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Silicon Whisker and Carbon Nanofiber Composite Anode for Lithium Ion Batteries

Physical Sciences Inc.

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November 17, 2009

2009 NASA Aerospace Battery Workshop, Huntsville, AL
No ITAR-Restricted Information
This research activity is funded by NASA Contract number NNX09CD30P

Current Silicon Anodes

VG00--1

Silicon anodes reported in the literature*:

1. Pure Si micro- and nano-scale powder anodes,
2. Si dispersed in an inactive matrix,
3. Si dispersed in an active matrix,
4. Si anodes with different binders,
5. Si thin films.

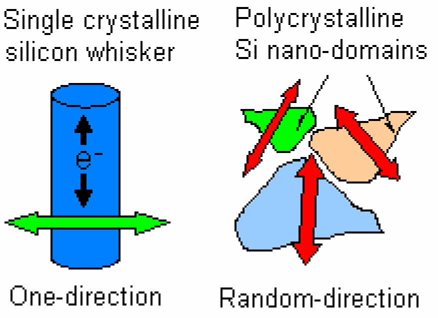
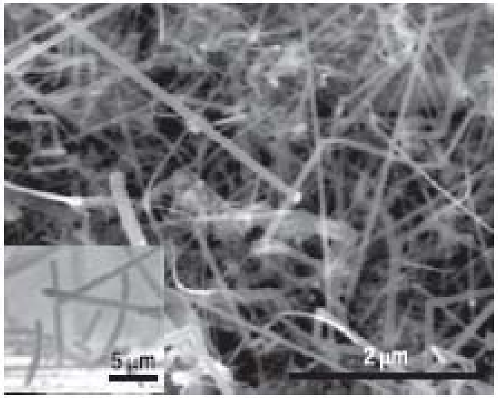
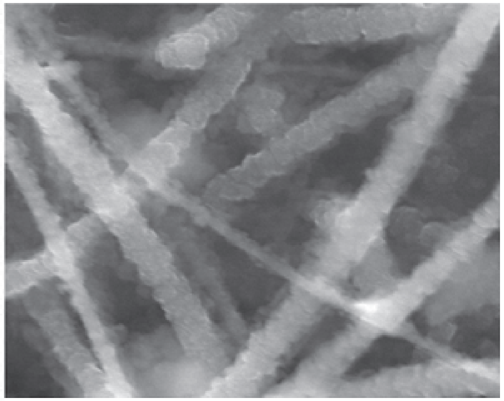


Illustration of destructive stress incurred by volume change during electrochemical cycling.

Silicon nanowire based anode By Chan et al. **:



Silicon nanowire on Stainless steel



After cycling

- Demonstrated high capacity and rate capability

* U. Kasavajjula, C. Wang and A. J. Appleby, *Journal of Power Sources*, 163, 1003–1039, (2007).

** C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R. A. Huggins and Y. Cui, *Nature Nanotechnology*, 3, 31 – 35. (2008).

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Phase I Concept: Silicon Whisker and Carbon Nanofiber Composite

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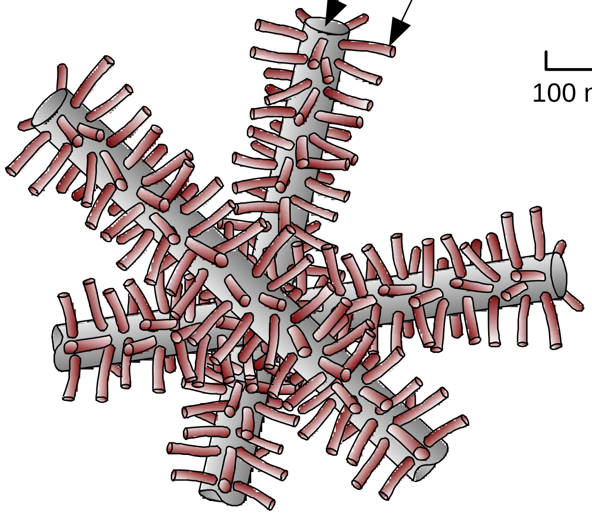

Silicon Whiskers/Nanowires on Carbon Nanofiber

J-8382

Material Concept Development Considerations:

- High in free volume;
- Free of polycrystalline domains (not achievable for silicon anode by CVD);
- 50% or higher loading of silicon;
- Supporting matrix forms an electronically conductive framework;
- Processable using established procedure and equipments.

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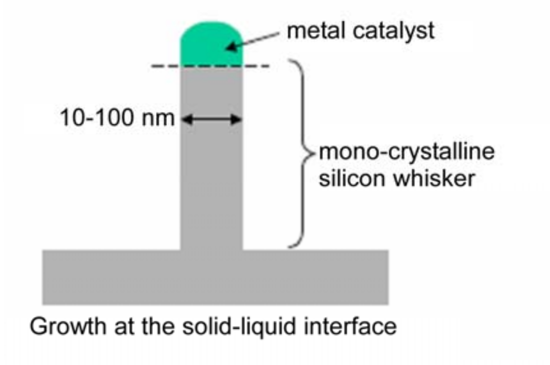
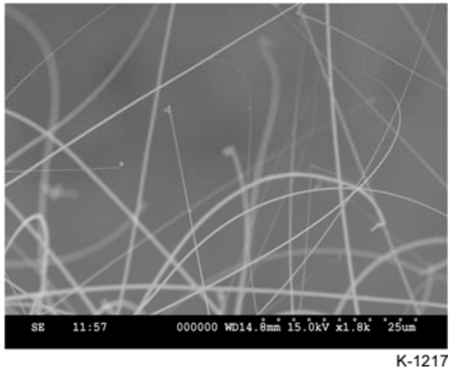
Technical Objectives

Silicon whiskers grow on carbon nanofiber; gold catalyzed Vapor-Liquid-Solid (VLS) process



