

# NASA Battery Workshop

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## C/Si Composite Anodes for Advanced Lithium Ion Batteries

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TDA Research

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# OUTLINE

- Introduction to TDA Research
- Technical Approach
- Results
  - Capacity
  - Power
  - Irreversible capacity
  - Capacity fade
- Future Work

# TDA Research, Inc.

[www.tda.com](http://www.tda.com)



**Wheat Ridge Facility**

**22,500 ft<sup>2</sup> offices and labs**  
**Synthetic Chemistry**  
**Catalyst/Sorbent Synthesis/Testing**  
**Ceramics Processing**  
**Machine and Electronics Shops**  
**SEM (w/EDX), TOF Mass Spec**



**Golden Facility**

**27,000 ft<sup>2</sup> offices and labs**  
**27 fume hoods**  
**Synthetic Chemistry**  
**Catalytic Process Development**  
**Pilot Scale Production**

# Goal Oriented Research

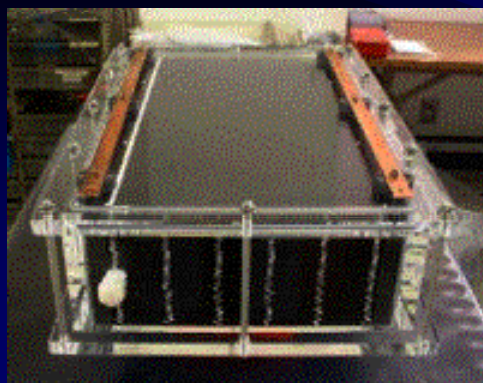
Private, founded in 1987

~ \$12.5 million/year revenue in 2008

Staff of 81, primarily chemists and engineers, 2/3 of whom have advanced degrees (24 w/ Ph.D.)

## Commercial Products

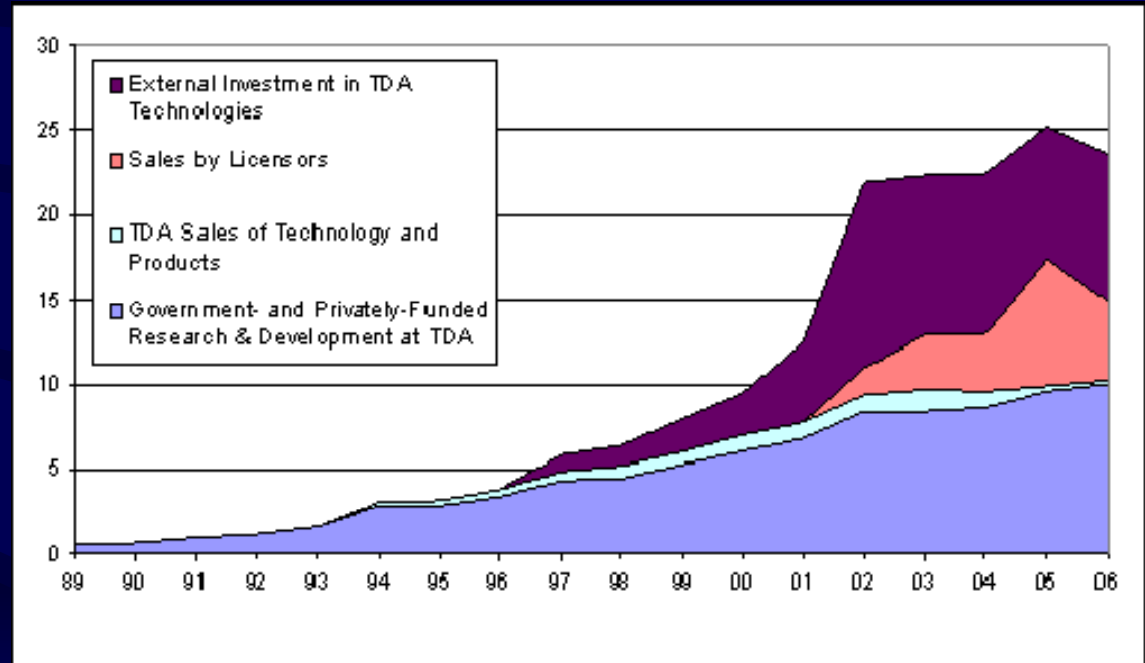
- SulfaTreat DO
- Fullerenes
- Conducting Polymers
- Self-Heating Products
- Sulfur Sorbents
- Carbon Electrodes for Desalination



