Structural Batteries for Hybrid Electric Propulsion System

Frank Ritzert and Randy Bowman
NASA Glenn Research Center
Cleveland, OH

Dan Steingart and Ben Hertzberg
Princeton University
Princeton, NJ

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Problem Definition

Parasitic Weight/Motivation

- Weight of batteries can be a large fraction of the overall aircraft weight
  - Ex. Electric aircraft that recently won the NASA/CAFÉ Green Challenge – batteries ~50% of empty weight of aircraft
- Batteries do not contribute to load carrying capability, and are therefore “parasitic”
- Goal is to create a load-bearing fiber-reinforced composite structure capable of energy storage
  - Fibers/foam will serve as the anode for energy storage functions

Innovation

Achieve a three-dimensional interpenetrating network of anode and cathode materials where the fibers provide load bearing capability using well established structural composite concepts.

Platform materials coated with suitable anodic materials that allow them to serve as the anode material in an energy storage system.

Alternative structural battery concept based on fiber-reinforced network for increasing strength while maintaining the energy storage capabilities of Li-ion battery system.

Structural Battery Concept

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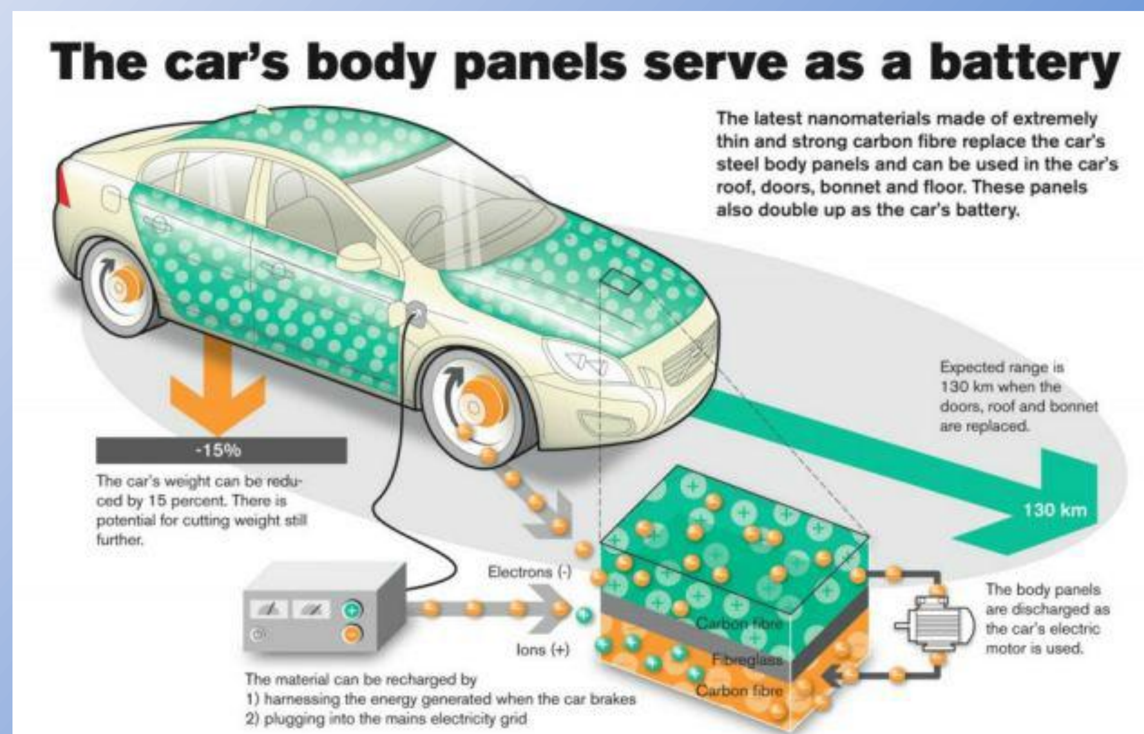
- Carbon-Carbon structural batteries are being studied.
- Currently have <u>poor electrical properties</u>
- Lots of room for improvement.
- More time is required to understand the current state of the art.

Emile Greenhalgh of [Imperial College, London], who is leading the research as part of a broader EU project called STORAGE into incorporating different battery materials into the bodywork of a car.



Structural Battery

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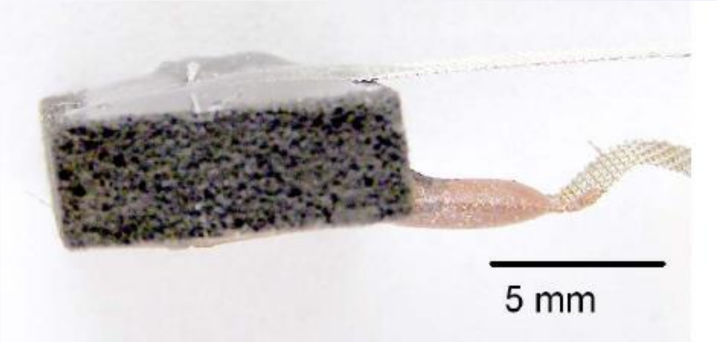
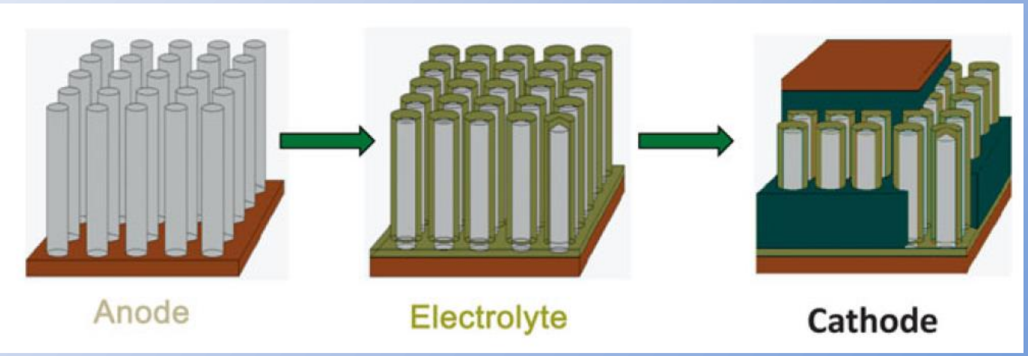
Foams

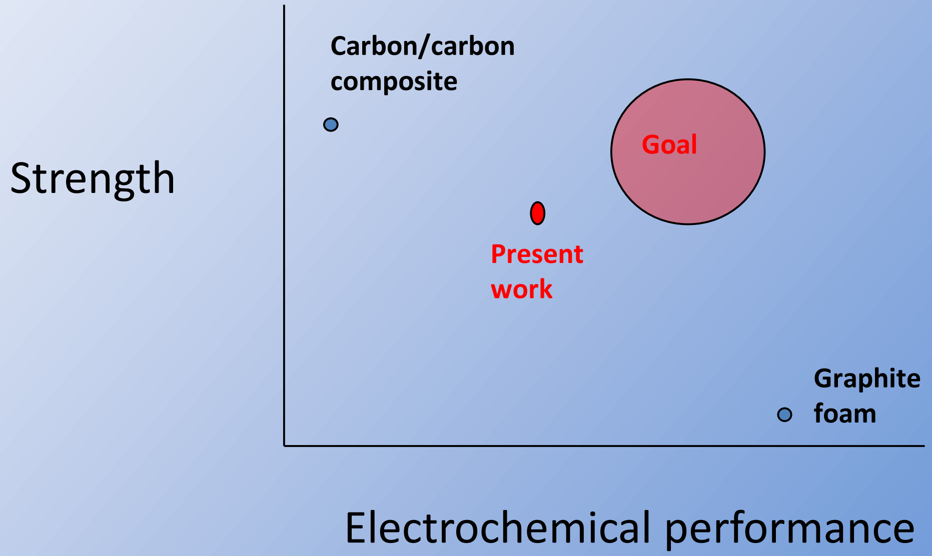


Poor strength
Marginal capacity

Fiber Mats



Difficult to coat and infiltrate
Marginal capacity



Objective/Strategy

- Establish energy storage feasibility of a structural Li-ion fiber-based anode incorporating three dimensional interpenetrating fiber-reinforced network

- Identify platform for 3-D battery concept
  - Must have structural integrity
  - Must show ability to cycle once active species is deposited

- Advantage of 3-D interpenetrating network:
  - Shorter diffusion distance for Li ions providing increased rate capability without sacrificing energy storage capability.

