Li-Ion Battery Anodes from Electrospun Nanoparticle/Conducting Polymer Nanofibers

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Overview

Timeline

- October 1, 2015
- September 30, 2019
- Percent complete: 95%

Budget

- Total project funding
  - DOE $590,000
  - Contractor $117,062 (VU)

Barriers

- Barriers addressed
  - Capacity fade when using Si as the anode material in a Li-ion battery
  - Achieving high volumetric, gravimetric, and areal energy densities at moderate C-rates
- Targets
  - Gravimetric capacity: 1,200 mAh/g (0.1C)
  - Areal capacity: 3 mAh/cm^2 (0.1C)
  - Volumetric capacity: 800 mAh/cm^3 (0.1C)
  - 40% capacity retention at 2C

Partners

- Lawrence Berkeley National Lab
- Oak Ridge National Lab
- e-Spin Technologies, Inc.
- **Project Lead: Peter N. Pintauro, Vanderbilt**

Project Relevance and Objectives

Project Objective: To fabricate and characterize nanofiber anode mats containing Si nanoparticles and an electronically conductive particles or conductive polymer binder for Li-ion batteries, where the mats exhibit:

- High gravimetric, areal, and volumetric capacities
- Long cycle life (90% capacity retention after 200 cycles at 0.1C)
- Good performance at high C-rates (500 mAh/g at 1C with an areal capacity of 1.0-2.0 mAh/cm^2)

Relevance:

Address problems with conventional thin film Si slurry anodes: (i) Low area capacity (the need to use only thin electrodes), (ii) Poor volumetric and/or areal energy densities at high C-rates, (iii) Si expansion/contraction result in electrode deterioration during cycling.

Collaborations and Coordination:

Oak Ridge National Laboratory (Dr. Jagjit Nanda and Dr. Ethan Self): Conduct electrochemical performance analysis of nanofiber anodes and provide microstructural and interfacial characterization of the electrospun materials.

e-Spin Technologies, Inc. (Dr. Jayesh Doshi): Conduct preliminary scale-up of the electrospinning process at his commercial facility in year 3.

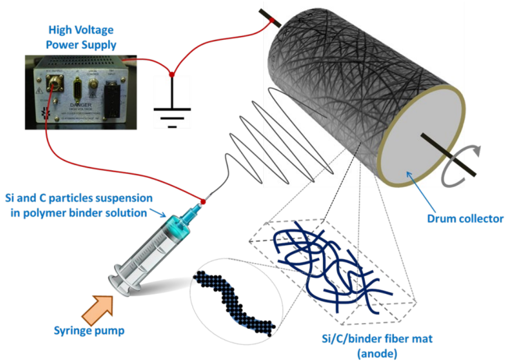
2018-2019 Project Tasks/Goals:

1. Electrospinning single fibers with Si/PAA (no carbon)
2. Electrospinning single fibers with Si/carbon/PAA (low carbon content)
3. Dual Fiber anodes (Si/PAA and Carbon/PAN)

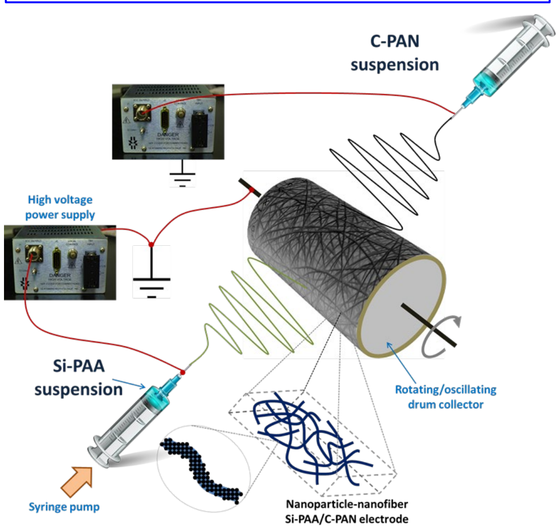
Approach: Single and Dual Fiber Particle/Polymer Electrospinning