# History of Commercial Success

*TDA's business plan is to develop new technologies and license them to leading industrial companies*

- 142 SBIR Phase IIs
- Of 107 completed, 87 have had Phase III funding or sales
- ~ \$91.5 million in Phase III funding
- Over \$11.3 million in direct sales; ~\$28.2 million of licensed customer sales



# Activated Carbons for Ultracapacitors



Capture regenerative braking energy in hybrid and fuel cell vehicles

Load level in cars and electronic, reducing wear on the battery, improving power system stability and reducing weight

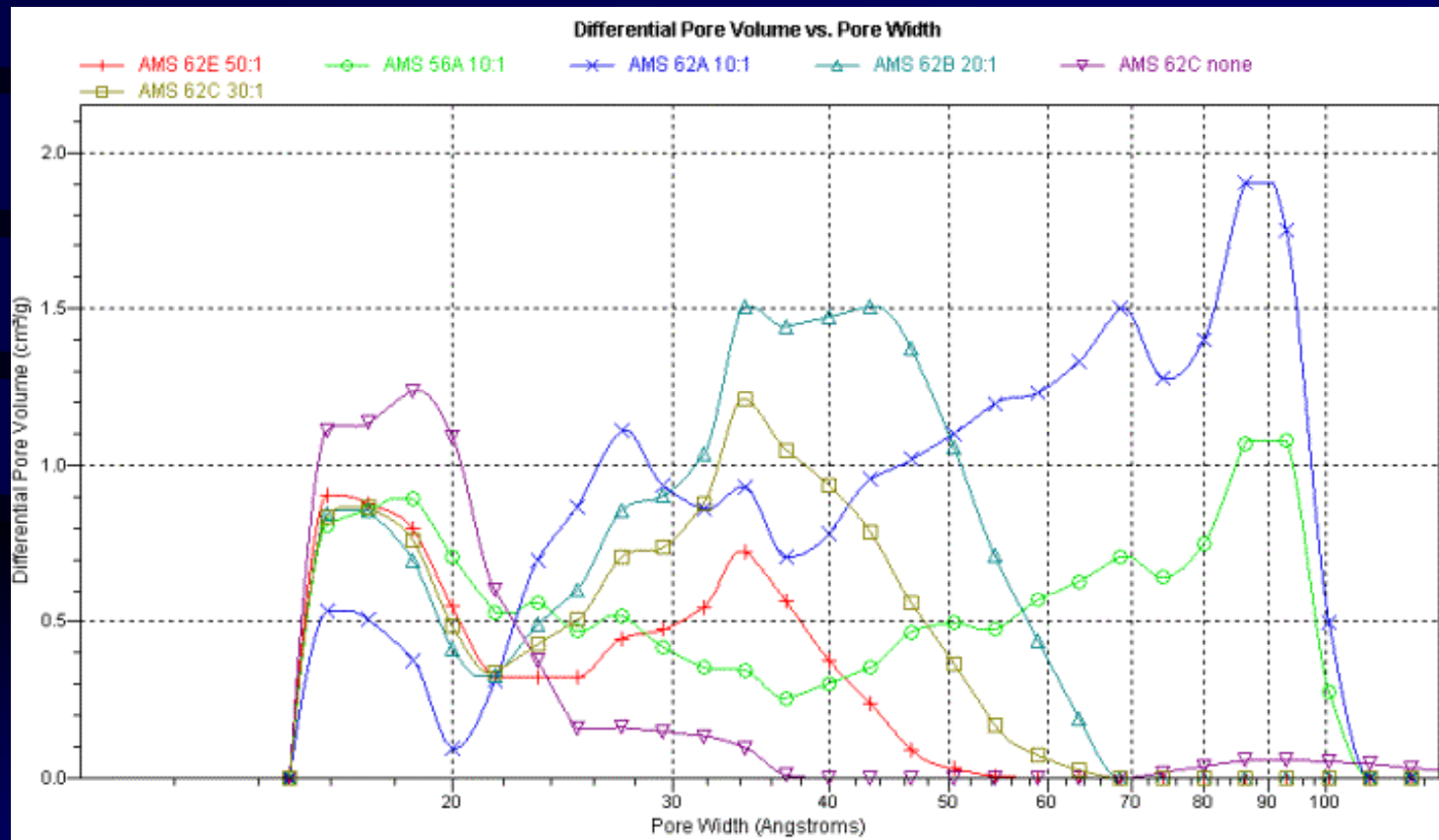
- PI: Dr. Steven Dietz
- Low-cost production from sugar precursors
- Larger voltage window than current carbons; 2.85 V vs 2.7 V
- Faster charge / discharge (lower internal resistance)
- Tailored pores allow liquid access to all the carbon's surface area
- Joint development agreement for ultracapacitors with MeadWestvaco
- Under evaluation by Maxwell Technologies and others

