Self-Assembling Rechargeable Li Batteries from Alkali and Alkaline – Earth Halides

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Project ID # bat326

Overview

Timeline

- Project start: 10/01/2017
- Project end: 12/31/2019
- Percent complete: 40%

Budget

- Total project funding
  - DOE share: $1,250,000
  - Contractor share: $138,889
- Funding for FY 2017: $456,742
- Funding for 2018: $462,912

Barriers

- A. Cost
  - Higher energy cells as a way to reduce costs
- C. Life.
  - Beyond Li-ion (BLI, cells containing Li metal anodes) technologies suffer major cycle and calendar life issues.
- B. Performance
  - Need improvement in XFC (eXtreme Fast Charging)

Partners

- 24M Technologies Inc.

Relevance

Overall Objective

- Investigate electrochemical formation of lithium halide based solid electrolyte interfaces, with the goal of enabling and demonstrating self-assembling/self-healing batteries using lithium metal negative electrodes

Current Objective

- Characterize morphological evolution of Li metal surfaces with halide additives
- Demonstrate Li-Li symmetric cell using halide additives that outperforms additive-free cell
- Structural and chemical characterization results for baseline halide films on Li metal
- Structural and chemical characterization results for self-healed halide films on Li metal

Impact

- The self-forming process is a ***simple and scalable***.
- Enables very high energy density (>350 Wh/kg) rechargeable lithium batteries that could improve the driving range and reduce the cost for electric vehicles.

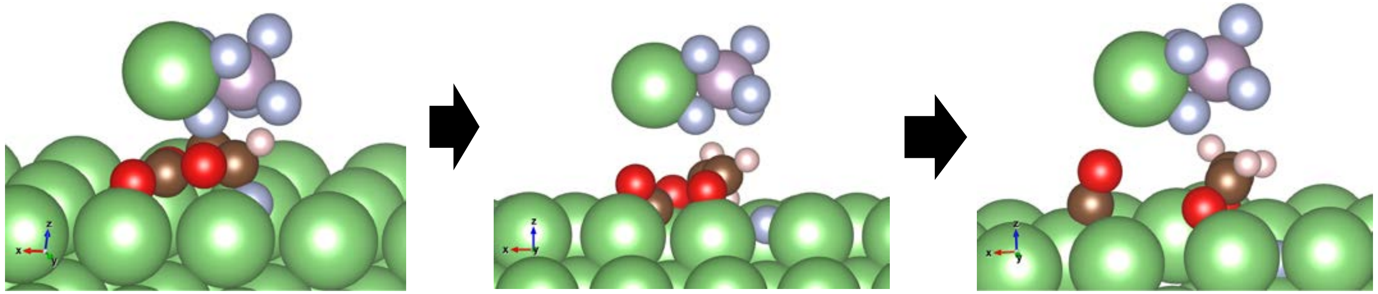
Milestones

Date	Description	Quarter	Status
March 2017	Complete initial computations and halide solubility studies and construct experimental matrix of halides and solvents.	Q2	Completed
June 2017	Demonstrate cell designs and electrochemical testing parameters that allow clear differentiation of dendritic and non-dendritic behavior of Li electrodes.	Q3	Completed
September 2017	Deliver characterization results for morphological evolution of Li metal surface showing that halide additives diminish Li dendrite formation.	Q4	Completed
December 2017 Go No/Go 2017	Demonstrate Li-Li symmetric cell using halide additives that outperforms additive-free cell	Q5	Completed
March 2018	Structural and chemical characterization of halide films on Li metal	Q6	Completed
June, 2018	Structural and chemical characterization of self-healed halide films on Li metal	Q7	On track
Sept, 2018	Establish quantitative criteria for effectiveness and reproducibility in dendrite-suppression	Q8	On track