STEP 1:
electrospinning

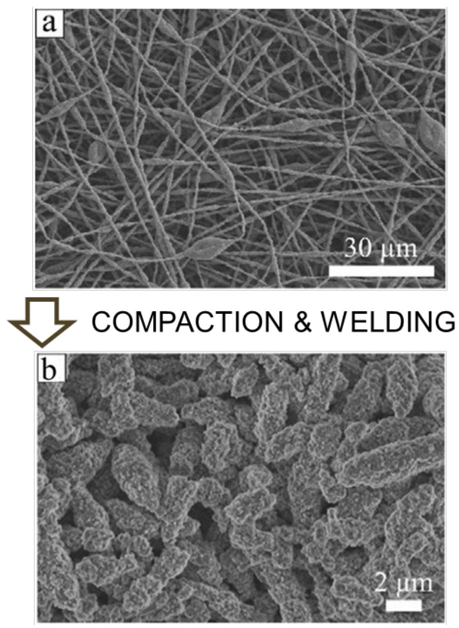
Single Fiber Electrospinning



Dual Fiber Electrospinning



STEP 2:
mat densification



The raw fibrous composite mats were densified through mechanical compaction followed by exposure to solvent vapor (fiber welding).

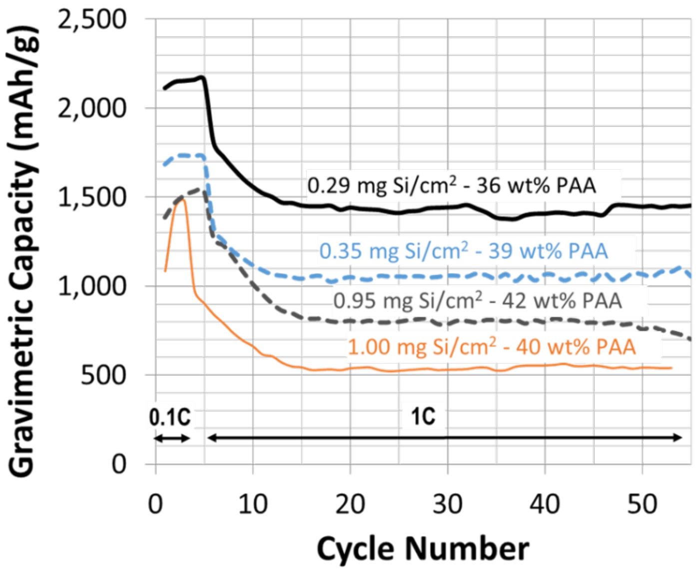
Advantages of Particle/Polymer Nanofiber Anodes:

- High surface area/volume ratio
- Short Li^+ transport pathways
- Controllable fiber volume fraction (for high areal and volumetric capacity)
- Simple fabrication (single fiber)
- Volume changes of Si/PAA network are stabilized by the elasticity of interpenetrating C/PAN network, for long cycle life (dual fiber)

