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Development of Electrolytes for Lithium-ion Batteries

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Project ID # ES067

Overview

Timeline

- 04/01/2009
- 12/31/2014
- 85 Percent complete

Barriers

- Barriers addressed
  - (Calendar Life (40 ^{o}C for 15 years)
  - Cycle life (5000 cycles)
  - Abuse Tolerance -Survival Temp Range (-46 to 66 ^{o}C)
  - Performance – Increased Energy Density

Budget

- Total project funding
  - DOE share $731 K
- Funding received in FY13 - $147 K
- Funding for FY14 - $0 K (No-Cost Extension)

Partners

- A. Garsuch (BASF)
- HV Spinel Focus group (LBNL-BATT)
- Silicon Focus group (LBNL-BATT)
- F. Puglia & B. Ravdel (Yardney)
- D. Abraham (ANL)
- M. Smart (NASA JPL)
- V. Battaglia (LBNL)

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Objective / Relevance

Develop novel electrolytes for lithium ion batteries that improve performance to meet or exceed DOE goals.

- Develop understanding of the mechanism of improved capacity retention for Si nano-particle electrodes in the presence of electrolyte additives FEC and/or VC.
- Conduct direct comparison of the cycling performance of electrolytes with different concentrations of added FEC and/or VC to allow determination of an optimized electrolyte for use with Si nano-particle electrodes.
- Suggest standard electrolyte formulation for BATT researchers to allow for better cross comparison of electrochemical cycling data for different novel Si anode materials.
- Conduct ex-situ surface analysis of Si-nanoparticle electrodes cycled with different electrolyte formulations.
- Use surface analysis and electrochemical data to develop a mechanism for capacity retention enhancement via addition of FEC or VC.

- The development of improved electrolytes is of critical importance for meeting the DOE goals for cycle life, calendar life, temperature of performance, capacity loss, and Increased energy density.

Template -- Milestones

FY 13

(a) Develop an understanding of the role of electrolyte in capacity fade for graphite/ $LiNi_{0.5}Mn_{1.5}O_4$ full cells cycled at moderately elevated temperature (55 ^{o}). **Completed**

(b) Design electrolyte formulations to decrease cell inefficiency (50 % of SOA) and decrease capacity fade (50 % of SOA) for graphite/$LiNi_{0.5}Mn_{1.5}O_4$ full cells. **Completed**

(c) Synthesize and characterize novel non-fluorinated lithium salts and test novel electrolytes In graphite/$LiNi_xCo_{1-2x}Mn_xO_2$ cells. **Sept 13, Due to significant difficulties in the preparation of the desired lithium salts and the creation of the new BATT silicon focus group our efforts were re-directed toward the investigation of the effects of electrolyte additives on SEI formation on Si anodes**

FY 14

(a) Complete electrochemical cycling of Si nano-particle electrodes with electrolytes containing added VC or FEC, **December 13, Completed**

(b) Determine the best electrolyte formulation for Si nanoparticle electrodes and suggest as standard for BATT researchers, **March 14, Completed**

(c) Complete surface analysis of Si nano-particle electrodes with electrolytes containing VC or FEC (6/30/14, **On Schedule**)

(d) Develop mechanism for the beneficial cycling performance for electrolytes with added FEC or VC for Si nano-particle electrodes (9/30/14, **On Schedule**)

Approach

- Study the mechanism of improved capacity retention for Si nano-particle electrodes in the presence of electrolyte additives FEC and/or VC.

- Conduct a direct comparison of the cycling performance of electrolytes with different concentrations of added FEC and/or VC.

- Utilize cycling results to determine optimized electrolyte for use with Si nano-particle electrodes.

- Conduct detailed ex-situ surface analysis of electrode surfaces after cycling Si-nano-particle electrodes via a combination of SEM, XPS, and FT-IR.

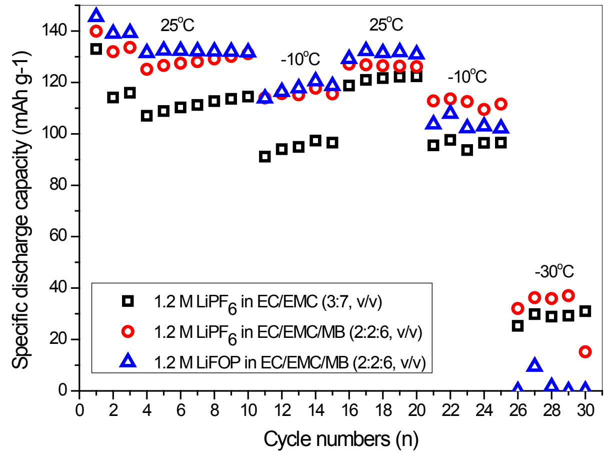
- Use surface analysis and electrochemical data to develop a mechanism for capacity retention enhancement via addition of FEC or VC.