Approach

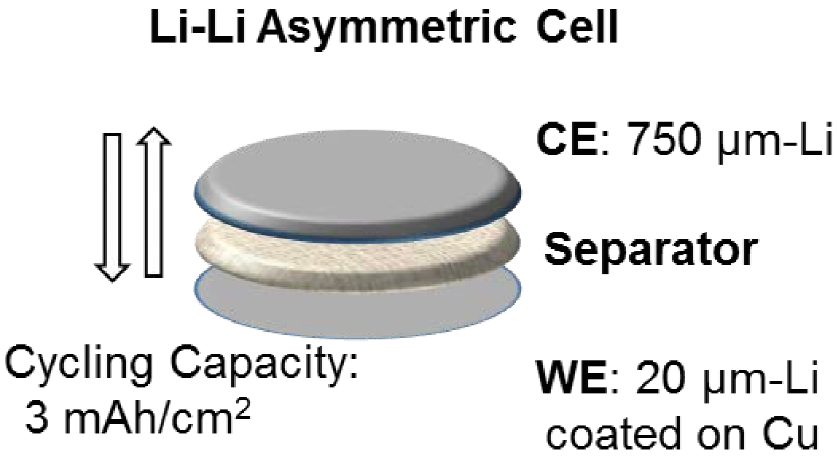
- Identify suitable combinations of solvents, Li-electrolyte salts, and halide and halogenated additives that can produce highly Li-ion conducting, mechanically robust solid electrolyte interfaces that are **self-formed** and possess **self-healing** properties.
- The development of these layers can lead to stable cycling of lithium metal that can lead to batteries with specific energy > 350 Wh/kg.

Theory Approach: Use Density Functional theory to identify and down-select self-forming and self-healing halogenated additives.



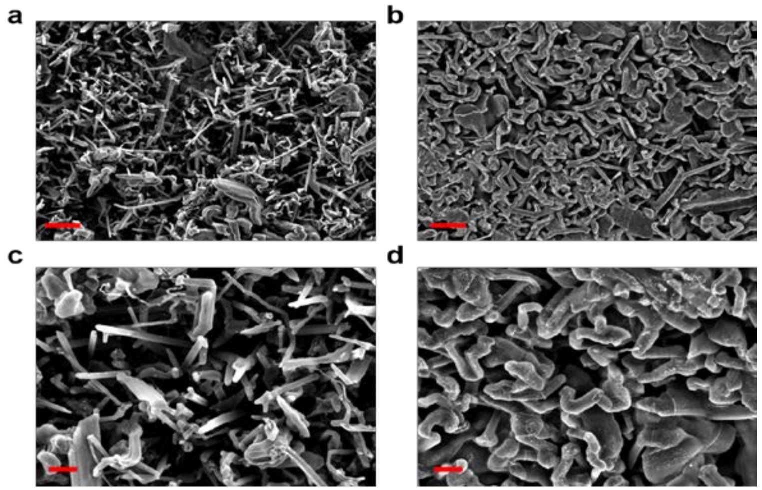
Density Functional theory simulation showing the decomposition of FEC additive on Li metal surface

Experimental approach: Assemble and test: 1) Asymmetric Li-Li cells and 2) Li metal batteries comprising a high areal-capacity cathode (> 3 mAh/cm^2) and a capacity-limited Li metal anode