Technical Approach

- Develop a 3-D interpenetrating network as a structural platform for a Li-ion Battery
- Develop method to deposit active anode onto the network
- Utilize advanced binders
- Evaluate in coin cells in conjunction with other standard cathode, electrolyte, separator components
- Perform mechanical testing to assess strength and electrochemical tolerance to deformation

Impact

- Reduce weight of hybrid electric aircraft
- Potential benefit of fuel burn reduction
- For same weight, structural battery enables increased range for aircraft

Li-ion Battery Anodes

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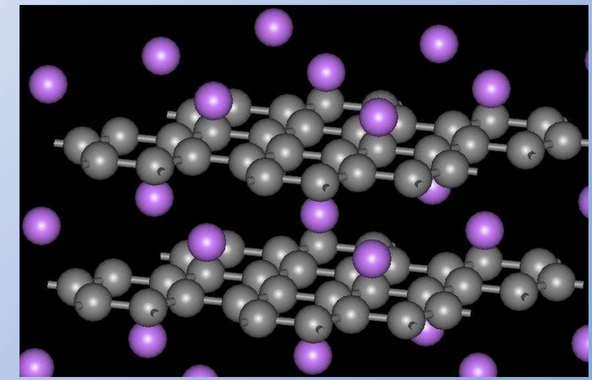
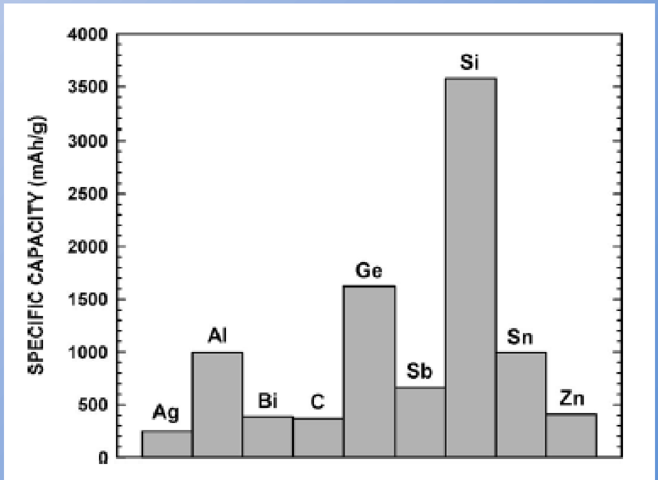
- **Lithium metal initially used as anode material, but too reactive**
- **Graphite is standard anode material – low cost, high conductivity, intercalates Li^+**
  - Li stored between crystal grains
  - Depending on crystal texture & grain size, up to 372 mAh/g
- **Increase in electrode capacity can reduce battery cost and weight**
  - Metals and semiconductors which electrochemically alloy with Li have greatly increased capacity
  - Si has high theoretical capacity – 3500-4200 mAh/g ($Li_{3.75}Si$ up to $Li_{4.4}Si$, depending on temperature)



Model of LiC_6 - intercalated graphite



Specific capacity of various potential negative electrode materials

R.A. Huggins. Lithium Alloy Negative Electrodes. J. Power Sources, 1999, 81-82, 13-19.

C. Lampe-Onnerud et al. Benchmark Study on High Performing Carbon Materials. J. Power Sources, 2001, 97-98, 133-136.

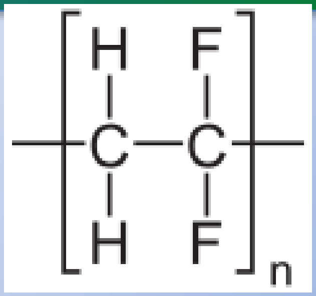
M. N. Obrovac, et al. Alloy design for lithium-ion battery anodes. Journal of the Electrochemical Societ,, 2007, 154, pp. A849-A855.

Novel Binder Materials for Advanced Anodes

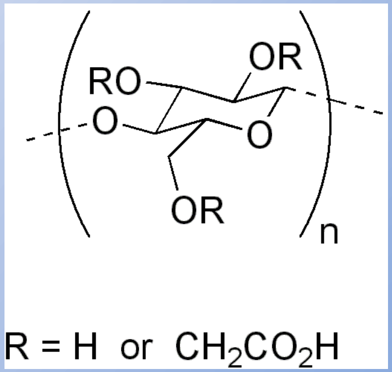
- Binder materials have a significant impact on performance of anodes
- Binder failure is significantly more likely in structural batteries – need stronger binders
- Binder has effect on electrode/active material surface chemistry
  - Surface chemistry has a significant impact on the performance of an electrode
- When SEI is unstable, conductivity and efficiency of electrode can be seriously affected

Role of Binders on Performance

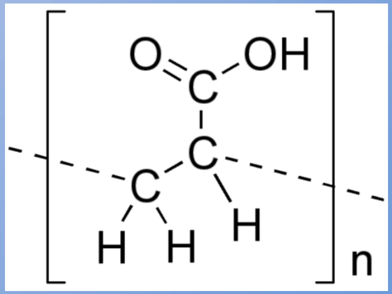
- Most common commercial binder is PVDF (Polyvinylidene Fluoride)
- New binders: PAA (polyacrylic acid), alginate
  - Both have carboxylic acid groups, improving adhesion
  - Water- and ethanol-soluble, easily sprayed
- PAA and alginate do not swell, lose mechanical strength in LIB electrolyte



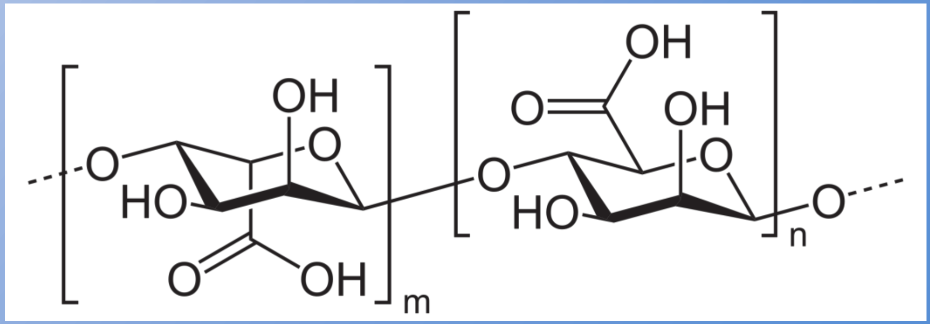
PVDF



CMC



PAA



Alginate

Potential Energy Density Improvements Over the Next 30 Years

	Wh/ kg (cell level)		
	Present	**15 years**	**30 years**
Lithium Ion	80 - 200	400	450
Lithium Sulfur		500 - 650	800 - 950
Lithium / Air		600 - 750	1200 - 1400

Boeing Hybrid Electric Study: Need 750 Wh/kg energy density, at least 600 Wh/kg

Projected Benefits of Structural Weight Reduction

	Baseline	15 Yr Projection	30 Yr Projection
Structural Weight Reduction		25 %	50%
Power Density	3 hp/lb	4 hp/lb	6 hp/lb

Assumes weight reduction benefits similar to that of aircraft structures by using nanotube/nanofiber reinforced composites

Results

Platform For Anode Development

Random Fiber and Foam

- Random fiber
  - Regenerator material
    - Metallic fiber composed of Fe-Cr-Al-Y
    - 90 percent porosity
  - Carbon fiber
    - 70+ percent porosity
- Foam
    - Carbon
    - 70+ percent porosity

Candidate Anode Materials/Configurations

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Material	Binder	Thickness
Regenerator material	PAA	0.020”, 0.050”, 0.080”, 0.125”
Random fiber	ALG	0.020”, 0.050”, 0.080”, 0.125”
Carbon fiber*	PAA	0.020”, 0.050”, 0.080”, 0.125”
Random fiber	ALG	0.020”, 0.050”, 0.080”, 0.125”
Carbon foam*	PAA	0.020”, 0.050”, 0.080”, 0.125”
	ALG	0.020”, 0.050”, 0.080”, 0.125”

PAA: polyacrylic acid
ALG: alginate

*Carbon concepts used in this work are proprietary. This limits the detail presented here. Regenerator material (metallic) will receive most attention for reporting at this time.