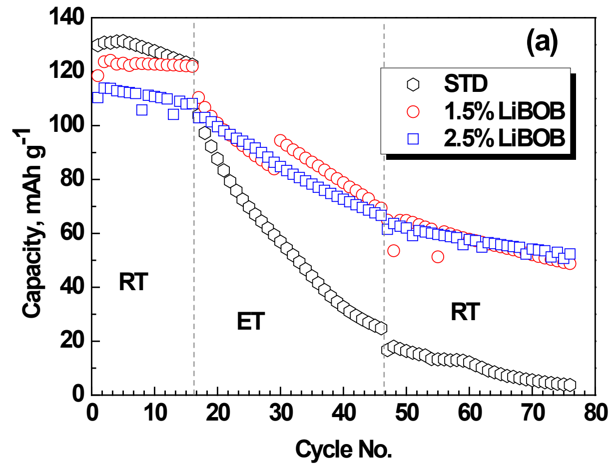
Previous Technical Accomplishments

- Investigated the performance of lithium tetrafluorooxalatophosphate in methyl butyrate electrolytes. The use of ester co-solvents can improve low temperature performance.
  J. Appl. Electrochem. **2013,** 43, 497-505.

- Investigated the failure Mechanism of Graphite/ $LiNi_{0.5}Mn_{1.5}O_4$ Cells at High Voltage and Elevated Temperature. Oxidation of the carbonate solvents and Mn dissolution are the primary sources of performance loss.
  J. Electrochem. Soc. **2013**,160, A3138-A3143

- Improved the Performance of Graphite/ $LiNi_{0.5}Mn_{1.5}O_4$ Cells at High Voltage and Elevated Temperature via incorporations Lithium bis(oxalato) borate (LiBOB) as an electrolyte additive. Addition of LiBOB results in the generation of a cathode electrolyte interface (CEI) which inhibits electrolyte oxidation and Mn dissolution.
  J. Electrochem. Soc. **2013**, *160*, A2005-A2013.





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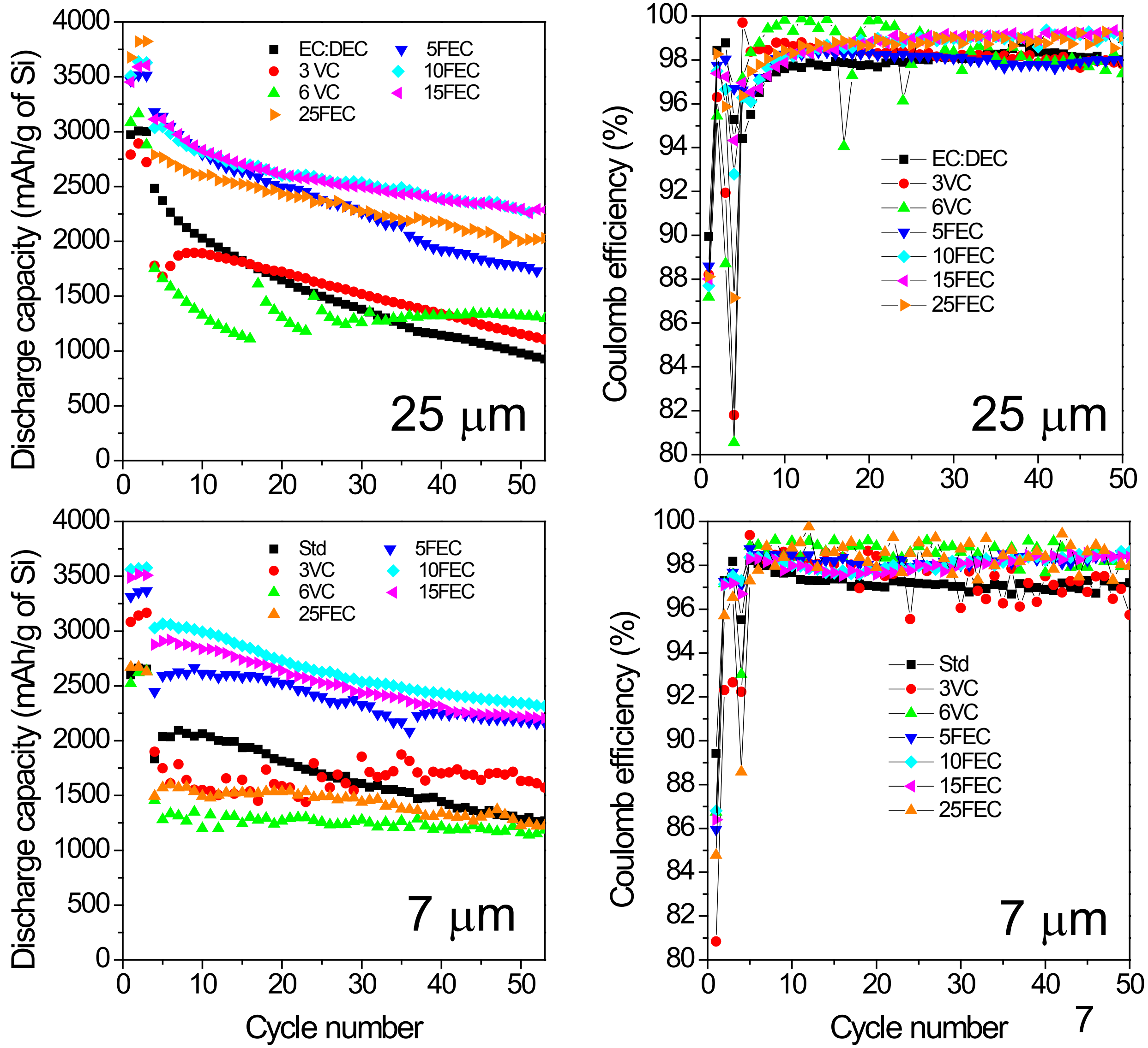
FY 13 Technical Accomplishments: Investigation of Electrolytes for Si Electrodes

