A Commercially Scalable Process for Silicon Anode Prelithiation

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June 8-12, 2015

ES250

Overview

Timeline

- Start date: October 2014
- End date: September 2015
- Percent complete: 50%

Budget

- Total project funding:
  $1,800,000
  - DOE share: $1,260,000
  - Contractor share: $540,000
- FY14 received: $0
- FY15 projected: $1,800,000

Barriers

- Performance
  - Manufacturing
  - Cost
  - Energy Density
- Life
  - Cycle life
  - Shelf life

Partners

- Amprius – project lead

Relevance:

Objectives

Project Objectives

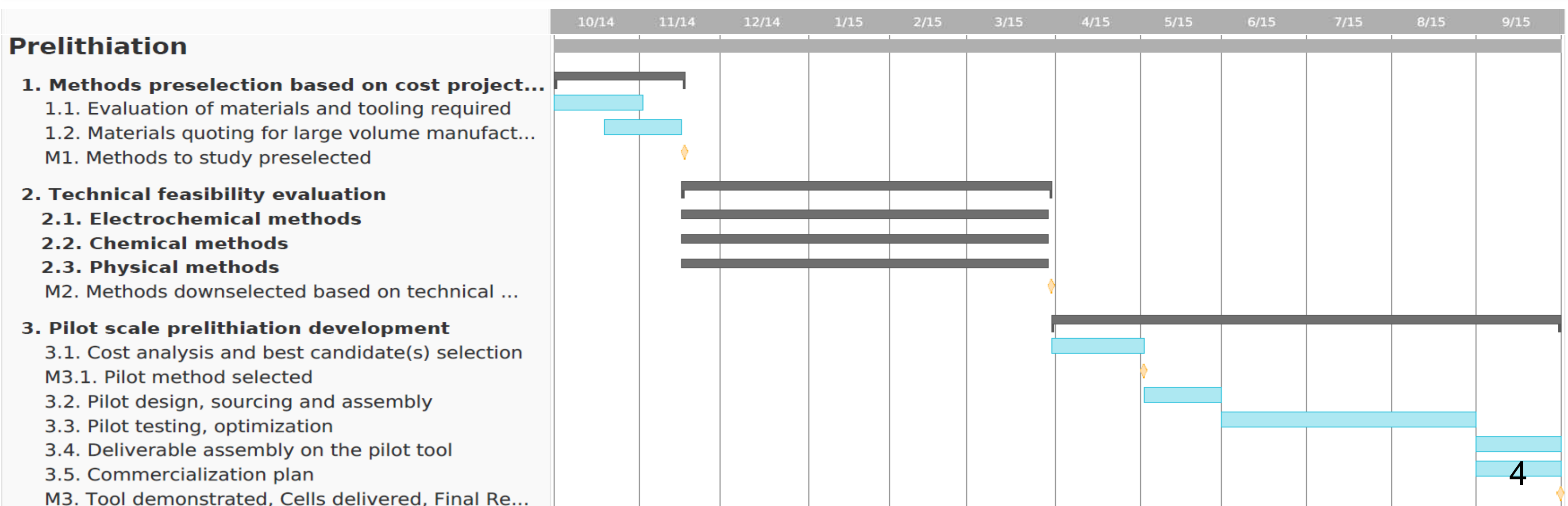
- **Develop and demonstrate a commercially scalable process for silicon anode prelithiation that will add no more than 10% to the cost of producing nanowires, facilitating production of silicon anodes that cost significantly less than today's premium graphite anodes**
- **Final performance targets:**
  - Pilot level prelithiation capacity (>100 cells/day)
  - <$0.1/Ah cost
  - >95% cathode utilization

Addresses Targets

- Facilitates the manufacturing of silicon nanowire cells by addressing capacity loss in formation
- Eliminates a key barrier to high-volume manufacturing of silicon cells
- Increases cathode utilization, reducing the cost per Ah
- Increases energy density by increasing the reversible capacity of the cell

