

Electrolytes - Advanced Electrolyte and Electrolyte Additives

P.I.: K. Amine

Presenter: L. A. Curtiss

Argonne National Laboratory

DOE merit review

June 7th to 11th , 2010

Project ID# ES066

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

Overview

Timeline

- Start April 1, 2009
- Finish Sept. 30, 2014
- 20%

Budget

- Total project funding
 - DOE: \$300 K
- FY10
 - DOE: \$ 300 K

Barriers

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

Partners

- Interactions/ collaborations
 - K Gering, INL
 - N. Romaro, ANL-ALCF
 - Jeff Moore, UIC
- Project lead: K. Amine

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 the model, characterize them and carry out extensive cycle and calendar life test.



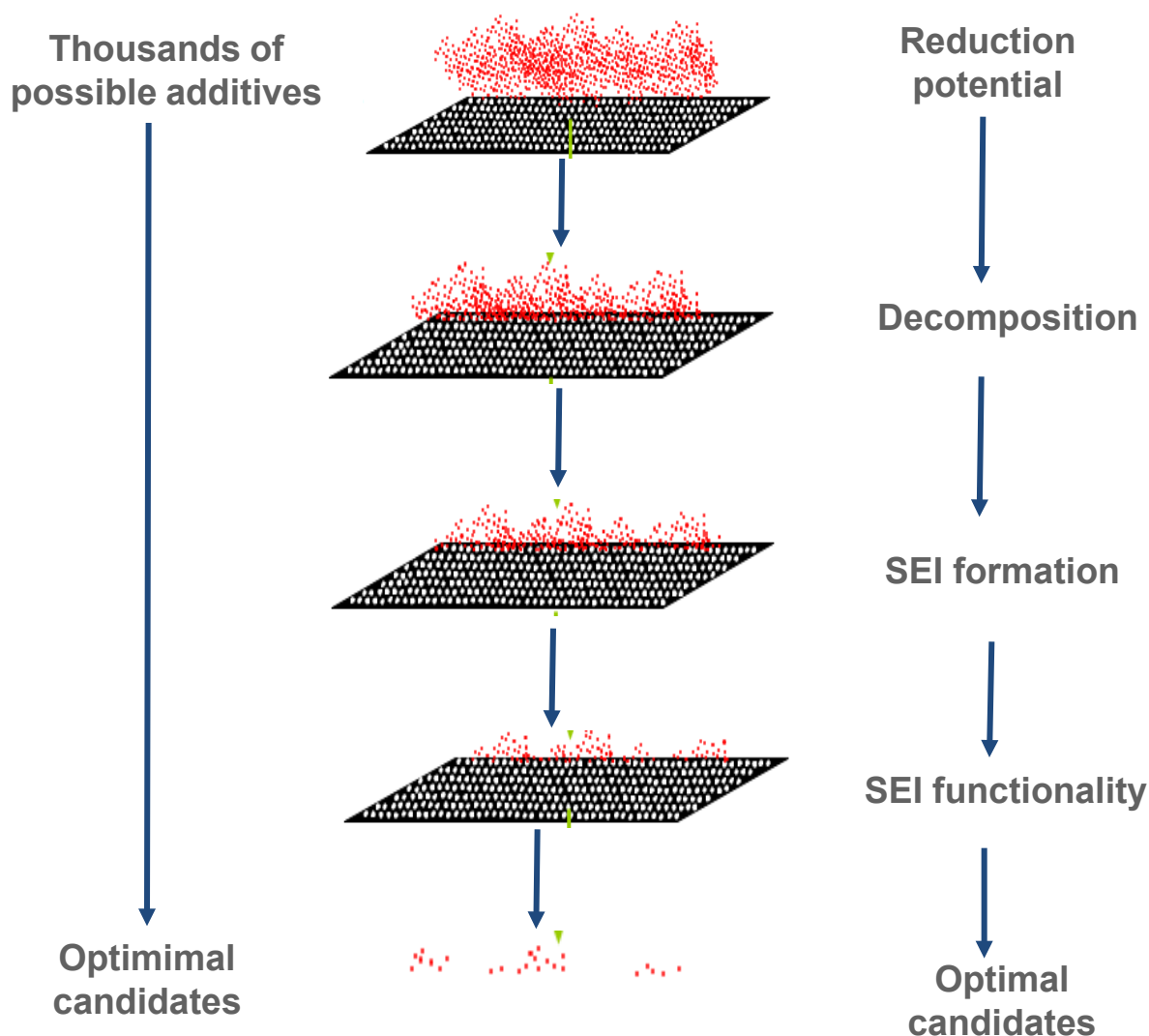
Milestones

- Screen over 100 candidate materials for reduction potentials. (Aug. 09) - delayed because work started in late April. (ongoing)
- Initiate investigation of reactions on electrode surface of decomposition products. (ongoing)
- Develop and optimize a quantum chemical model that helps identify new functional electrolyte additives. (Sep. 10)
