A Disruptive Concept for a Whole Family of New Battery Systems

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ES242

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: 2/01/2015
- Project end date: 7/30/2017
- Percent complete: 35%

Budget

- Total project funding
  - DOE share: $600,000
  - Contractor share: $150,000
- Funding received in FY 2015
  - $160,000
- Funding for FY 2016
  - $250,000

Barriers

- In order for EV's to compete with IC vehicles the batteries needs to be significantly improved
- We are developing a chemistry-agnostic cell-system level architecture to significantly improve performance with acceptable cost & life of batteries
- Our goal is to achieve 1000 Wh/L with our novel cell architecture and using commercially available chemistries, with acceptable rate and Wh/kg performance.

Partners

- Caltech
- UCLA
- JPL, Hydro Québec, Argonne, OakRidge

Relevance

Overall Project Objectives:

- Introducing a novel chemistry-agnostic cell architecture, called Scell, to circumvent limitations by the traditional planar plates cell architecture, and thus significantly increase performance of EV batteries: Wh/L
- Perform fundamental research to design optimum cell architecture resulting in highly packed cells
- Developing fabrication methods for anode, cathode, current collectors, separator and full cell integration
- Demonstrating 50% improvement in volumetric energy density by introducing a novel chemistry-agnostic cell architecture, achieving 1000 Wh/L at 5Wh cell level, with clear path to 1000 cycles, with acceptable rate
- Developing a scalable low cost fabrication method for the said architecture, with clear path to 150 $/kWh cost at cell level, manufacturing volume

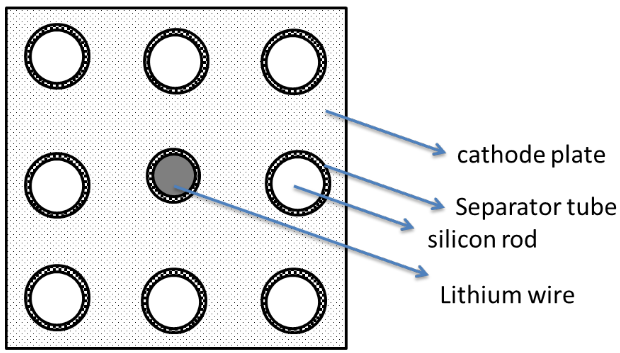
Project Objectives, Budget Period 1:

- Develop a realistic numerical model to design optimized Scell cell-level architecture, based on commercially available chemistries: *Accomplished*
- Develop a fast testing method, implementing commercial cell shapes, coincell-18650 and pouch cell, to rapidly test Scell architecture: *Accomplished*
- Develop low cost fabrication methods for anode rods, cathode plates & current collectors: *Accomplished*
- Demonstrate full capacity of each of anode array and cathode layers in half cells: *On going*
- Demonstrate promising early results and clear paths for low cost fabricating of separator coating: *On going*

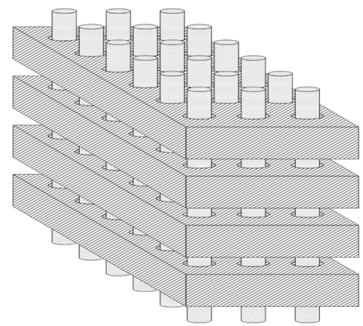
Milestones

Budget Period	Milestones & Go / No Go	Status
1	Complete Perforated Plate Fabrication	Complete
1	Complete Anode Array Fabrication	Complete
1	Half S-cell Testing the Novel Rod Electrode (GO)	On going Cells are made and are running Will be completed by the end of Budget Period 1
2	Complete Half S-cell Testing; Perforated Plates Cathode	On going
2	Complete Testing Full S-cells	On track
2	Initial S-cells Testing Complete	On track
2	Final S-cells Testing Complete	On track

Introducing the Supper Cell (Scell™) 3-D Architecture



Top view

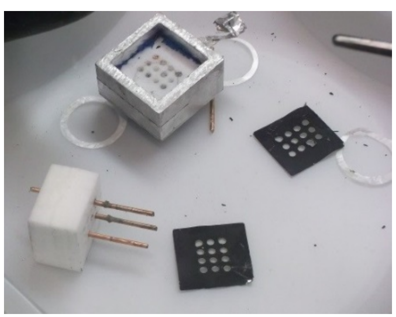


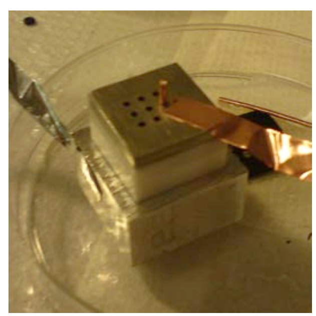
Chemistry Agnostic

Fabrication challenges:

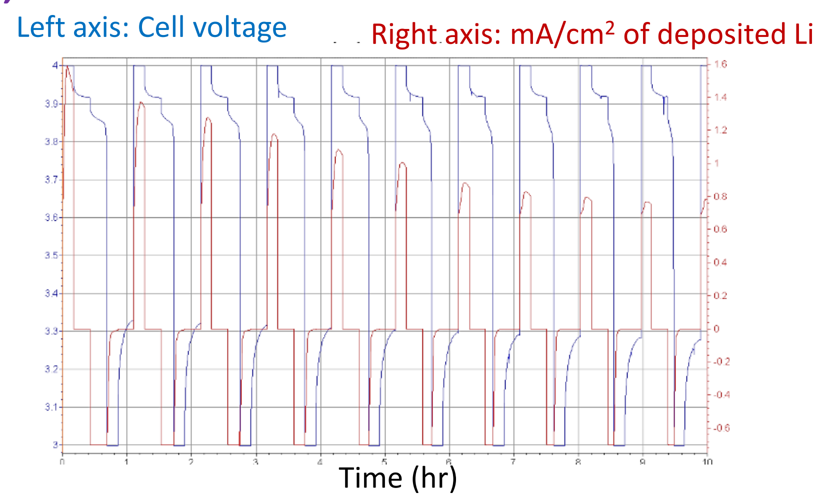
- Anode rod array
- Layered cathode
- Conformal separator
- Current collectors
- Full cell integration

Early proof of concept, full cell





3 layers, 8 rods; Cathode: $LiCoO_2$; Anode: In-situ lithium deposited on copper c.c.; Commercial electrolyte; Designed gaps instead of separators



Designing an optimized cell architecture to fully utilize the chemistries of the batteries

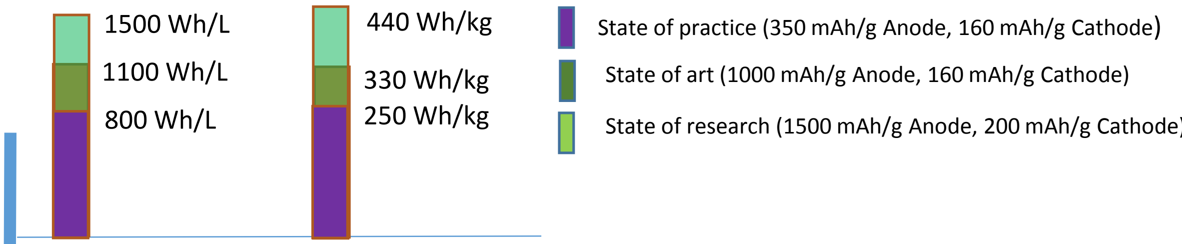
Scell, Uniquely enables:

