Perfluoro Aryl Boronic Esters as Chemical Shuttle Additives

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Project ID: ES107

Overview

Timeline

- Project start date 10/01/2009
- Project end date 3/21/2013
- Percent completed 20%

Budget

- Total project funding
  - DOE share: $ 2,565,912
  - EnerDel share: $ 3,158,408
  - FFDRC share: $ 900,000
- Federal funding received:
  - FY10 $ 320,063
  - FY11 $ 1,029,409 (planned)

Barriers

- Barriers addressed
  - D. Abuse Tolerance, Reliability and Ruggedness
  - A. Cost
  - E. Life
- Technical Target
  - to employ a redox shuttle molecule in a large format Li ion cell

Partners

- Argonne National Laboratory
- Purdue University Birck Nanotechnology Center
- Project Lead: EnerDel, Inc.

Relevance: Safety, Life, Cost

- Overcharge could be a safety hazard
  - Instability of cathode and anode due to overcharge can result in a thermal event
- Overcharge reduces the lifetime of Li ion batteries
  - Cathode materials degrade irreversibly when overcharged
  - Lithium dendrites can form at the anode when overcharge outside the design specifications occurs
- Overcharge protection is provided by the battery management system (BMS)
  - Electronics add weight, volume, and cost to the pack
- Redox shuttle compounds could eventually replace or reduce the role of the BMS

Relevance: Redox Shuttle Additives

- Redox shuttle (RS) compounds have a reduction-oxidation reaction at the potential where overvoltage protection is desired
- When this overpotential voltage is reached during cell charging, the extra charge is used to oxidize the RS additive at the positive electrode instead of further charging the cell; the cell voltage is pegged
- The oxidized form of the redox shuttle additive migrates to the anode, where it is reduced
- This process could occur indefinitely for a species that exhibits completely reversible electrochemical behavior and has chemically stable oxidized and reduced forms

Relevance: Objectives

- To make lithium ion batteries more robust, lighter, smaller, and less costly
- To confirm shuttle behavior using abuse testing
- To understand the mechanism of loss of overcharge protection using analytical characterization techniques
- To understand the mechanism of reduction of the oxidized redox shuttle molecule at the anode
- To use this information to choose the redox shuttle molecule and optimize its performance in cells
- To scale up from coin cells to packs
- Milestone FY10: test the initial candidate molecules
- Milestone FY11: identify redox shuttle(s) for scale up

Approach: Challenges/Concerns

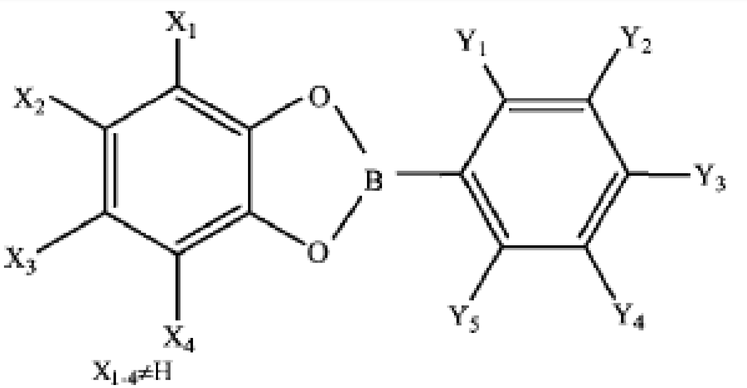
Challenge/Concern	Approach
Electrochemical reversibility at desired E_0	Theoretical molecular orbital calculations (ANL); confirm using cyclic voltammetry
Chemical and electrochemical stability in voltage window of cell	Confirm using cyclic voltammetry and cell testing
Negative effect on performance	Check formation, charge and discharge rate, cycling, power, high and low temperature performance, self-discharge
Current density limitation	Since I_{max} /A= nCDF/L, use a concentrated solution of redox shuttle, maximize the diffusion coefficient, maximize number of charges on oxidized molecule, minimize distance between electrodes
Heat generation	Take advantage of cooling system in vehicle

Challenges/Concerns from J. Dahn, J. Jian, L. Mosherchak, C. Buhrmester, and R.L. Wang, Electrochemical Society Interface, Winter 2005, pp 27-31.

