A Commercially Scalable Process for Silicon Anode Prelithiation

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ES250

Overview

Timeline

- Start date: October 2014
- End date: September 2016
- Percent complete: 75%

Budget

- Total project funding:
  $1,800,000
  - DOE share: $1,260,000
  - Contractor share: $540,000
- FY15 received: $609,887
- FY16 projected: $650,113

Barriers

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

Partners

- Amprius – Project Lead

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 silicon 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 Barriers

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

Relevance:

Milestones and Timing

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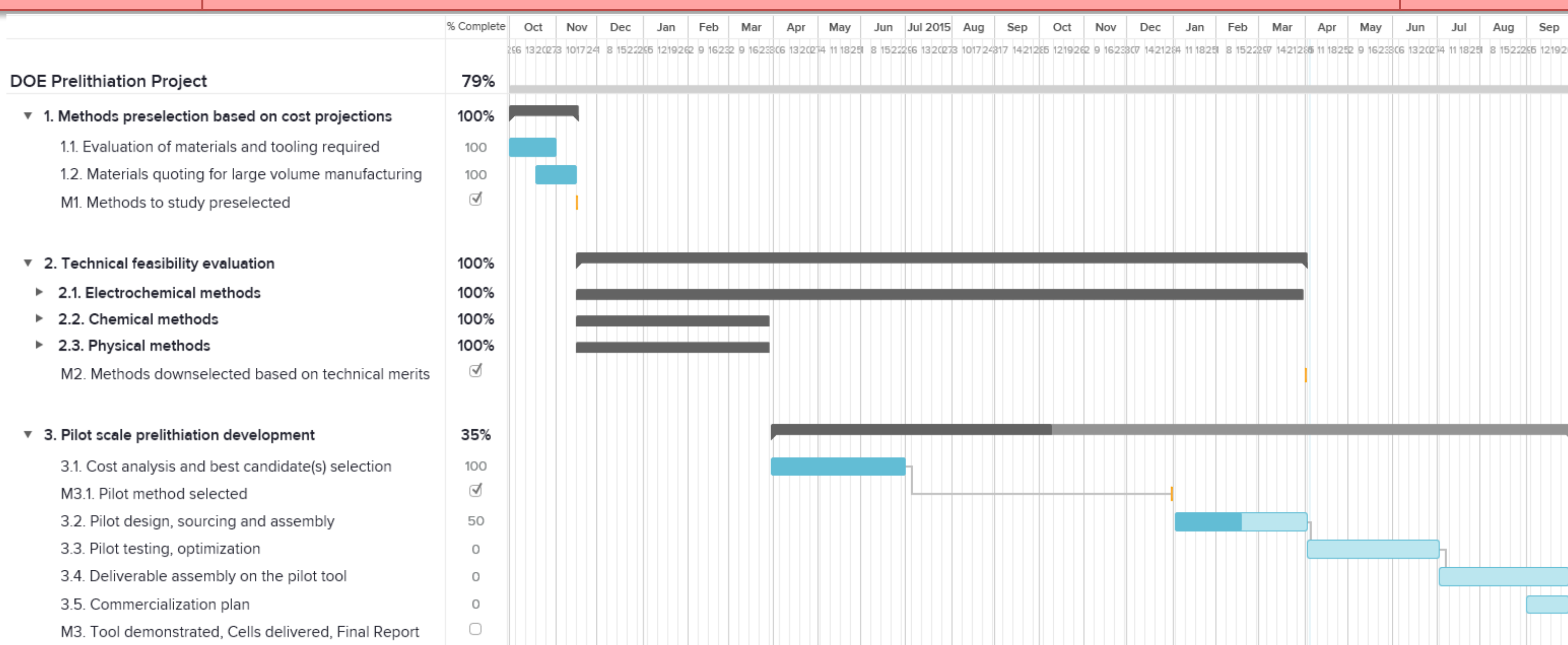
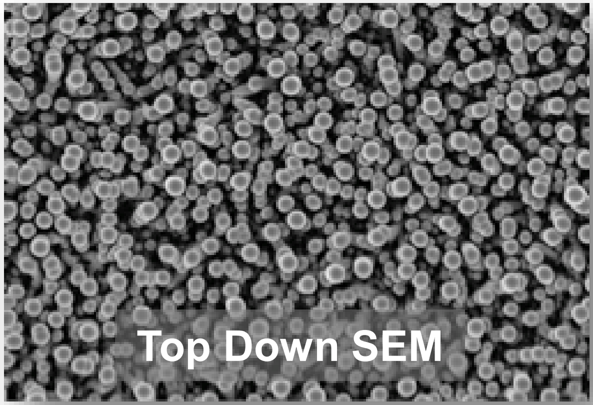
Month/Year	Milestone or Go/No-Go Decision	Status
Nov-14	Milestone: Prelithiation methods preselected	Complete
Mar-16	Milestone: Methods down selected based on technical feasibility	Complete
Mar-16	Milestone: Pilot method selected	Complete
Sep-16	Milestone: Pilot tool/machine/setup demonstrated 10 cells delivered with a capacity over 2Ah, prelithiated in pilot tool Final report submitted	On Track