- "lithium metal depot" inside the cell: In-situ lithiation & Non lithiated cathode and anode
- Thick electrodes: multi-layered electrode
- Conversion chemistries: Accommodating large shape changes of electrode materials, such as silicon, inside the cell (space between layers and the cylindrical array structure)
- Slow kinetics chemistries: Increasing the surface area of plate and rod electrodes by two orders of magnitude

Notes:

1. Addressing the development of thick electrodes with a unique method
2. Each of the rods: Solid rod or bundle of micro-nano featured rods
3. Multiple different chemistries for each plate or rod can be used in one cell

Expected Energy Density



Developed a **realistic** numerical model to optimize the Scell design by varying key parameters:

Rods spacing:

Rods spacing is the most important design parameter dictated by physics and defines the rods radius

Ionic diffusion between plates & electrochemistry dependence of distance from the rods

Smaller spacing improves the performance but more challenging fabrication (cost)

Rods length:

Homogeneity through the height

Larger height improves performance but more challenging fabrication (cost)

Rods diameter:

Ionic diffusion inside the rods & homogeneity through the diameter

Smaller dimeter improves performance but more challenging fabrication (cost)

Cathode plates thickness

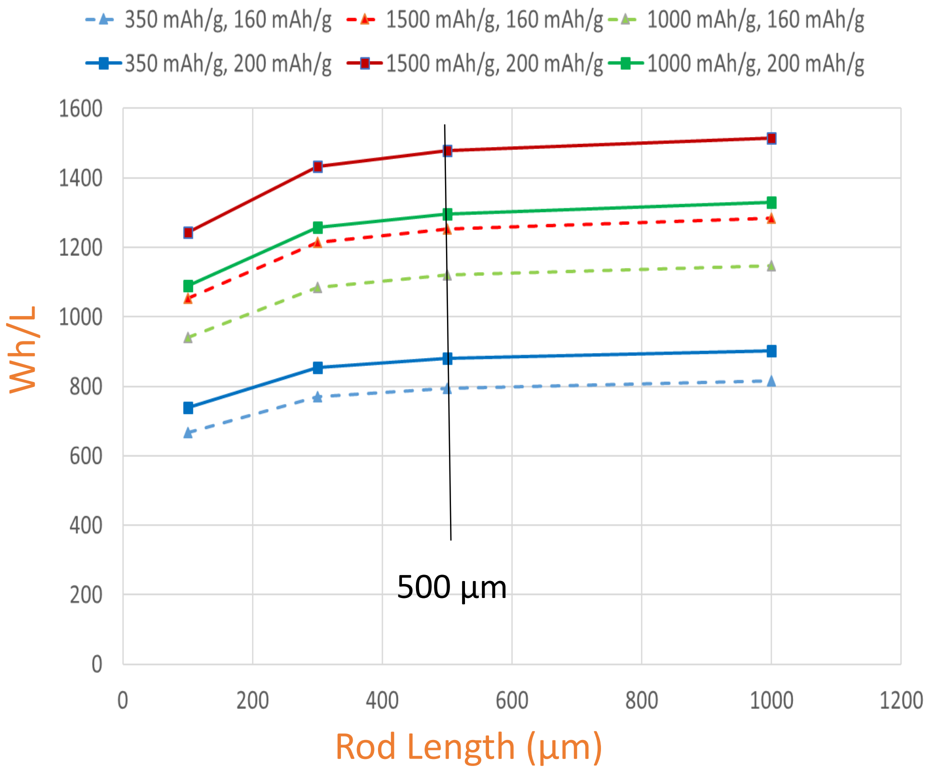
Porosity of Plates & Rods

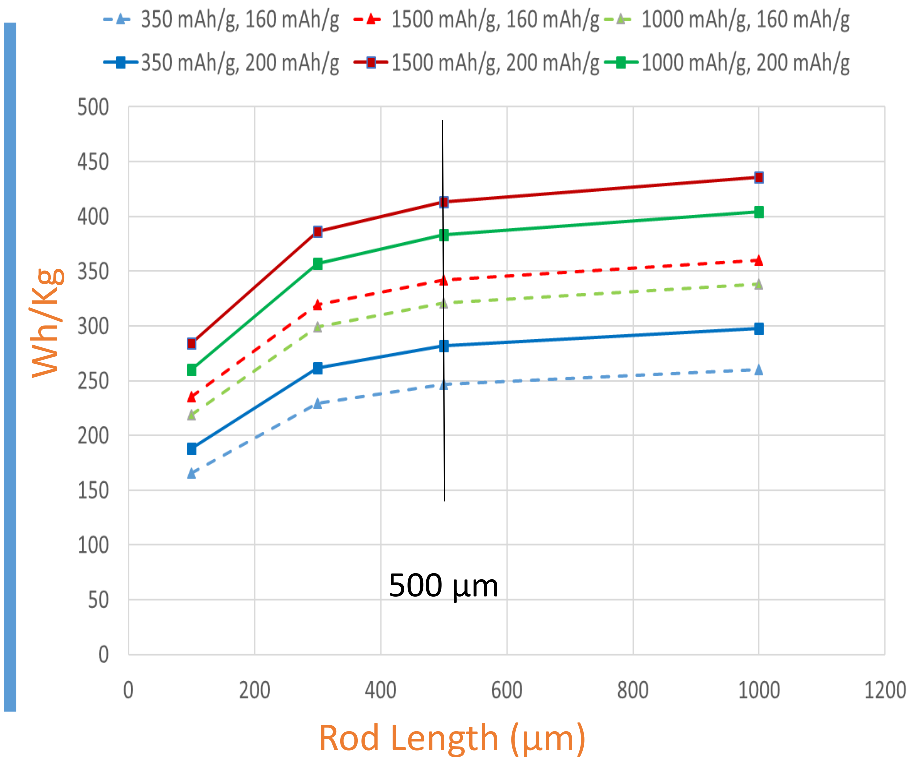
Numerical model is designed to adjust the values to 700 Wh/L and 250 Wh/kg, when the format becomes 18650