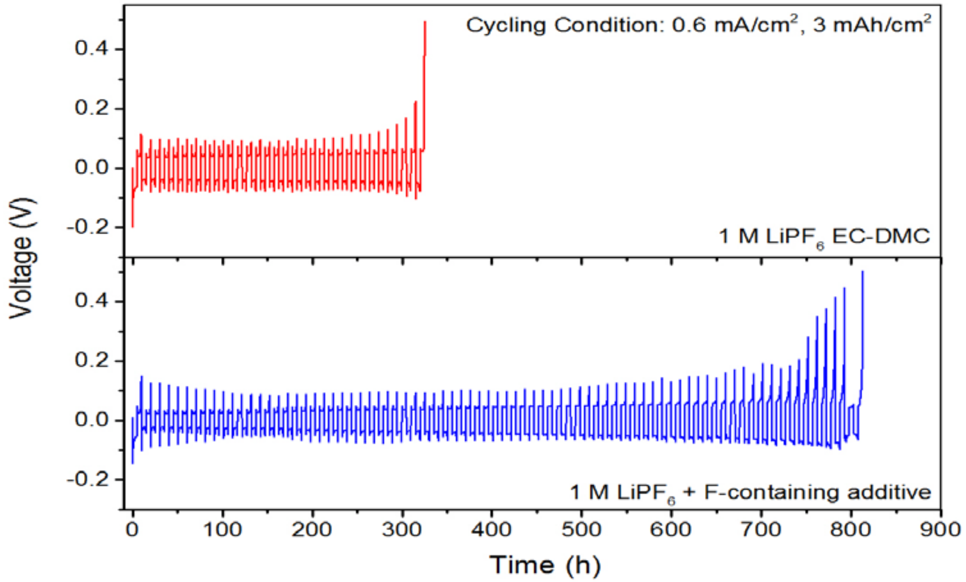


Technical Accomplishments

- Completed initial computations and halide solubility studies and construct experimental matrix of halides and solvents. **(March 2017)**
- Demonstrated cell designs and electrochemical testing parameters that allow clear differentiation of dendritic and non-dendritic behavior of Li electrodes. **(June 2017)**
- Delivered characterization results for morphological evolution of Li metal surface showing that halide additives diminish Li dendrite formation. **(Sept 2017)**
- Delivered chemical characterization of the solid electrolyte interface using XPS. **(Sept 2017)**
- Demonstrated Li-Li cell using halide additives that outperforms additive-free cell. **(Dec 2017)**
- Identified new halogenated solvents for self-forming and self healing. (**Mar 2018**)

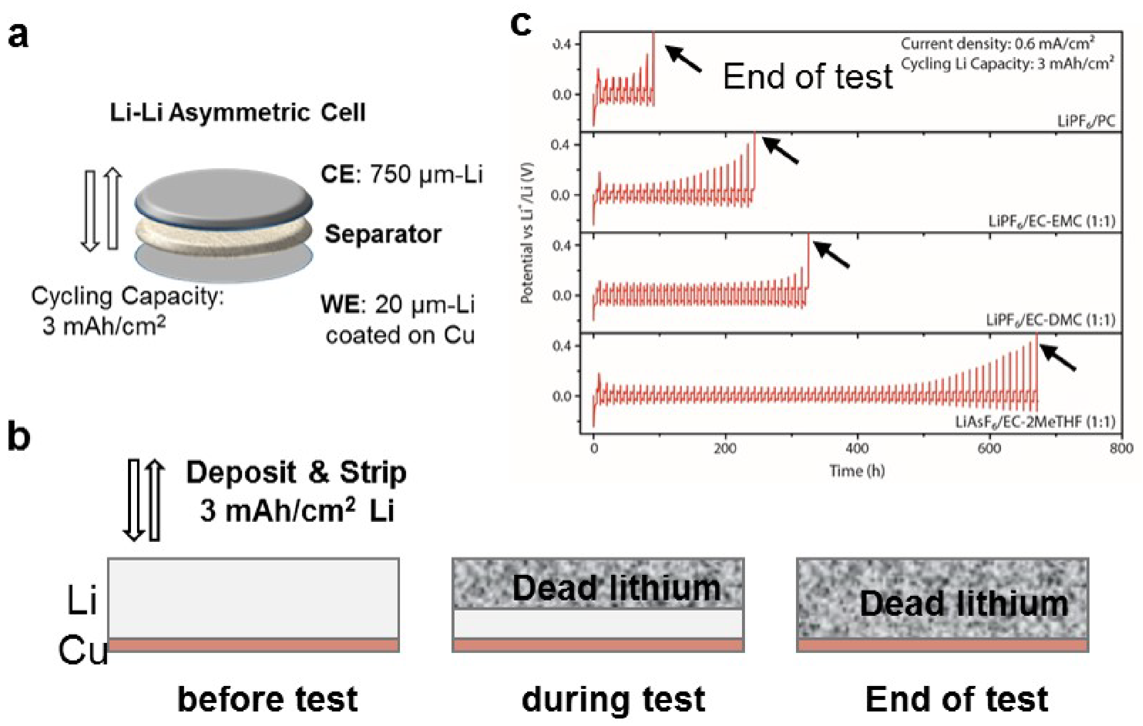


Without Halide **With Halide**



TECHNICAL ACCOMPLISHMENTS

DEVELOPMENT OF An Li-Li ASYMMETRIC CELL TEST



Measurement of average CE

$$E_{average} = 1 - \frac{Q_D}{nQ_T}$$

Q_D : Total Li capacity ($Q_D = Q_T + Q_{excess}$)

Q_T : Cycling Li capacity (3 mAh/cm^2 in our tests).

n: Number of deposition/stripping cycles when there is a sudden and significant increase in (over)potential for lithium stripping.