Development funded by DOE, NSF

Proprietary – TDA Research

**TDA**  
Research

# Engineered Pore-Size Optimizes Performance



Proprietary – TDA Research

**TDA**  
Research

# Key Personnel Are Experienced

- Dr. John Olson – PI, Electrochemist
  - Joined TDA Research in 2007
  - 15 years experience in battery industry; Optima Batteries, Boundless Corp.
  - Lithium-ion, VRLA, Ultracapacitors, battery management, charge algorithms
  - 3 patents
- Dr. Steve Dietz – Carbon Synthesis
  - Invented pore size engineering of activated carbons
  - Applied to ultracapacitors and capacitive de-ionization
  - TDA scientist from 1993
  - 4 patents, 1 patents pending

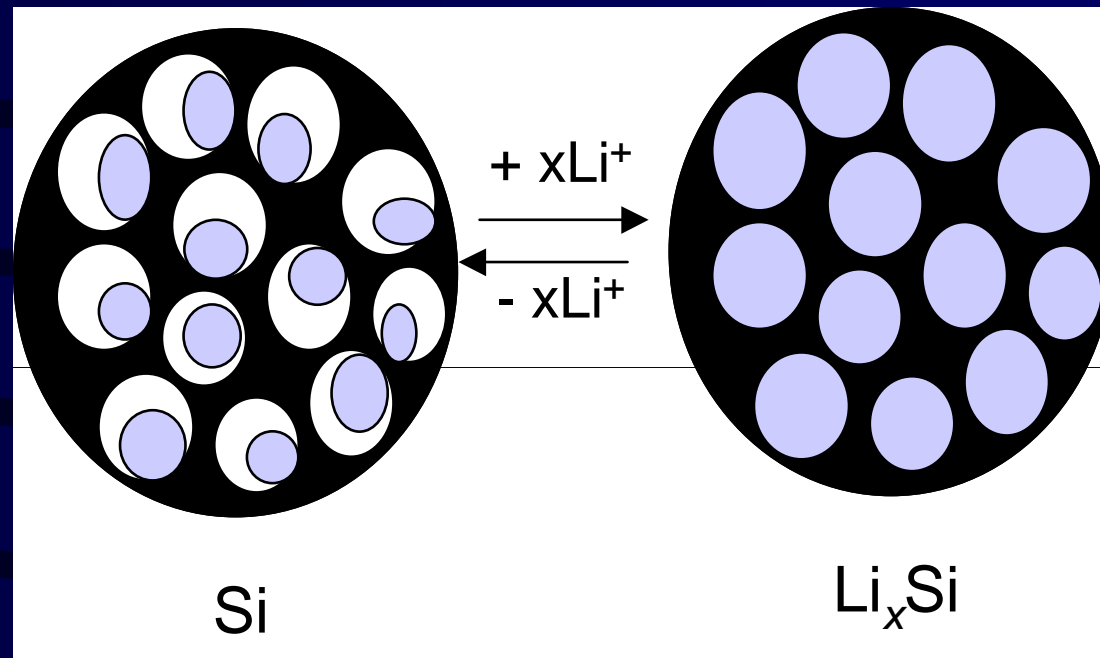
# Silicon as an Anode

- 4200 mAh/g capacity (theoretical)
- Li forms alloy, rather than intercalating
- 4.4 Li atoms per Si atom
- Large expansion 280%
- Cycling leads to rapid capacity loss due to cracking and loss of conductive matrix

# Efforts to Engineer Silicon for Li-Ion Battery Anodes

- Nanoscale particle size – effectively extends life, but Oswald ripening and agglomeration lead to capacity fade and high surface area results in SEI formation and large irreversible capacity loss
- Graphite carbon matrix or coatings – also effective, but capacity fade still needs improvement and SEI growth an issue