Random Fiber Platform Material

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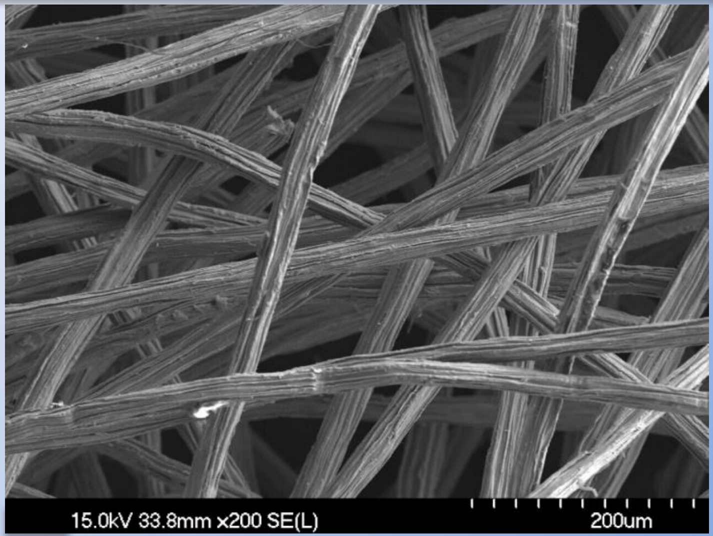
Metallic random fiber



~90 percent porosity

Carbon platforms

~70 percent porosity

- Good compressive strength
- Fibers/foam need to be coated with active material
- Energy density is limited by the amount of active material that can be deposited

Anode Design Approach

- Materials
  - State-of-the-Art Binders
    - Alginate
    - Poly(acrylic acid) (PAA)
  - Conductive additive
    - Graphite (anode)
    - Carbon black

Macro and Microscopic Representation of Structure

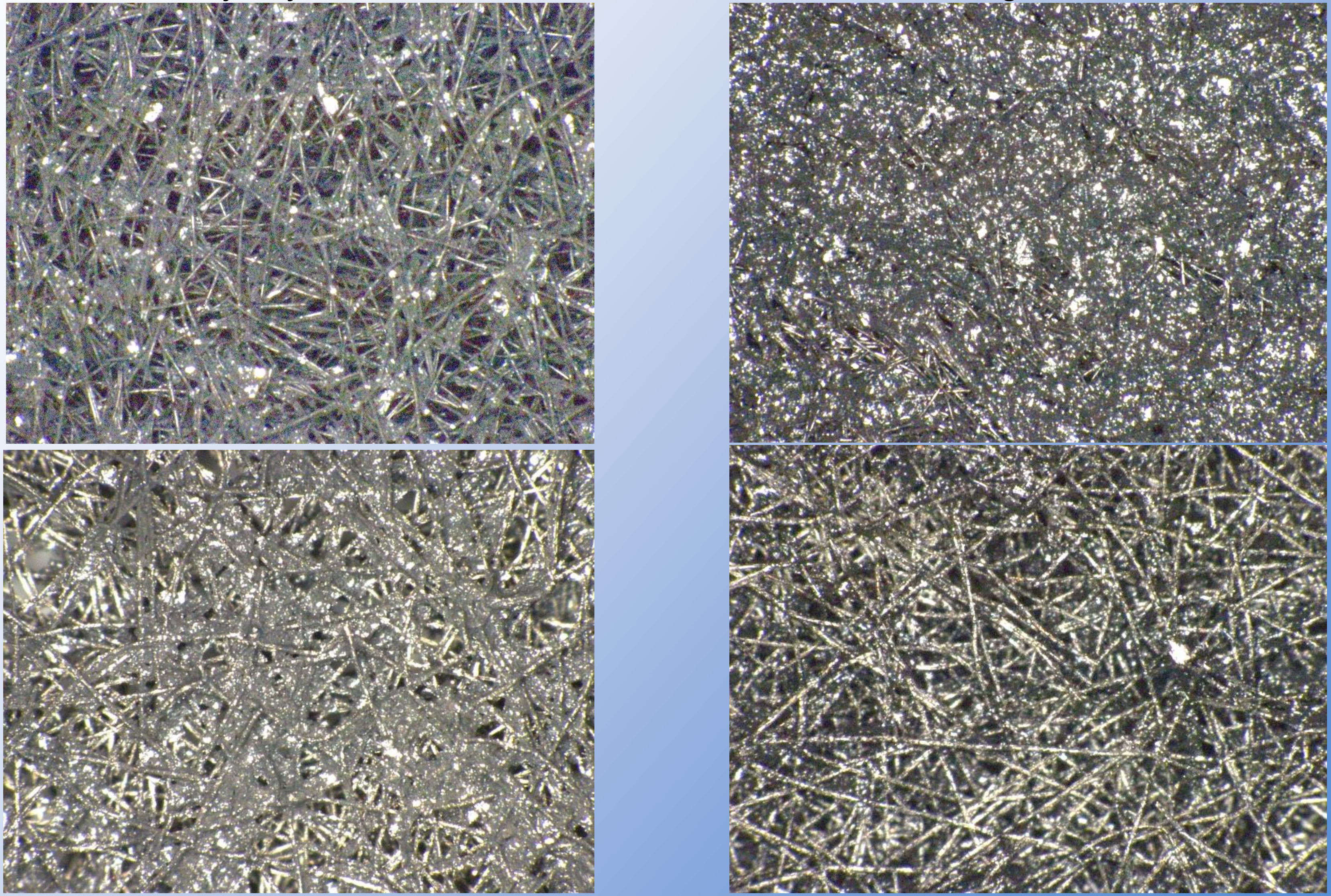
- Regenerator material selected to give microscopic representation of coating process
- Permissions not yet secured to show proprietary C-fiber and C-foam material architectures at a structural level
- Strategy: Examine 0.080” thick specimens first to assess characteristics of coating, including uniformity and amount of deposition across the full thickness of specimen. Proceed to thicker 0.125” specimens to see what, if any, of the observations in the 0.080” samples changed.

Coating of Fiber Substrates With Binder Materials

Polyacrylic Acid | Alginate

C fiber

Metallic fiber



Metallic Regenerator Material SEM, Polyacrylic Acid Binder

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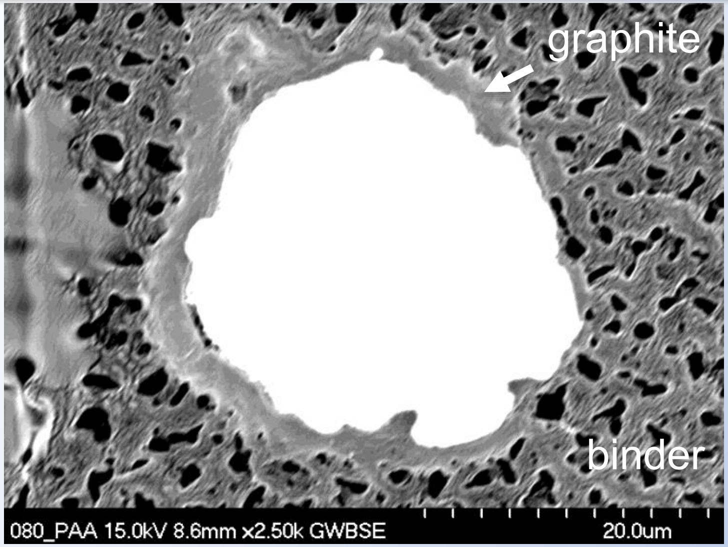
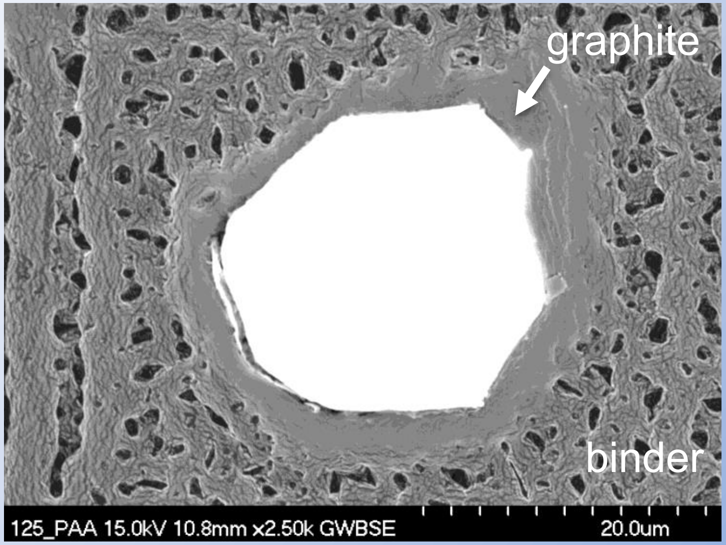
0.080”



Outside edge of specimen:
- Fiber: 30μm/31μm, 27μm/27μm
- Graphite: 1.5μm/14μm, 0μm/4μm

Center of specimen:
- Fiber: 25μm/26μm, 29μm/33μm
- Graphite: 0.5μm/2.5μm, 0μm/4.5μm

0.125”



Outside edge of specimen:
- Fiber: 25μm/28μm, 22μm/23μm
- Graphite: 1μm/4μm, 1μm/5μm