Scell may enable long cycle life and lower inactive/active ratio

Performance as a function of rod length

For different electrode capacities; cell level

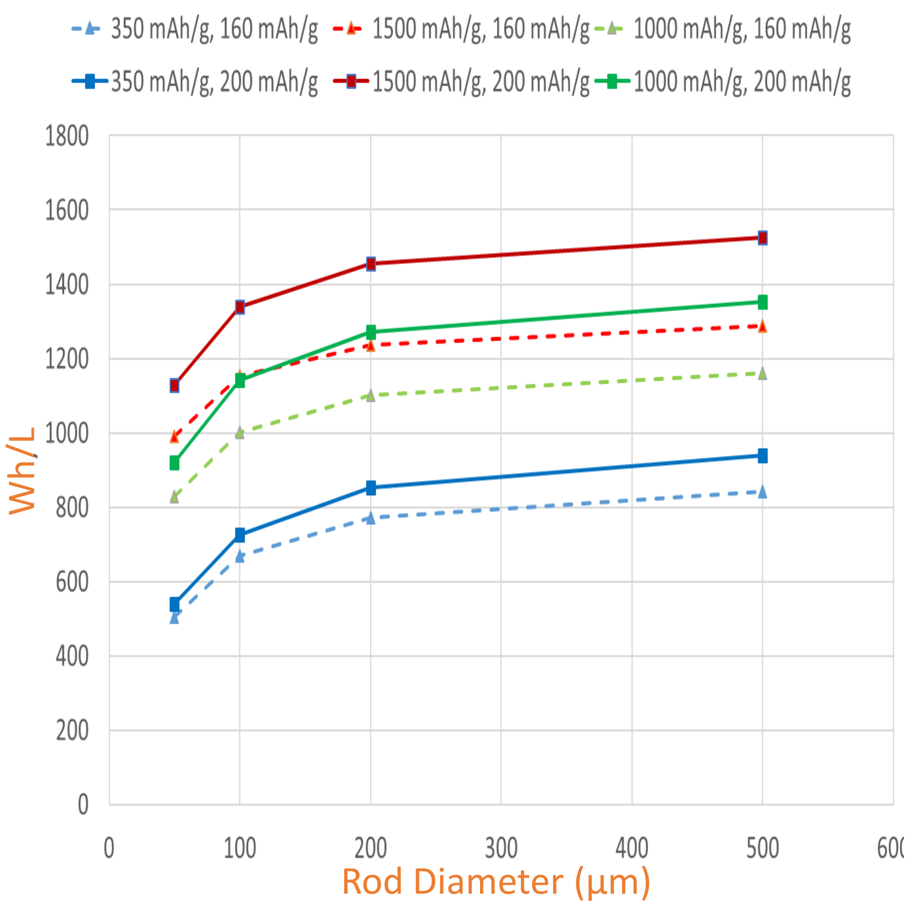


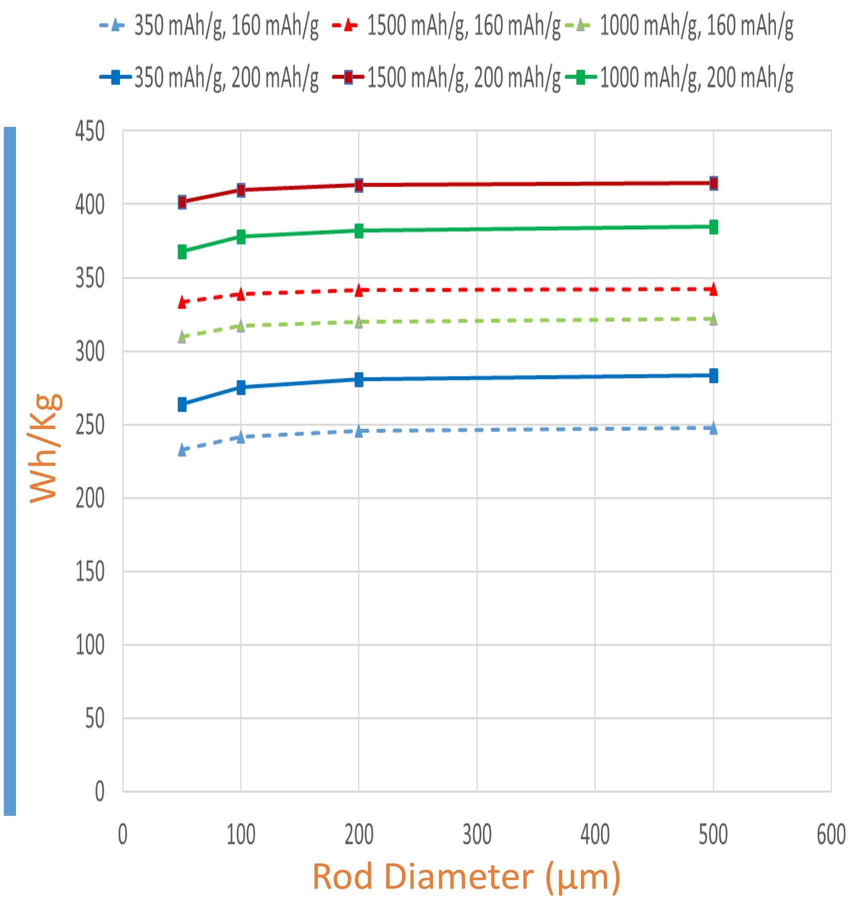


- Anode: commercial Carbon+ Silicon; Cathode: commercial $LiCoO_2$ or commercial high capacity LNMC
- Rods diameter: 250 um; Pitch: 350 um; array substrate thickness: 25 um; Cathode porosity: 25%; Carbon anode porosity: 25%; Silicon-Carbon anode porosity: 50%; “Core copper to rod” diameter ratio: ¼ [conservative; we try making cells with 1/10 ratio]; Separator thickness: 16 um; Case thickness: 0.25 mm

Performance as a function of rod diameter

For different electrode capacities; cell level

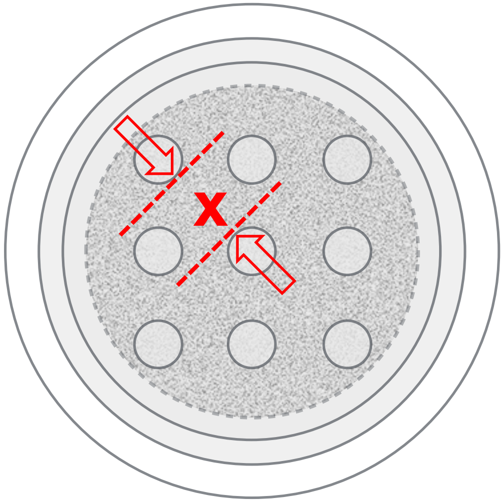




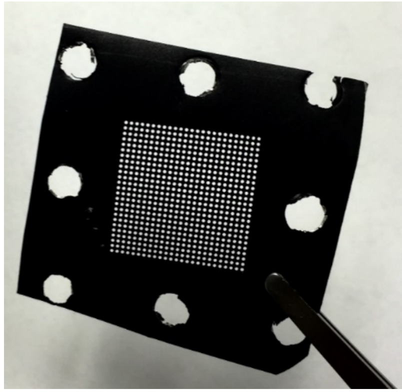
Anode: commercial Carbon+ Silicon; Cathode: commercial $LiCoO_2$ or commercial high capacity LNMC

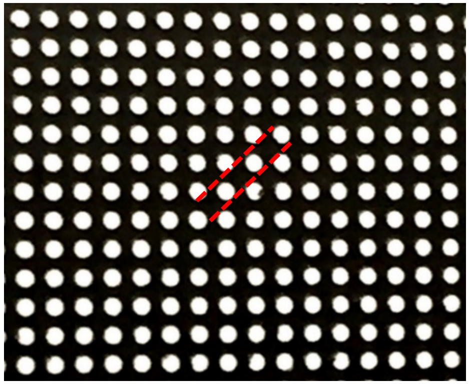
Rods height: 500 um; Pitch: 350 um; Rods array substrate thickness: 25 um; Cathode porosity: 25%; Carbon anode porosity: 25%; Silicon-Carbon anode porosity: 50%; “Core copper to rod” diameter ratio: 1/4; Separator shell thickness: 16 um; Case thickness: 0.25 mm