# Si/C Composites



Hard carbon matrix with encapsulated silicon

- Prevent SEI layer formation/re-formation on Si particles
- Provide highly conductive matrix
- Prevent agglomeration of dispersed Si particles

# Hard (non-graphitizable) Carbon vs Graphites

- Higher specific capacity and better charge acceptance
- Lower energy density
- Better cycle life, less volume change and more stable SEI layer
- Higher irreversible capacity due to surface groups and water adsorption
- Higher surface area leading to increased SEI formation
- Hydrogen incorporation causes cycling hysteresis

# Synopsis of Work Effort

There were three major factors studied:

- (1) Composites fired at different temperatures ( $> 1200$  C or  $1000$  C)
- (2) Composites made with nano Si versus  $44$   $\mu\text{m}$  Si particle sizes
- (3) Composites using different carbon sources

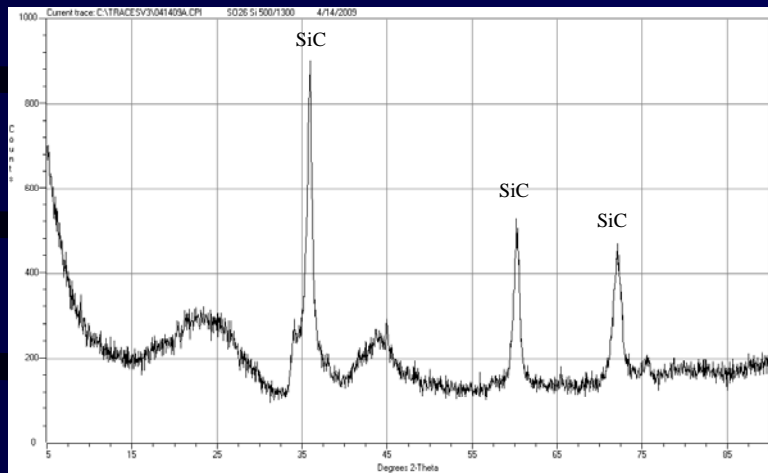
# Experimental Test Methods

- Anode formulation: 87.5% active, 5% Super P, 5% PVDF in NMP cast onto Cu foil (25 um)
- Half 2025 cells: Li foil, Celgard separator, 1 M LiClO<sub>4</sub> EC:DEC 1:1 (Dahn charge method)
- Full 2025 cells: Commercial LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode, Celgard separator, 1 M LiClO<sub>4</sub> EC:DEC 1:1
- Typical charge/discharge rates: C/2 – C/4
- Resistance measurements using current pulse at 20 ms
- Irreversible capacity expressed as Ah<sub>charge</sub>/Ah<sub>discharge</sub>

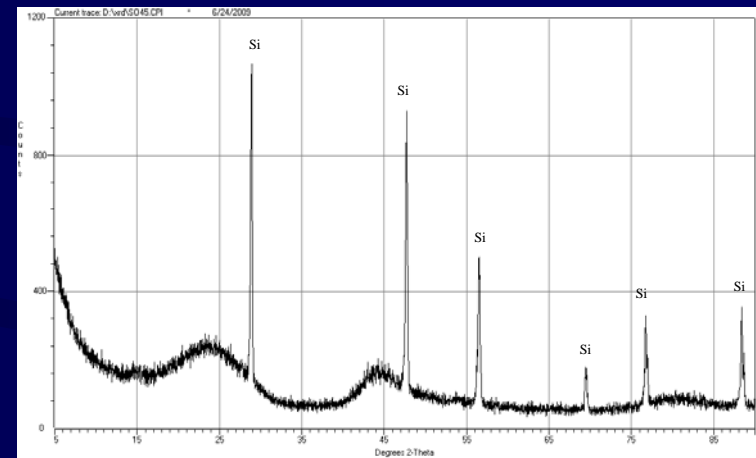
# Started with Control Carbons Fired at 1200 – 1400 C