VLS mechanism

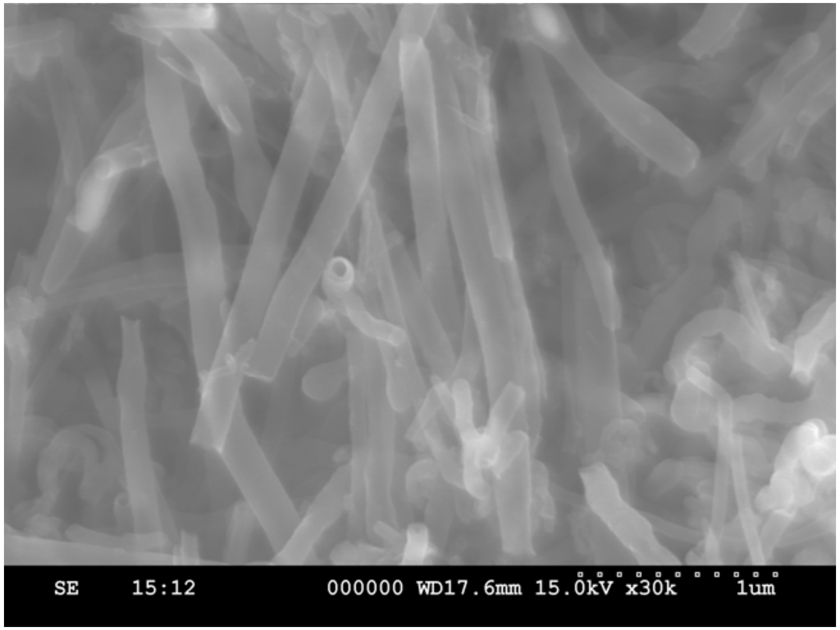


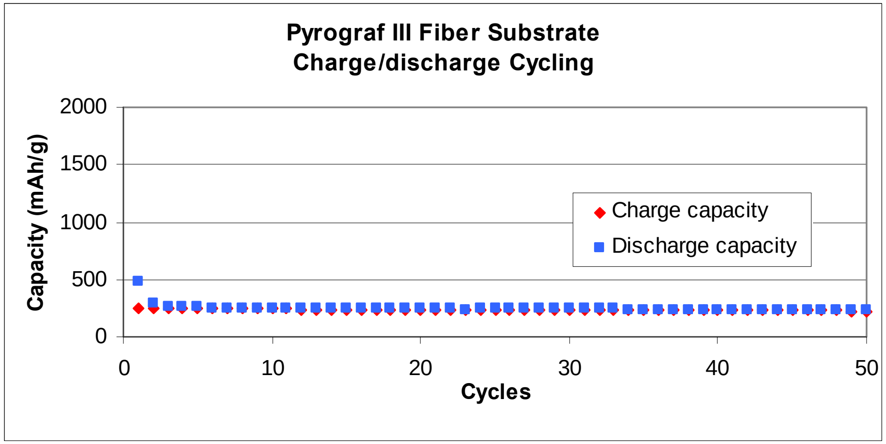
PSI Si whiskers / nanowires

Phase I Objectives:

- Demonstrate silicon whisker on carbon nanofiber composites with 1:1 weight ratio.
- For an anode in half cell, demonstrate a capacity of greater than 1000 mAh/g based a C/2 charge/discharge rate and an irreversible loss of <10% for the 1st cycle.
- Demonstrate a cycle life of over 100 cycles with less than 20% capacity fade.
- In a lithium ion battery, achieve an anode capacity greater than 950 mAh/g at C/2 and 0^{o}C.

The Carbon Nano-fiber Substrate

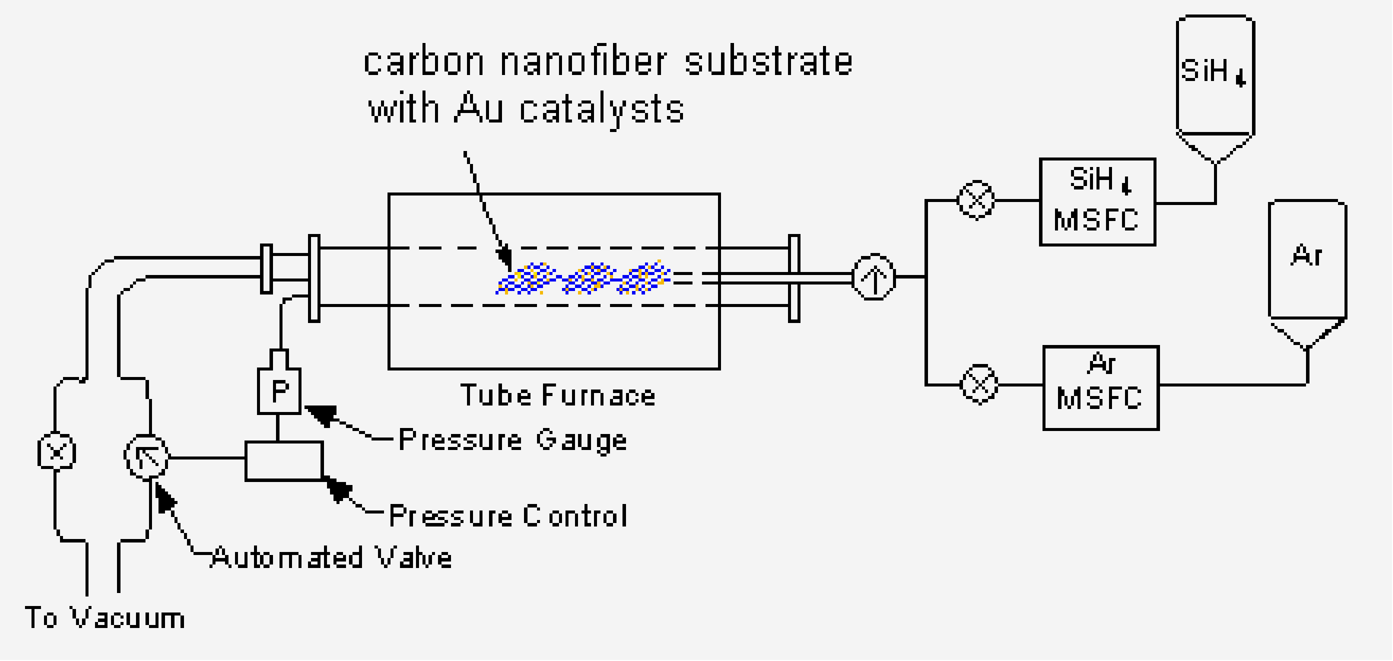




Pyrograf® III Carbon fiber (Pyrograf Products, Inc. / Applied Sciences Inc.)