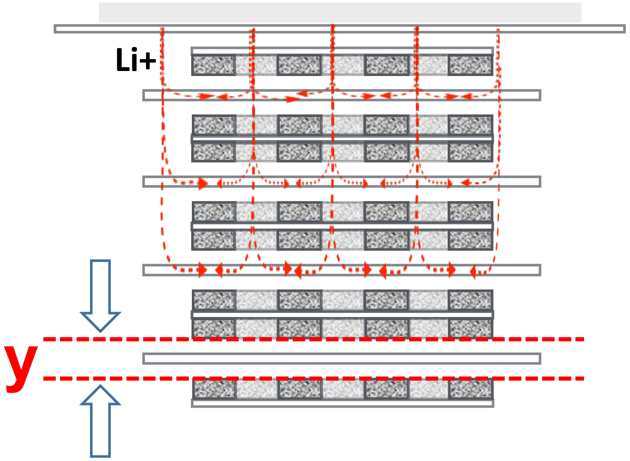
Most critical design issue: Ionic diffusion access to the entire surface layers, affected by x & y, below:



- **Maximum edge-to-edge spacing, x**
- Number of lithium ions between the layers depend on the available electrolyte in **y** thickness
- Lithium ions must travel a maximum distance **x/2** through channels with height **y** through electrolyte solution





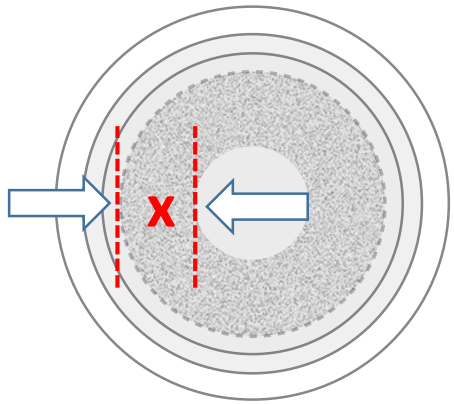


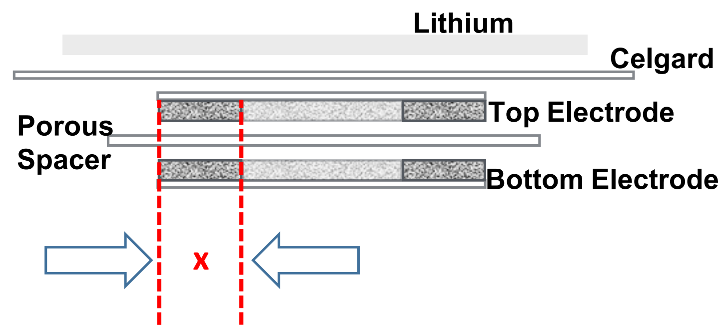
$LiCoO_2$ with 300 μm holes, **x**= 550 μm

Determining parameter x

The ionic diffusion study experiment

- **Studying the maximum allowable distance ions can travel (diffusion limits)**
- **Stacked and aligned layers** with **electrodes facing each other** so that Li must diffuse through a distance x/2 in the electrolyte.

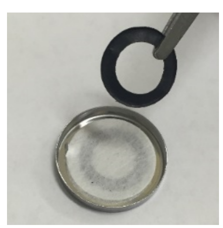




Bottom Electrode

Porous Spacer

Top Electrode



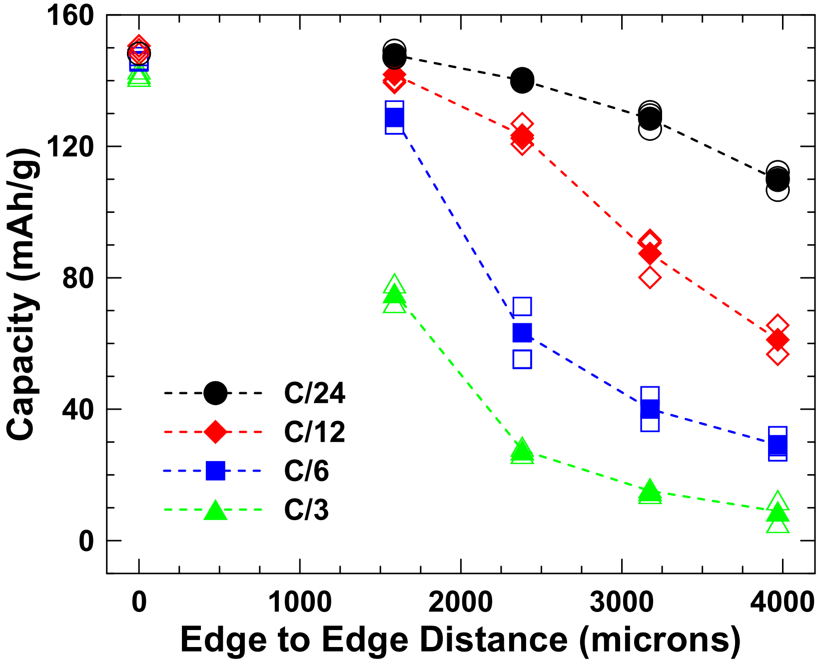
Al current collector

Celgard Separator

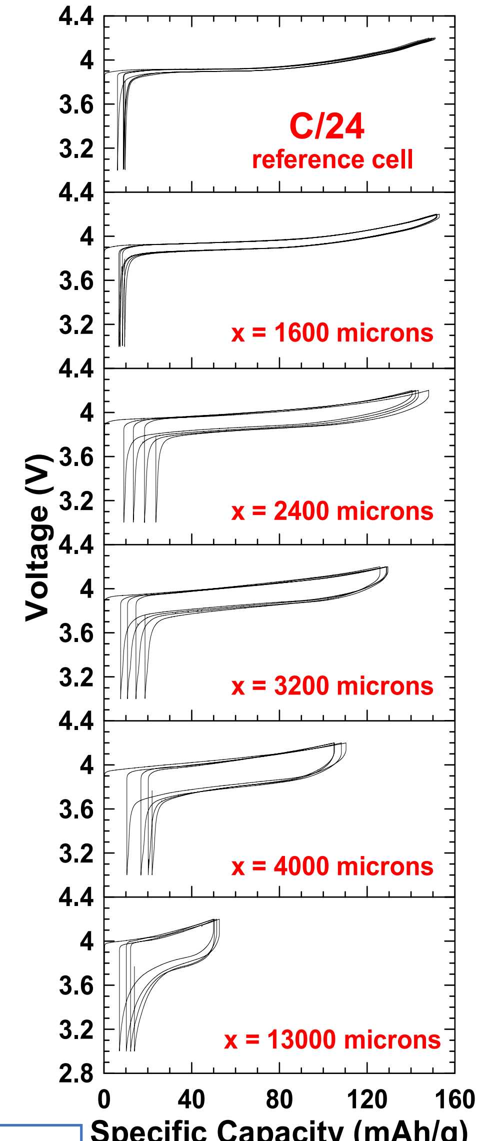
Lithium and Spacer

Spring

Experimental results



- Right: reference $LiCoO_2$ sample vs. stacked electrodes for given values of **X** at C/24.
- Left: first charge capacity as a function of **X** for different rates.