Milestones and Timing

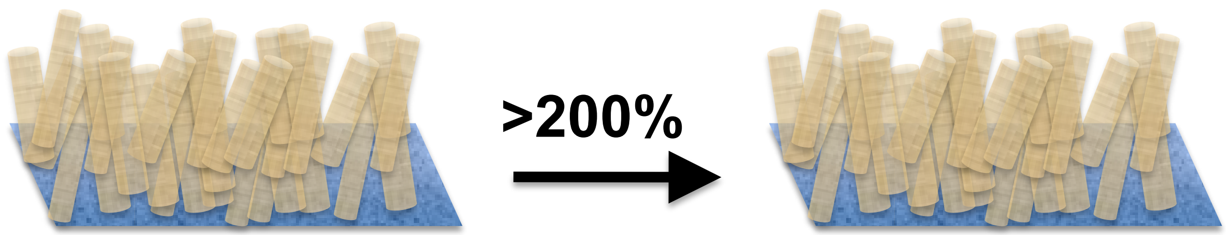
Month/Year	Milestone or Go/No-Go Decision	Status
Nov-14	Milestone: Prelithiation methods preselected	Complete
Mar-15	Milestone: Methods down selected based on technical feasibility	On Track
Apr-15	Milestone: Pilot method selected	On Track
Sep-15	Milestone: Pilot tool/machine/setup demonstrated Deliver 10 cells with a capacity over 2Ah, prelithiated in pilot tool Final report	On Track



Approach:

Silicon Nanowires enables high energy

Amprius' growth-rooted silicon nanowires enable silicon to swell and contract successfully, without compromising the battery's mechanical stability