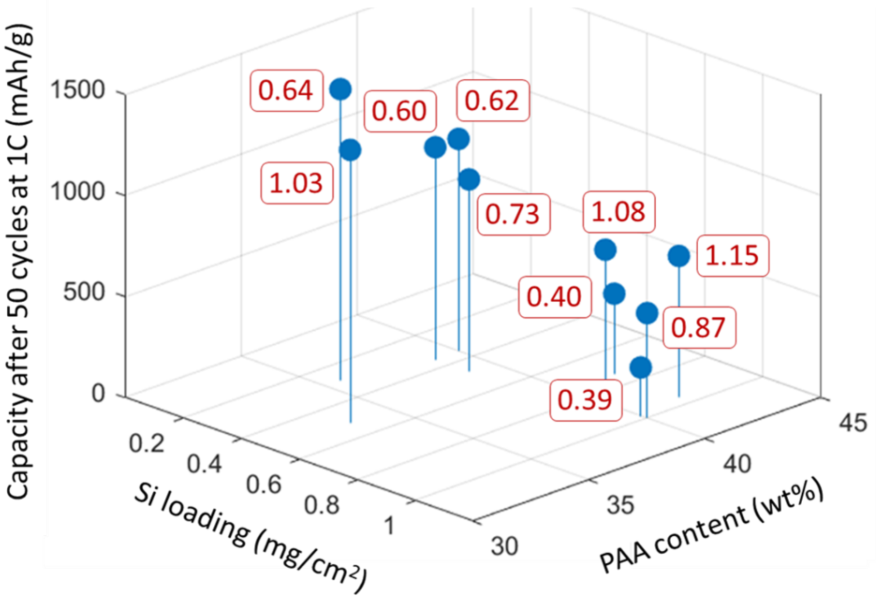
Accomplishment: Single Fiber Si-PAA Nanofiber Anode (no carbon)

Charge/discharge cycling results for Li-ion half-cells with electrospun singe fiber Si-PAA anode mats with different Si nanoparticle loading and various PAA contents.

Discharge curves for selected anodes



Summary comparison of discharge capacities after 50 cycles at 1C vs. Si loading and PAA content. The labels next to the data points in show areal discharge capacities in mAh/cm^2.



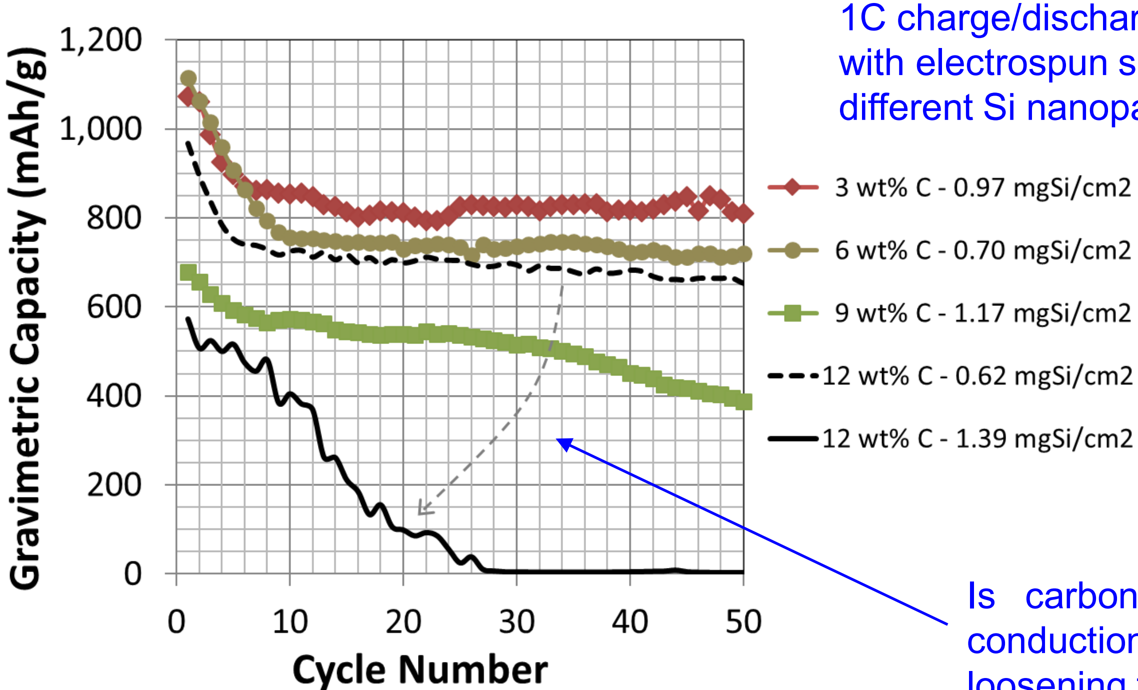
The best anode in terms of areal capacity (1.15 mAh/cm^2) contained 42% PAA, with a Si loading of 0.95 mg/cm^2.