- Develop quantum chemical models for polymerization pathways of electrolyte additives that can be used for screening. (Sep 10)
- Develop a model to predict the potential of redox shuttle to improve safety. (Sep. 10)

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/Strategies - Screening



Theoretical methods: highly accurate G4 methodology, and density functional theory for electron affinities, ionization potentials, and reaction energies, continuum model for solvation effects, periodic calculations, high performance computing including massively parallel codes

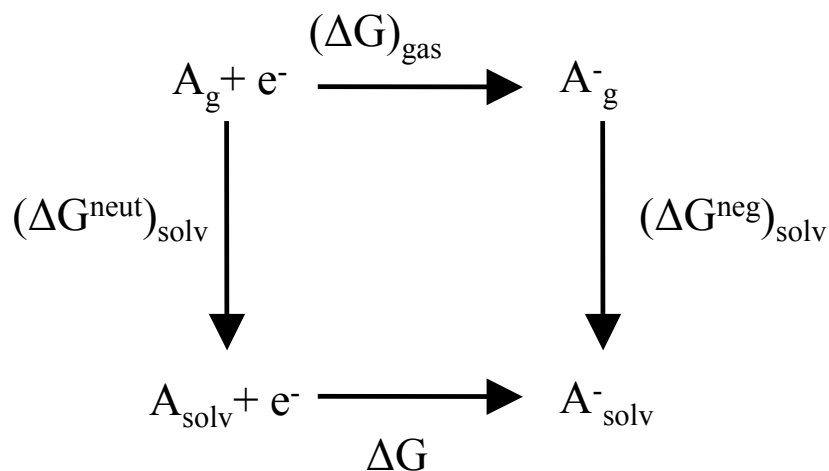
Exoerimental methods: cell testing, CVs, FTIR, NMR, X-ray crystallography, organic synthesis,

Accomplishments: improved method for calculation of reduction potentials

- Improvements to our method* for calculating reduction potentials have been made
 - Better geometries and zero point energies
 - New solvation models
 - Assessments of accuracy using high level G4 calculations

* Vollmer et al JECS 2004.