Center of specimen:
- Fiber: 25μm/26μm, 24μm/29μm
- Graphite: 1.5μm/3μm, 2μm/5μm

Metallic Regenerator Material SEM, Alginate Binder

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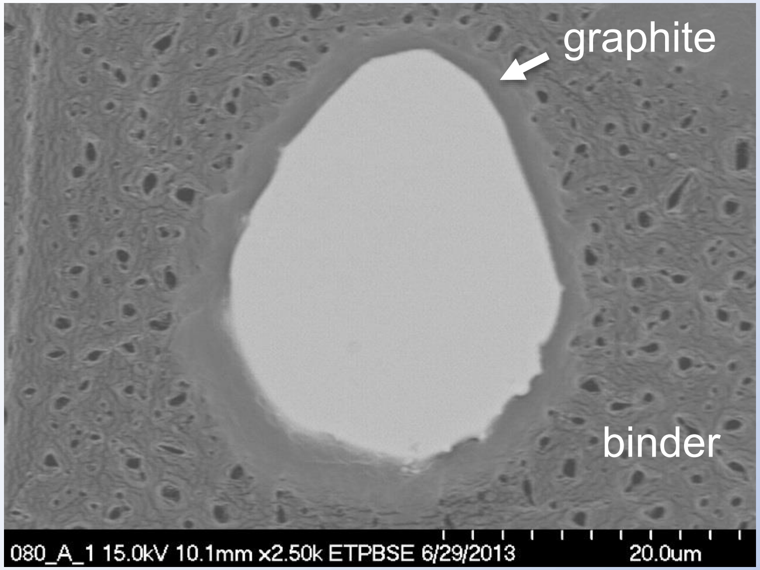
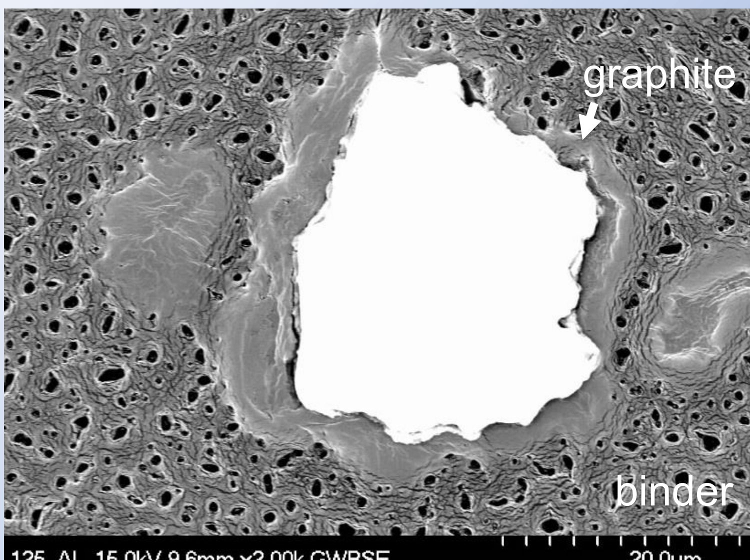
0.080”



Outside edge of specimen:
- Fiber: 26μm/22μm, 23μm/27μm
- Graphite: 2μm/3μm

Center of specimen:
- Fiber: 25μm/25μm
- Graphite: 2μm/5μm

0.125”



Outside edge of specimen:
- Fiber: 25μm/29μm
- Graphite: 1.5μm/5μm

Center of specimen:
- Fiber: 29μm/29μm
- Graphite: 0μm (trace)

GRC Mechanical Evaluation

Three point bend

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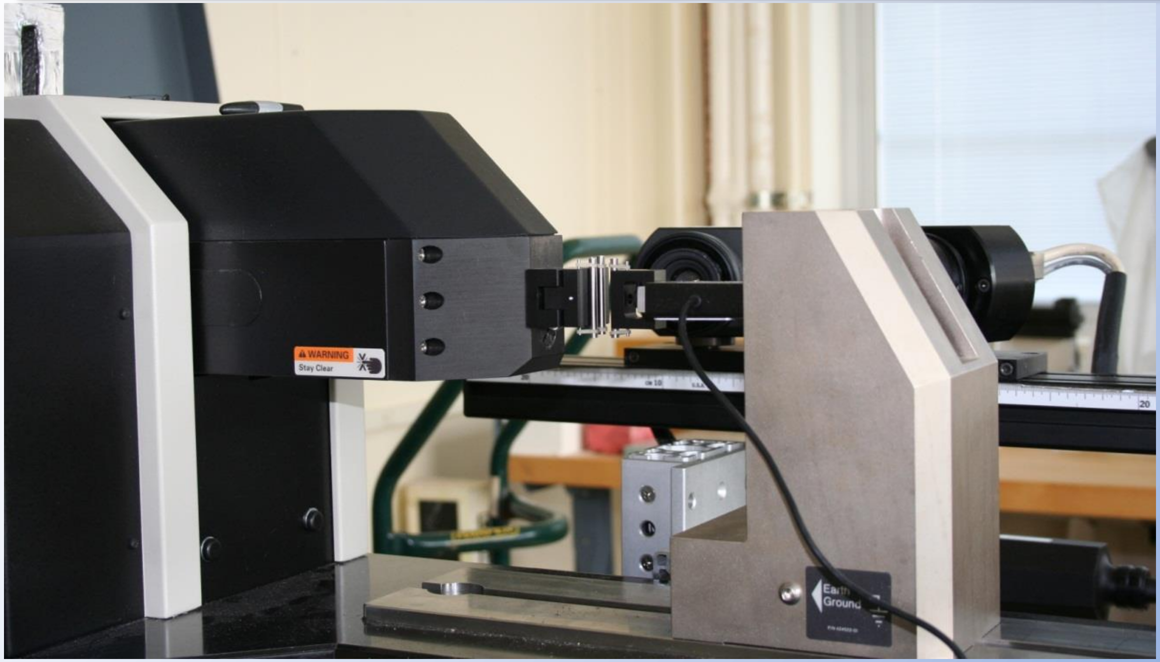

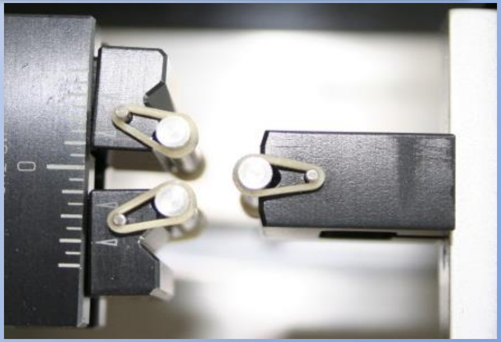

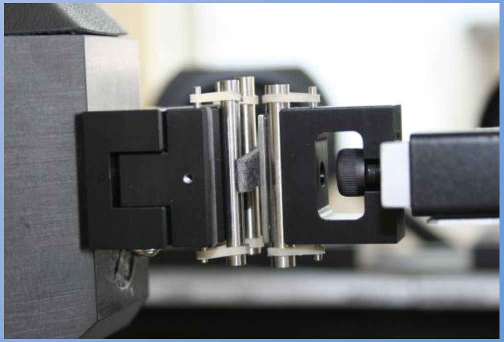

FeCrAlY Fiber	Uncoated	4.59 lbf
	PAA	3.43
	Alg	2.62
Carbon Fiber*	Uncoated	
	PAA	
	Alg	
Carbon Foam*	Uncoated	
	PAA	
	Alg	

* Performance less than metallic fiber; carbon fiber could possess some promise. Degradation in carbon performance from processing is not seen.

FeCrAlY, Alginate, 0.125”

Bend Testing

Although eventual structural battery concepts will not necessarily see bending loads (likely compression), this test was chosen to give a qualitative comparison of structural capability.