	<u>Cycle</u>	<u>1200</u>	<u>1300</u>	<u>1400</u>	<u>Commercial</u>
Density (g/ml)		0.645	0.594	0.683	0.691
BET (m <sup>2</sup> /g)		0.69	0.42	0.14	
Capacity (mAh/g)	1st	375	512	Bad data	566
	2nd	379	471		545
	3rd	371	442		578
	4th	387	384		
Capacity (mAh/ml)	1st	244	304		325
	2nd	238	280		313
	3rd	248	262		332
	4th	260	228		
Irrev. Cap: (%)	1st		131		125
	2nd	103	105		103
	3rd	104	100		104
	4th	103	102		

# C/Si Composites Fired at 1300 C Were Inactive



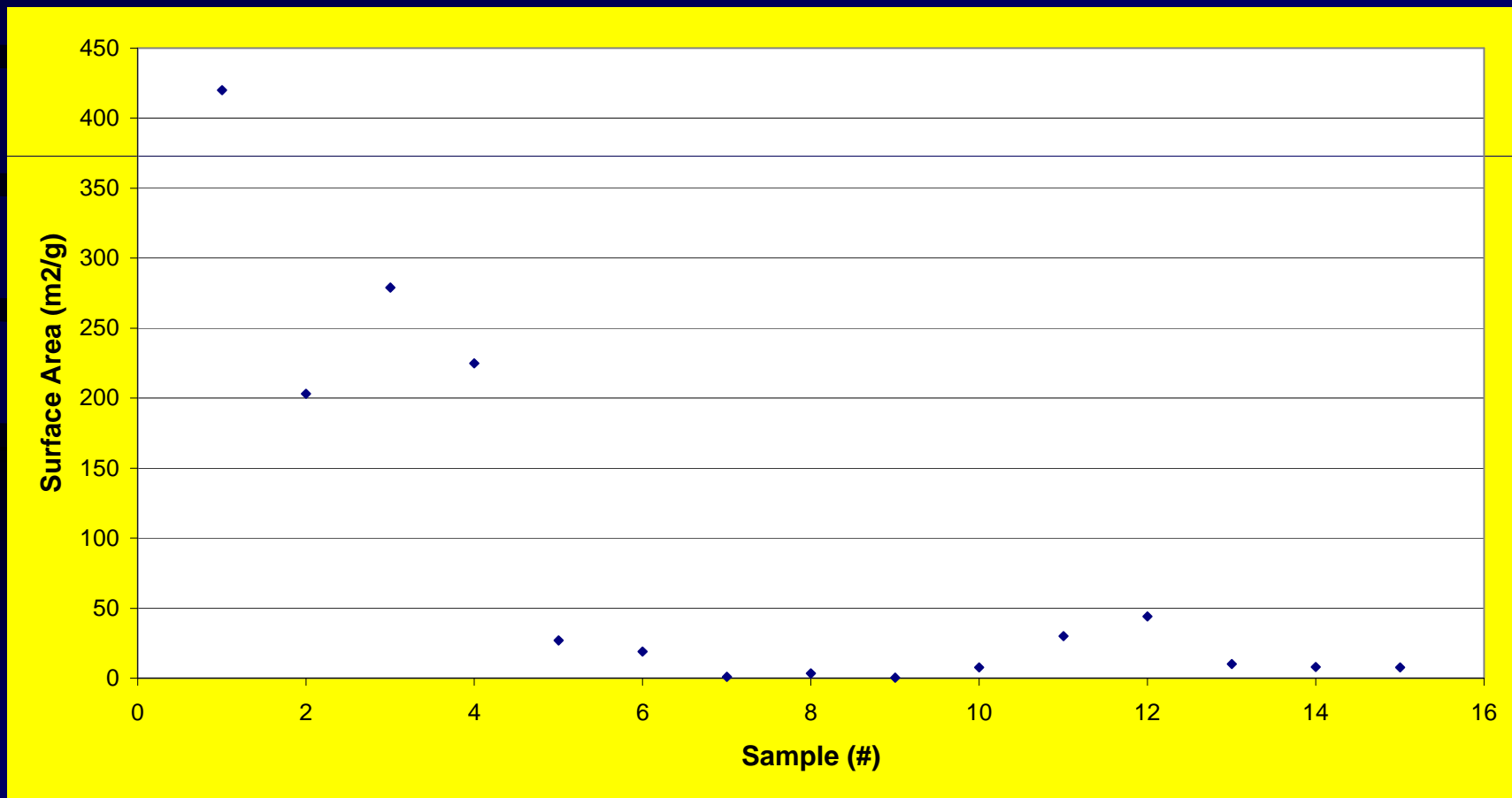
1300 C



1000 C

SiC formed at 1300 C, but not at 1000 C

# Process Conditions Changed to Reduce Surface Areas

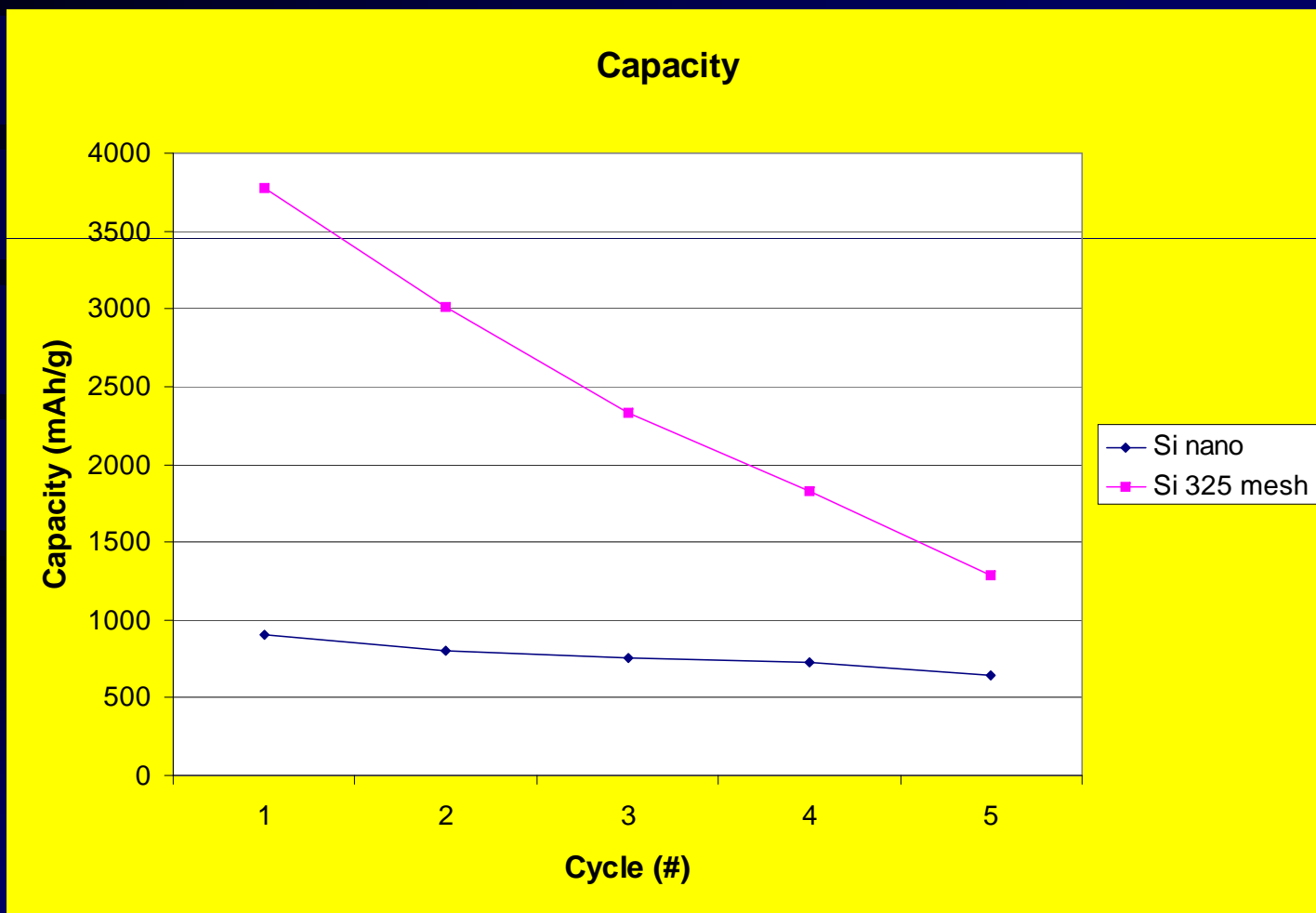


# Initial C/Si-nano Composites had Relatively Low Capacities

<u>Sample</u>	<u>mAh/g</u>	<u>mAh/ml</u>	<u>% Si</u>
SO26	618	147	20
SO27	545	140	20