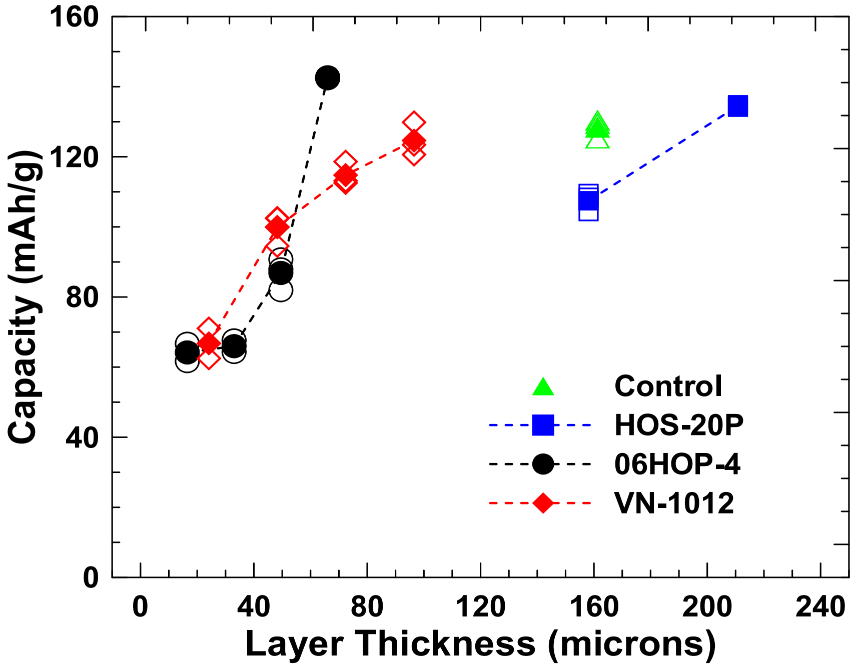


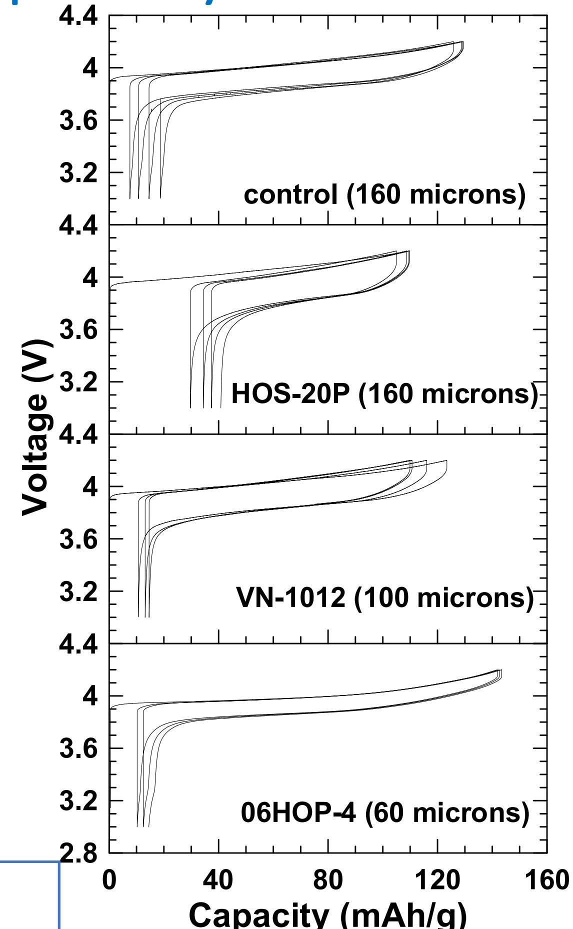
- 1M $LiPF_6$ in 1:1:1 EC:DMC:DEC by volume electrolyte.
- $LiCoO_2$ cathode with 34 mg/cm^2 active mass loading.
- Spacer: S1; 160 µm thick

Demonstrated that full cathode capacity <u>can</u> be achieved in the final S-Cell design.

Experimental result: Demonstrating 100% half-cell capacity

- x= 3200 um
- **Achieved theoretical capacity, 145 mAh/g at C/24, when y=60um, i.e. x/y=53**



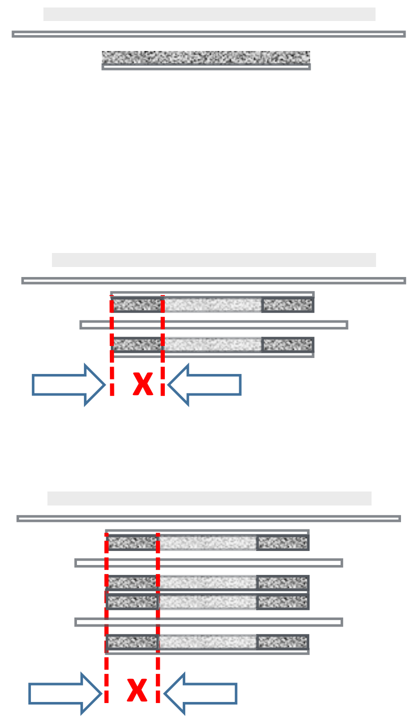


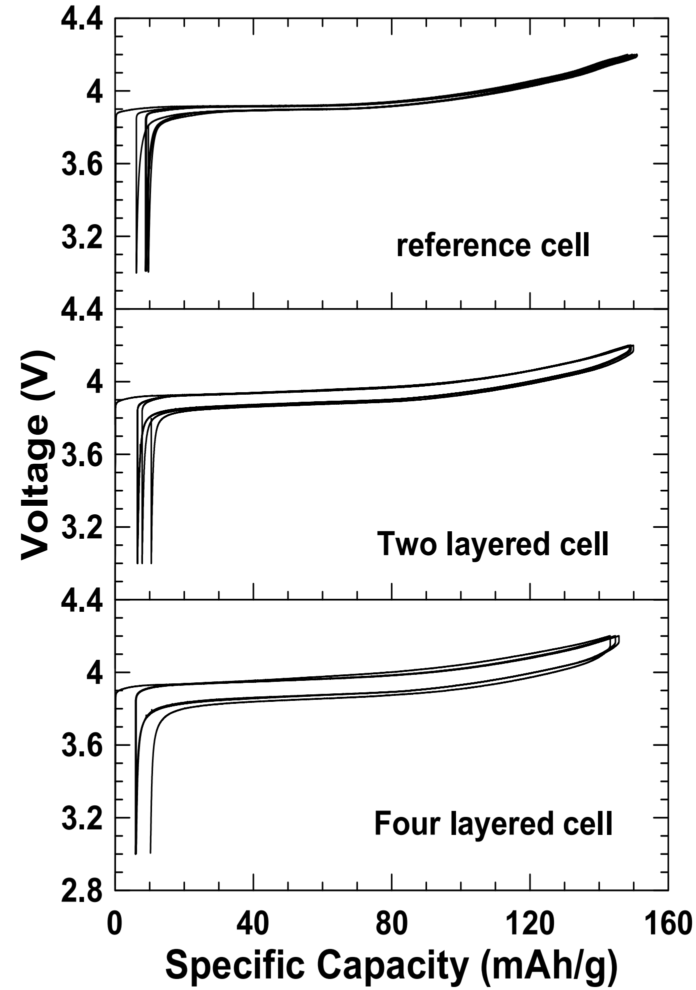
Demonstrated full cathode capacity is achievable for the x/y ratio of 50 or smaller

Effect of Adding Layers

- In half cell performance, the addition of layers resulted in a small increase in hysteresis at C/24, when x = 1600 microns, but no capacity loss.