Discharge capacity vs. cycle number plots and cycling efficiency of Si electrodes

Best electrolyte formulation for cycling Si anodes was determined to be 10 % FEC in 1.2 M $LiPF_6$ 1:1 EC/DEC

No significant improvement with thinner electrodes



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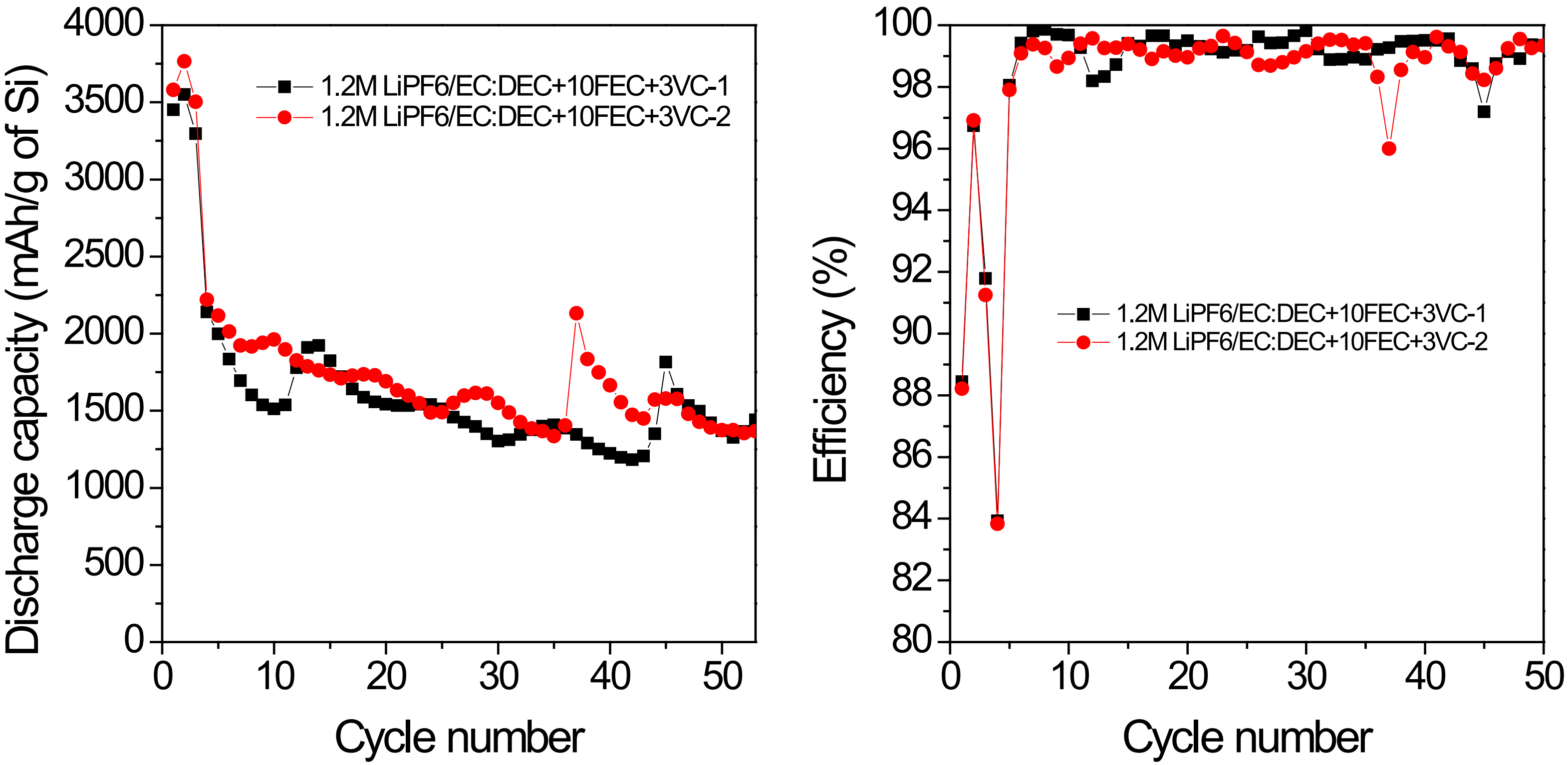
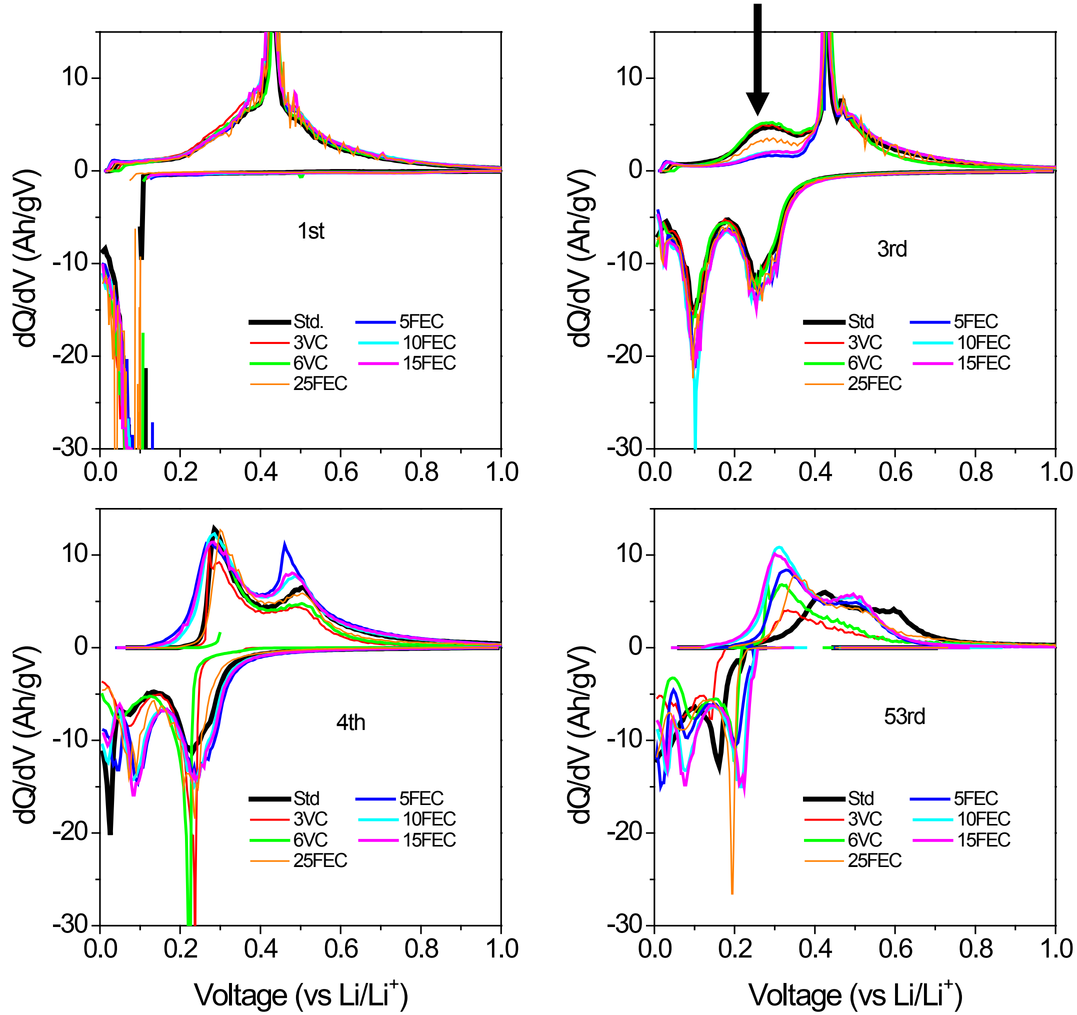
FY 13 Technical Accomplishments: Investigation of Electrolytes for Si Electrodes