- Developed a new, more reliable approach to measure CE and compare effect of Li salts, solvents, and additives
- Final voltage spike can be used to confirm the absence of short-circuit during the cycling test.
- Used this methodology to completed Q2 milestone “Demonstrate cell designs and electrochemical testing parameters that allow clear differentiation of dendritic and non-dendritic behavior of Li electrodes”

TECHNICAL ACCOMPLISHMENTS

MEASUREMENT OF AVERAGE CE USING LI-LI ASYMMETRIC CELL

Table 1. Li cycling efficiency with various electrolyte compositions

Lithium salt (1 M)	Solvent & Additive	Average Li cycling CE*
$LiPF_6$	A	73.6%
LiTFSI	B	83.0%
$LiPF_6$	C	90.1%
$LiPF_6$	C	92.6%
$LiPF_6$	D	95.1%
LiTFSI	E	95.5%
$LiAsF_6$	F	95.9%
$LiAsF_6$	G	96.4%
LiTFSI	H	96.7%
$LiPF_6$	I	97.0%

Test Conditions:
Cycling Capacity: 3.0 mAh/cm^2
Current Density: 0.6 mA/cm^2
40 μL electrolyte per cell
Tonen or Celgard 3501 (for PC-based electrolytes) separator

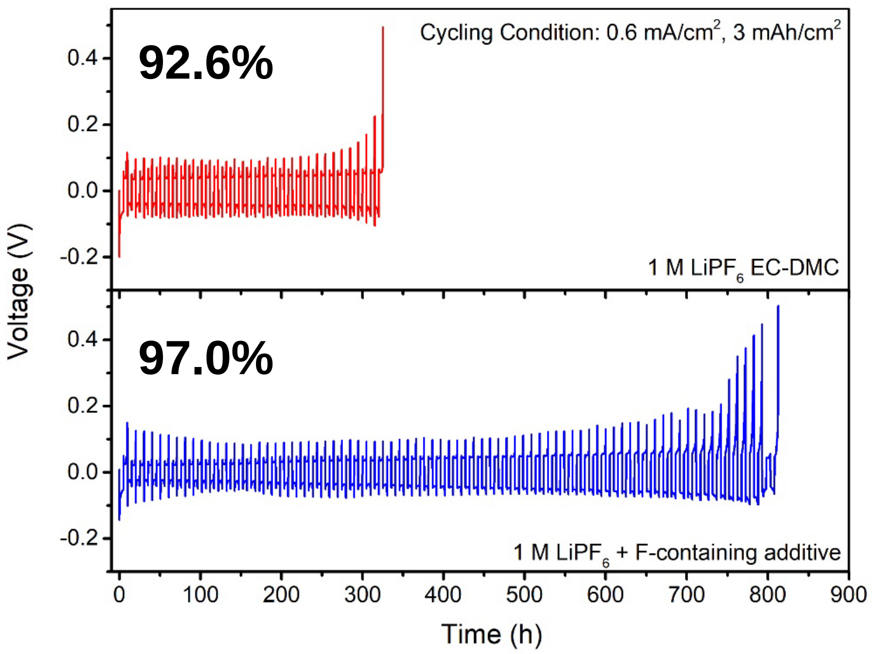
*This test gives the average coulombic efficiency (CE) over all cycles counted, including initial cycles which typically have lower CE.