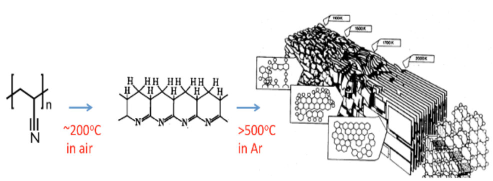
- In the final S-Cell, the anode will be inserted into the rods. Therefore the additional vertical distance will not affect performance.





While addition of layers improves the Wh/L, we have demonstrated that it does NOT adversely affect the rate performance

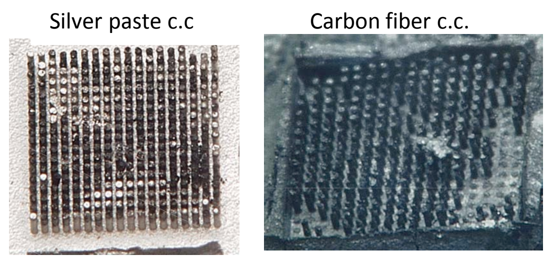
Anode Rods & Current Collector



polyacrylonitrile-derived amorphous carbon

Prepare slurry:

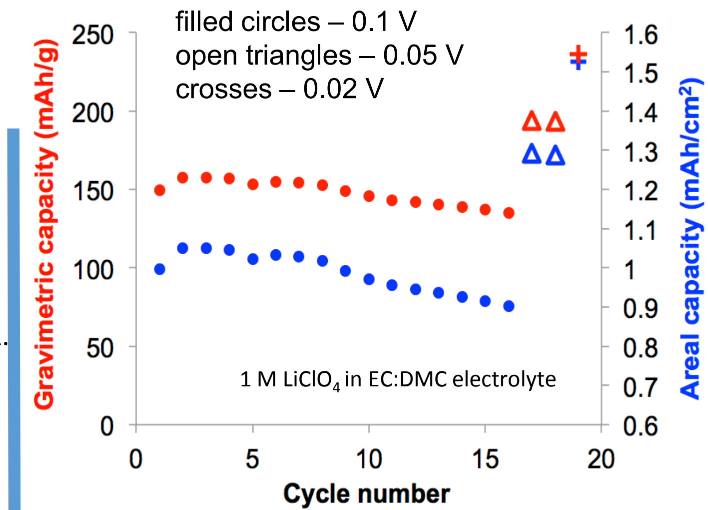
0.1 g/ml solution of polyacrylonitrile in DMSO
separately mix active materials (graphite microbeads and silicon nanoparticles)
mix for total solids concentration of 4.8 g/ml
Fill into mold using pressure vacuum
Heat 280°C in air, 800°C in inert atmosphere
Conversion to amorphous carbon, seen in FTIR.

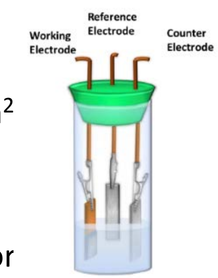


80% active material; 10% conductive carbon; 10% binder; 100 um diameter, 350um length

Current collector:

- Silver paste adhesive: Not suitable (Electrochemically active; Weak adhesion
- Impregnate PAN slurry directly into carbon fiber paper: <u>successfully fabricated 3D array</u>



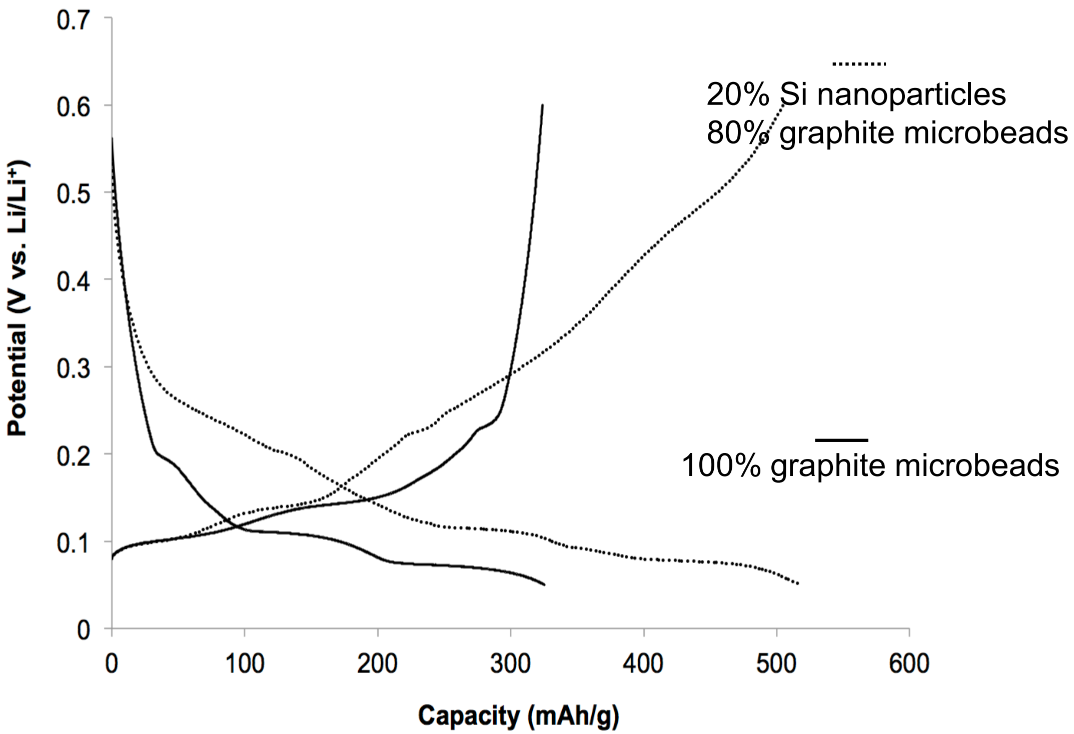


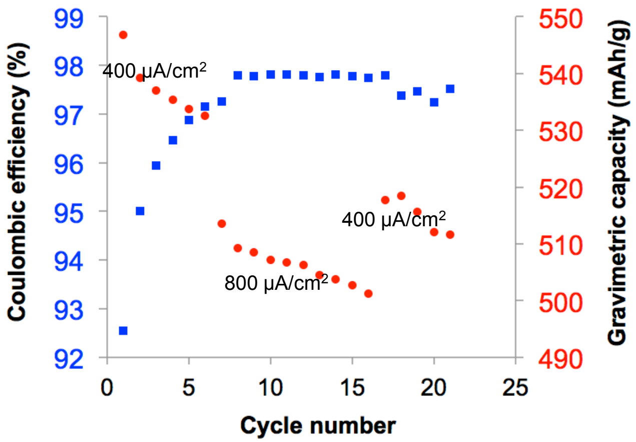
- 0% Si / 100% graphite
- current density = 0.4 mA/cm^2
- Post dimensions:
  - 100 μm diameter
  - 200 μm pitch
  - 350 μm tall
- mounted on current collector using silver paint adhesive
- broken posts: mass is overestimated
- limit lower voltage to prevent lithiation of silver paint