So we evaluated some Si anode  
controls

# Initial Si-nano Controls Also Showed Low Capacity

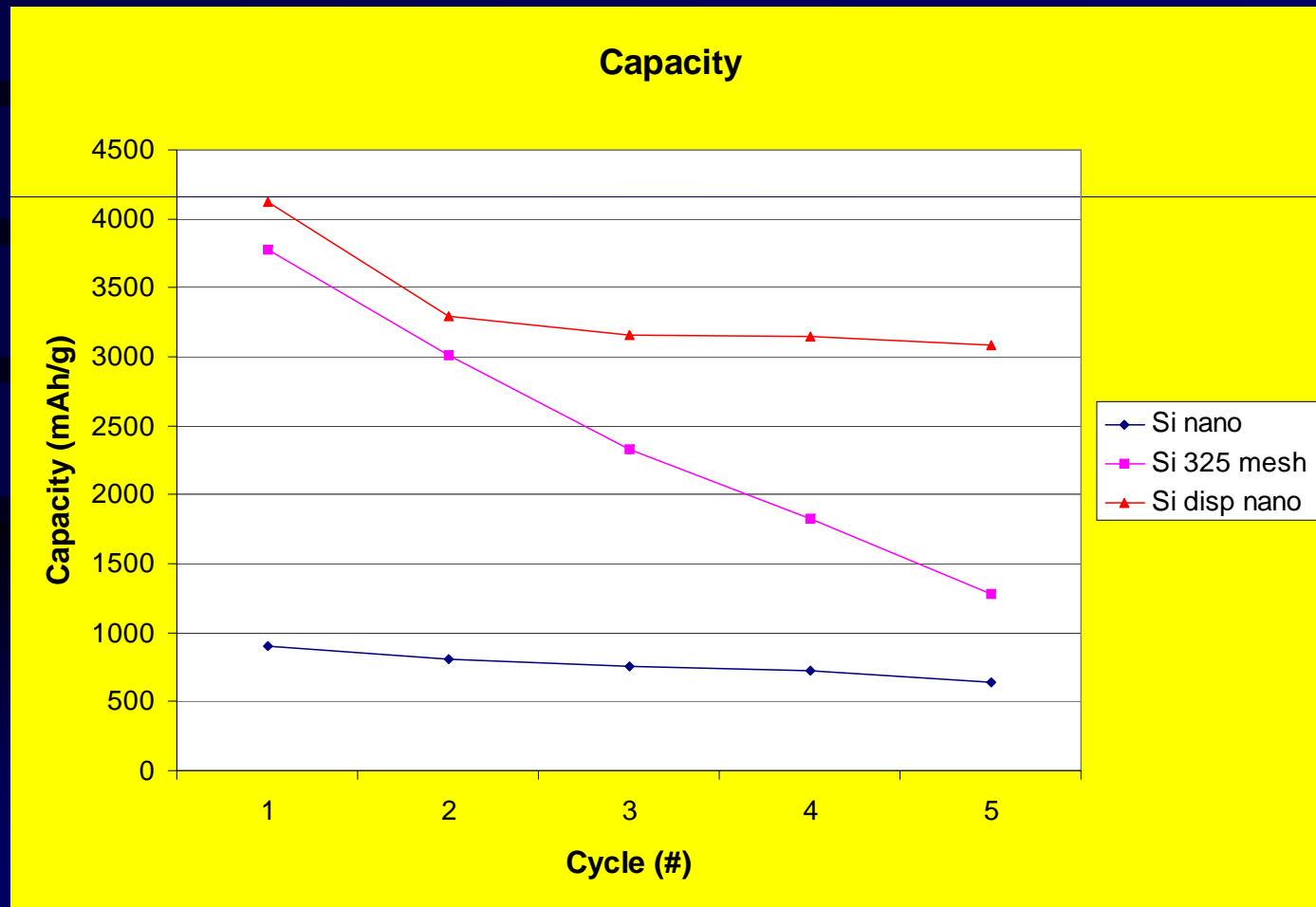


# C/Si Composites With 44 um Si Particles Showed Good Capacity

<u>Sample</u>	<u>mAh/g</u>	<u>mAh/ml</u>	<u>% Si</u>
SO32	1080	305	20
SO36	1510	595	40
SO38	1270	500	40

But high capacity fade!