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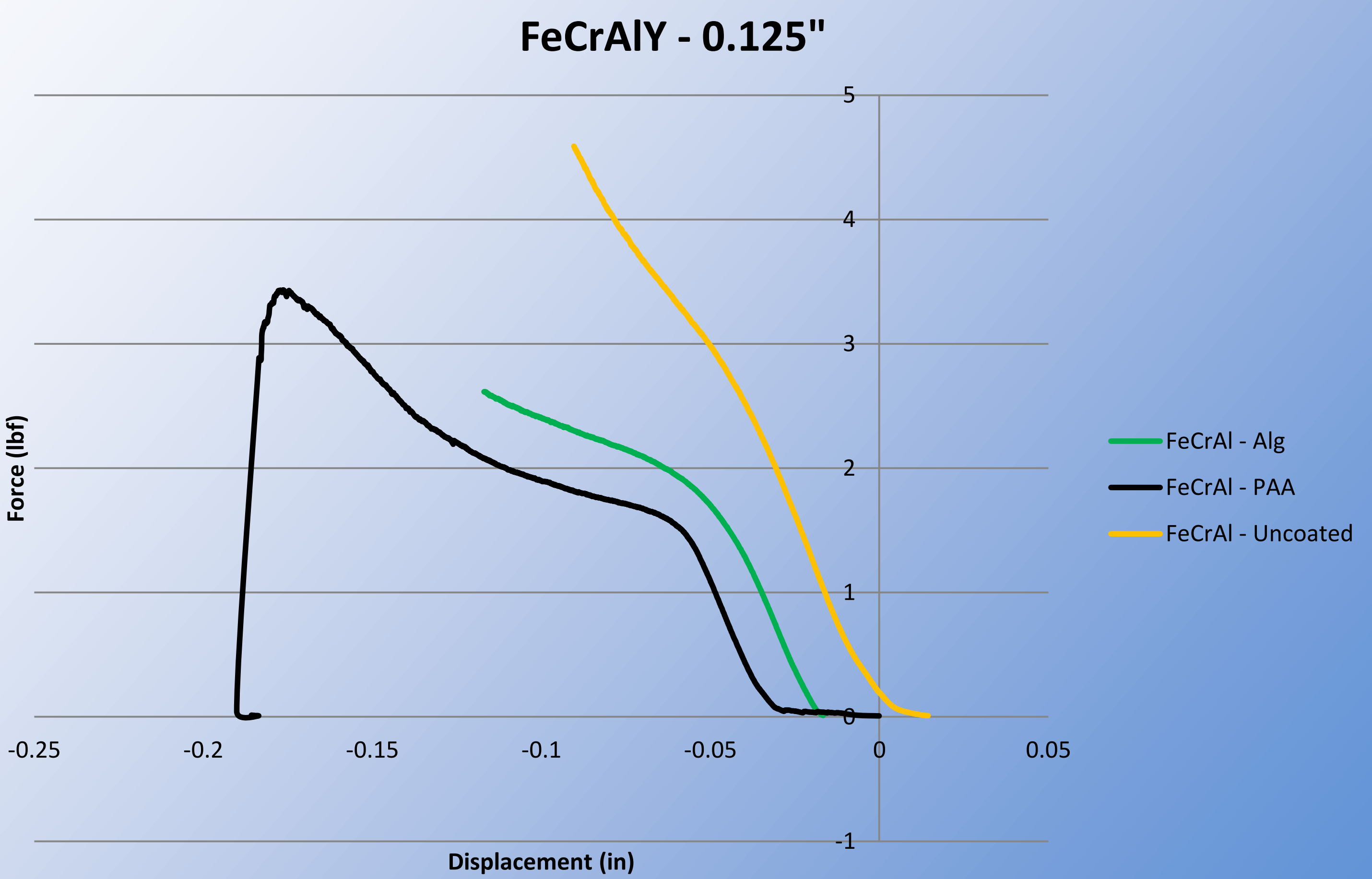

Thicker Sections Will Provide Structural Integrity

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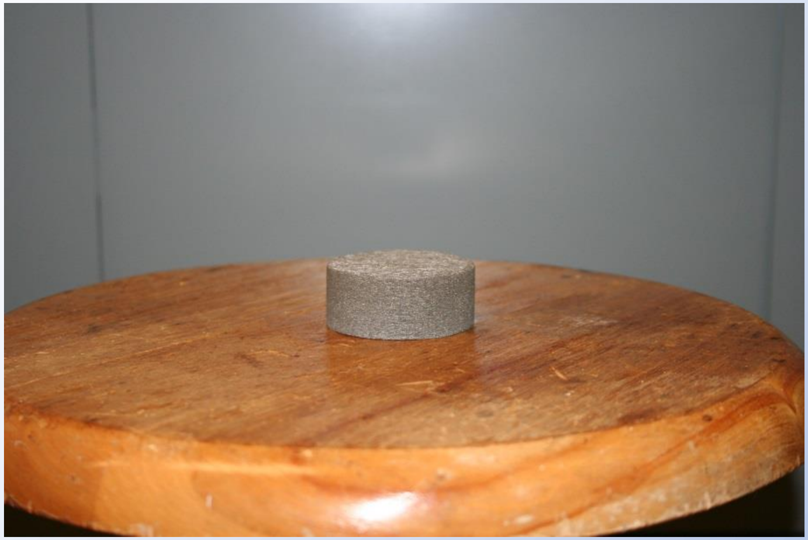

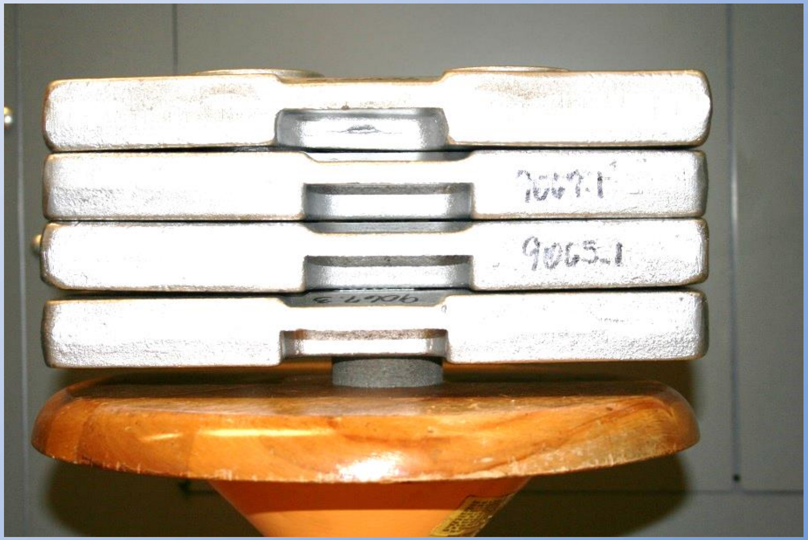

- Thin sections tested as candidates for the anode layer in a structural layup.
  - expected to have limited individual strength
  - data used as a qualitative guideline
- Final application will be a sandwich structure incorporating multiple layers
- Thicker sections have much better structural resistance
  - Example. FeCrAlY regenerator material (shown)

    Compact withstands 2000 lbs force in fabrication and more

    Only 80 pounds shown in picture above (showing potential)

    Image above gives indication of structural potential

    Carbon fiber compacts will have similar characteristics

Electrochemical Data

- NASA GRC data presented here
  - Electrochemistry Branch/RPC
    - Lead for electrochemical evaluation at GRC
  - James Wu, Patricia Loyselle and Vadim Lvovich (Branch Chief)
- Princeton data similar

Sample Preparation

- The samples were dried at 60^{o}C under vacuum overnight
- Then, the samples were transferred to glovebox with argon
- Samples were punched as 0.5” diameter disks, got the weight of disks, and the disks were used as working electrode

Coin Cell Configuration

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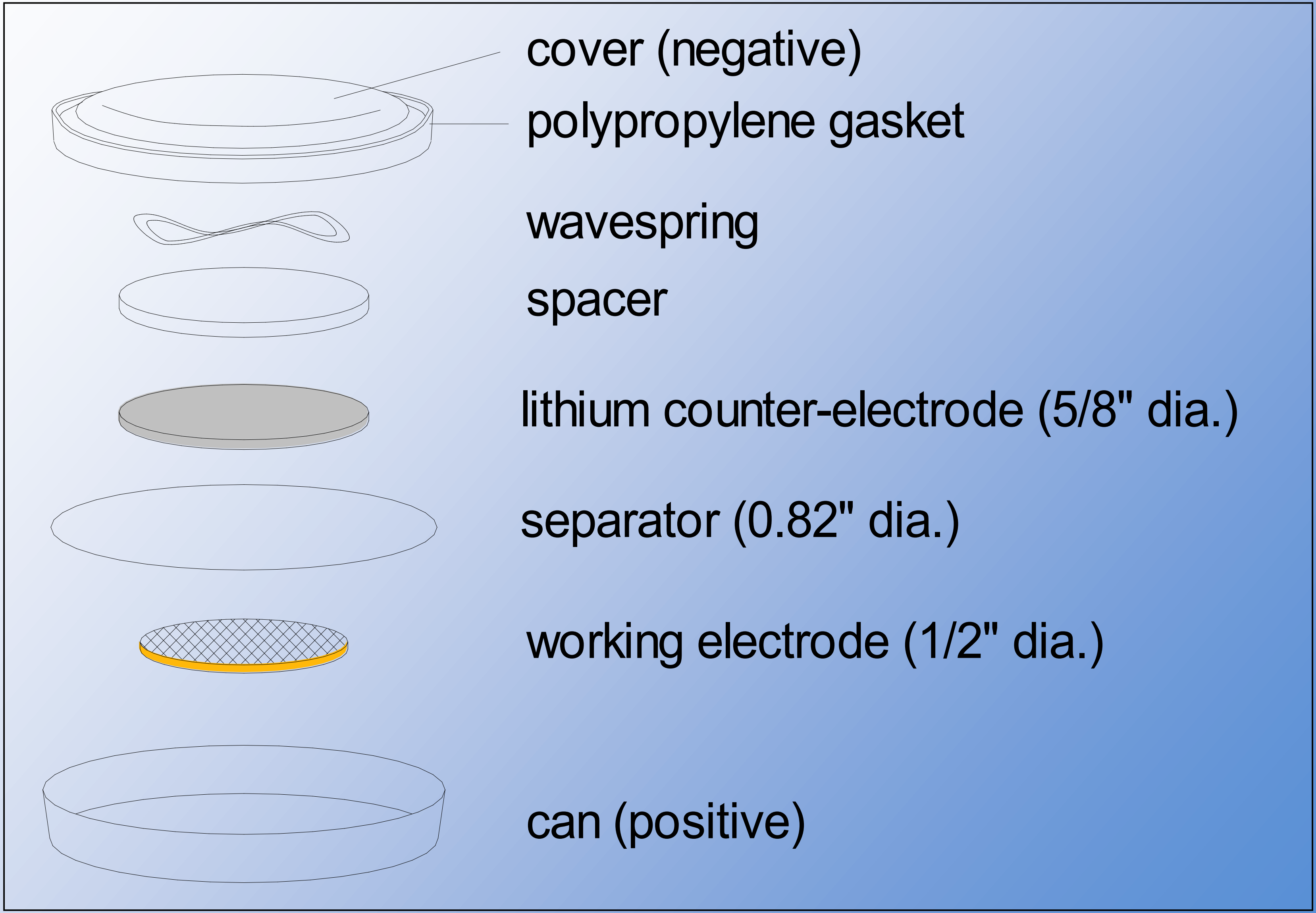