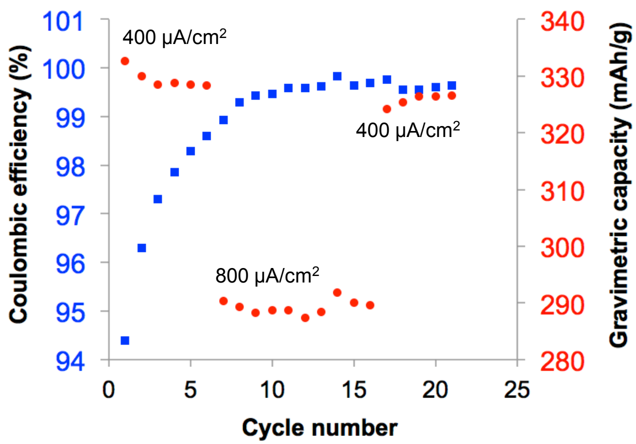
Demonstrated scalable anode array fabrication for carbon and its current collector

Anode: silicon added carbon, 2D results

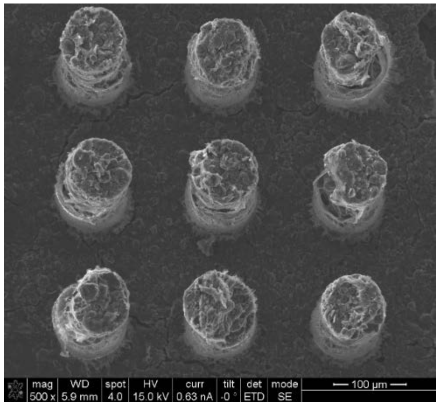
- Thick (10 mg/cm^2) samples prepared on stainless steel mesh
- Cycled in half-cell configuration with 1 M $LiClO_4$ in EC:DMC electrolyte





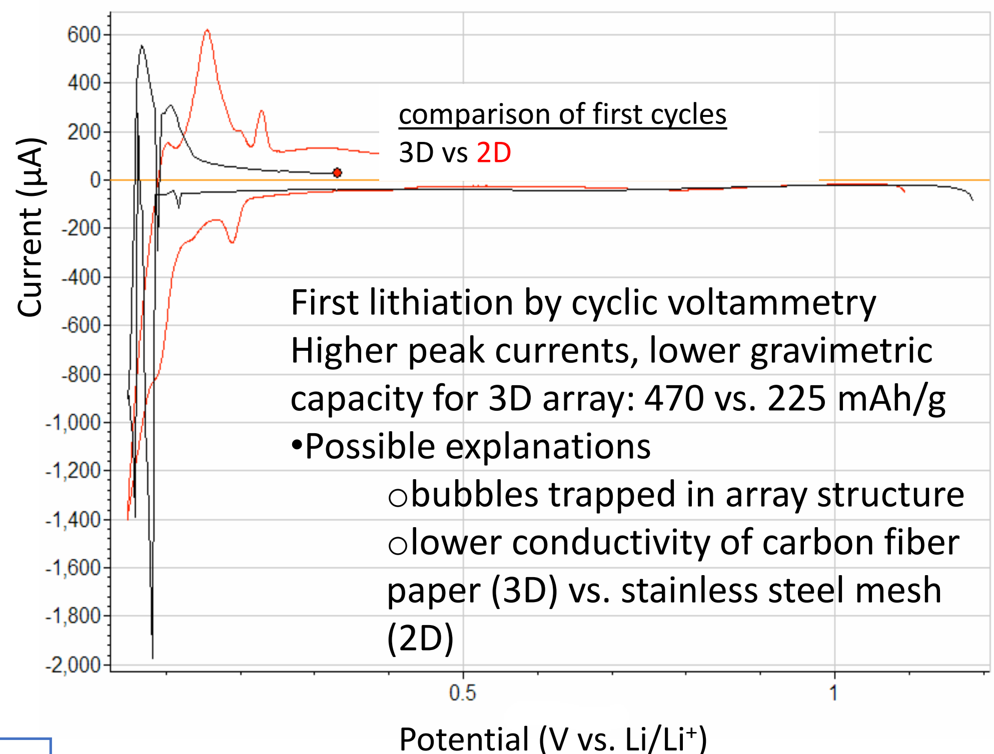


Anode rod fabricated with silicon nanoparticles



20% silicon / 80% graphite Si nanoparticles embedded in amorphous carbon matrix.

Carbon fiber current collector



Demonstrated scalable anode array fabrication for silicon added carbon

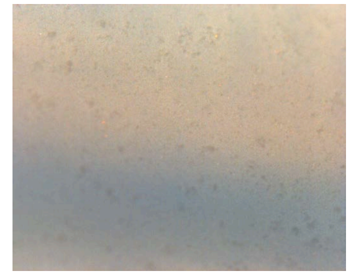
Separator In Situ Fabrication

- Electrophoretic deposition on Stainless steel substrate
- Dispersion: 0.5 mg/ml of 700 nm PS beads in ethanol
- 1 V/mm applied for one hour;
- 2 mg/cm^2 or ~ 20µm thick; surface area = 0.25 cm^2
- PS bead annealing should occur above the glass transition point of PS: TG = 107°C
- tested the conductivity of PS coating after various annealing treatments
  - electrolyte = 1 M butyl methylimidazolium in PC
  - Approx. doubling of electrolyte resistance for 120°C anneal: PS film conductivity σ = 0.3 mS/cm; comparable to liquid electrolytes; infinite electronic resistance

9/16” SS counter electrode

1/2” SS mesh working electrode

3 days @ 100 C



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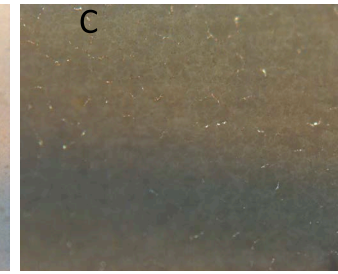
4 min @ 120 C



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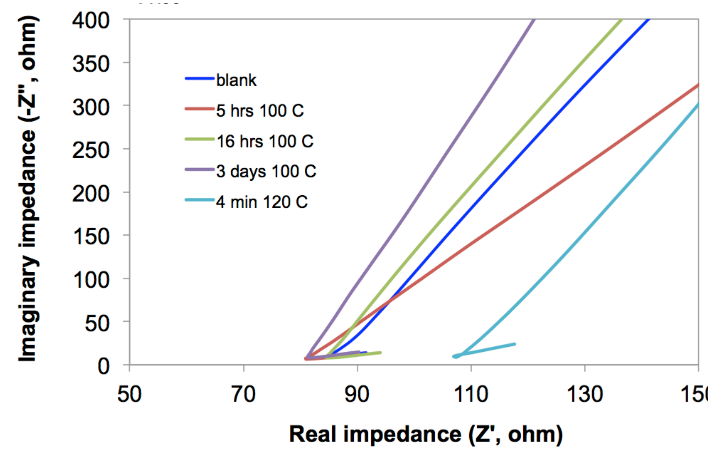
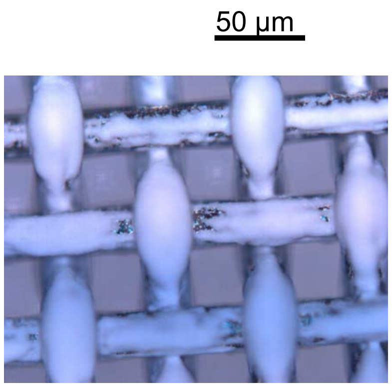
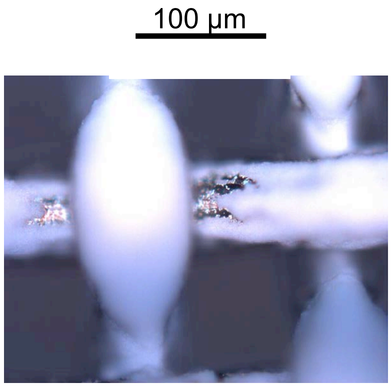