The best anode in terms of Si utilization (highest gravimetric capacity) is at 0.64 mAh/cm^2 (with a Si loading of 0.29 mg/cm^2), where the gravimetric capacity is 900 mAh/g after 50 cycles at 1C.

At low-to-moderate Si loadings, we can achieve a stable areal capacity at 1C with a fiber anode that does not contain carbon.

Accomplishment: Single Fiber Si-C-PAA Nanofiber Anode (with low carbon content)

Carbon black was added to increase conductivity at higher electrode loading and to improve areal capacity. It worked but was not as effective as expected.



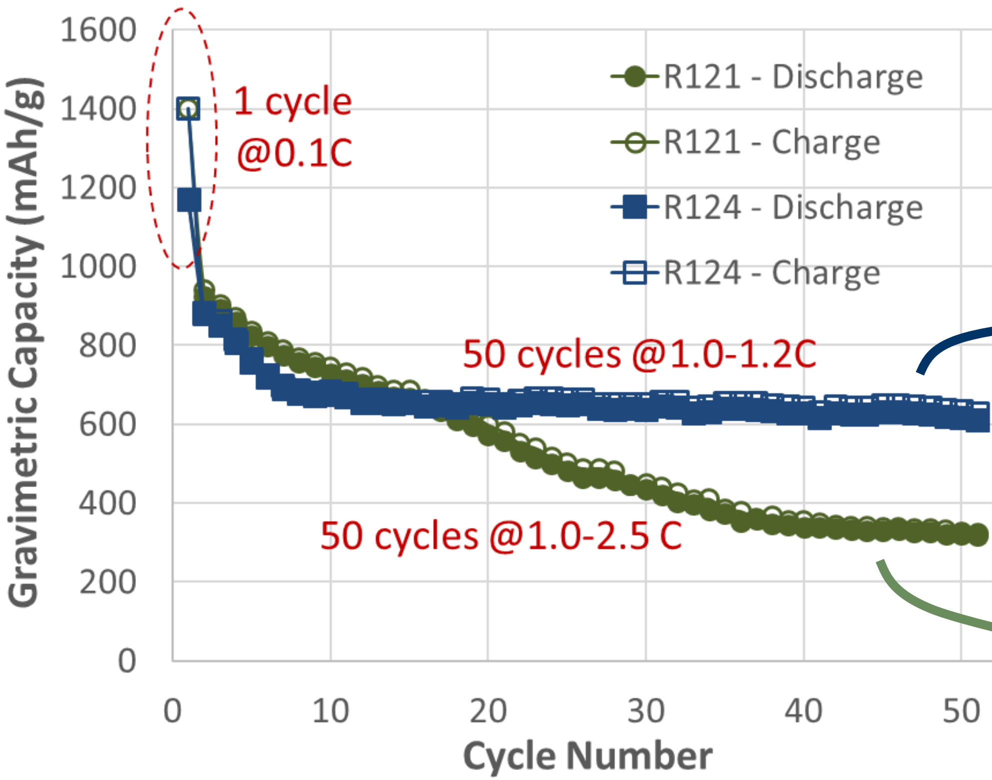
1C charge/discharge cycling results for Li-ion half-cells with electrospun singe fiber Si-C-PAA anode mats with different Si nanoparticle loading and various C contents.