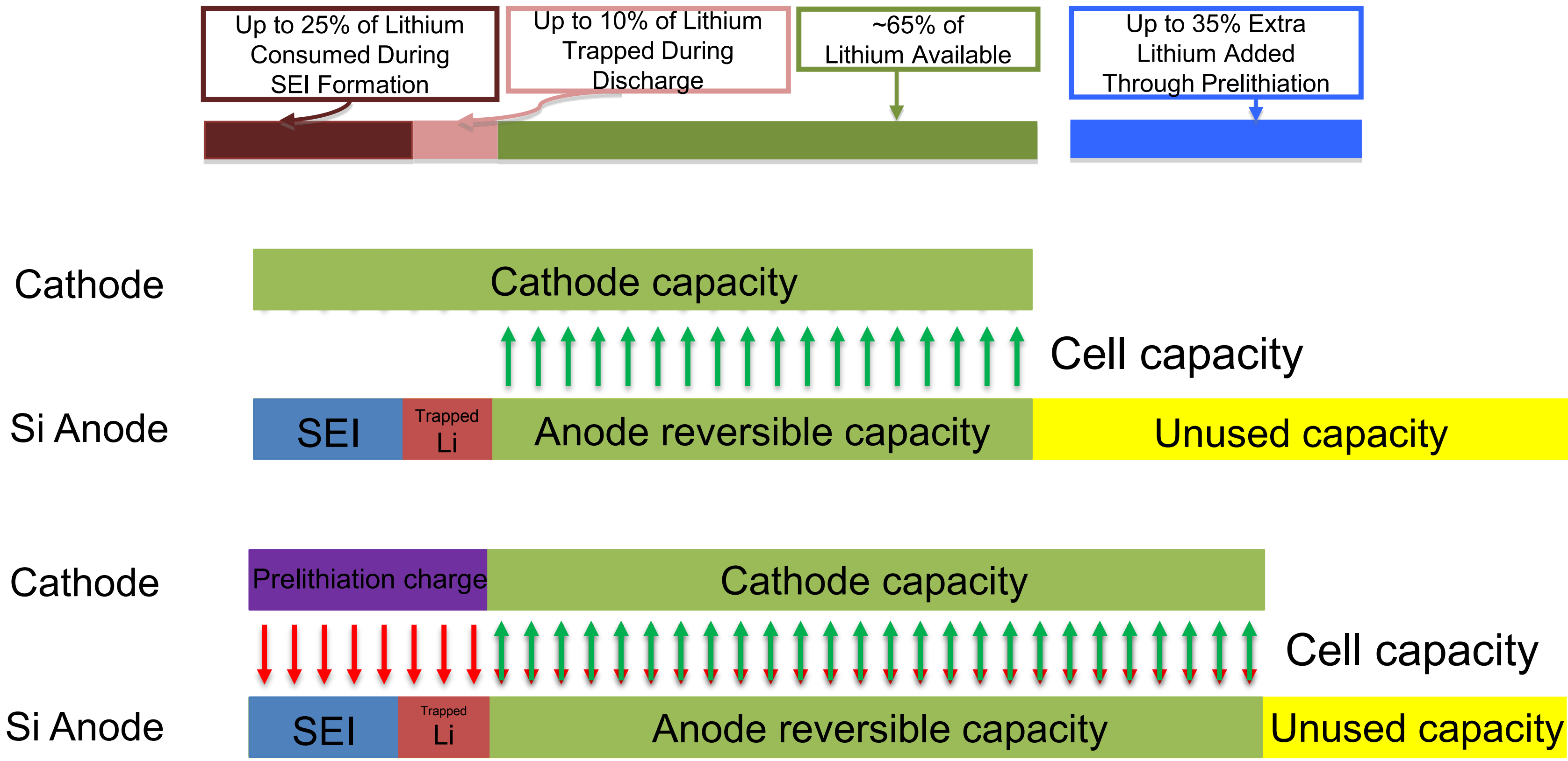
Si $+Li^+ + e^-$ Si_xLi_y

- 1/3-1/5th of graphite anode thickness
- High content active silicon materials (100%)
- Ideal and adjustable porosity distribution
- High mass loading (2-3 mg/cm^2)
- High conductivity and connectivity
- Low tortuosity – high rate capability

Approach:

Prelithiation Concept

Increase cell capacity without an increase in cathode size by compensating anode losses through anode prelithiation



Approach:

Prelithiation Methods Considered

Type	Method	Options
Electrochemical	Ex-situ (before cell assembly):	• Lab scale – individual anodes in fixtures • Industrial – R2R electrochemical bath
	In-situ (in cell):	• Auxiliary electrode source of lithium • Oversized cathode • Cathode embedded lithium source – lithium rich materials as secondary phase • Sacrificial salt in electrolyte as lithium source
Chemical	Lithium from active reactants:	• Organometallic compounds • Lithium salts, reactive or unstable
	Lithium metal:	• Direct contact, dry • Direct contact, with electrolyte • Lithium powders or films, in cell
Physical	Vacuum methods:	• Evaporation • Sputtering
	Inert atmosphere:	• Molten metal mix, spray, dip-coating

Q1-Q2 Accomplishments

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Selected two electrochemical and one physical method for prelithiation, based on cost and manufacturing process impact

Evaluated the impact of prelithiation on cell capacity and cycle life

Started technical feasibility evaluation and development of preselected methods

Task 1: Methods Preselection

- Lithium metal does not have a spot price and has a wide range depending on source, purity and shape
- Common lithium compounds include Li2CO3 and LiOH*H20 and are available in large quantities at prices that are 10-20 times lower than those of lithium metal
- Prelithiation added cost cannot exceed the cost of added capacity by oversizing the cathode

LCO capacity	165	mAh/g
LCO price	30	$/kg
Charge price	0.18	$/Ah

Task 1: Methods Preselection

Step	Condition	Environment	Prelithiation type
Finished electrode	Full roll, coated and calendered or deposited (NW)	Electrode dried before calendaring; no air exposure (NW)	• **Bath prelithiation, rinse and seal (or protection)** • **Wet contact with lithium foil** • Lithium evaporation, sputtering, molten spray plus protective layer • Li powders in anode • Unstable Lithium salt on anode
Slitting or Punching	Narrow rolls or sheets	Requires dry room if prelithiated; typically not a dry room	No prelithiation method applicable
Jelly roll assembly, tabbing	Stack or roll accessible through the sides	Requires dry room if anode is prelithiated; typically not dry	• Bath prelithiation with slow or pulsed current after jelly roll drying • Contact foil inserted in cell on anode or separator
Pouch & tab sealing	Stack or roll accessible through one side	Requires dry room if anode is prelithiated; typically not dry	• Electrochemical with auxiliary electrode
Electrolyte injection	Stack or roll accessible through one side	Done in dry room or sealed machine	• **Electrochemical with concentrated Li salt and reactive anion**
Pouch sealing & hot press	Anode not accessible	Sealing done in inert or dry vacuum	No prelithiation method applicable

Task 2: Feasibility Evaluation

Work directions:

1. Find the optimum prelithiation charge level by electrochemically dosing the charge and evaluation of the effects on reversible charge and cycle life
2. Increase the concentration of prelithiation salt by optimizing the solvent formulation
3. Optimize the prelithiation protocol for cell fabrication process integration
4. Study thermal and optical properties of LiN3 for physical prelithiation application
5. Evaluate roll-to-roll industrial processes that can be adapted to prelithiation