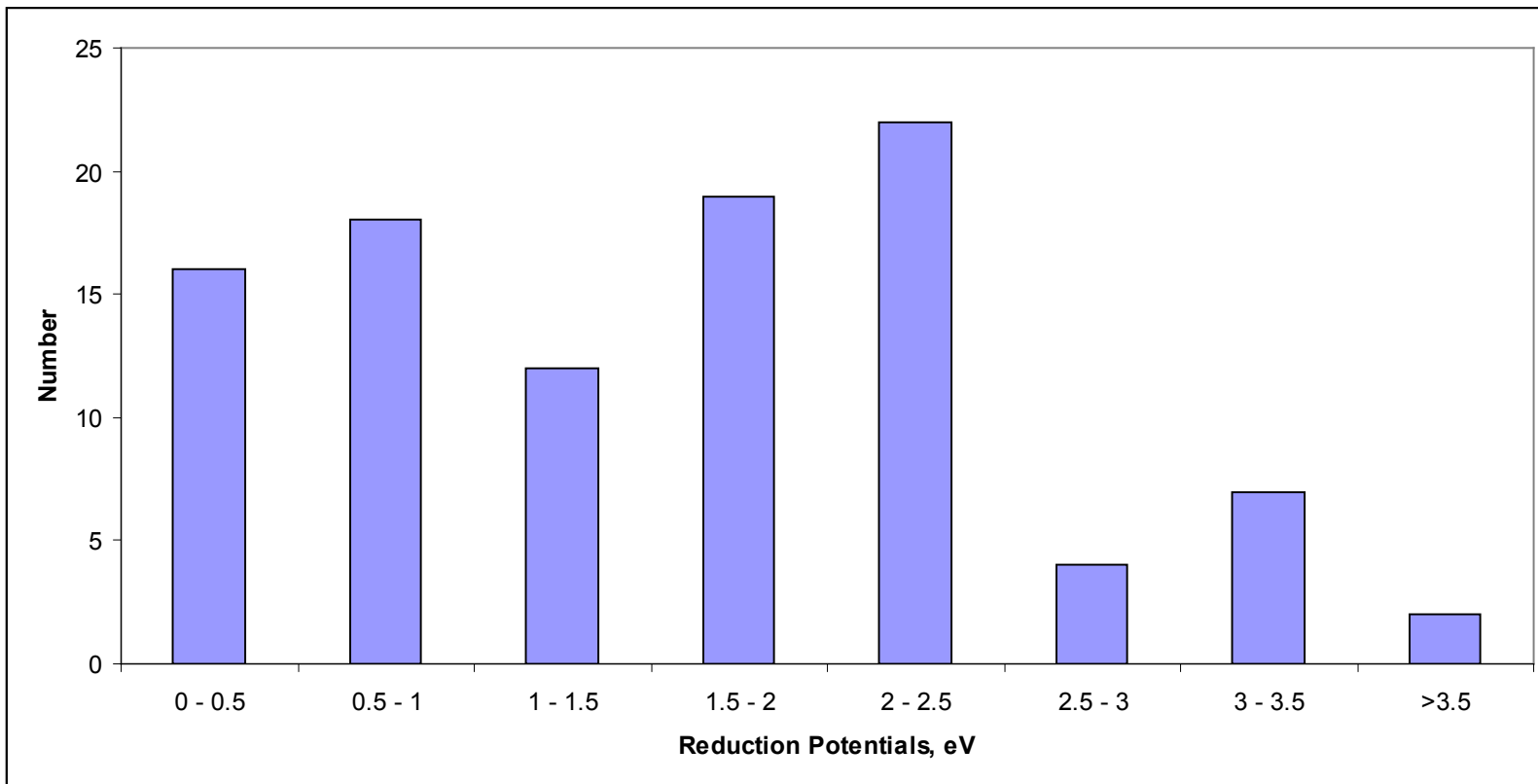
Thermodynamic Cycle Used to Calculate Reduction Potentials



$$\Delta G = (\Delta G)_{\text{gas}} + (\Delta G^{\text{neg}})_{\text{solv}} - (\Delta G^{\text{neut}})_{\text{solv}}$$