Approach: Perfluoro Aryl Boronic Esters

- Class of redox shuttle agents
- A fluorinated 1,3,2-benzodioxaborole (BDB)
- Redox voltage is about 4.43 V
- Good redox shuttle candidate for NMC cathodes which operate at 4.1 to 4.2 V
- Patented by Argonne National Laboratories

Zonghai Chen, Qingzheng Wang, K. Amine, "Understanding the Stability of Aromatic Redox Shuttles for Overcharge Protection of Lithium-Ion Cells," *Journal of the Electrochemical Society*, **153** (12) A2215-A2219(2006).

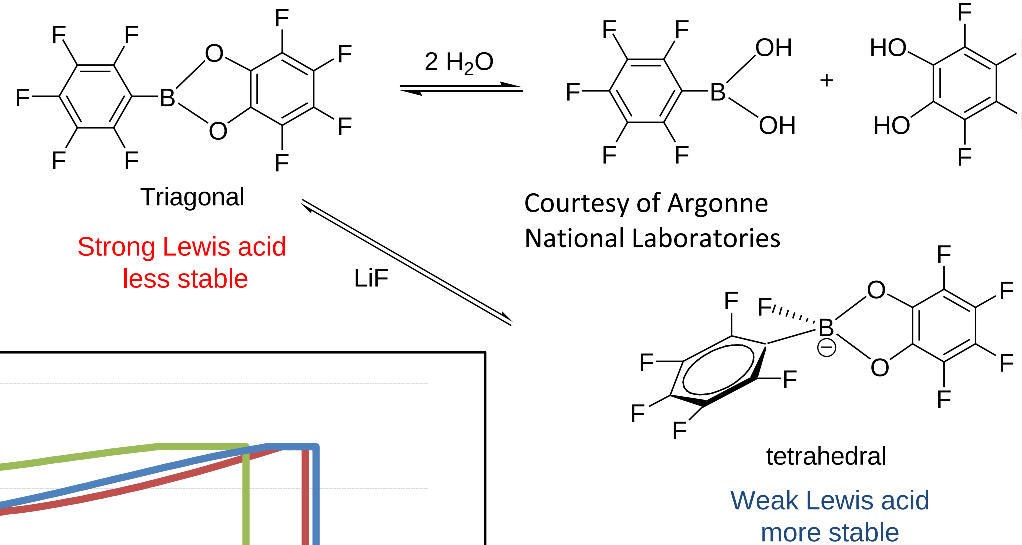


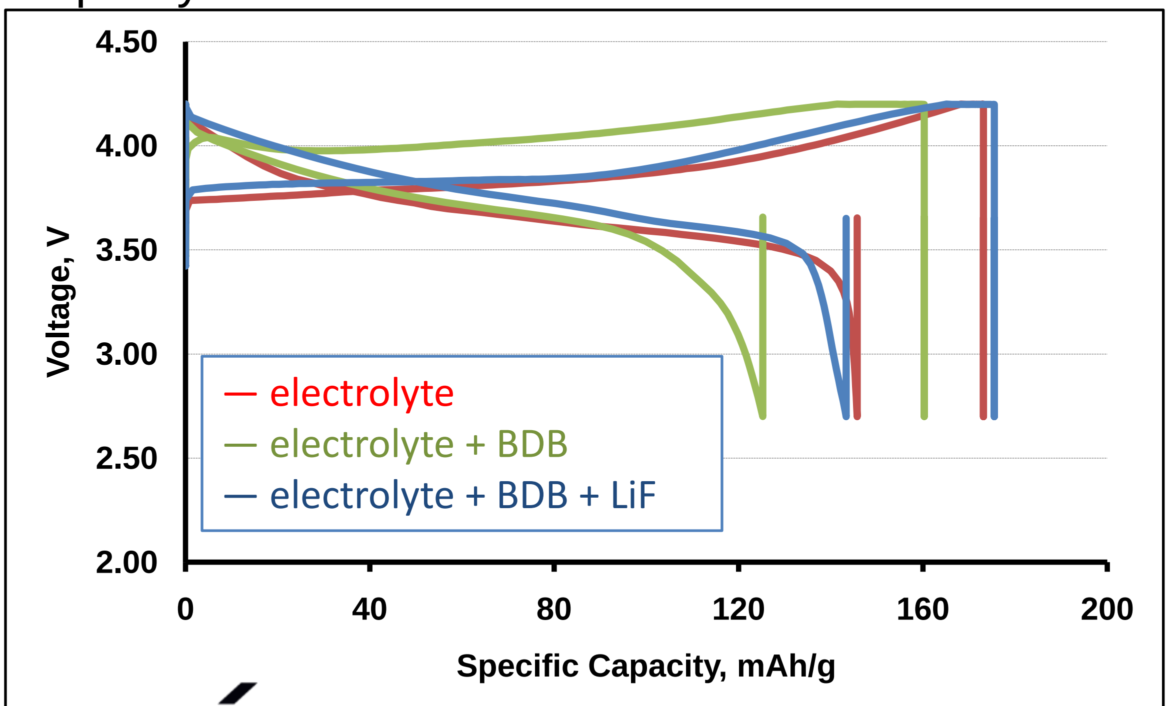
Approach: Test Methodology

Test	Method
Confirmation of E_0, diffusion coefficient, and electrochemical stability	Cyclic voltammetry of RS molecule in electrolyte using Pt electrode