Task 2: Feasibility Evaluation

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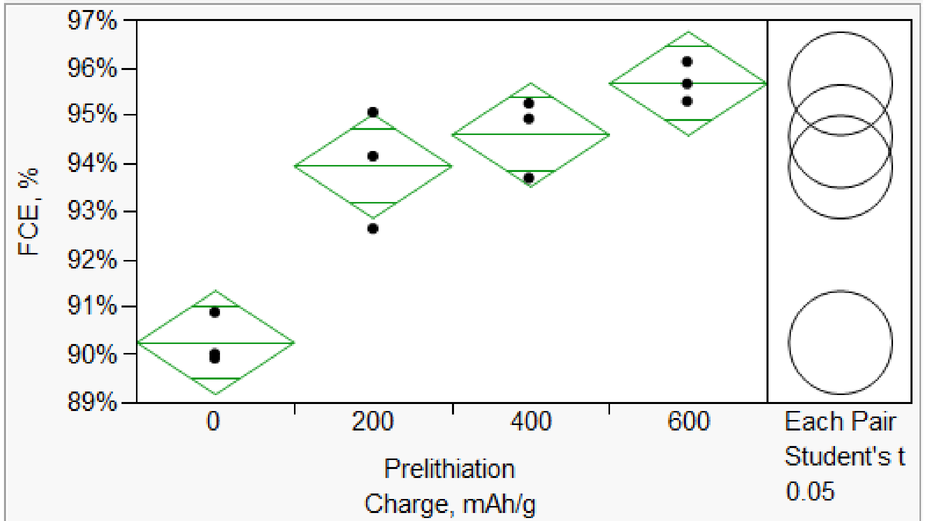
Prelithiation charge optimization:

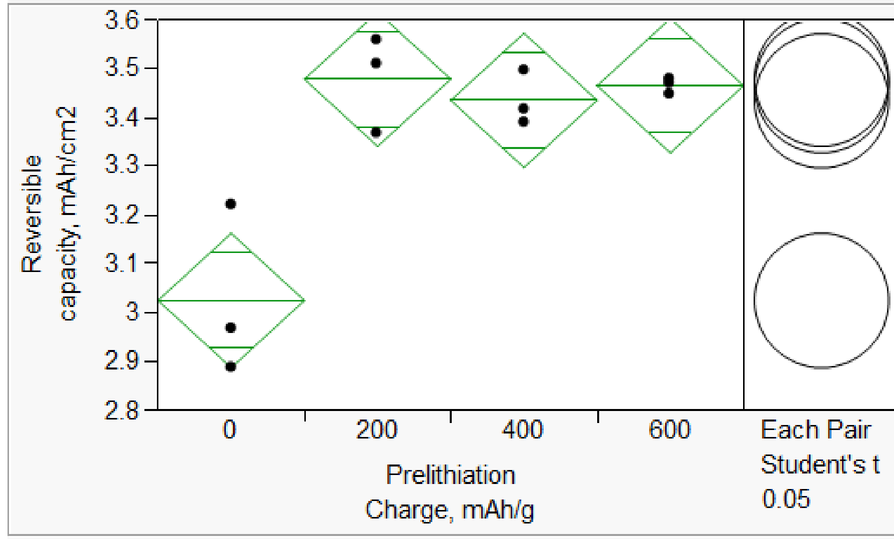
Oneway Analysis of FCE, % By Prelithiation Charge, mAh/g



Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
0	3	0.902667	0.005508	0.00318	0.88899	0.91635
200	3	0.939600	0.012261	0.00708	0.90914	0.97006
400	3	0.946167	0.008259	0.00477	0.92565	0.96668
600	3	0.956900	0.004104	0.00237	0.94671	0.96709