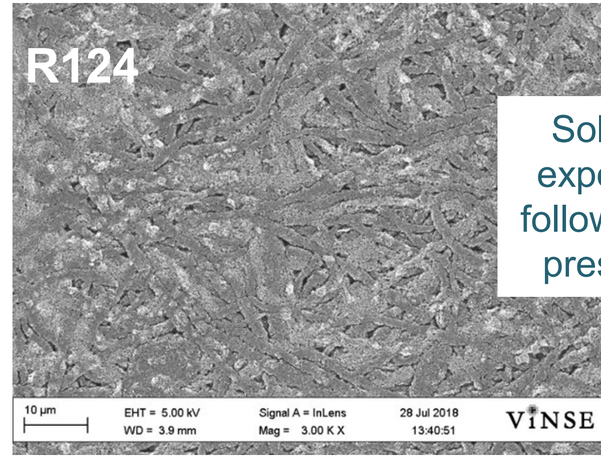
Is carbon not forming percolating conduction pathways but instead loosening the Si-PAA fiber structure?

The best anode (3 wt.% C, 40 wt.% PAA, and 57 wt.% Si = 0.97 mg_{Si}/cm^2) had areal capacity of 1.32 mAh/cm^2 and a gravimetric capacity of 811 mAh/g after 50 cycles.

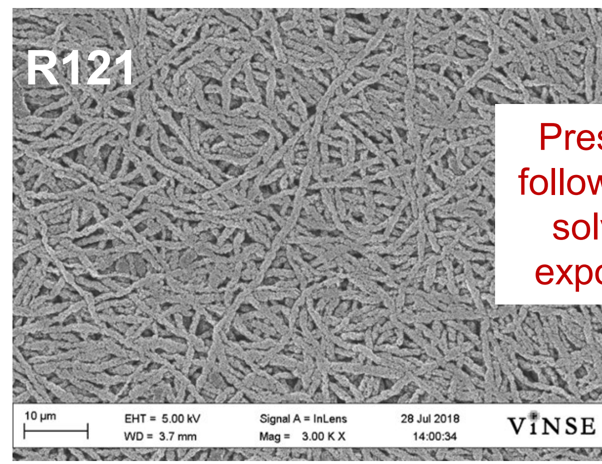
Addition of a small amount of carbon improves the capacity if the anode is not too thick – the anode with 1.39 mg_{Si}/cm^2 and 12 wt.% C failed within 30 cycles at 1C.

Accomplishment: Dual Fiber Si-PAA/C-PAN Anode Mats – Effect of Densification





Solvent exposure followed by pressing



Pressing followed by solvent exposure

R124 & **R124 -** 0.81 mg_{Si}/cm^2, 1.5 mAh/cm^2
57 wt..% Si-PAA fibers (with 40 wt..% PAA binder)
43 wt..% C-PAN fibers (with 39 wt..% PAN binder)

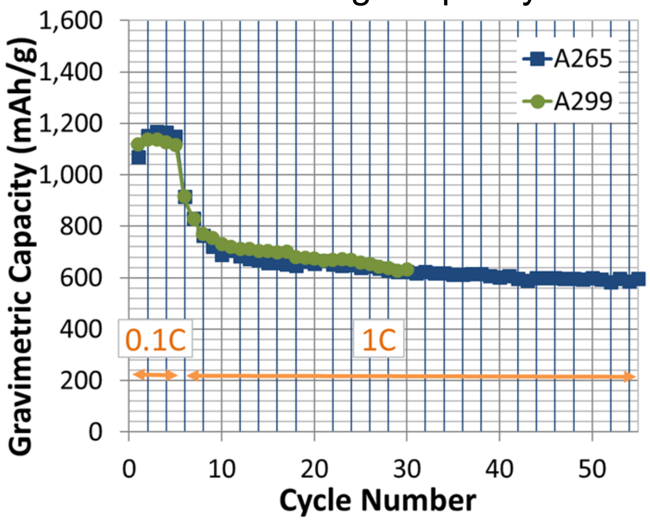
The **presence of residual solvents** in the fiber mat during welding for sample R124 led to improved interfiber contacts at fiber cross points and better compaction, thus creating a mechanically stronger anode with better resistance against expansion and shrinkage during charge/discharge cycling.