- Tested in 2mAh half cells;
- Pyrograf base line evaluated – capacity 250 mAh/g

Vapor-Liquid-Solid Process



Reaction conditions in a VLS reactor:

- Reactor temperature: 500^{o}C
- Pressure: 30 Torr (~4000 pascal)
- Flow rate of SiH_4(2% in Argon) mixture gas 80 cc/min
- Reaction time: 60 minutes

Silicon Whisker/Carbon Fiber Composite – SEM -1

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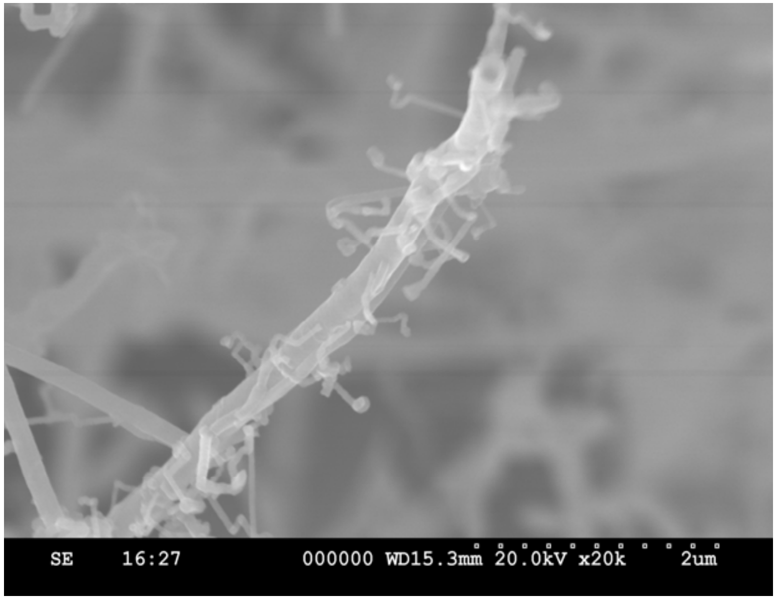
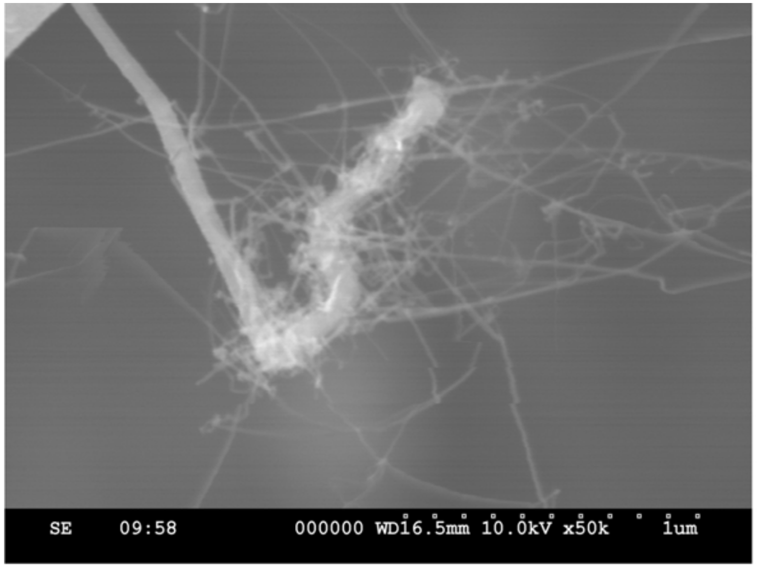


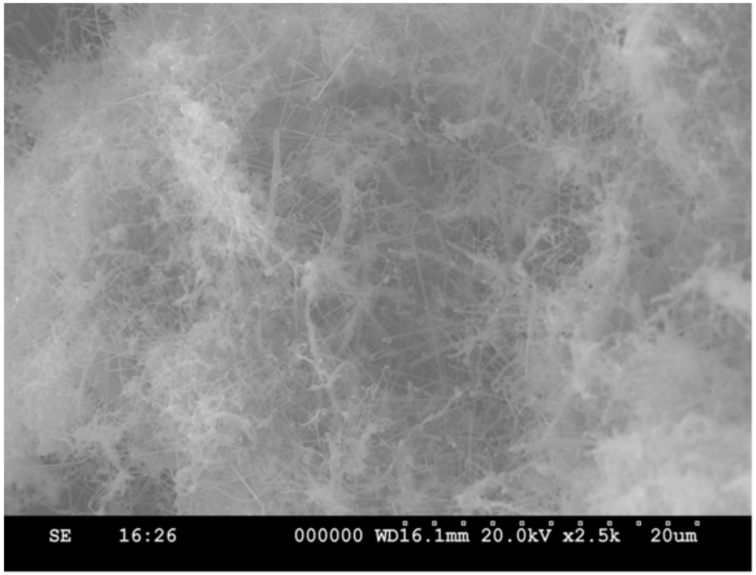
1. It is feasible to grow silicon whiskers on carbon nanofibers by VLS.