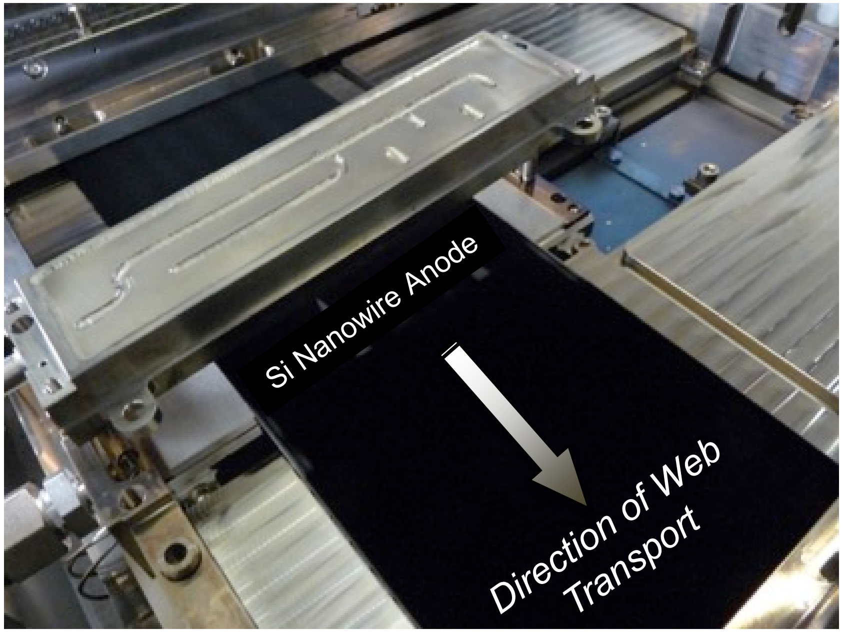


Approach:

Silicon nanowires enables high energy

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





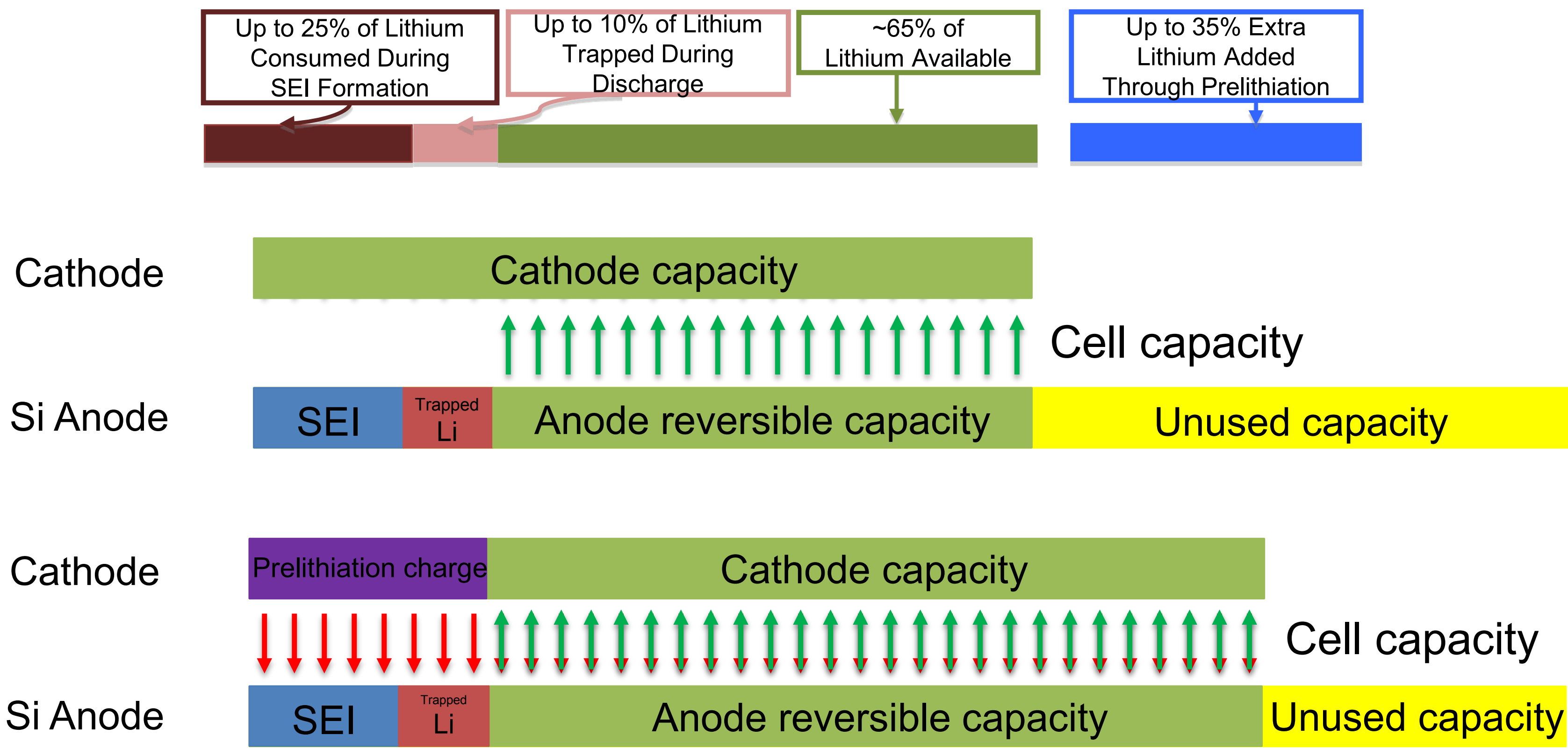
- 1/3-1/5th of graphite anode thickness
- High content active silicon materials (100%)
- Ideal and adjustable porosity distribution
- High mass loading (2-3 mg/cm^2)
- High conductivity and connectivity
- Low tortuosity – high rate capability

During Q1 2016, Amprius tested a first of its kind pilot line tool for roll-to-roll production of double-sided, rooted silicon nanowire anodes

Approach:

Prelithiation Concept

Increase cell capacity without increasing cathode size by using anode prelithiation to address lithium losses



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

FY 2015 Accomplishments

- Selected two electrochemical, one chemical and one physical method for prelithiation, based on cost and manufacturing process impact
- Evaluated the impact of prelithiation on cell capacity and cycle life
- Confirmed/infirmed technical feasibility of preselected methods
- Demonstrated potential pathways for scale-up of selected method

Task 1: Methods Preselection

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•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

The cost of prelithiating the anode should not exceed the cost of adding 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 calendared 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 reagents or salts 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

Amprius favors methods that have a limited impact on current industrial production process flow and equipment, i.e. introduce prelithiation late in cell assembly process

Task 2: Feasibility Evaluation

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Work directions:

- Find the optimum prelithiation charge level by electrochemically dosing the charge and evaluation of the effects on reversible charge and cycle life – reported at AMR 2015
- Verify feasibility of selected methods:
  - Electrochemical prelithiation using sacrificial salt
  - Chemical prelitiation using Lithium reagents
  - Physical prelithiation using unstable salts
- Design and build a pilot scale setup for selected method
- Evaluate roll-to-roll industrial processes that can be adapted to prelithiation