Performance of the Si electrodes worse with the combination of FEC and VC

FY 13 Technical Accomplishments: Investigation of Electrolytes for Si Electrodes

- Si anodes cycled with either 10 or 15 % FEC have best retention of cycling profile
- Crystalline $Li_{15}Si_4$ is preferably formed in electrolytes containing added FEC



Differential capacity plots of Si electrodes at different cycle number

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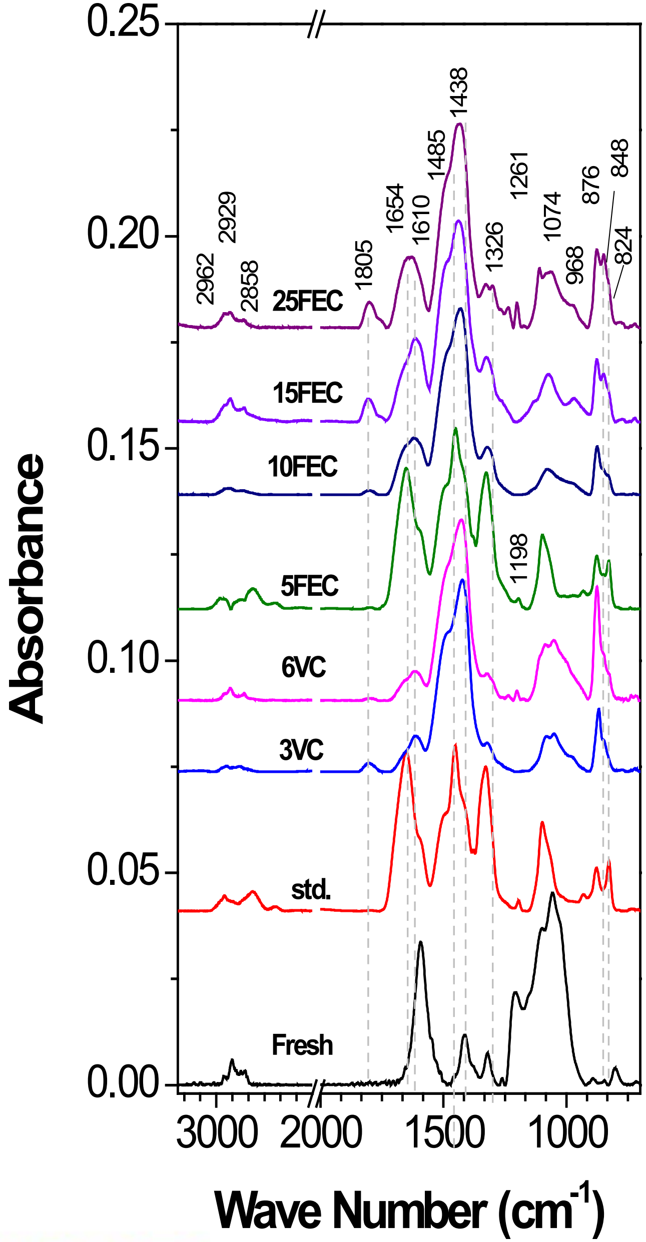
FY 14 Technical Accomplishments: FT-IR spectra of silicon anodes