Structural Battery Fabrication

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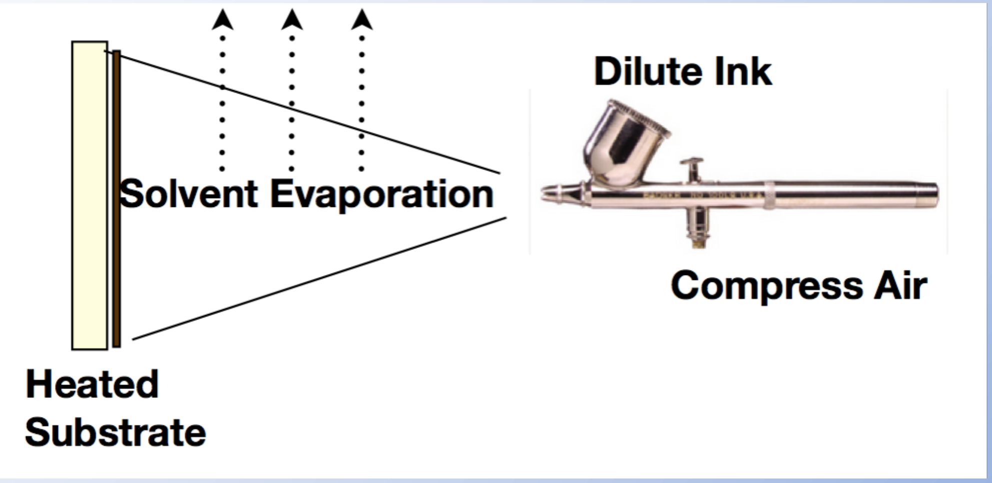
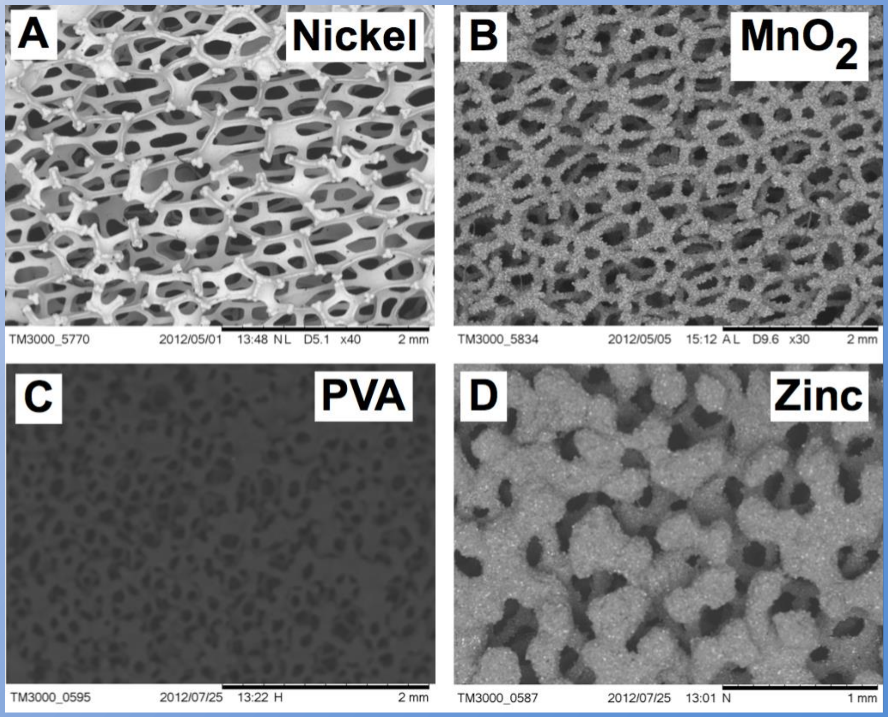
- Spray coating - dilute ink is sprayed onto heated substrate
- Permits conformal coating of thick, porous substrates



(above) schematic of spray-coating process; (right) 3D MnO2 - Zn alkaline battery on Ni foam made via spray coating



Coin Cells Built With The Following Samples

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Coin Cell ID#	Sample ID#	Description	weight* (g)	OCV (V)
60513-5A			0.0124	0
60513-5B	060513-5	Alginate 15% + C fiber	0.0122	0
60413-3	060413 3	PAA 15% + EMD Metal Fibers	0.0332	0
60513-7A	060513-7	Alginate 15% + C Fiber	0.0341	0
60513-7B			0.0358	0
60413-1	060413-1	Alginate 15%+EMD Metal Fibers	0.0369	0
60413-2	060413-2	Alginate 15%+EMD Metal Fibers	0.0355	2.367
60413-4	060413-4	PAA 15% + EMD Metal Fibers	0.0349	2.943

* Weight of 0.5” disk

0V OCV implying that
either the cells were shorted or no active materials were coated

Experimental for Electrochemical Performance

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- Coin cell as testing vehicle:
  - Anode: C-fibers or EMD metal fibers w/Alginate or PAA
  - Counter: Lithium metal foil
  - Electrolytes:
    - Baseline electrolyte:

      1M $LiPF_6$ in EC:DEC:DMC (1:1:1)

- Electrochemical techniques:
  - Electrochemical impedance spectroscopy (EIS)
  - Galvanistic charge/discharge (C/10)

Initial Formation Cycling Result for Sample 060413-2

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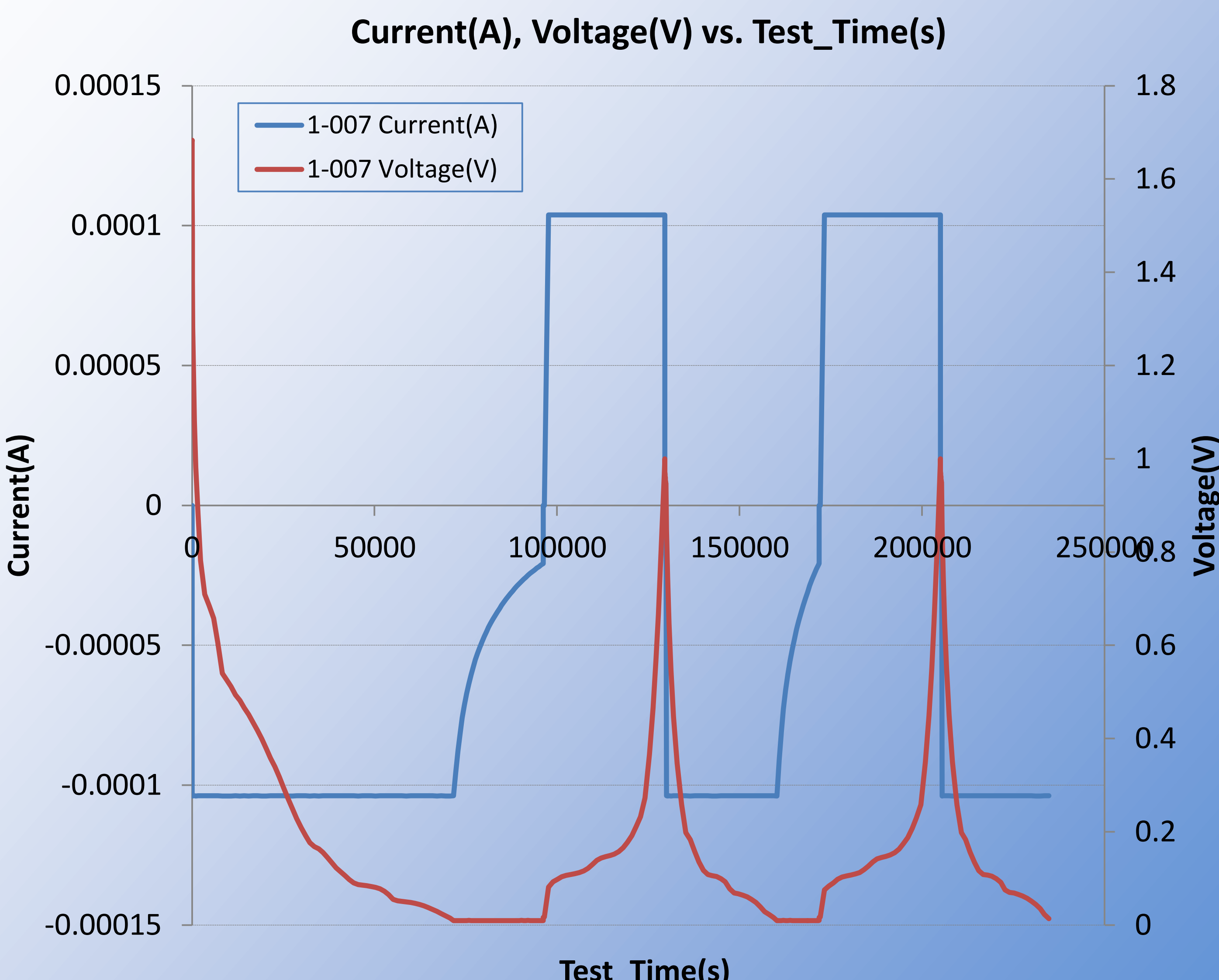