2. Silicon-on-fiber architecture demonstrated.

3. The 1:1 silicon / carbon nano-fiber weight ratio target was achieved.

4. Weight gain is proportional to reaction time.





Silicon Whisker/Carbon Fiber Composite – XRD

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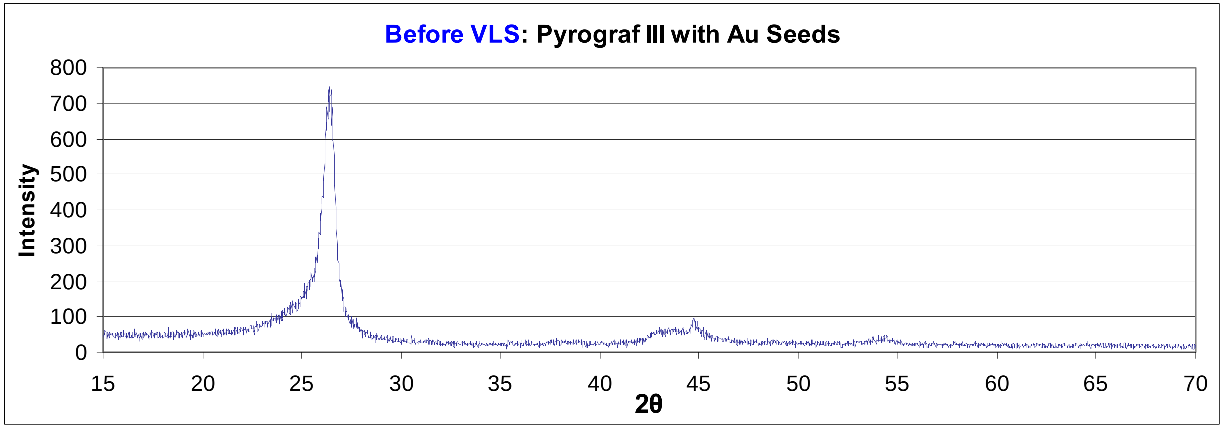

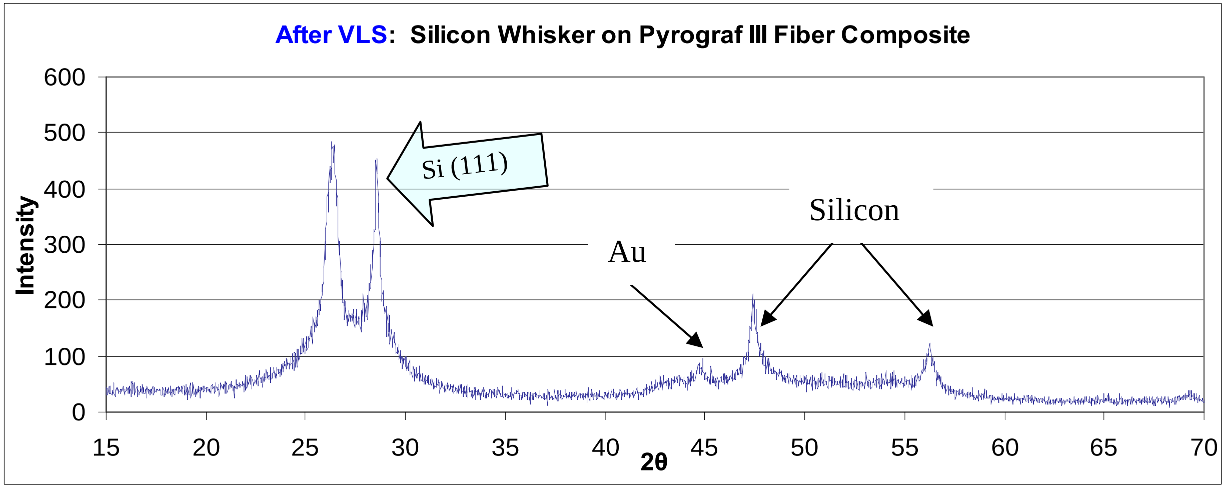

XRD before and after VLS confirms formation of single crystalline silicon.

* C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R. A. Huggins and Y. Cui, *Nature Nanotechnology* 3, 31 - 35 (2008).

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Silicon whisker Composite Electrode and Testing

Electrode formulation (wt%):

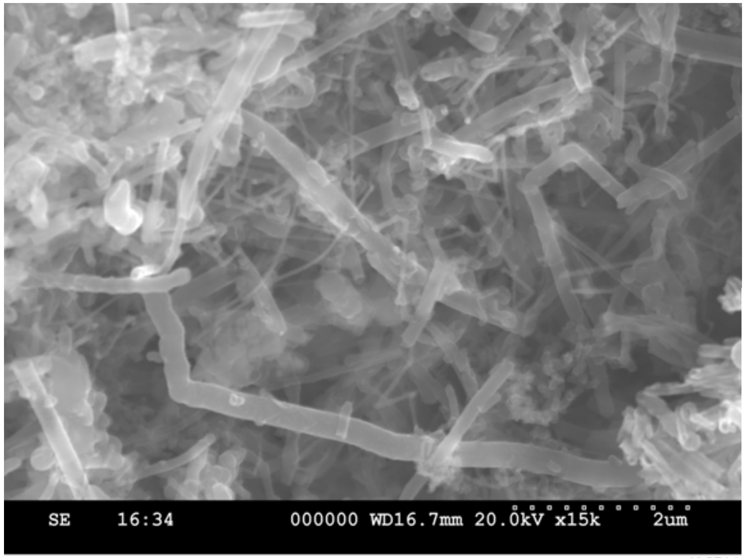
78% Composite
11% Acetylene black
11% polymer binder

Composite loading in electrode:

0.5 - 1.7 (mg/cm^2)

Cycling rate: C/10 to 1C
Voltage range: 2 - 0.05 volt
Electrolyte: 1M $LiPF_6$ in EC/DEC + 5 % VC

Tested in spring-loaded puck-cells and 2325 coin cells (shown right).