FT-IR spectra for silicon anode before and after 53 cycles

- ❑ **Standard electrolyte:**
  - ✓ SEI is mainly composed of lithium alkyl carbonates (ROCOOLi) and Li_2CO_3
- ❑ **Electrolyte with added VC**
  - ✓ Main SEI component: Li_2CO_3 with smaller amount of poly VC and lithium alkyl carbonates.
- ❑ **Electrolyte with added FEC**
  - ✓ SEI in the presence of 5wt.% FEC resemble to that of standard electrolyte
  - ✓ With higher FEC concentration, lithium alkyl carbonates, Li_2CO_3 and poly FEC were increased.

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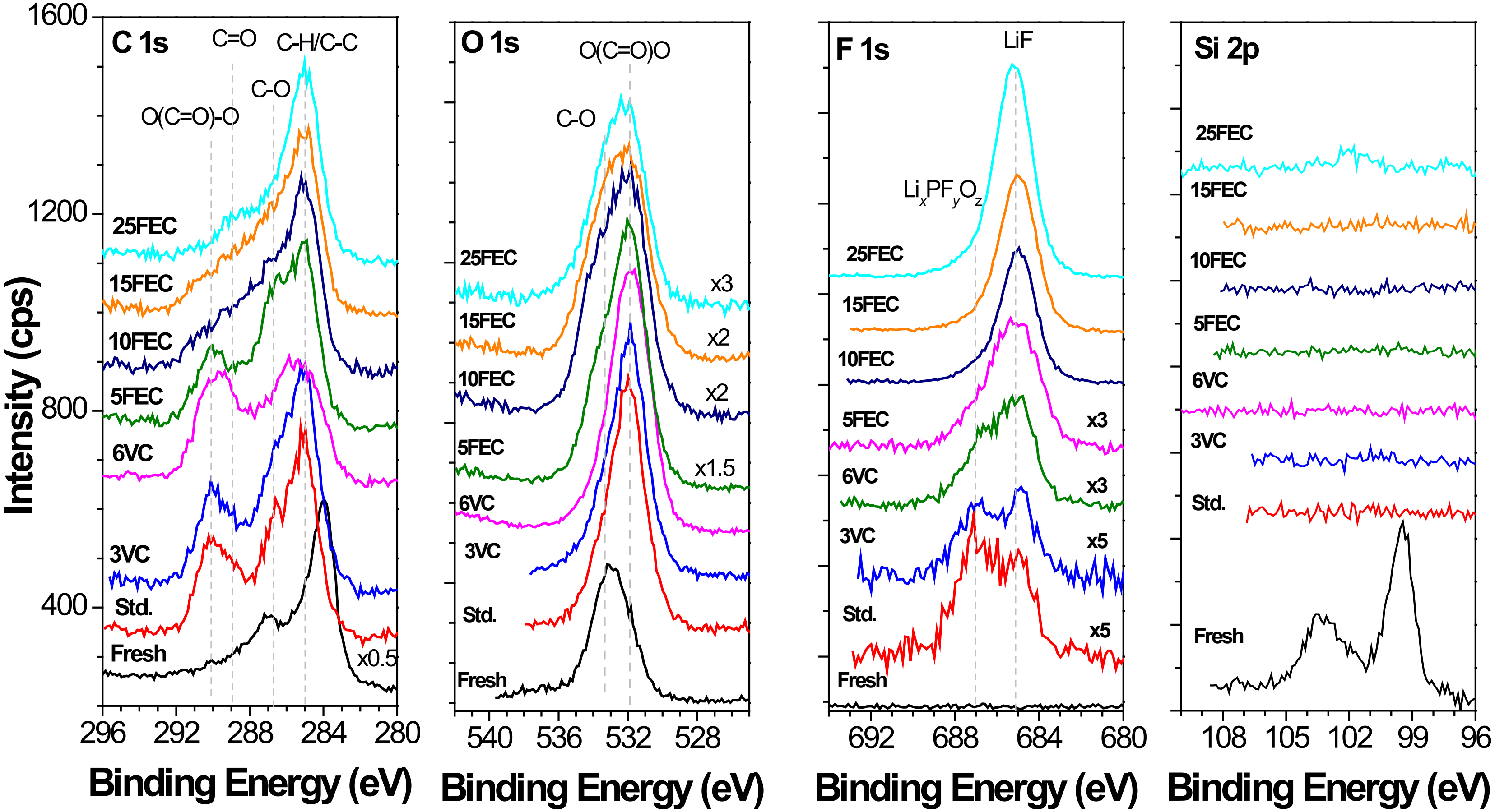
FY 14 Technical Accomplishments: XPS of Silicon Anodes



Electrolytes containing FEC have less Lithium alkyl carbonates.
Electrolytes containing added VC have more lithium carbonate