Task 2: Feasibility Evaluation

Chemical Method:

- Silicon anodes were exposed to a preselected list of organometallic compounds
- Prelithiated charge was measured by delithiation and/or by comparing full cell capacity with non-prelithiated cells

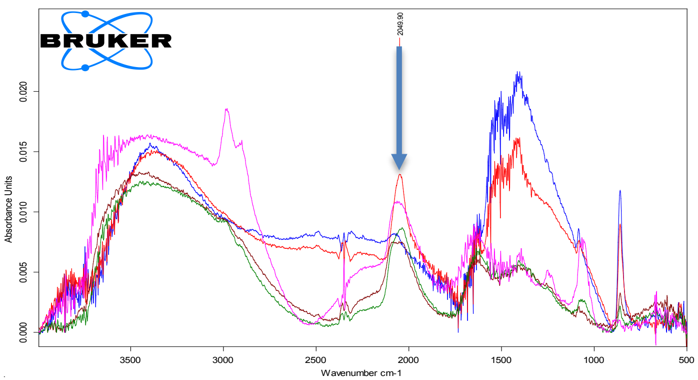
Results and Conclusions:

- Chemical treatment of the anode resulted in reactions at the surface and no or very low prelithiation charge
- Reagents are relatively expensive and produced in low volumes
- Method was not considered feasible technically

Task 2: Feasibility Evaluation

Physical Method:

- Decomposition of lithium salts (ex. LiN_3) at temperature and/or radiation
- Salt condition was monitored by FTIR before and after exposure to UV



Peak disappears after two hour of UV exposure

However:

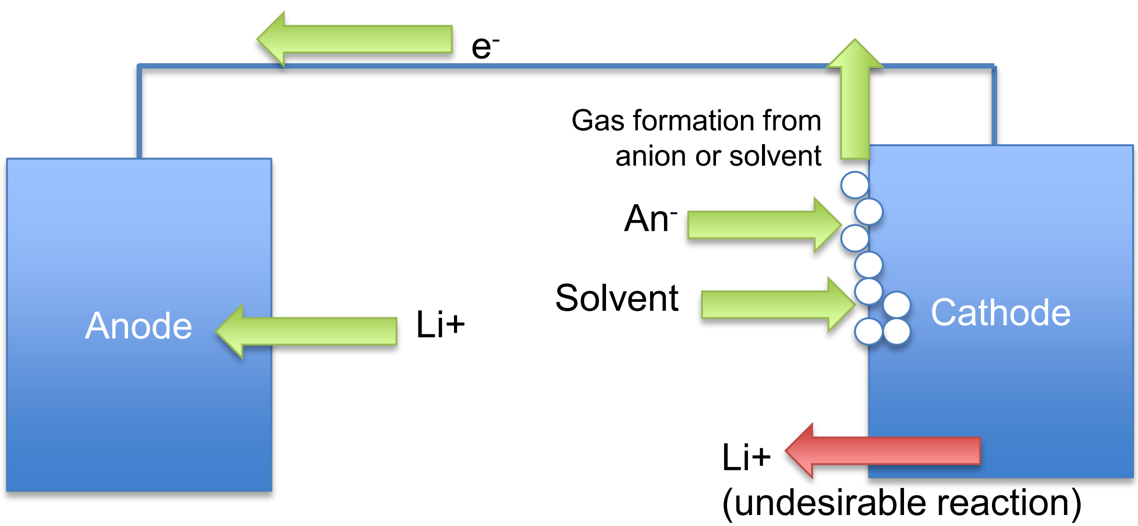
- The prelithiation charge requires about 2 mg/cm2 of azide = >1 mL of solution per cm2
- Solid azide is explosive and toxic → difficult working environment and possible health hazard
- Difficult to confirm that all azide was decomposed and may leave residues that produce gassing in cell
- *Conclusion*: not feasible