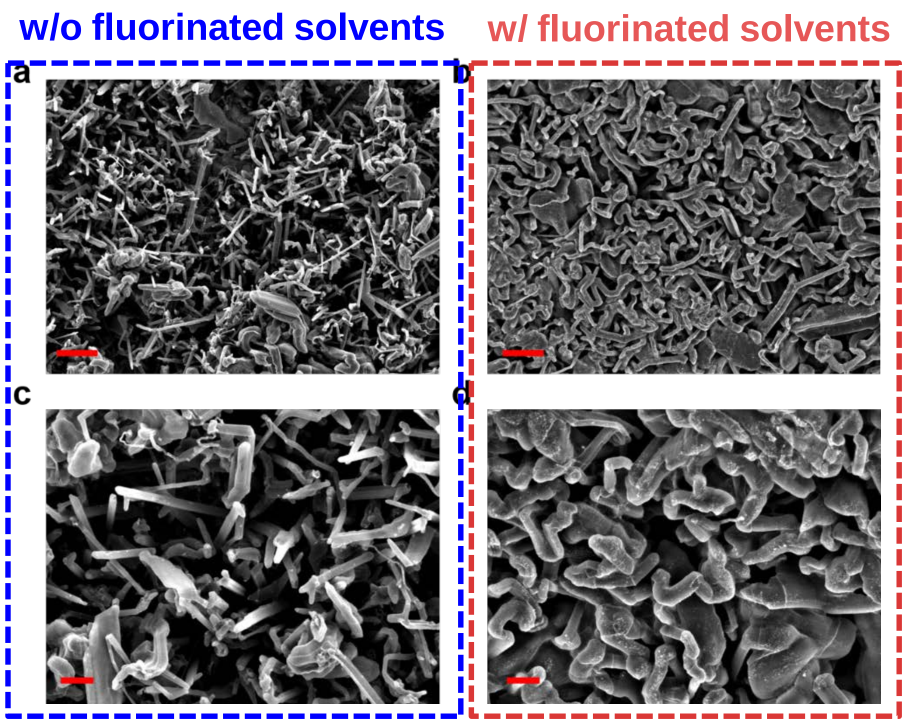
- More than 20 different electrolyte compositions （Li-salt/solvent/additive combinations) have been tested using Li-Li asymmetric cell.
- Established a database of CE of different electrolyte compositions