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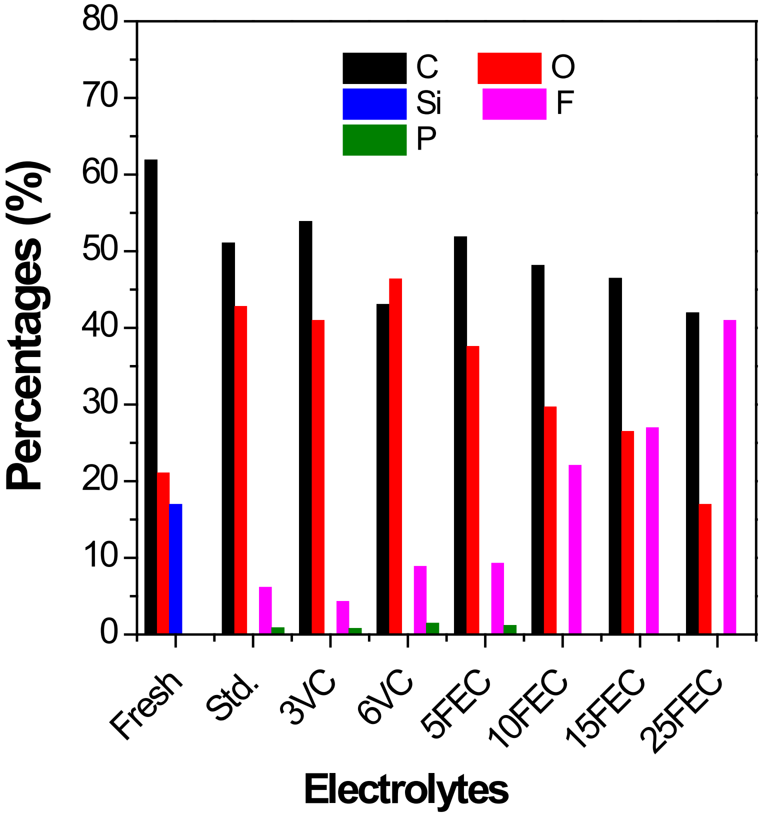
FY 14 Technical Accomplishments: XPS of Silicon Anodes



Elemental concentrations on the surface of cycled electrodes

Si concentration is very low after cycling

LiF is dominant with added FEC

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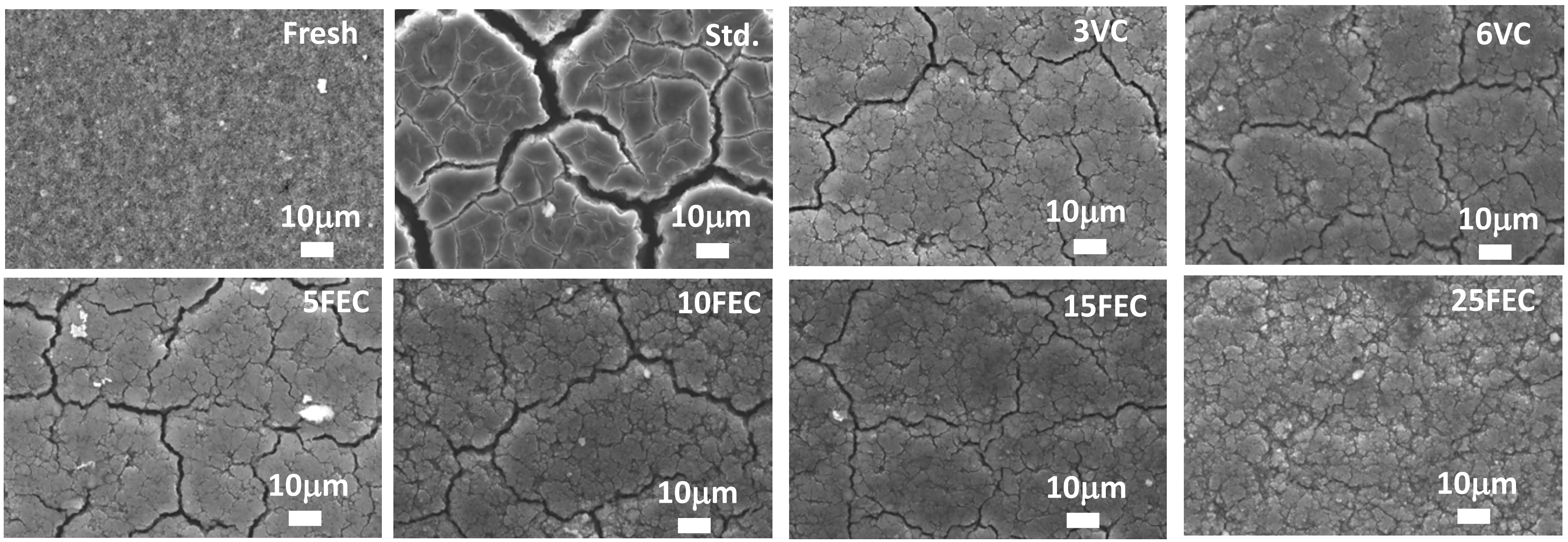
FY 14 Technical Accomplishments: SEM images of electrodes