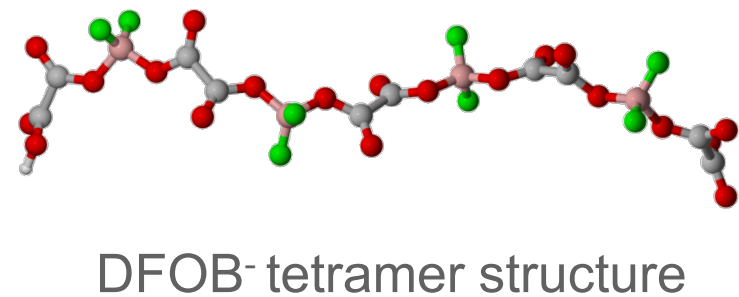
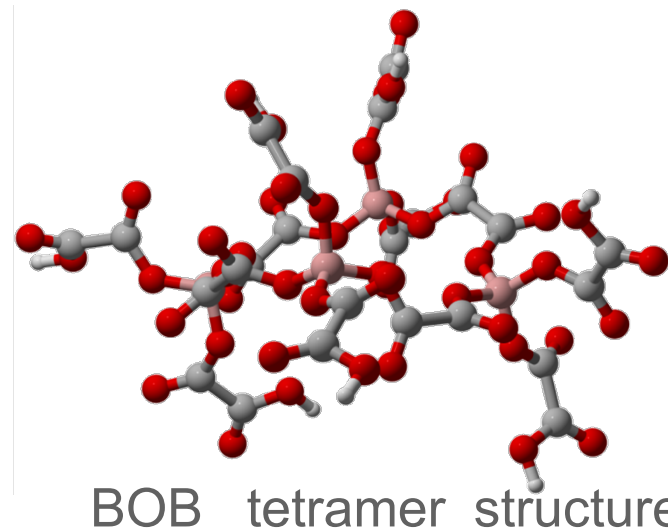
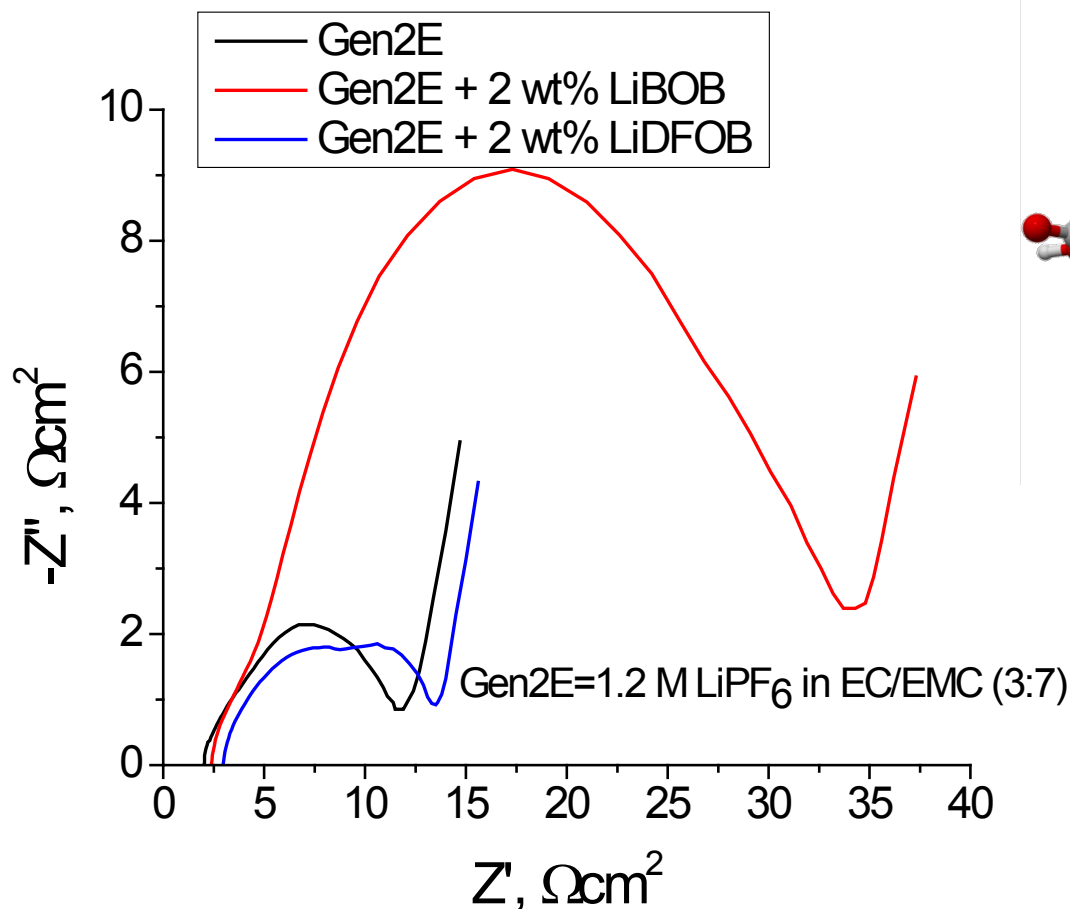
Accomplishment: screening of reduction potentials of over 100 additive candidates