Performance in R&D half cells (cathode or anode material vs. Li metal)	Determine initial, reversible, and irreversible specific capacity with and without the RS molecule
Performance in R&D full cells (about 5 to 50 mAh capacity)	Determine charge and discharge rate capability and cycle life; high and low temperature; storage; overcharge
Performance in larger cells (about 1 to 20 Ah)	Formation, cycle life, and power testing; storage; self-discharge; high and low temperature
Abuse testing in larger cells (about 1 to 20 Ah)	Overcharge testing

Technical: LiF Stabilizes BDB

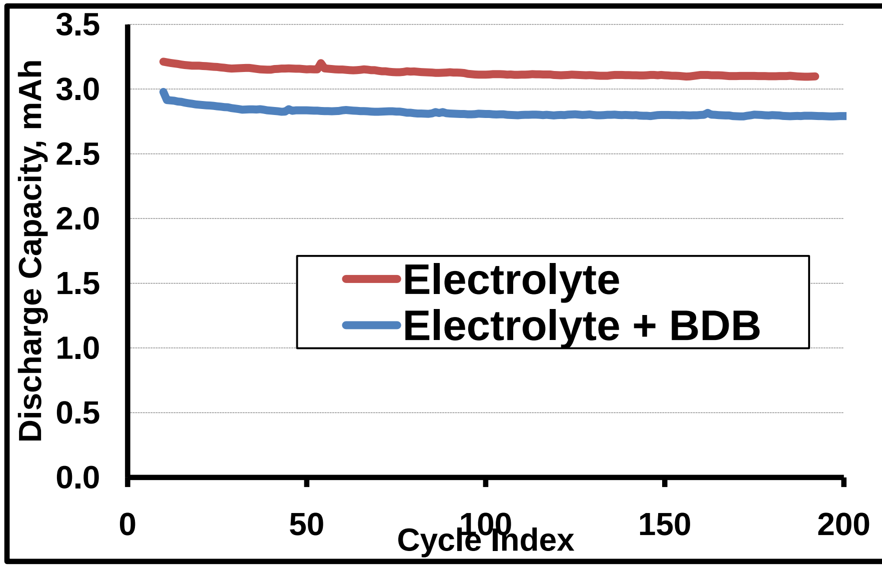
- NMC half cell results
- The presence of BDB resulted in lower initial and reversible specific capacity and higher irreversible capacity