Oneway Analysis of Reversible capacity, mAh/cm2 By Prelithiation Char



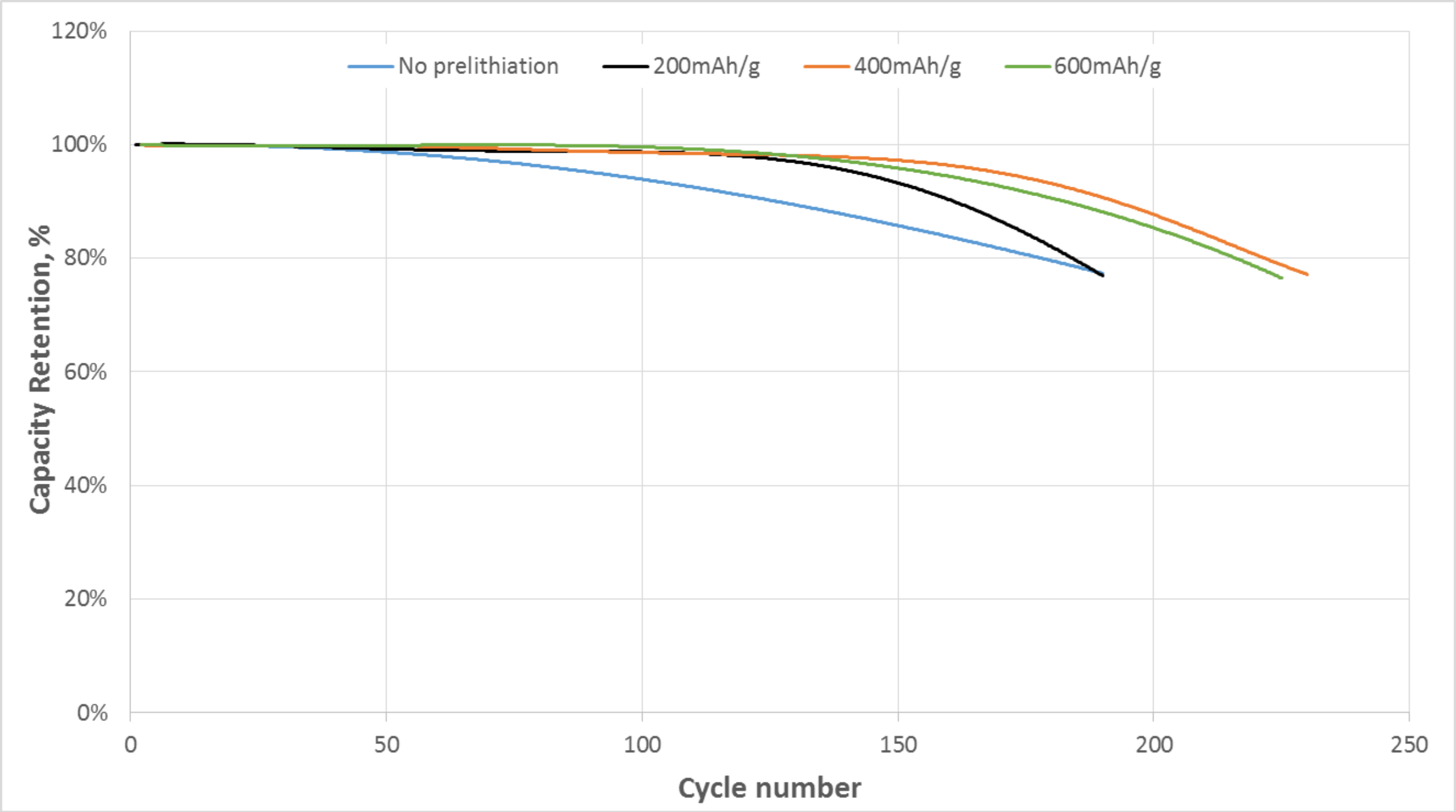
Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
0	3	3.02667	0.172143	0.09939	2.5990	3.4543
200	3	3.48000	0.098489	0.05686	3.2353	3.7247
400	3	3.43667	0.056862	0.03283	3.2954	3.5779
600	3	3.46667	0.015275	0.00882	3.4287	3.5046

There is no significant difference in reversible capacity or first cycle efficiency → 200mAh/g is enough to compensate for SEI formation

Task 2: Feasibility Evaluation

Prelithiation charge optimization:



Cycle life seems to be affected by prelithiation charge → the amount of trapped charge probably acts as a lithium reservoir

400mAh/g prelithiation level compensates lithium loss in formation and results in improved cycle life at 97% cathode utilization