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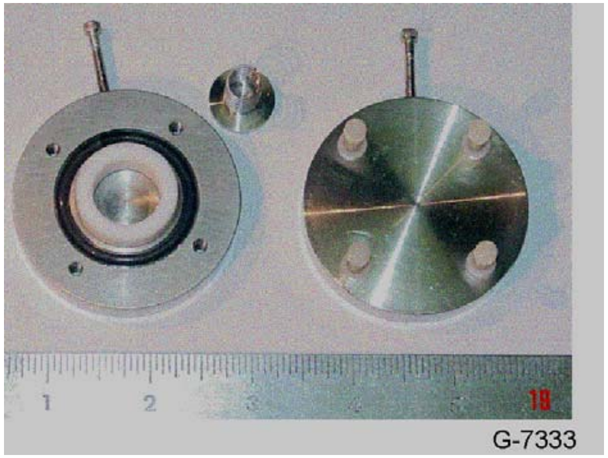
SEM photograph of silicon whisker electrode



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VC in Electrolyte

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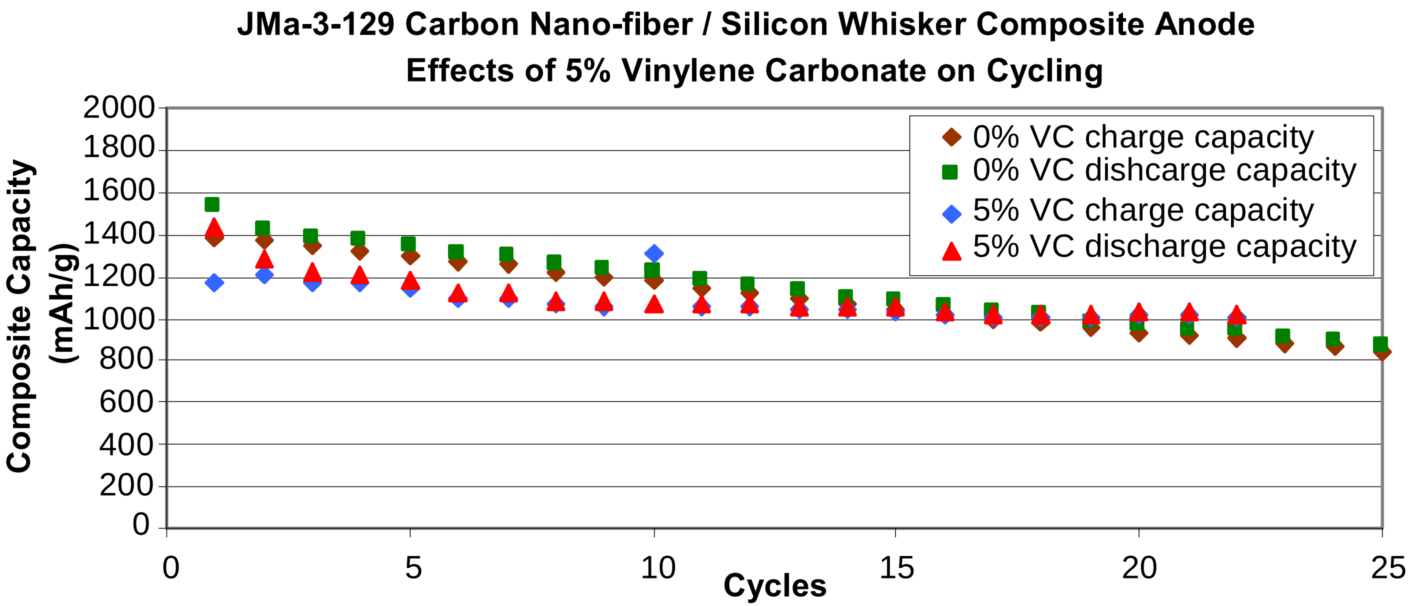

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- The addition of VC doesn't improve capacity
- VC additives improves cycling

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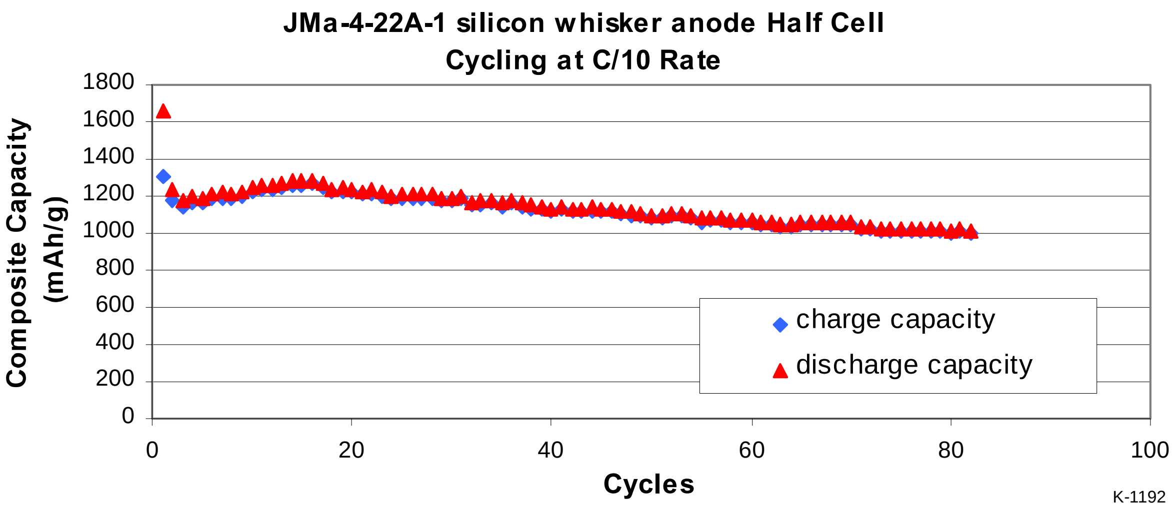
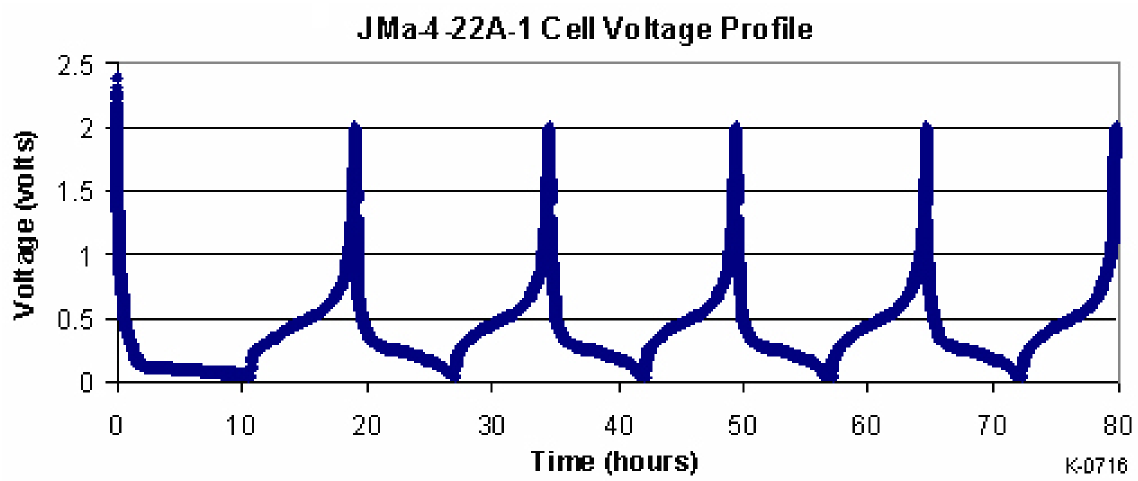
2nd generation Electrode