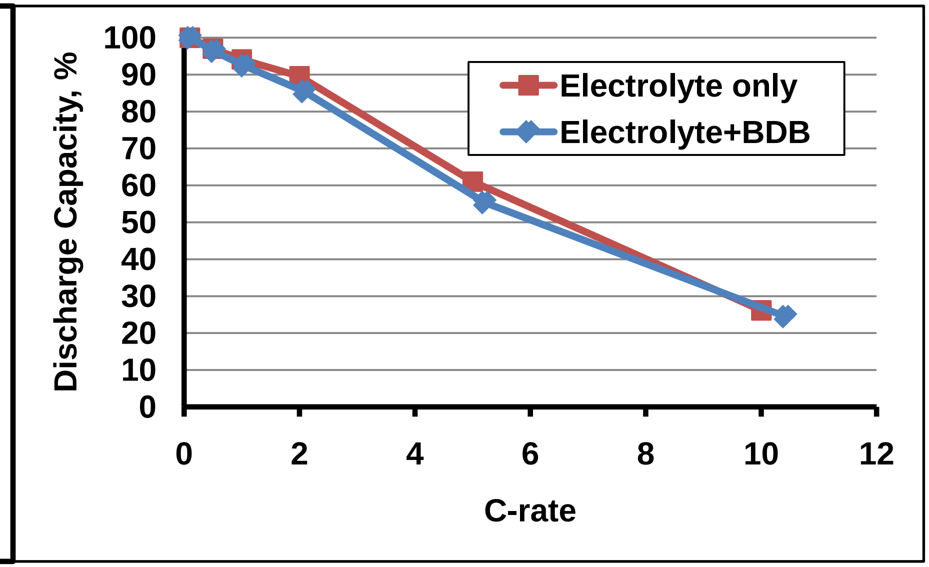




- The addition of LiF stabilizes the BDB
- Half cell results for NMC material are improved with the addition of LiF

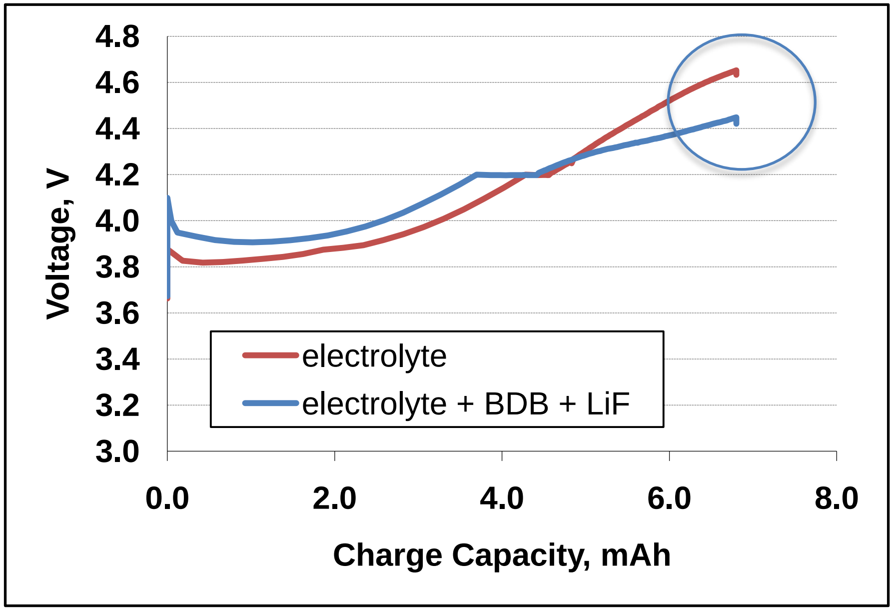
Technical: BDB Effect on Cell

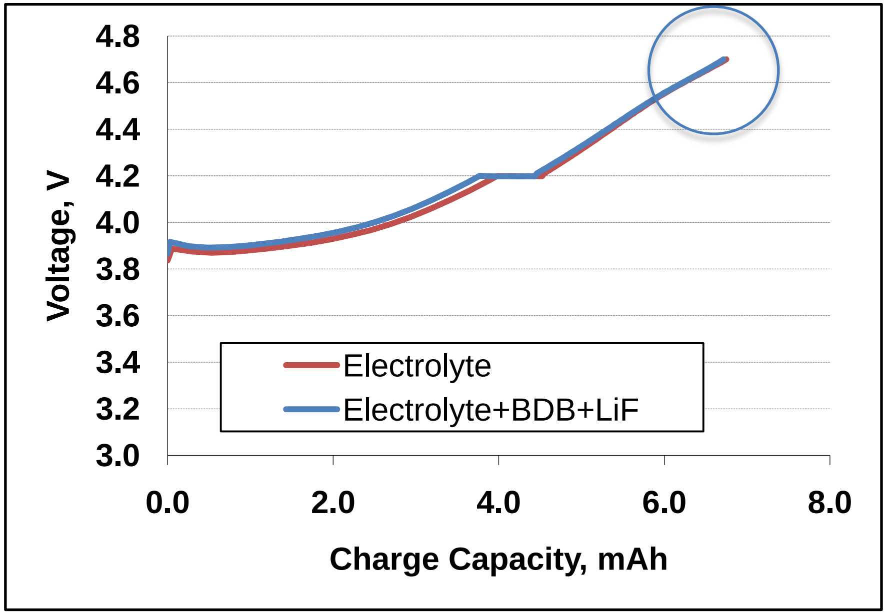




- This data was generated for full cells with NMC cathodes and hard carbon anodes
- The presence of BDB does not affect the cycleability but does decrease the capacity
- The presence of BDB does not affect the discharge rate capability