Accomplishment: Half- and Full Cell Performance with Dual Fiber Si-PAA/C-PAN Anodes

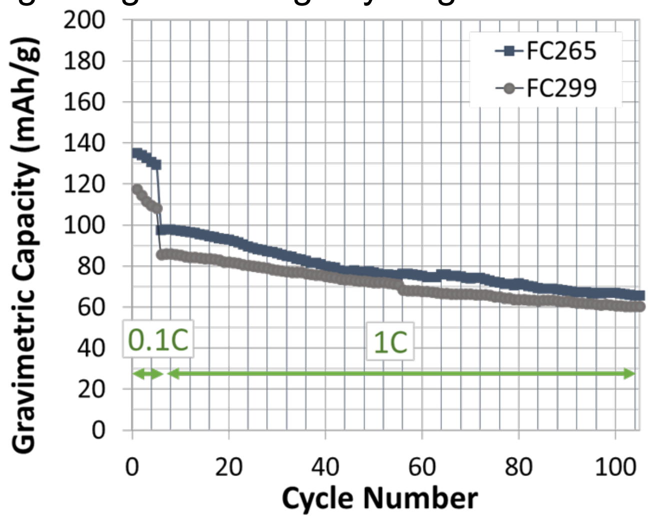
A265 - 78.4 wt.% Si-PAA fibers + 21.6 wt.% C-PAN fibers (55.3 wt.% Si, 12.9 wt.% C, 31.8 wt.% PAA+PAN)

A299 - 73.3 wt.% Si-PAA fibers and 26.7 wt.% C-PAN fibers (45.5 wt.% Si, 15.9 wt.% C, 38.6 wt.% PAA+PAN)

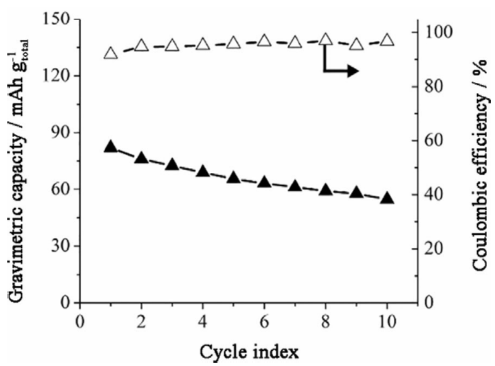
Discharge capacity loss during charge/discharge cycling



Two half cells with dual fiber Si-PAA/C-PAN anodes



Two full cells with the dual fiber pre-lithiated anodes and an NMC 622 cathode, where the **N/P ratio was 1.2**. Gravimetric capacity is based on **anode+cathode weight** (cycled between 3.0V and 4.2V)



Full cell performance improved by moving from a single-fiber (previously reported) to a dual-fiber anode:

60 mAh/g after 100 cycles at 1C with a **dual fiber anode** and NMC cathode

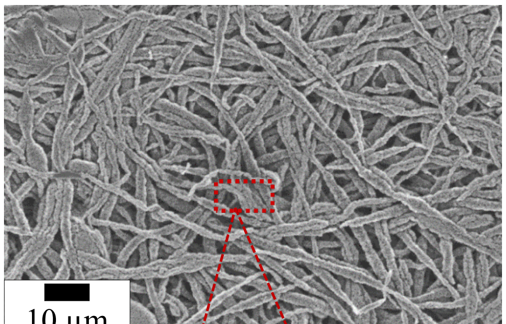
vs

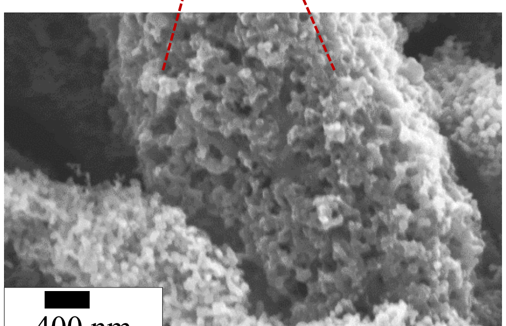
60 mAh/g after 10 cycles at 0.1C. with a Si-C-PAA **single fiber anode** and a $LiCoO_2$ fiber cathode.