- High in capacity: discharge capacity of 1300-1600 mAh/g;
- Good 1st cycle coulombic efficiency: 80 – 90%.

Silicon Whisker/Carbon Fiber Composite – Cycle life

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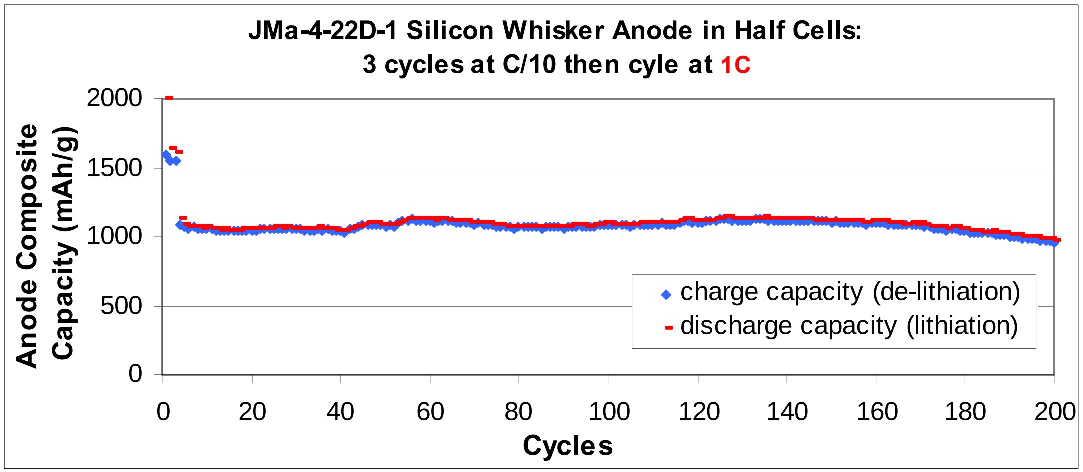
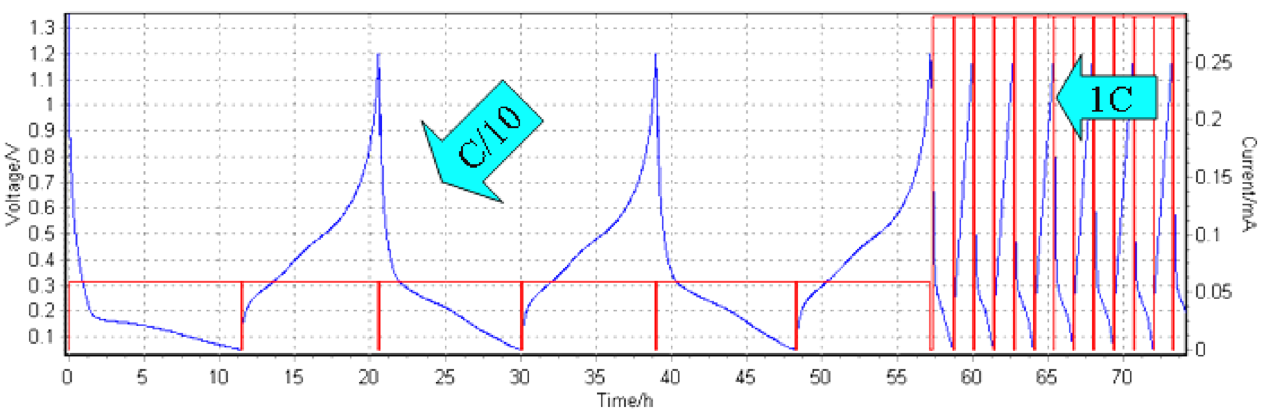
Discharge: anode lithiation; Charge: anode de-lithiation

All capacity values were calculated based on composite weight (50% silicon whisker and 50% Pyrograf fiber)





- Good cycle life achieved for > 200 cycles;
- C/10 cycles seems to be necessary to stabilize the cell;
- Single crystalline silicon whiskers are capable of cycling at high rate of 1C

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Silicon Whisker Composite Anode in Full Cells