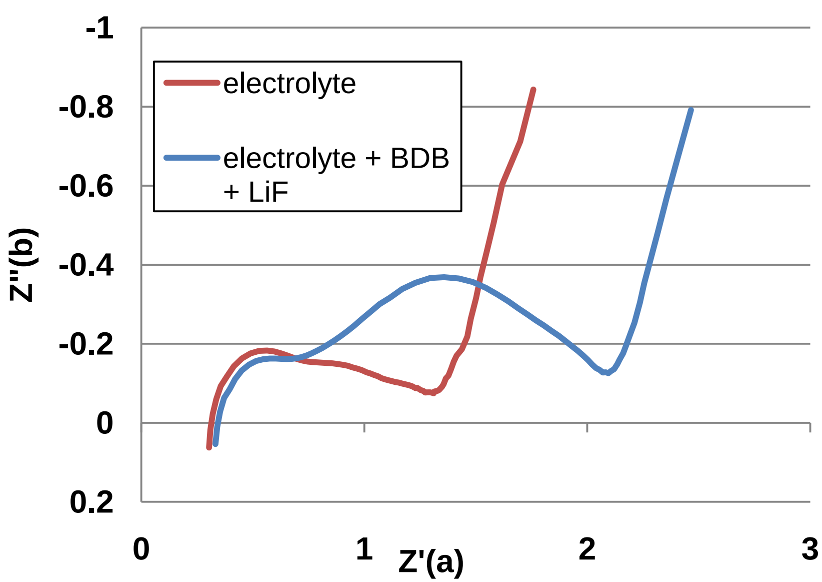
Technical: Overcharge (BDB)

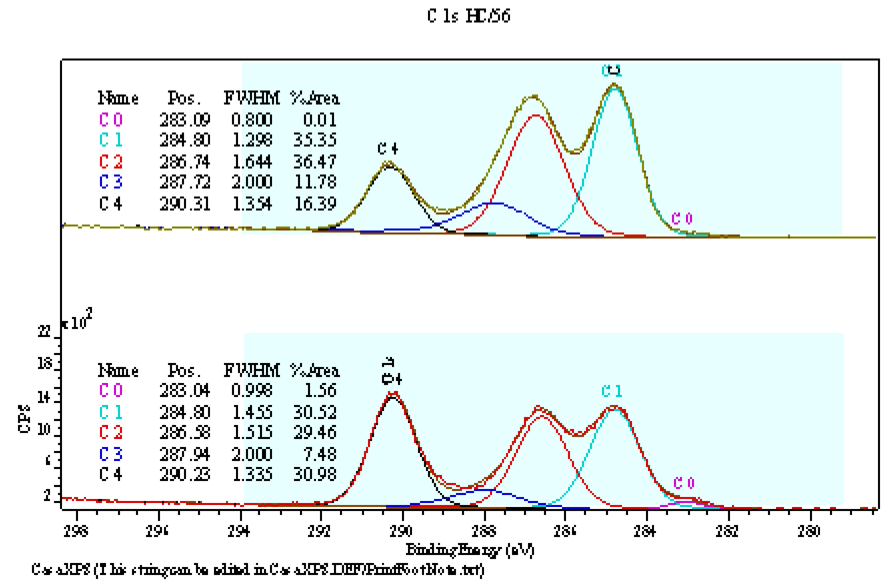




- Full cells NMC – hard carbon charged at 1C to 4.2 V then 0.1C to 4.7 V or 150% state of charge, whichever occurred first
- The BDB provided overcharge protection on the 1st cycle (left), but the protection was gone on subsequent cycles (right)
- The BDB did not exhibit the stability needed for many overcharge cycles, even with the addition of the LiF