Accomplishment: Post-Mortem Electrode Characterization of Dual Fiber Electrodes (ORNL)

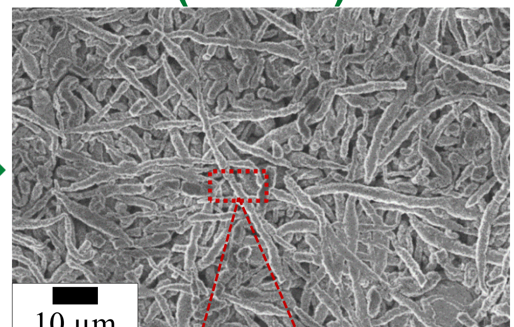
Goal: Determine how mat morphology changes upon cycling

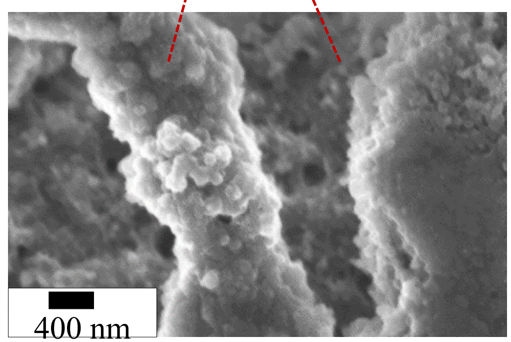
Pristine Mat





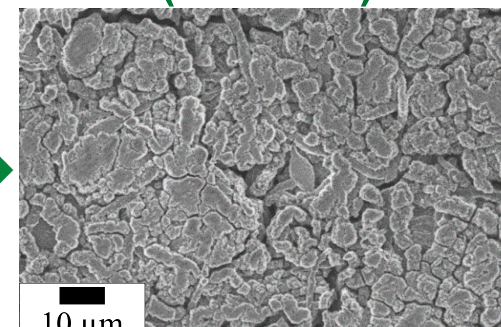
After 60 Cycles (0.1-1C)





SEI overgrowth on surface of individual fibers/particles

After 185 Cycles (0.1-8.2C)



SEI overgrowth throughout but interfiber void space is still present

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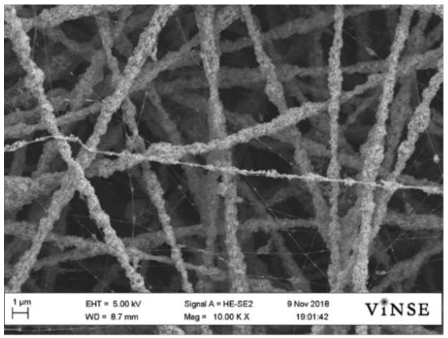
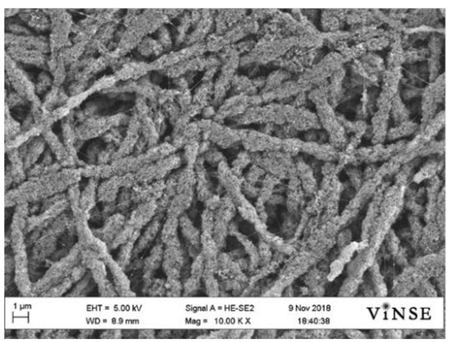
Conclusions:

A longer cycling test results in a thick SEI layer which disrupts the electrode's pore structure. Regardless, the dual fiber anode exhibits a stable capacity of ~375 mAh/g at 8.2C after 185 cycles.