Task 2: Feasibility Evaluation

Electrochemical Method: Sacrificial lithium salt in electrolyte

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



Task 2: Feasibility Evaluation

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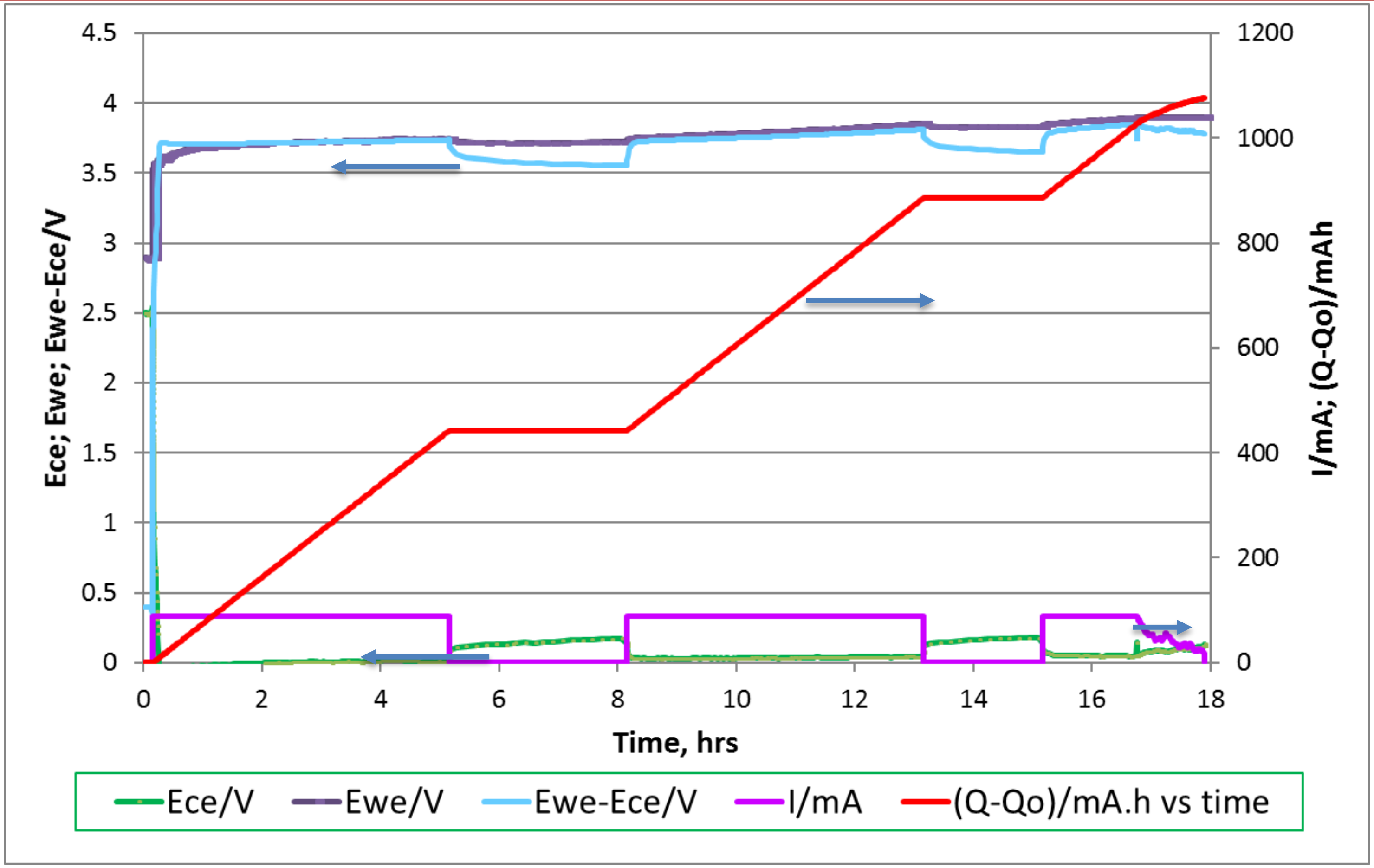
Amprius' project steps to feasibility demonstration:

- ☑ Find a salt that meets electrochemical criteria and has high solubility
- ☑ Proof of concept in single layer cell – capacity
- ☑ Proof of concept in single layer cell – cycle life
- ☑ Proof of concept in >2Ah cell - capacity
- ☑ Proof of concept in >2Ah cell - cycle life

Task 2: Feasibility Evaluation

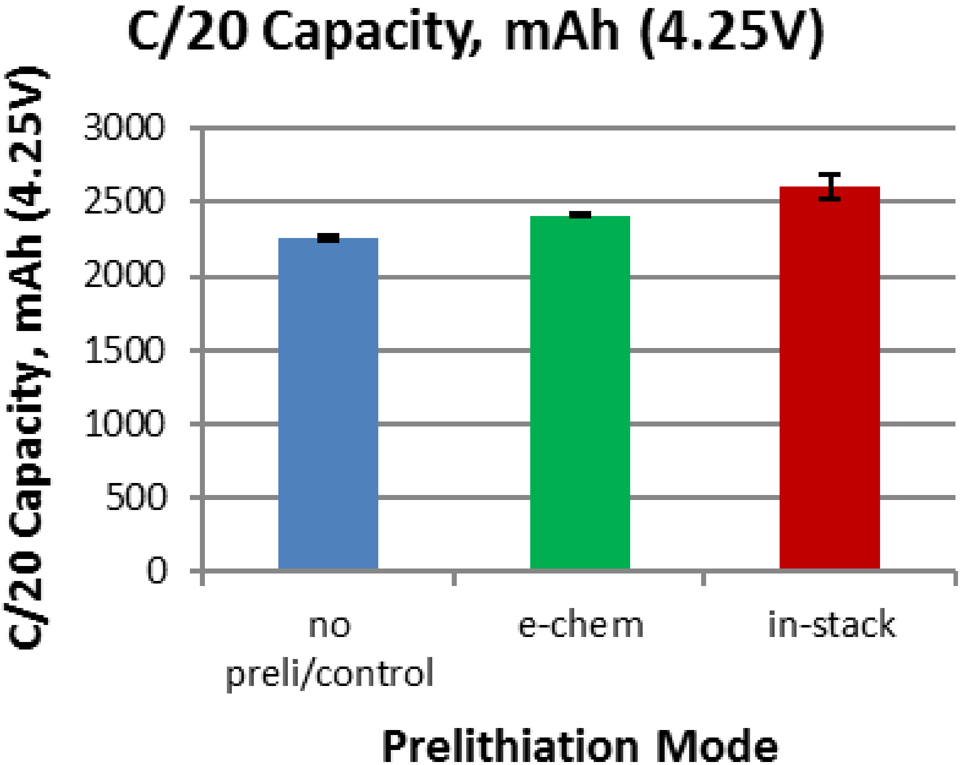
Prelithiation protocol and cell response