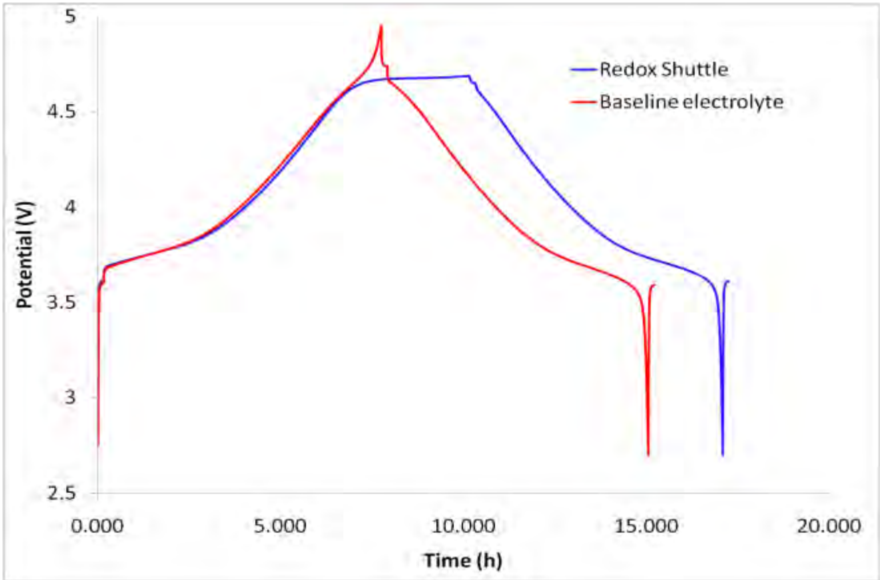
Technical: Effect on SEI Layer

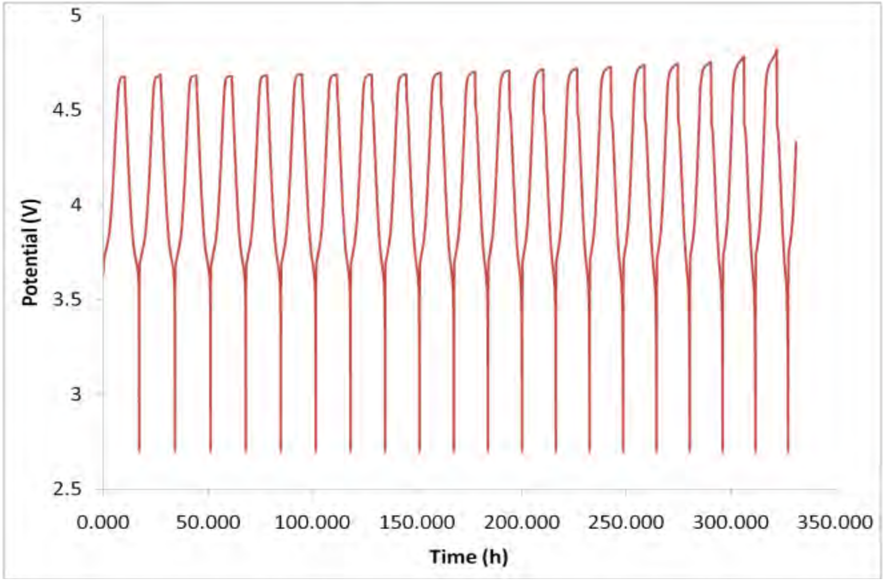




- Electrochemical impedance spectroscopy (left) and X-ray photoelectron spectroscopy (right) both show that the SEI layer is changed when formation occurs in the presence of the BDB redox shuttle molecule
- The SEI layer has a higher impedance in the presence of BDB (EIS data)
- The SEI layer components have different chemical states in the presence of BDB (carbon region, top spectrum is electrolyte + BDB, bottom is electrolyte only)

Technical: Overcharge ($Li_2B_{12}F_{12}$)