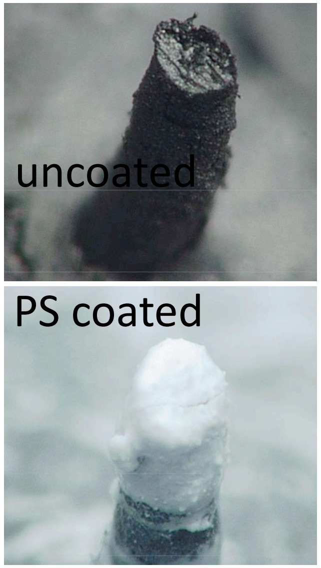
Proof of concept tests: EPD conformality



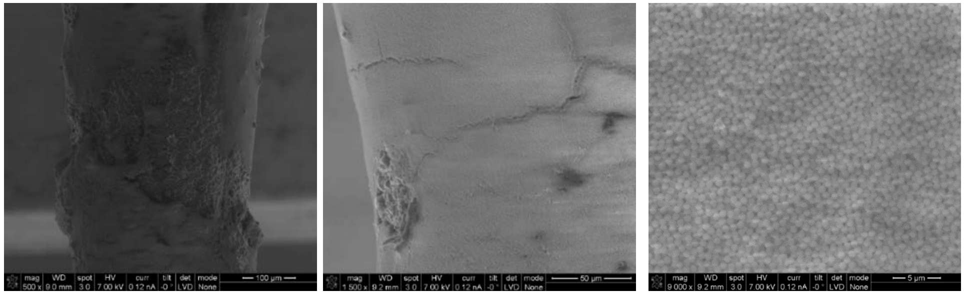


roughness of SS mesh ~ 1.9; ½" diameter SS mesh has surface area 240 mm^2
close packed spheres 74% dense; for 10 um thick coating → 1.9 mg
0.4 mg/ml; 10 V/cm deposition for 80 min; 1.1 mg deposit mass

- EPD conformality test; 500 µm diameter post
- 0.5 mg/ml PS dispersion; Deposit one hour @ 1 V/mm; 0.5 mg / cm^2 (Approx. ½ the mass of the 2D stainless steel deposits
- Conformality can be improved by using stronger and alternating (AC) electric fields
- Will adapt to 100 µm diameter arrays
- May need eletro-deposition to fill the large pinholes in EPD method



Demonstrated a potential scalable conformal separator coating method



Responses to Previous Year Reviewers' Comments

- Developed scalable fabrication methods for anode arrays, cathode layers & current collectors. Experiments are under way (will be completed on schedule by June 2016) to demonstrate 100% of each of anode & cathode capacity in half cells
- Developed an electrophoresis conformal method for coating the separator. Experiments are running
- Developed an extensive numerical model that in conjunction with the experimental verifications shows a clear path to cell level performance of 1100 Wh/L, 330 Wh/kg, 1000 cycles at 80% DoD to 80% capacity retention at the end of the project. Experiments are running.
- Significant collaboration started and is running with UCLA
- Collaboration formed with JPL, Hydro Québec, Argonne, OakRidge
- Identified two distinct fabrication methods of full-cells, new Scell architecture:
  - Separate fabrication of anode arrays and cathode perforated plates and then integration of the full cell
    - Developed scalable anode and cathode fabrication methods
    - Developed current collectors integration methods
    - Developing the separator coating and full cell integration
    - Patents are filed
  - Fabrication of anode arrays and then fabrication of cathode layers on it
    - Will Develop the method later. Patents are filed.
- Detailed future experiments are designed with clear path to the project objectives

Collaborations and Coordination with Other Institutions

Academic: UCLA (Project subcontractor)
Development of anode array; Development of separator thickness

Government Lab/ Final user: JPL-NASA
Project Management, Scell design, Parameter optimization, Designing experiments, Data analyses

Industry: HydroQuebec
Fabrication and supplying Electrode Materials based on the optimized Scell requirements

National Lab: Argonne
Supplying Electrode Materials; Studying the materials performance; Technical discussions

National Lab: Oak Ridge
Implementing their 3-dimentional software to simulate the performance of Scell to optimize the design

Remaining Challenges and Barriers

- Fabrication of a novel architecture is extremely challenging. For this reason, instead of one, we identified “two” distinct fabrication methods of full-cells for Scell architecture:
- Separate fabrication of anode arrays and cathode perforated plates and then integration of the full cell
  - Challenge 1: developing the separator coating: Conformal, homogeneous, maximum hole sizes, low ionic resistance.
    - Electrophoresis: Conformality and homogeneity are challenging tasks
    - Electrodeposition: Ionic resistance can be very high
  - Challenge 2: developing precise placing methods to integrate anode and cathode. We have identified an industrial (electronics manufacturing based) method.
  - Challenge 3: Full cell integration may damage the conformal separator
  - Challenge 4: Cycle life of anode array is still under evaluation; if the posts break we will need to further assisting techniques
  - Challenge 5: Working with perforated plates with 100um holes array requires extreme caution
- Fabrication of anode arrays and then fabrication of semi-solid cathode layers on it
  - Challenge 1: The viscosity control of the cathode formation and ensuring adequate ionic and electronic conductivities in the entire layer
  - Challenge 2: Homogeneous coating of cathode
  - Challenge 3: Separator, conformal, homogeneous, electrochemically inactive

Proposed Future Work

On going:

1. Fabrication and half-cell testing of silicon+ carbon anode rods with different sizes: ½” circular molds are prepared; Achieving 100% theoretical capacity
2. Fabrication and half-cell testing of conformal separator on rod arrays with electrophoresis; also without any adverse effects on the array electrochemical performance
3. Fabrication and half-cell testing multi-layer cathode with 100-500um arrays of holes; Achieving 100% theoretical capacity

Future:

1. Fabrication of separator-solid electrolyte with electrodeposition
2. Full-cell integration implementing with solid cathode (pick & place, borrowed from electronics manufacturing). Optical testing techniques may need to be implemented
3. Investigating semi-solid cathode with Scell architecture

Summary

- In order for the EV cars to compete with IC vehicles they need to significantly improve their battery performance.
  - Improve energy density by 50% (from 750Wh/L to better than 1,000 Wh/L)
- Traditional parallel plate batteries can introduce incremental improvement by adjusting battery chemistry
- We are introducing a disruptive, novel 3D battery platform that may significantly improve EV performance.
- The project has made impressive progress addressing the challenges that need to be overcome to introduce this battery to market.
  - Development of a numerical model needed for defining optimum battery parameters; demonstrated at least one method each for producing anode rods; cathode plates; application of current collector and separator; and testing of the anodes and cathodes in half cells.
- We are on target to produce a scalable prototype ahead of final project end date