In cell prelithiation

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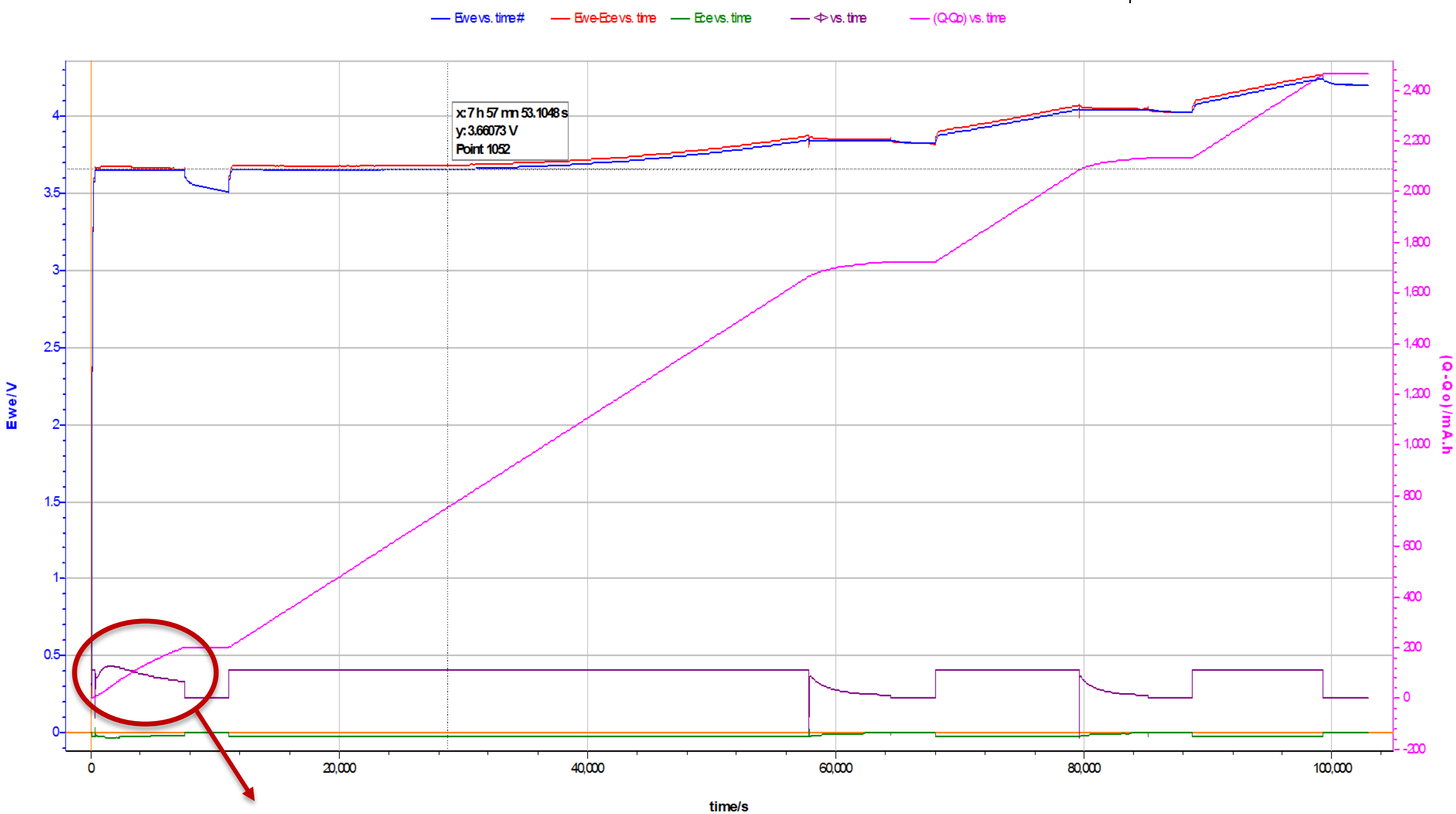
Uses sacrificial salt for prelithiation

The electrolyte formulation, electrochemical protocol and physical setup have to meet all conditions:

- Lithium ions are driven into the anode for prelithiation
- No solvent reduction on the anode or reaction that forms stable SEI
- Oxidize the solvent or anion salt on the cathode, as counter-reaction
- Counter-reaction products should be inactive, so gas-forming reactions are ideal
- Counter-reaction at low voltage so that there is no driving force to pull lithium out of the cathode