Initial Formation Cycling Result for Sample 060413-4

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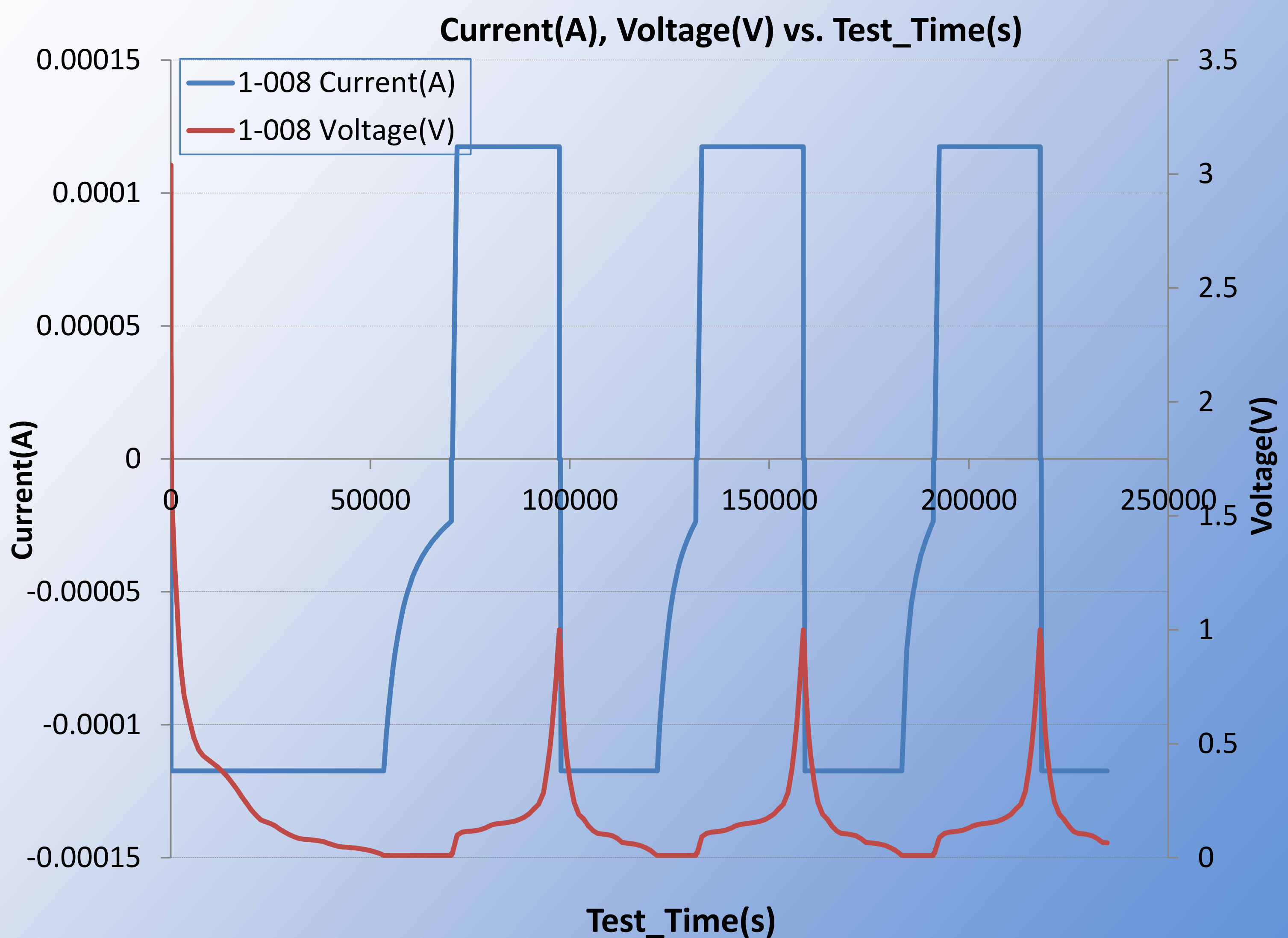

Summary of Initial Formation Cycling Result

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Cycle#	Sample 60413-2			Sample 60413-4		
	Capacity (mAh/g)		Coulombic Efficiency (%)	Capacity (mAh/g)		Coulombic Efficiency (%)
	measured	theoretical		measured	theoretical	
1	228.7	250	40.2	213.25	250	44.4
2	228.7		92.1	211.5		93.1
3				210.7		95.7

Initial Cycling Results

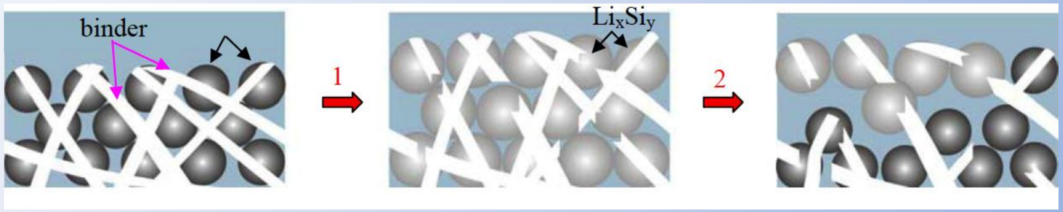
- Capacity ~88% of theoretical value – excellent
- Initial Coulombic efficiency ~40% – product of SEI formation, could be improved by using electrolyte additives
  - Subsequent cycles show 90-95% CE – good start
- Very little difference between PAA, Alginate samples
- Excellent open circuit potential for Metal Fiber samples – highly conductive substrate improves performance
- Carbon fiber samples have high tendency to short, low OCV due to poor conductivity and mechanical properties

Distribution/Dissemination

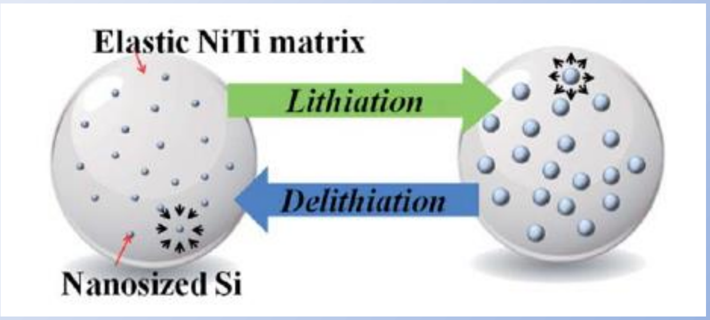
The authors/investigators will look for opportunities to report and present this research.