Electrodes cycled with additives have much less cracking

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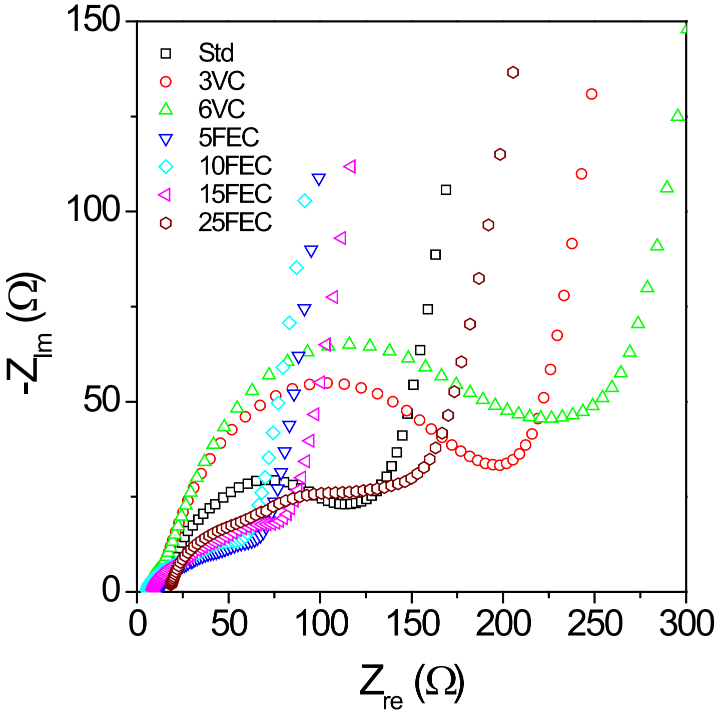
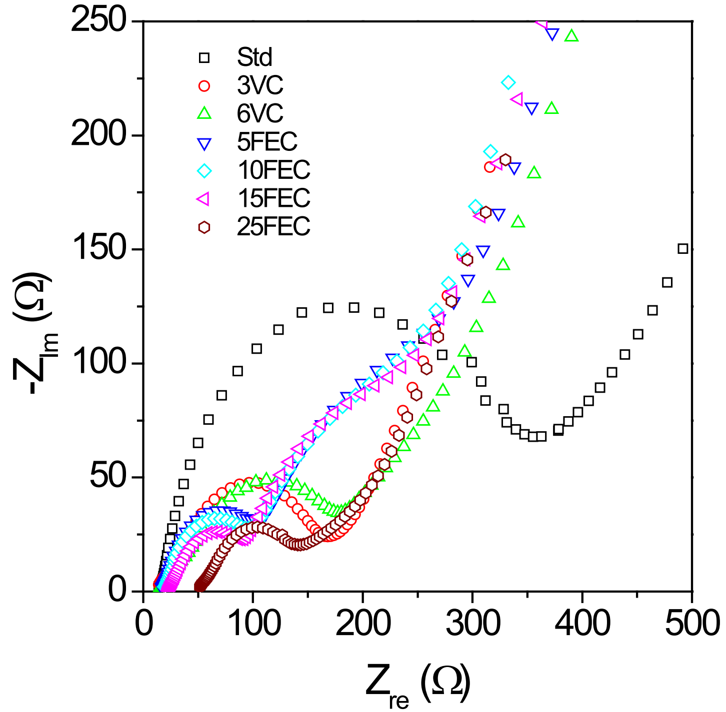
FY 14 Technical Accomplishments: Electrochemical Impedance Spectroscopy



After 3 cycles



After 53 cycles

- Cells with added FEC (≤15 wt.%) show smaller impedance
- 25 wt.% of FEC causes larger impedance

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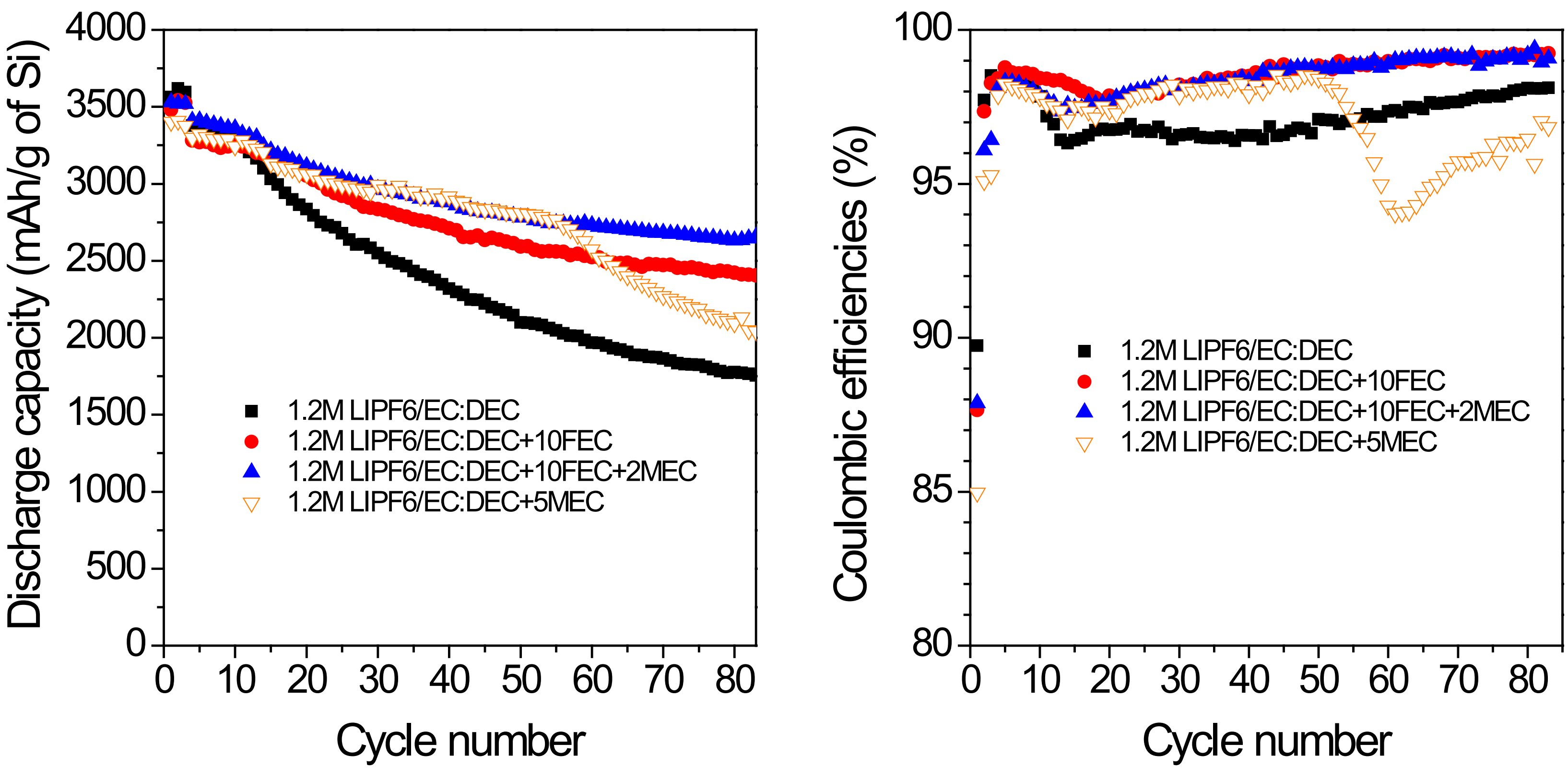
FY 14 Technical Accomplishments:
New additive for enhancing cycling performance of Si anodes: Methylene ethylene carbonate (MEC)