TECHNICAL ACCOMPLISHMENTS

FLUORINATED SOLVENTS CAN IMPROVE LI METAL ANODE

Li-Li Asymmetric Cell Test

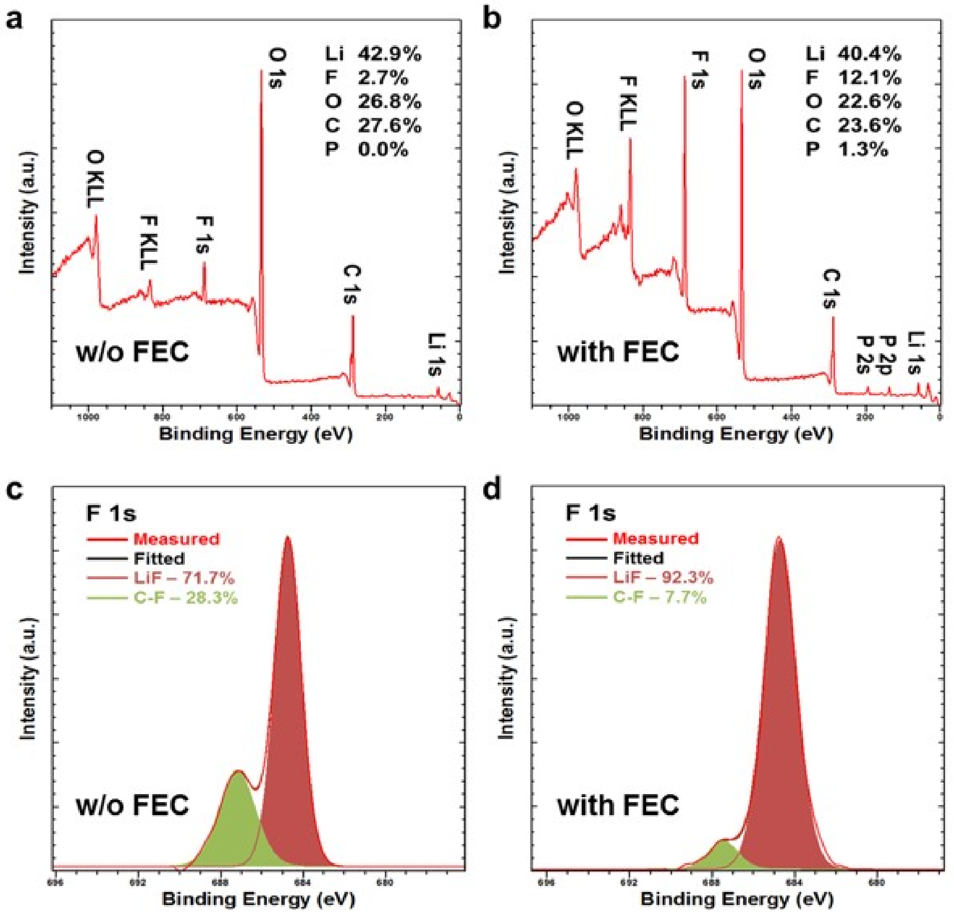




- Fluorinated solvents (such as FEC) significantly improved CE of Li metal anode
- Fluorinated solvents can change the morphology (less dendritic) and compactness (denser) of the deposited lithium.
- Completed milestone Q4 and Q5 (Go/No-Go milestone)