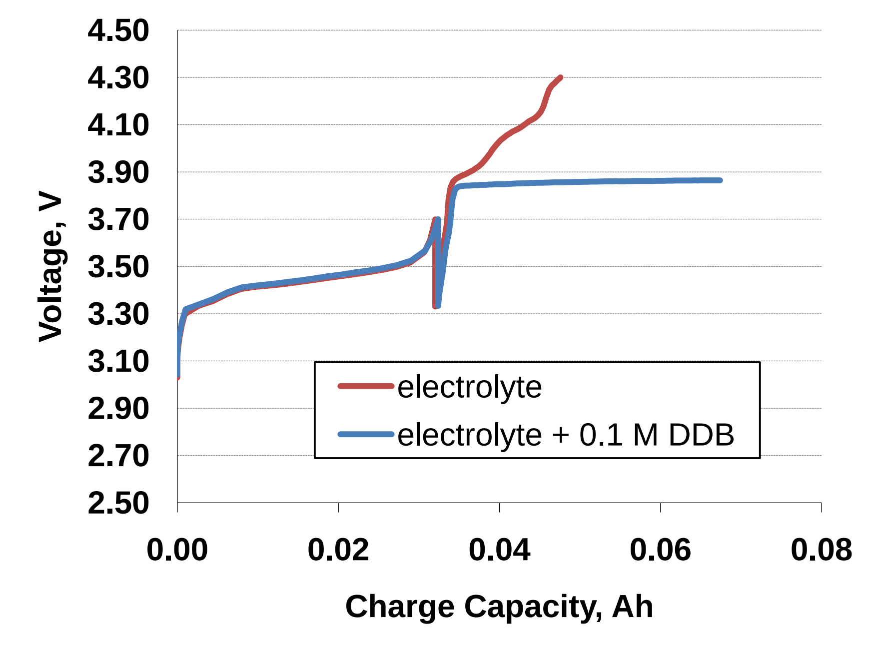


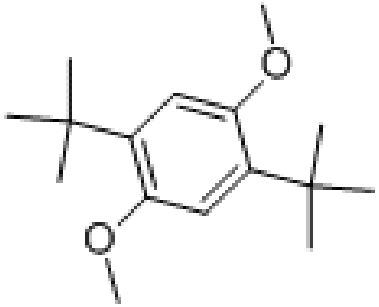


- NMC half cell testing with redox shuttle $Li_2B_{12}F_{12}$ (LBF) which has an E_0 of about 4.7 V, which is a little high to protect NMC cathode materials
- This data shows that the 0.1 M LBF is fairly stable
- Potential vs. time (left) shows the clamping at 4.7 V provided by the LBF
- Cycling data (right) shows that LBF is effective for about 20 cycles before the voltage starts increasing upon overcharge

Technical: Overcharge (DDB)

- 2,5-Di-tert-butyl-1,3-dimethoxy-benzene (DDB) is a well-known, well-characterized redox shuttle compound
- Its E_0 of about 3.9 V is too low for NMC cathodes but well-suited for LFP cathodes



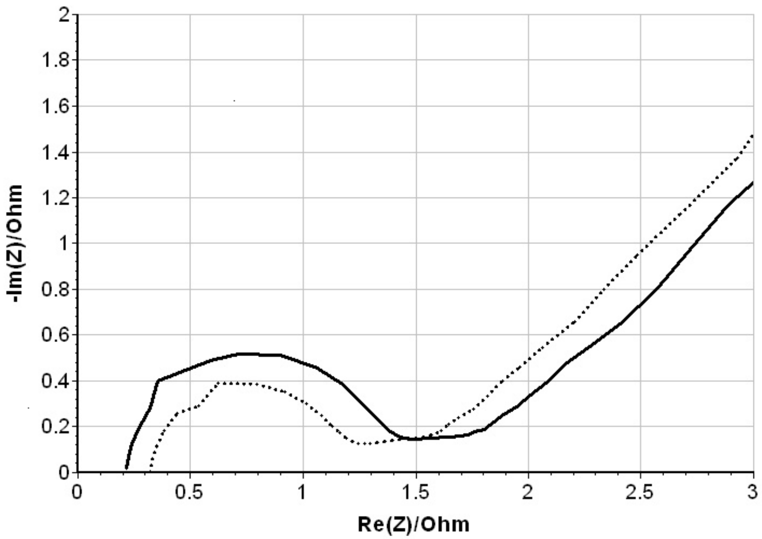


- NMC – graphite full cell overcharge behavior
- Note that the voltage is pegged at about 3.85 V
- The charge rate to 3.7 V was 1C and the overcharge rate to 4.3 V or 200% state of charge was 0.2 C

