation

+ CH_4 -0.69ev

+ CH_3OH -0.30ev

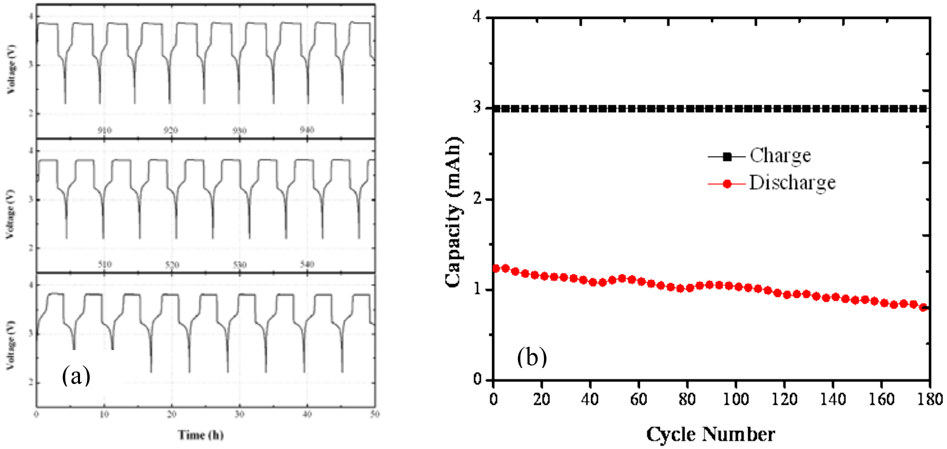
+ CH_3CHO -0.98ev

+ $CH_3OCH{=}CH_2$ -0.80ev

+ CH_3OCH_2CHO -0.50ev

- Five different decomposition reactions involving one methoxyethoxy arm of the DBBB cation were investigated.
- Barriers for these reactions are expected to be very large since they involve either hydrogen transfer over more than one bond or more complicated rearrangements.
- Thus, DBBB is likely to be quite stable as a redox shuttle molecule

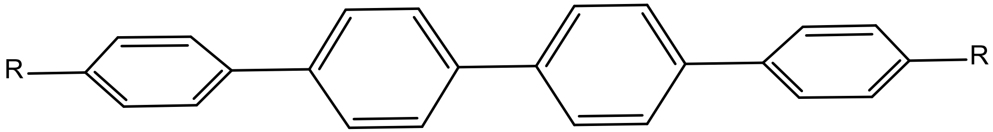
DBBB – experimental studies



(a) Voltage profiles of MCMB/LiFePO4 cells containing 0.1 M DBBB in Gen 2 electrolyte during the course of 0-960 h. charging rate is C/2 and overcharge ratio is 100%. (b) Capacity retention profiles of MCMB/ LiFePO4 and Li/LiFePO4 cells containing 0.4 M DBBB in Gen 2 electrolyte. Charging rate is C/2and overcharge ratio is 100%.

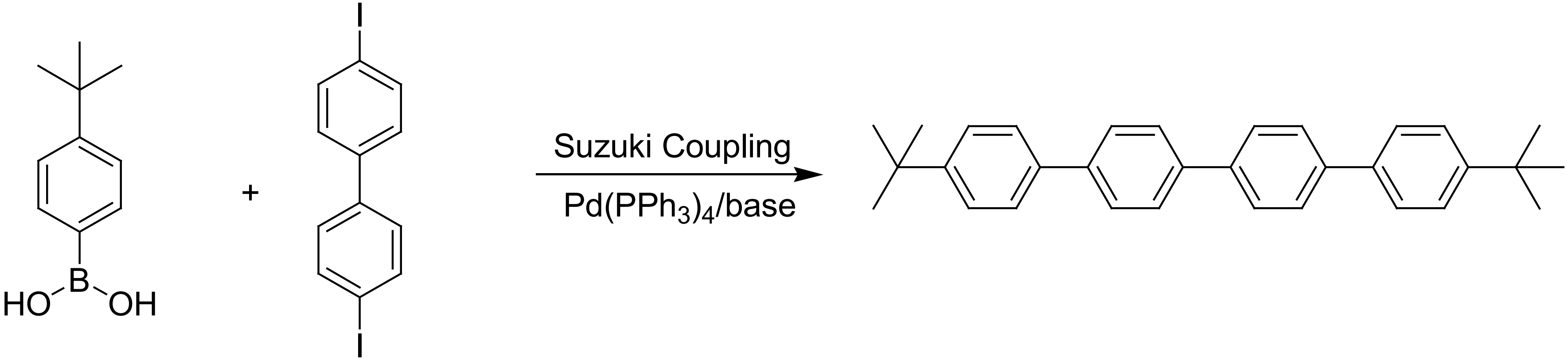
- DBBB displays reversible redox potential at 3.9 V, which close to theory
- Over 180 overcharge cycles can be achieved under C/2 rate and 100% overcharge ratio using 0.4M DBBB redox shuttle in Gen 2 electrolyte
- DBBB does not negatively impact the cell system.