TECHNICAL ACCOMPLISHMENTS

FLUORINATED SOLVENTS CAN IMPROVE LI METAL ANODE

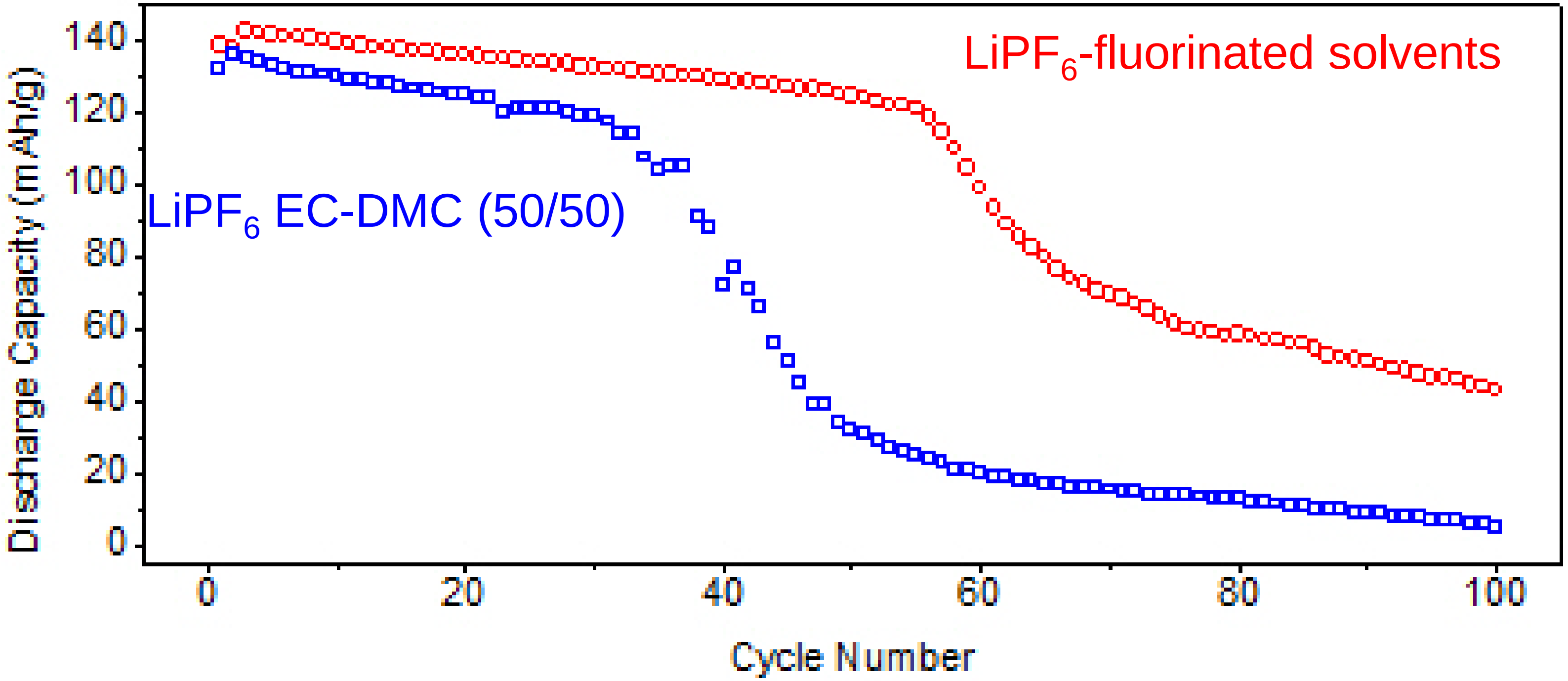


- $3.0\ mAh/cm^2$ lithium is deposited onto a copper substrate for XPS measurements. XPS is a surface-sensitive technique that can probe the composition of the SEI on the surface of the deposited lithium.
- A much higher LiF concentration is observed at the surface at the presence of the baseline FEC additive.
- A LiF-rich SEI is beneficial to improving CE of lithium metal anode.

- Completed the Q6 milestone “Deliver structural and chemical characterization results for baseline halide films on Li metal”.

TECHNICAL ACCOMPLISHMENTS

$LiCoO_2$ – Li metal full cell tests



- LCO cathodes, 22.5 mg/cm^2 LCO loading (>3 mAh/cm^2); 20 µm-thick Li anode; <40 µL/cell electrolyte, 2025 coin cell
- Cycling conditions: 0.1 C × 2 cycles then 0.2 C cycling between 4.3 and 3.0 V
- **LCO-Li full cell cycling performance is improved by fluorinated solvents**

Response to Previous Year comments

No previous year comments.

Collaboration and Coordination with Other Institutions

24M Technologies Inc.

- Received thin lithium metal foils for experiments to date
- Preparation and testing of 18 cm^2/80 cm^2 pouch cells (future work)

Remaining Challenges and Barriers

- Establish quantitative criteria for effectiveness and reproducibility in dendrite-suppression.
- Identify new halide additives for self-healing to improve coulombic efficiency and quantify their effectiveness.
- Deliver 12 baseline cells of >10 mAh capacity.
- Develop Li-Li asymmetric cells or Li-ion cells cycling $\geq$ 5 mAh/cm^2 at C/5 rate over 100 cycles.

Proposed Future Research

- Theoretical identification and quantification of better fluorinated solvents for self formation and self healing
- Structural and chemical characterization of lithium metal surface with different fluorinated solvents.
- Further develop asymmetric Li-Li cell cycling methodology to resolve coulombic efficiency at different stages of cycle life.
- Demonstrate Li-Li asymmetric cells that meet established criteria cycling at $\geq$ 3 mAh/cm^2 at C/5 rate over 30 cycles.
- Operation of Li-NMC full cells with high areal capacity > 3mAh/cm^2 for more than 100 cycles.

Any proposed future work is subject to change based on funding levels

Summary

Relevance

- Self-formed lithium halide based solid electrolyte interface, with the goal of enabling and demonstrating self-assembling/self-healing batteries using lithium metal negative electrodes.
- This provides a ***simple and scalable*** way towards enabling lithium metal electrodes and batteries with very high energy density (>350 Wh/kg).

Technical Accomplishments

- Integrated theory-experiment driven selection of halogenated electrolyte additives for improving Li metal electrode stability and cycle life.
- Demonstrated new asymmetric Li-Li cell methodology to differentiate dendritic and non-dendritic behavior of Li electrodes.
- Identified electrolytes (>20 tested) that outperform baseline electrolyte in Li-Li asymmetric cells

Approach

A tightly integrated experiment-theory approach towards enabling self-formed lithium electrodes.

- **Theory Approach:** Use density Functional theory calculations to down-select self-forming and self-healing halogenated electrolyte additives.
- **Experimental approach:** Assemble and test asymmetric cells as a screening approach to determine overall columbic efficiency. Test downselected electrolytes in full cells.

Proposed Future Work

- Theoretical identification and quantification of better fluorinated solvents for self formation and self healing.
- Structural and chemical characterization of lithium metal surface with different fluorinated solvents.
- Demonstrate Li-Li asymmetric cells cycling at ≥ 3 mAh/cm^2 at C/5 rate over 30 cycles.