- Bar chart shows the distribution of the reduction potentials relative Li electrode of more than 100 candidate additives; data is stored in a database



- More than 60% of the candidate additives have favorable reduction potentials of greater than 1 eV and are being considered in further screening for decomposition/polymerization reactions

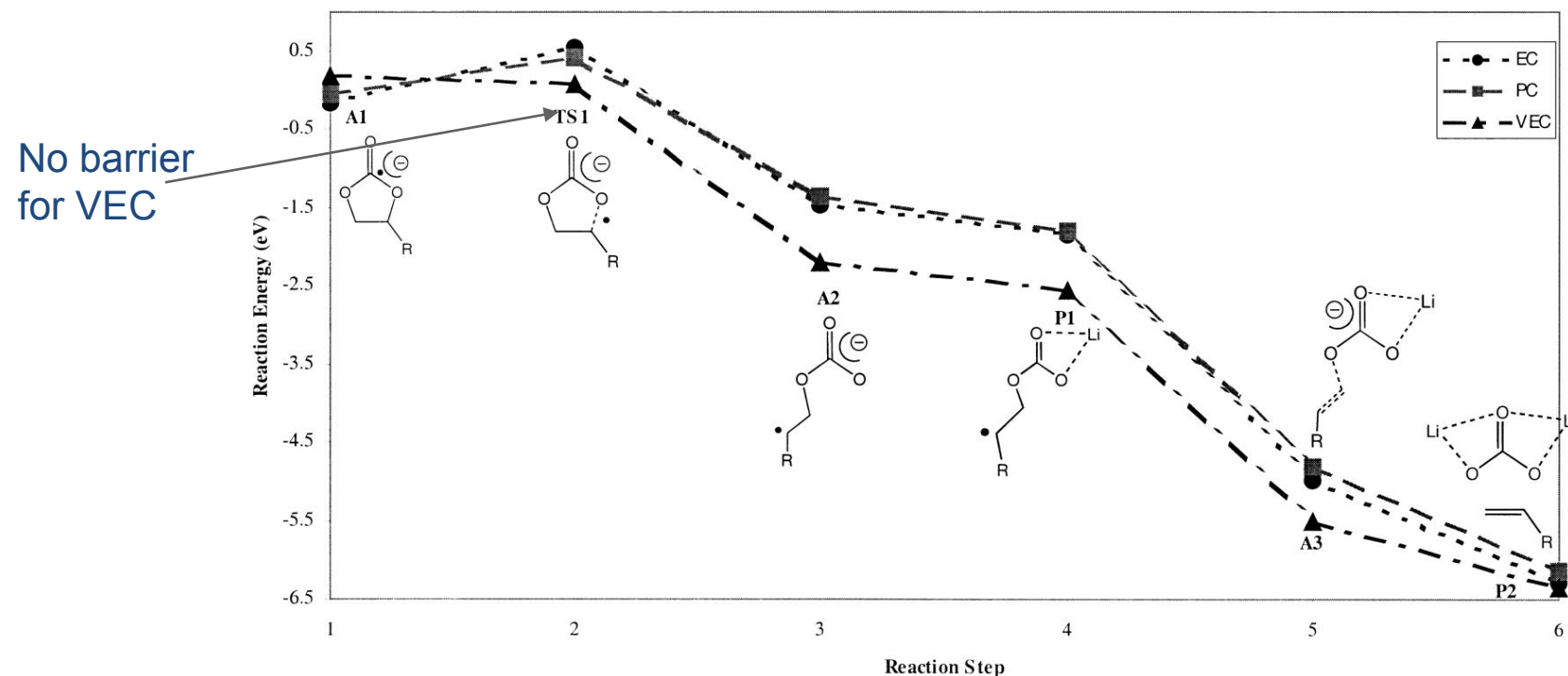
Accomplishment: understanding the reason for the large difference in impedance of SEI films formed from polymerization of LiBOB and LiDFOB



- Density functional calculations show that fluorine termination prevents 3-D polymeric structure growth. This explains the low observed impedance for LiDFOB compared LiBOB