Exploration of substituted quaterphenyls for redox shuttles



- A series substituted (R) quaterphenyls was examined theoretically
- The calculated free energy of solvation for R=t-butyl is -9.9 kcal/mol.
- The calculated oxidation potential for R=t-butyl is 4.05 V.

4PH (R=t-butyl) – synthesis and properties



- Advantages
  - Low Solubility in Gen2 Electrolyte
  - High Voltage (~4.6 V vs Li/Li^+)
  - Small charge and discharge voltage hysteresis (Reversible)
- Disadvantages
  - Low electronic conductivity (needs more conductive additive in Cell Fab)
  - Low specific discharge Capacity: ~64 mAh/g (due to high molar mass for 1e process)

Test 4PH as Redox Shuttle Molecule

- **4PH** not soluble in Gen-2 Electrolyte (<0.005 M), can not be directly used as electrolyte additive
- **4PH** dissolved in CHCl3, spin coated on cathode laminate
- 0.5 mg **4PH** can be deposited

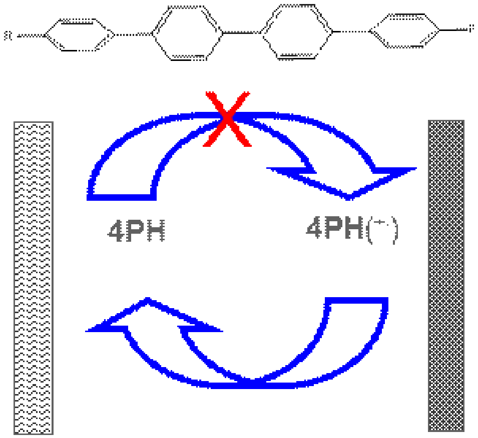
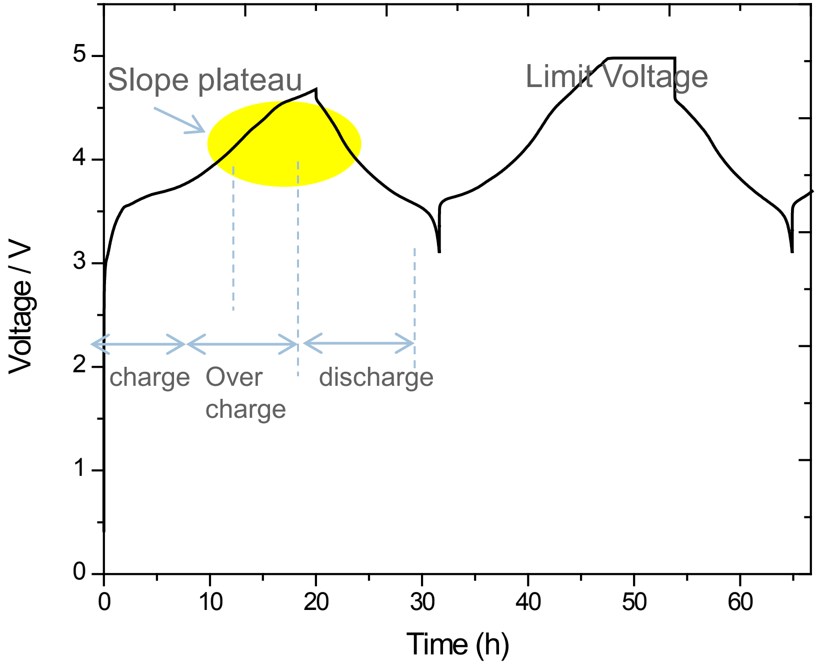


Illustration of redox failure mechanism for the t-butyl substituted quaterphenyl



- c/10 rate, 100% overcharge
- Overcharge plateau observed in 1st cycle
- **4PH** deposited on anode, can not cycle

Proposed Future Work

- Improved modeling of decomposition reaction pathways leading to SEI formation
    - Collaboration with Bedorov (Utah) and Borodin (Army)to integrate high level quantum chemical studies with larger scale methods for modeling SEI formation mechanisms
- Redox shuttles
    - Combined experimental theoretical studies to find new shuttles based on our extensive database
- Additives for SEI formation
    - Combined experimental theoretical studies to find new SEI additives based on our extensive database

Summary

- Exploration of new additives for SEI formation
  - Screening of over 370 candidate materials
  - Many new candidates identified from high level quantum chemical screening
  - Experimental testing
    - Example: **TTT (**3,5-triallyl-[1,3,5]triazinane-2,4,6-trione **) has confirmed its value as an additive**
- Exploration of new additives for redox shuttles
  - DBBB
    - Calculations of oxidation potential and stability
    - Experimental synthesis and testing has revealed that it has excellent properties as a redox shuttle
  - Quaterphenyls
    - Calculations of oxidation potentials and solubility products
    - Experimental synthesis and testing of the 4PH quaterphenyl has found it to fail due to formation of a coating
- Further quantum chemical modeling of ethylene carbonate decomposition pathways for simulations of SEI formation (with Bedrov, Utah)