In cell prelithiation



The prelithiation starts before lithium is extracted from the cathode

In cell prelithiation

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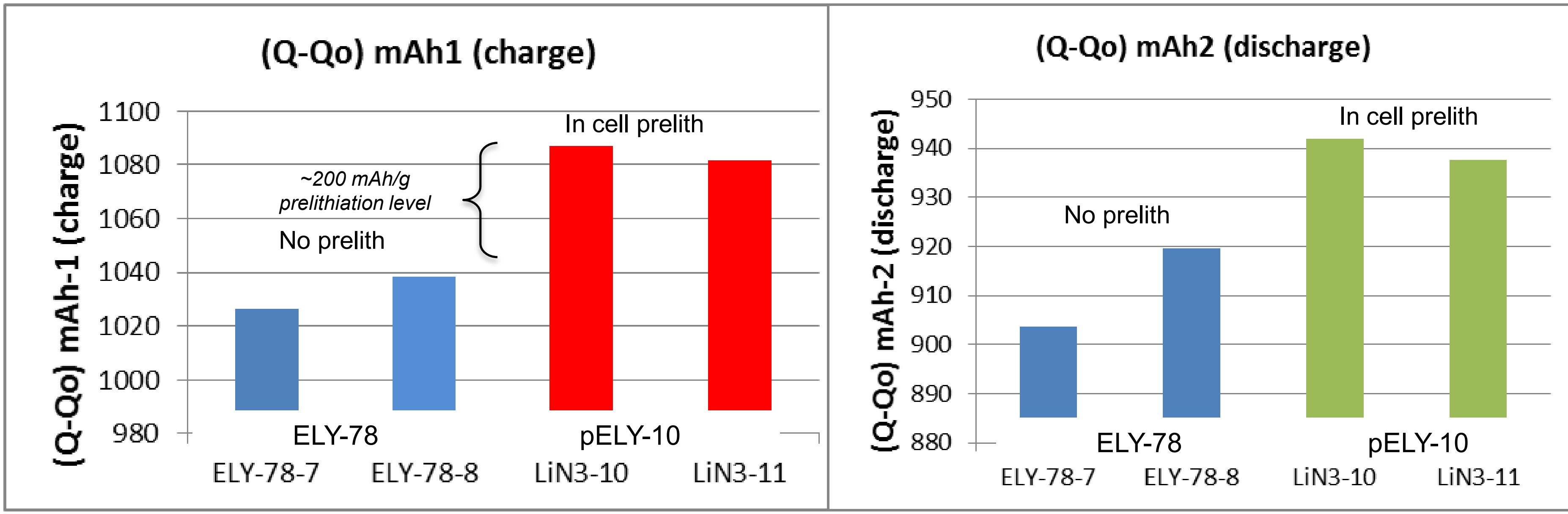
In cell prelithiation applied to wound cells made from full frame foils

Prelithiation formulations increase capacity by about 3%



- Currently in cycle life

Response to Reviewer Comments

New Project, Not Applicable
(No Prior Comments)

Amprius Looks Forward
to Replying to your Comments

Collaborations:

Team Overview

Amprius is the only team member; there are no subcontractors on the project

Amprius has to date performed the overwhelming majority of project work. However, Amprius will engage external vendors to assist with the design and assembly of a pilot prelithiation chamber

Remaining Challenges and Barriers

Sourcing materials for prelithiation

- Prelithiation is a new process step and, with the exception of lithium metal, the chemicals needed for the prelithiation step are not available in quantities required by the battery industry

Process integration

- Prelithiation affects the properties of anode materials and requires special conditions and handling
- Potential impact on downstream process steps is difficult to quantify

Feasibility

- A 3-6 months feasibility evaluation may be too short to fully evaluate potential secondary effects of prelithiation and new chemical formulations of the electrolyte
- 3-6 months may also be not enough time to complete design, development and demonstrate of a pilot prelithiation chamber

Activities – Through September

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Down-select method for prelithiation scale-up

- Finish technical feasibility evaluation of selected methods
- Analyze cost impact of each method tested

Pilot prelithiation development

- Design, test and optimize a pilot setup and equipment that can be integrate with current cell assembly processes

Pilot prelithiation demonstration

- Produce and deliver cells prelithiated using the pilot process developed

Summary

Amprius analyzed the cost and process impact of a variety of prelithiation methods, and selected three for technical feasibility evaluation

Amprius optimized the prelithiation charge level and started feasibility evaluation with the optimized level as target

A new prelithiation method with minimum process impact was invented and is under development