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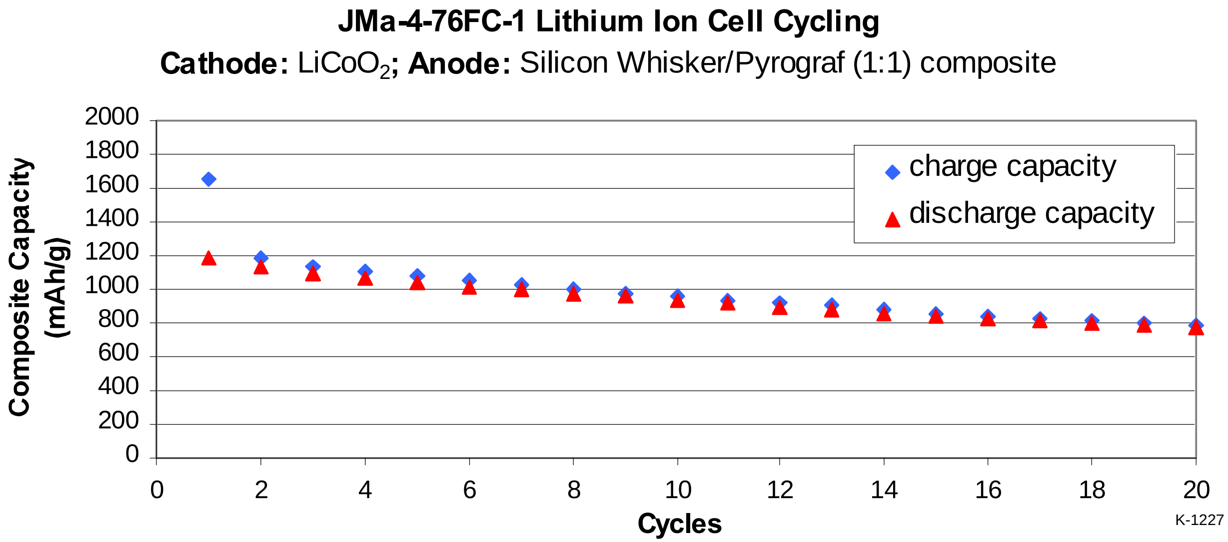

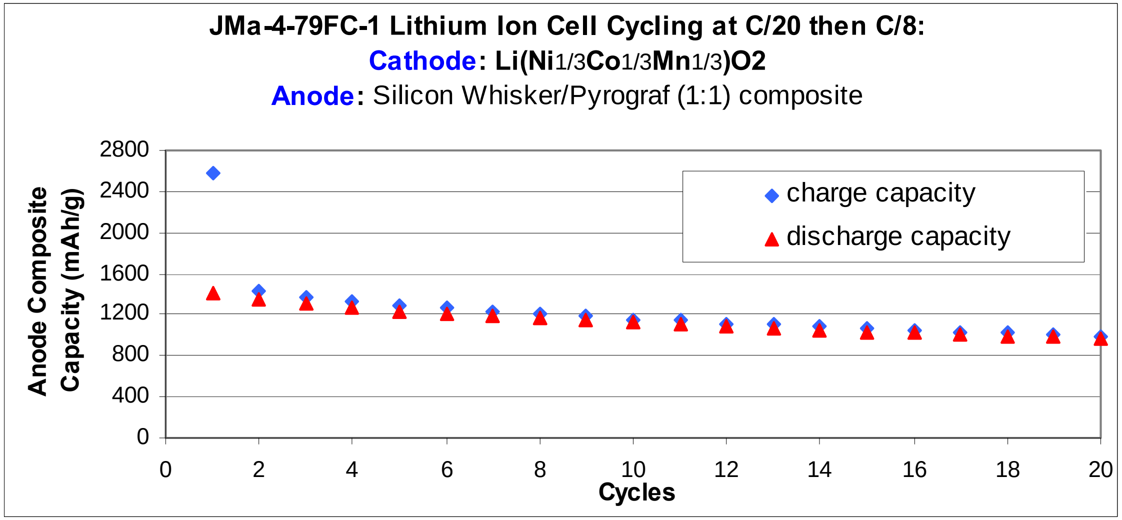

- 1200 – 1300 mAh/g in capacity;
- Good cycling performance demonstrated in full cells;
- Need to improve 1st cycle efficiency.

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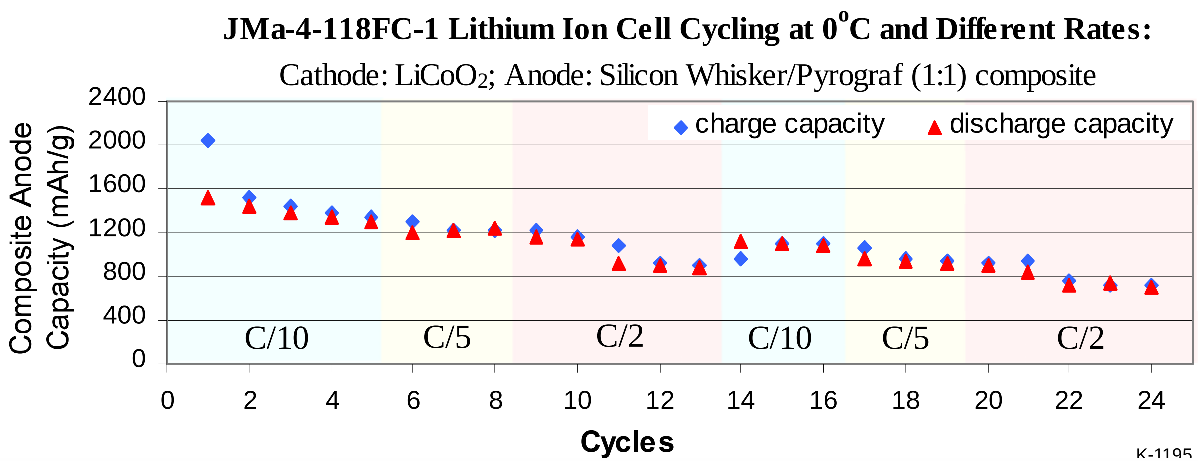
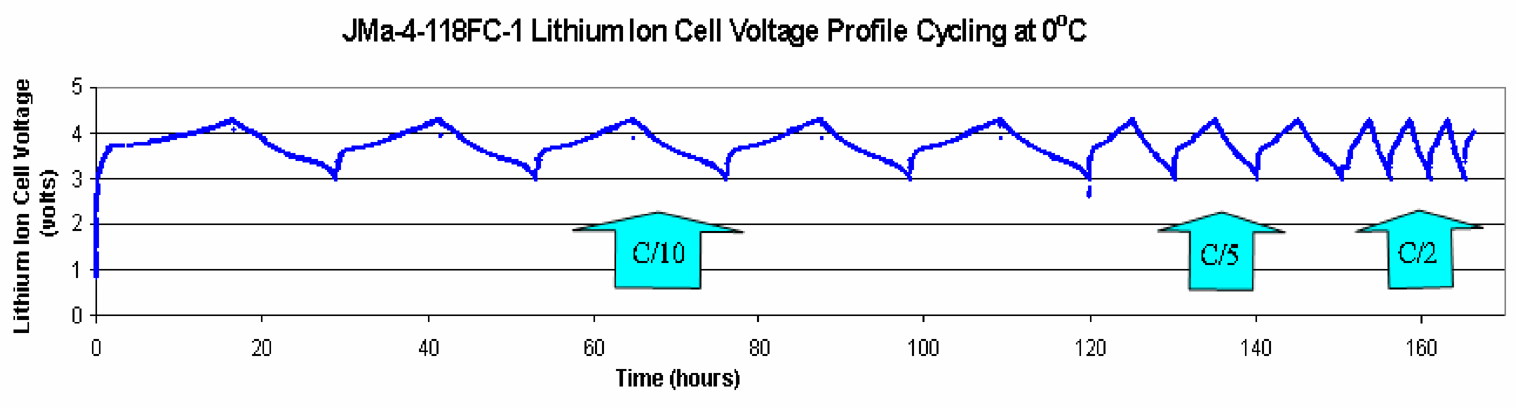
Lithium Ion Cell at 0°C