- MEC improves cycling performance of Si anodes significantly
- 5 wt.% MEC appears to be insufficient to maintain good cycle life

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Response to reviewers comments

- ***Reviewers comments were favorable, weighted average score of 3.71***

- The reviewer suggested that the evaluation of accelerated aging along with impedance and XPS studies would be valuable to apply to this situation.

  We have expanded our impedance investigations and continued XPS.

- The reviewer commented that Lewis base additives improved performance, but asked whether this depended on how much water has leaked in.

  Related investigations have been conducted with industrial partners on commercial cells which confirmed improved performance.

- The reviewer criticized that insufficient effort to decide whether changes in SEI should be good or bad, rather than just being different.

  We are working to develop a better understanding of how changes in electrolyte composition result in changes to the SEI structure. We then correlate this to cycling performance to allow for a better understanding of how the SEI structure effects the cycling performance. This will allow us to systematically design electrolyte formulations to yield an SEI with desired properties.

Collaborations

- D. Abraham (ANL, National Lab, ABRT Program): Collaborations on the investigation of novel salts, solvents and additives in lithium ion battery electrolytes.
- M. Smart (NASA JPL, National Lab, ABRT Program): Collaborations on the investigation of novel salts, solvents and additives in lithium ion battery electrolytes.
- V. Battaglia (LBNL, National Lab, BATT Program): Collaboration on performance testing of novel salts and additives in BATT program cells.
- A. Garsuch (BASF, Industrial): Collaboration on the development of novel electrolytes for high voltage cathodes.
- F. Puglia and B. Ravdel (Yardney, Industrial): Collaboration on testing novel electrolytes in large format cells and investigation of high voltage LNMS (7 – 12 Ah).
- High Voltage Spinel Focus Group (LBNL, National Lab, BATT Program)
- Silicon Focus Group (LBNL, National Lab, BATT Program)

Remaining Challenges and Barriers

- Improving the capacity retention upon cycling for silicon based anode materials is needed to afford the use of these high capacity electrode materials

- The reactions of the electrolyte with the surface of lithiated silicon are particularly problematic due to the large volumetric changes of silicon upon lithiation/delithiation

- The development of an electrolyte formulation which allows high efficiency cycling and good capacity retention of silicon anodes is a significant challenge

- Generating a better understanding of how current electrolyte additives improve the cycling performance of silicon anodes will lead to the systematic development of improved electrolyte formulations

Proposed Future Work

- The ex-situ surface analysis of silicon nano-particle electrodes cycled with electrolytes containing VC or FEC will be completed and a manuscript will be submitted for publication
- A mechanism to explain the beneficial properties of added VC and FEC on the structure and performance of the anode SEI will be proposed.
- The effect of added methylene ethylene carbonate (MEC) on the cycling performance of silicon nano-particle electrodes will be expanded
- Ex-situ surface analysis of silicon nano-particle electrodes cycled with electrolytes containing added MEC will be conducted

Summary

- The mechanism of improved capacity retention for Si nano-particle electrodes in the presence of electrolyte additives FEC and/or VC has been investigated
- The cycling performance of electrolytes with different concentrations of added FEC and/or VC has been studied
- ***The optimal baseline electrolyte formulation for cycling Si anodes was determined to be 10 % FEC in 1.2 M $LiPF_6$ 1:1 EC/DEC***
- Detailed ex-situ surface analysis of electrode surfaces after cycling silicon nano-particle electrodes has been conducted using a combination of SEM, XPS, and FT-IR
- The optimized electrolyte formulation results in an SEI containing lithium alkyl carbonates, Li_2CO_3, LiF and a cosslinked polymer. The ratio of insoluble lithium salt and polymer appears to be critical for performance optimization. Very high polymer content leads to high impedance while low polymer content leads to poor capacity retention