Next Steps

- Further optimization of spray coating anode processing
- Phase II objectives
  - Build on successful spray technique to include active anode material with higher capacity (e.g., nano-silicon)



  - Evaluate electrochemically active current collectors – Si in NiTi matrix



  - Pursue technique to consider active Al and Mg substrates for nano-silicon deposition through de-passivation techniques

Summary/Lessons Learned

- Spray coating of anode material onto 3-D substrate demonstrated
- Additional optimization of processing, assembly is necessary to give better microstructural consistency
- Sample substrates based on fiber architecture demonstrates potential to support load
- Cells that contain 3-D sprayed anode were able to cycle – capacity ~90% of theoretical values
- Metallic regenerator platform exhibited the best mechanical and electrochemical characteristics
- C-fiber platform showed poor electrochemical properties, but we need a current collector that contributes to the overall capacity of the cell

Extra Slides

Princeton University Results

Princeton University Coin Cell Samples

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Coin Cell ID#	Sample ID#	Description	Active Mass* (g)	OCV (V)
0627 - 5	060513-5	Alginate + .02" Metal Fibers	0.0017	2.29
0627 - 7	060413-3	Alginate + .05" Metal Fibers	0.0052	2.38

* Mass of active material on 7/16" disc

Other samples still under testing –
these are the ones that have completed full charge-discharge cycles

Carbon fiber samples still prone to shorting

Initial Formation Cycling Result for Sample #5

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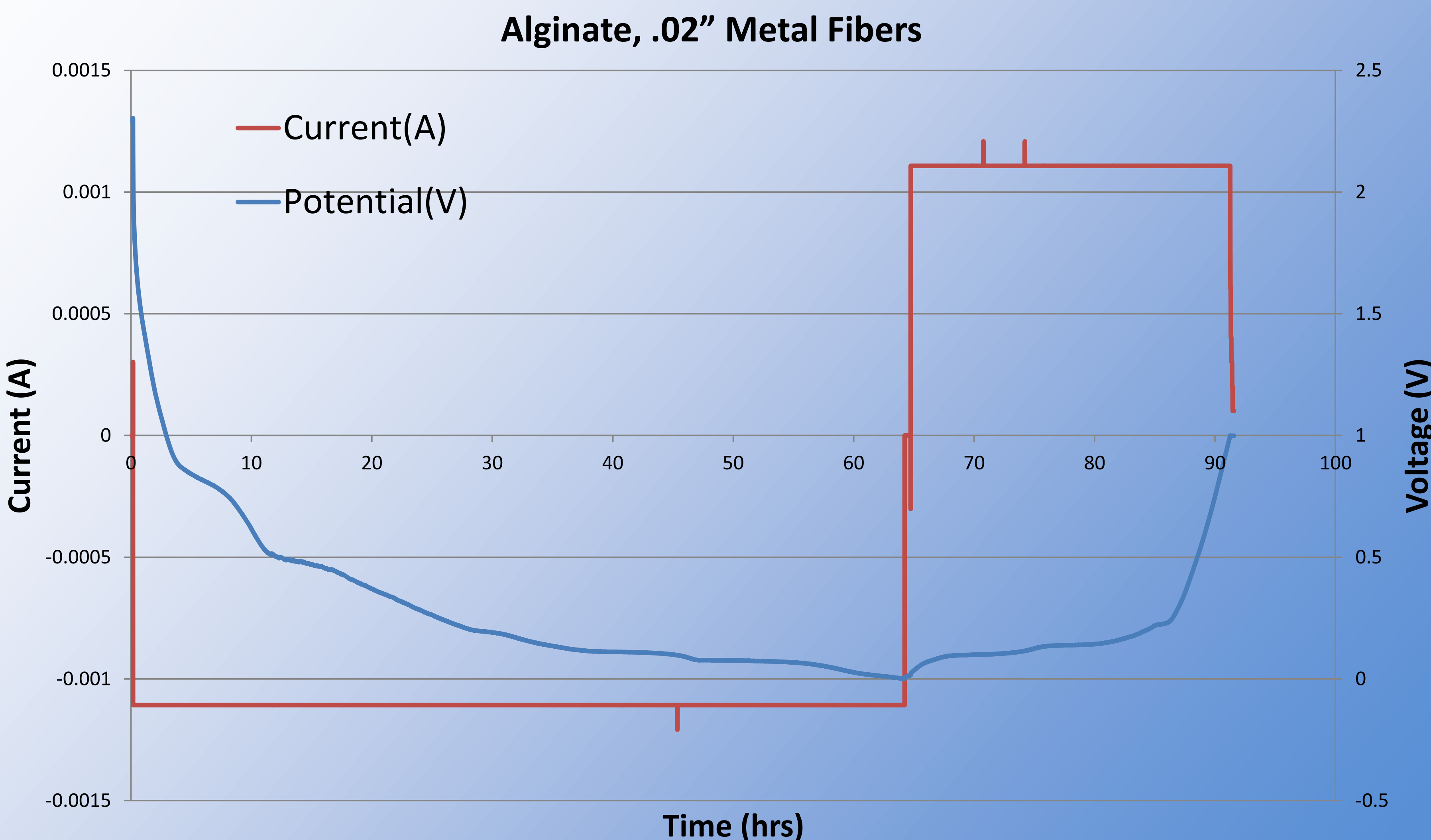

Initial Formation Cycling Result for Sample #7

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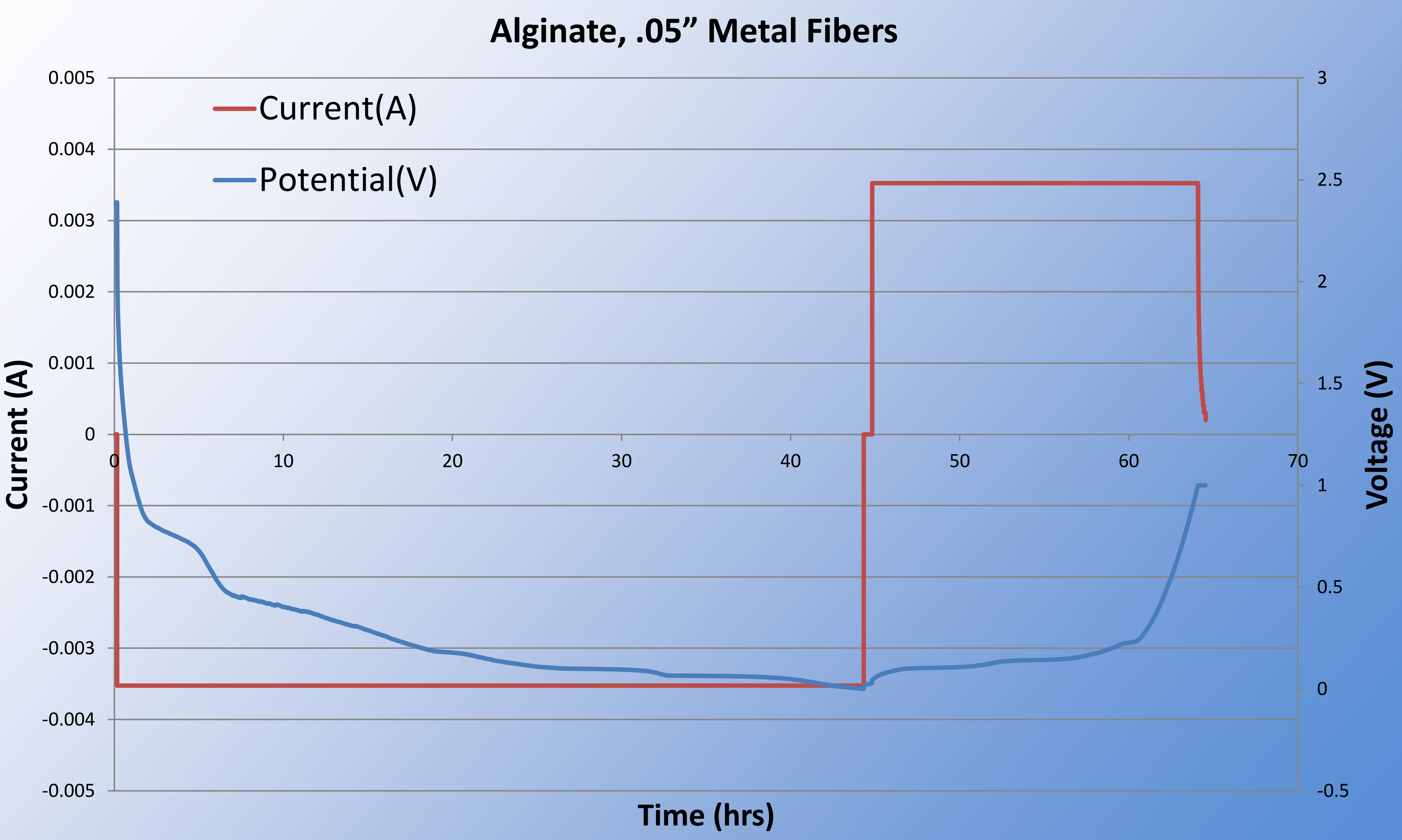

Summary of Princeton Cycling Results

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Cycle#	Sample #5			Sample #7		
	Capacity (mAh/g)		Coulombic Efficiency (%)	Capacity (mAh/g)		Coulombic Efficiency (%)
	measured	theoretical		measured	theoretical	
1	173.38*	146	41.5	131	146	44.4

* Extra capacity product of solid electrolyte interface formation

Electrochemical Testing

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- Testing capacity: charge/discharge cycling
  - C-rate: Current set to fully charge cell at theoretical capacity in X # of hours
- Qualitative testing of electrochemical properties: cyclic voltammetry
  - Change voltage at a constant rate (V/s) within a certain range repeatedly
  - Used to determine change in surface area of electrode after spraying