Accomplishment: 2nd level screening for decomposition to lithium carbonate

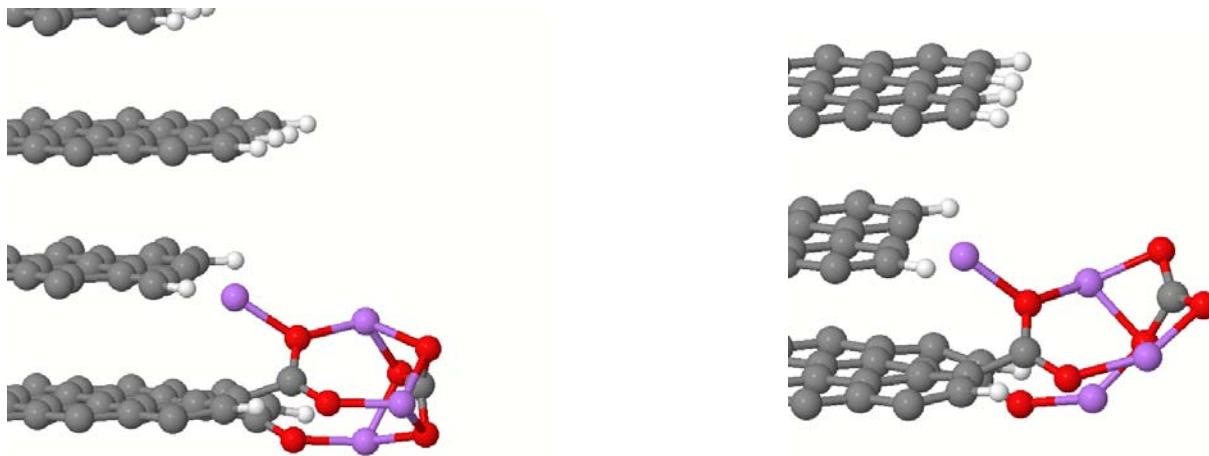
- The candidates from the 1st level screening were screened for their reaction barriers to decomposition to form Li_2CO_3 to find candidates with properties similar to that found for vinyl ethylene carbonate, which forms good SEI films (Vollmer et al, JECS 2004)



- The screening process identified nine candidate fitting the criteria and 4 of these surpassed the criteria. These will be tested in future work.

Accomplishment: initiated investigation of reactions on electrode surface of decomposition products

- The initial reactions of Li_2CO_3 on the edge surface of graphite was investigated. Many different configurations of monomers and dimers have been investigated. Two are shown below.



- Defect sites (missing hydrogens) on the graphite edges are very reactive towards Li_2CO_3 and are likely nucleation sites for lithium carbonate SEI growth.

Collaboration/Interactions

- Dr. Kevin Gering, INL
 - Collaborations on modeling of properties of electrolytes
- Prof. Jeffrey Moore, University of Illinois
 - Synthesis and testing of shuttles for overcharge protection
- Prof. Dana Dlott, University of Illinois
 - Spectroscopic characterization of SEI growth on graphite
- Prof. Michael Bedszk, Northwestern University
 - X-ray characterization of SEI growth on graphite
- Dr. Nichols Romero, Argonne Leadership Computing Facility
 - Codes for highly parallel computer clusters

Proposed Future Work

- The screening will be continued. We will expand our database to more than 200 candidate materials with inclusion of decomposition and polymerization in the screening as well as reduction potentials
- The reaction mechanisms of SEI growth on anode surfaces from decomposition products will be investigated for incorporation into our quantum chemical screening model.
- We will develop a quantum chemical model to screen for redox shuttle to improve safety.
- Experimental studies will be carried out to assess additive candidates for SEI formation as well as shuttles.



Summary

- An improved quantum chemical model for the calculation of reduction potentials has been tested and used in the screening of over 100 candidate materials.
- Further screening based on decomposition pathways has identified 9 new promising candidate additives for testing by experiment and our calculations have also provided insight into polymerization of additives found in experiments.
- Density functional studies are being used to provide new insight into formation at the molecular level of lithium carbonate SEI films.