Anode voltage and prelithiation charge reached target values

Task 2: Feasibility Evaluation

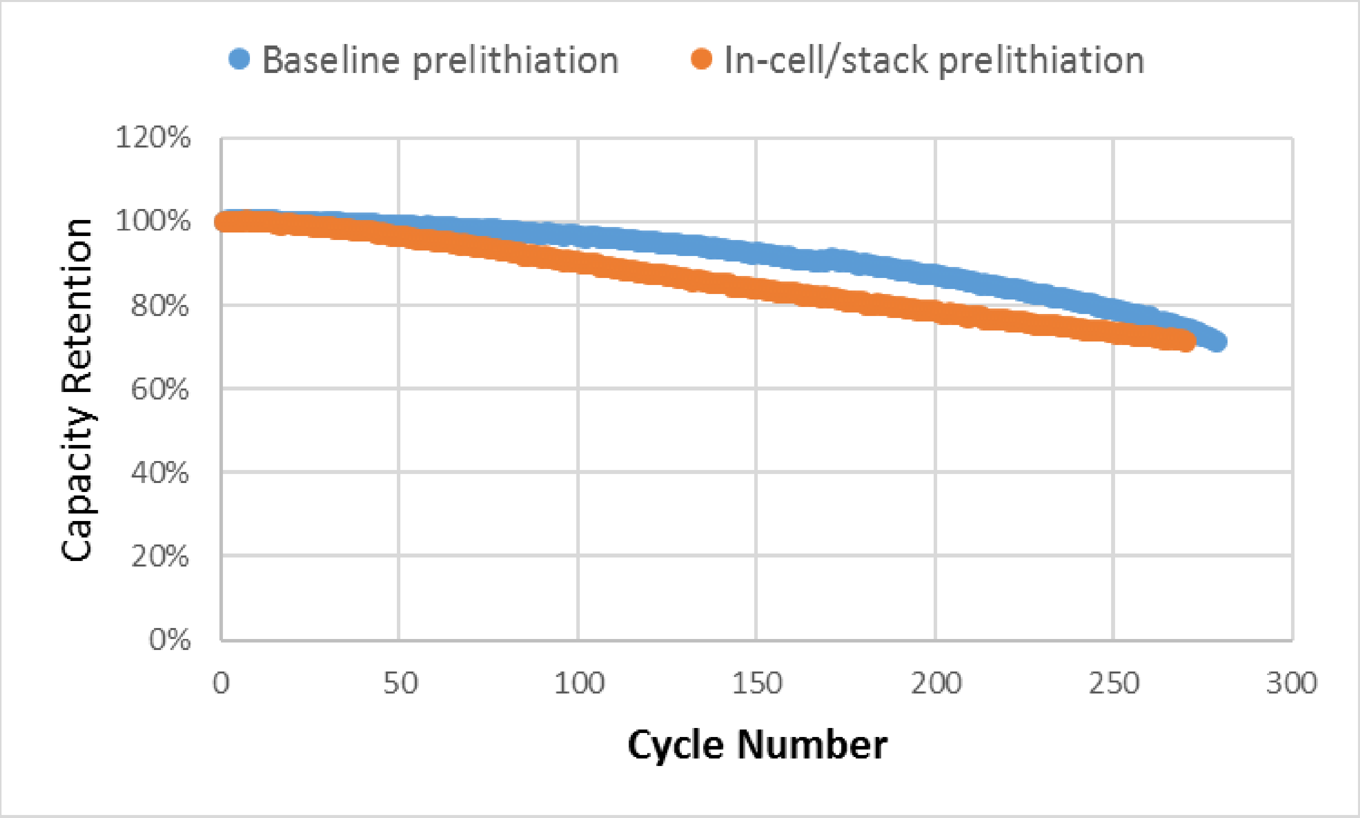
Cell capacity achieved target values



Capacity can be increased by 5-7% by prelithiation for silicon nanowire cells

Task 2: Feasibility Evaluation

Prelithiated cell cycle life approaches baseline target value



Cycle life can be further improved by optimizing the prelithiation solvent and additive formulation, as well as protocol conditions

Response to Reviewer Comments

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•**The project was reviewed positively in most respects. Amprius thanks reviewers for their comments and suggestions**

•**"More legible figure for electrochemical protocol" – machine produced plots were replotted for better presentation**

•**"More data on cycle life" – full cycle life data is available**

•"The project has a short length of only one year, so there may not be sufficient time to identify the cost-effective prelithiation process and demonstrate it on a pilot scale" – **project extended for a second year**

•**"Not clear if the method can be applied to other materials" – Amprius is focused on the development, scale-up and manufacturing of silicon nanowire anodes. However, Amprius' prelithiation formulations are based on commonly used solvents that should be compatible with other battery anodes**

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

Scale-up to pilot

- The in cell/stack method requires a new piece of equipment that should provide environmental, mechanical and electrochemical conditions for the process to take place – scaling from one cell at a time to multiple cells requires design and development

Feasibility

- Long term feasibility, including process reproducibility over a larger number of cells and distribution of capacities and cycle life can be proven only after the method is scaled up to a higher throughput

Future Work:

Activities – Through September

Continue to optimize process conditions

- Analyze the impact of process variables, formulations and protocol

Pilot prelithiation development

- Design, test and optimize a pilot setup and equipment that can be integrated 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

Amprius created and developed a new prelithiation method with minimum process impact