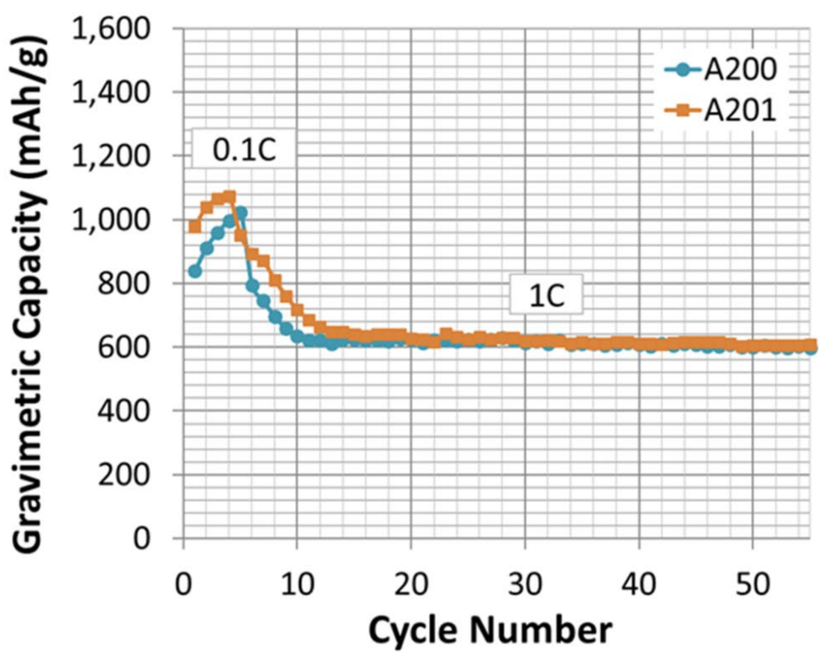
Accomplishment: Concurrent Electrospinning of Si/PAA and Electrospraying C-PVDF

61 wt..% Si-PAA fibers (with 40 wt..% PAA binder)
39 wt..% C-PVDF droplets (with 37 wt..% PVDF binder)





Upper SEM - Surface image of the raw mat
Lower SEM - Surface of the compacted/welded mat



Cycling results (discharge curves) for two Li-ion half-cells with anodes prepared from the compacted and welded mat. The first 5 cycles were at 0.1C and the remaining 50 cycles at 1C; terminal discharge capacity at 1C was <u>600 mAh/g (gravimetric) and 1.2 mAh/cm^2 (areal).</u>

- Electrospraying carbon while electrospinning Si fibers works well.
- Carbon-PVDF droplets are deposited on Si-PAA fibers.

Summary

- Electrospun Si-PAA fiber mat anodes with no carbon showed moderately high capacity at Si areal loadings ≤ 0.5 mg/cm^2; electrospun anodes have higher gravimetric capacity by about 25% than Si-PAA slurry electrodes at the same loading. Above 1.0 mg Si/cm^2, both types of anodes loose capacity.
  - Best Si anode Si-PAA nanofiber result: 1.03 mAh/cm^2 and 900 mAh/g after 50 cycles at 1C
- A new dual fiber anode mat morphology was created and successfully tested, for use in Li-ion batteries.
  - Separate fibers were electrospun, for Li alloying (Si-PAA fibers) and for electrical conduction (C-PAN fibers).
  - Results show that there are sufficient contact points between Si/PAA fibers and C/PAN fibers in a dual fiber mat electrode (a random distribution of the two fiber types) for good isotropic electron flow throughout the anode, with good electrolyte infusion between fibers.
  - 15-20% carbon fibers in a dual fiber mat is sufficient for acceptable electron conduction.
  - Dual fiber anode results after 50 cycles at 1C: 611 mAh/g (gravimetric) and 1.7 mAh/cm^2 (areal capacity).
- A combination of electrospinning (of Si-PAA fibers) and spraying/electrospraying (of C-PVDF droplets) also works.
  - After 50 cycles at 1C: 600 mAh/g (gravimetric) and 1.2 mAh/cm^2 (areal)