- Anode capacity greater than 950 mAh/g at C/2 and 0°C;
- 1st cycle efficiency needs improvement;
- Electrolyte used is 1.0 M $LiPF_6$ solution in a 1:1:1 by volume mixture of EC/DEC/DMC+ 5% VC

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High Loading Silicon Anode

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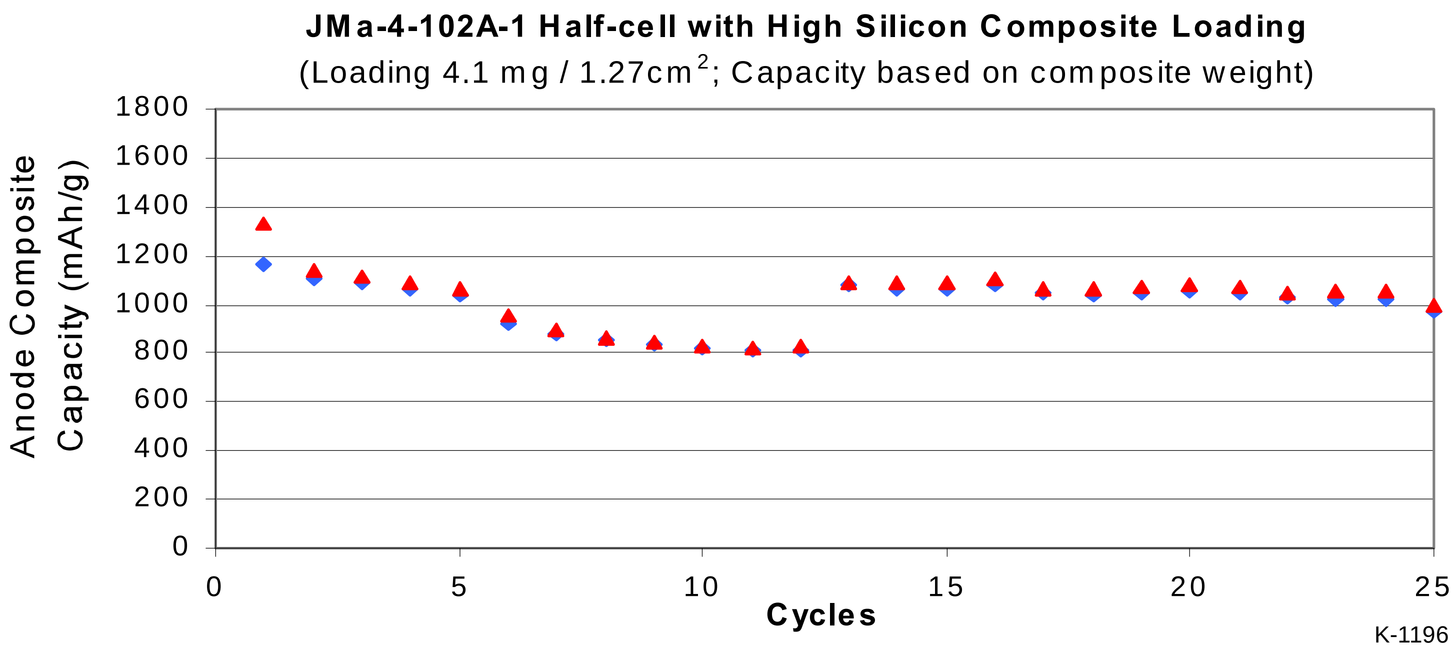

- Five cycles at C/10, 7 cycles at C/5 and 12 cycles at C/10
- **Achieved a discharge capacity of 22.86 mAh/in^2** for the high loading silicon whisker composite anode

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Conclusions

- A novel silicon whisker on carbon nano-fiber composite anode material was successfully demonstrated in this program.
- It is feasible to grow silicon whiskers on carbon nanofibers by VLS processes to achieve a high silicon loading of 50%.
- The silicon whisker anode composite shows a high capacity of greater than 1000 mAh/g.
- The silicon whisker composite anode shows a good cycle life at high rate.

Acknowledgements

- NASA SBIR Phase I Contract Number: NNX09CD30P
  100K; Jan. 22, 2009 – July 22, 2009

- Dr. Richard Baldwin, William Bennett and the NASA Glenn Battery Group
  Electrochemistry Branch
  NASA Glenn Research Center, Cleveland, Ohio