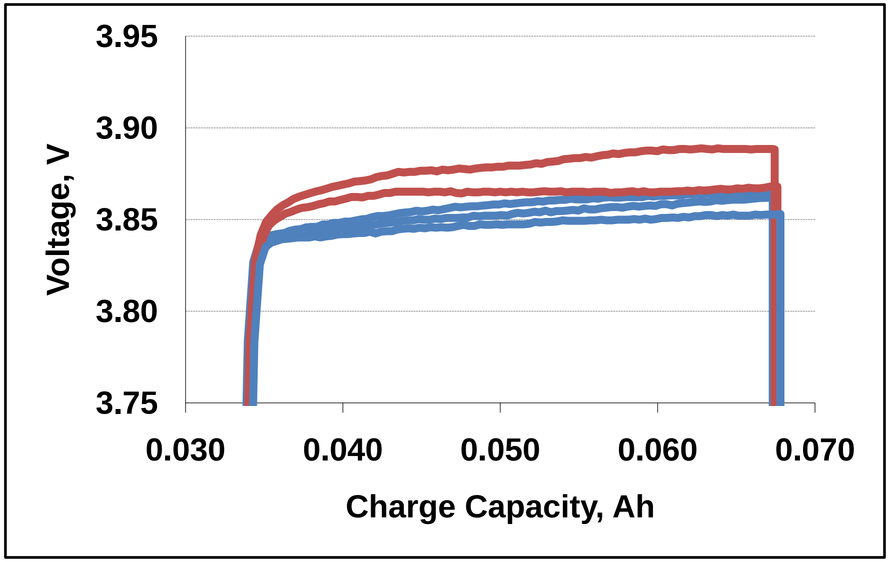
Technical – Molecular Imprinting

- How are redox shuttle molecules reduced at a carbon anode when it is covered by the SEI layer, which is supposed to be insulating?
- Molecular imprinting (MI) may explain the mechanism
  - MI occurs when polymerization occurs in the presence of a molecule
  - The resulting polymer film has enhanced recognition and transport properties toward that molecule due to shape and electrostatic recognition
  - SEI films have the correct thickness (40 to 100 nm) to exhibit this phenomenon
  - Heavily crosslinked films have better MI properties (like VC)
  - MI is used for sensors, chromatography, etc. and there is a large body of experimental and theoretical work available

Technical - Molecular Imprinting



EIS spectra for LFP-graphite cells. Solid line: formed in the presence of DDB. Dotted line: formed in the absence of DDB.



Overcharge voltage profiles for LFP-graphite cells. Blue: formed in the presence of DDB. Red: formed in the absence of DDB.

- The EIS spectra show that the impedance of the SEI layer is increased by the presence of DDB during formation
- When overcharged, cells formed in the presence of DDB have a lower voltage than those formed in the absence of DDB

➢Electrolyte is 1.2 M $LiPF_6$, 30:70 EC:DEC, and 0.1 M DDB (2,5-di-tert-butyl-1,3-dimethoxybenzene).

Collaborations

- Argonne National Laboratory (federal)
  - Dr. Khalil Amine
  - Dr. Zonghai Chen
  - Dr. Wei Weng
  - Dr. Zhengcheng (John) Zhang
  - design and synthesis of redox shuttle compounds

Argonne NATIONAL LABORATORY

- Purdue University Birck Nanotechnology Center (academic)
  - Dr. Dmitry Zemlyanov
  - XPS data acquisition and interpretation

PURDUE UNIVERSITY

Proposed Future Work

- Pursue new redox shuttle molecules
  - inorganic
  - organic
- Test new redox shuttle molecules from ANL
- Test redox shuttle molecules against NMC and other cathodes, such as NCA or LFP
- Characterize how the SEI layer on the anode and cathode changes in the presence of the redox shuttle molecules
- Complete molecular imprinting study
- When promising redox shuttle molecules are identified, test and scale up

Summary

- Relevance: Redox shuttles can improve the robustness of lithium ion batteries while making them smaller, lighter, and less costly
- Approach: We are evaluating redox shuttle molecules using electrochemical and cell testing methods
- Technical Accomplishments: We have evaluated three redox shuttle molecules; this work resulted in one peer-reviewed publication and one conference presentation
- Collaborations: We are collaborating with partners Argonne National Laboratory and the Birck Nanotechnology Center at Purdue University
- Future work: We are seeking a robust organic or inorganic redox shuttle molecule suited for 4.2 V cathodes and also are performing fundamental mechanistic studies on redox shuttle molecules