# Dispersion of NanoSi Resulted in Theoretical Capacity



# Evaluated a Second Sugar Source to Obtain Better Dispersion

## 44 um Si

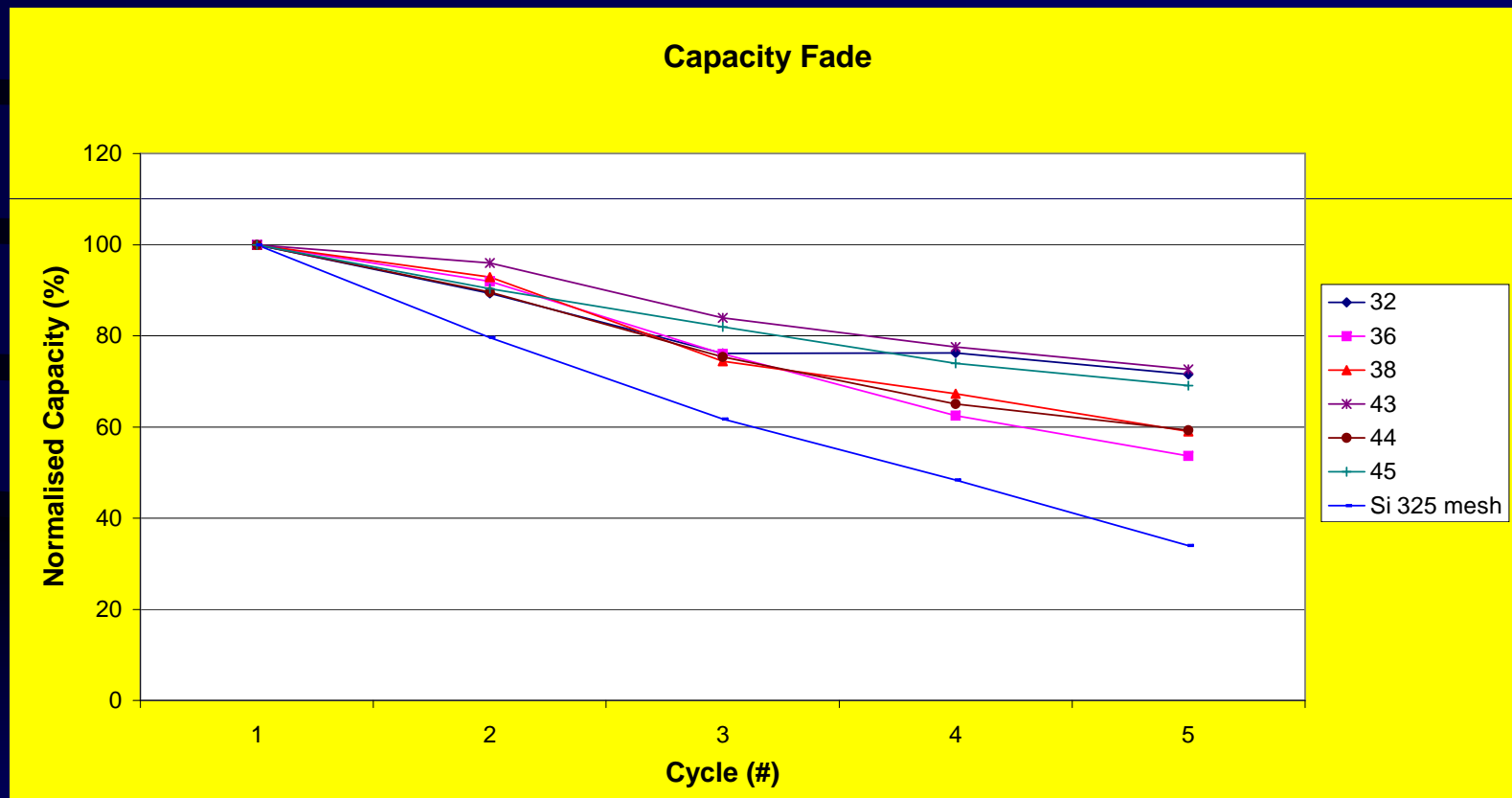
<u>Sample</u>	<u>mAh/g</u>	<u>mAh/ml</u>	<u>Carbon Source</u>	<u>% Si</u>
32	1080	305	Type 1	20
43	1060	436	Type 2	20
44	993	426	Type 2	20

## Nano Si

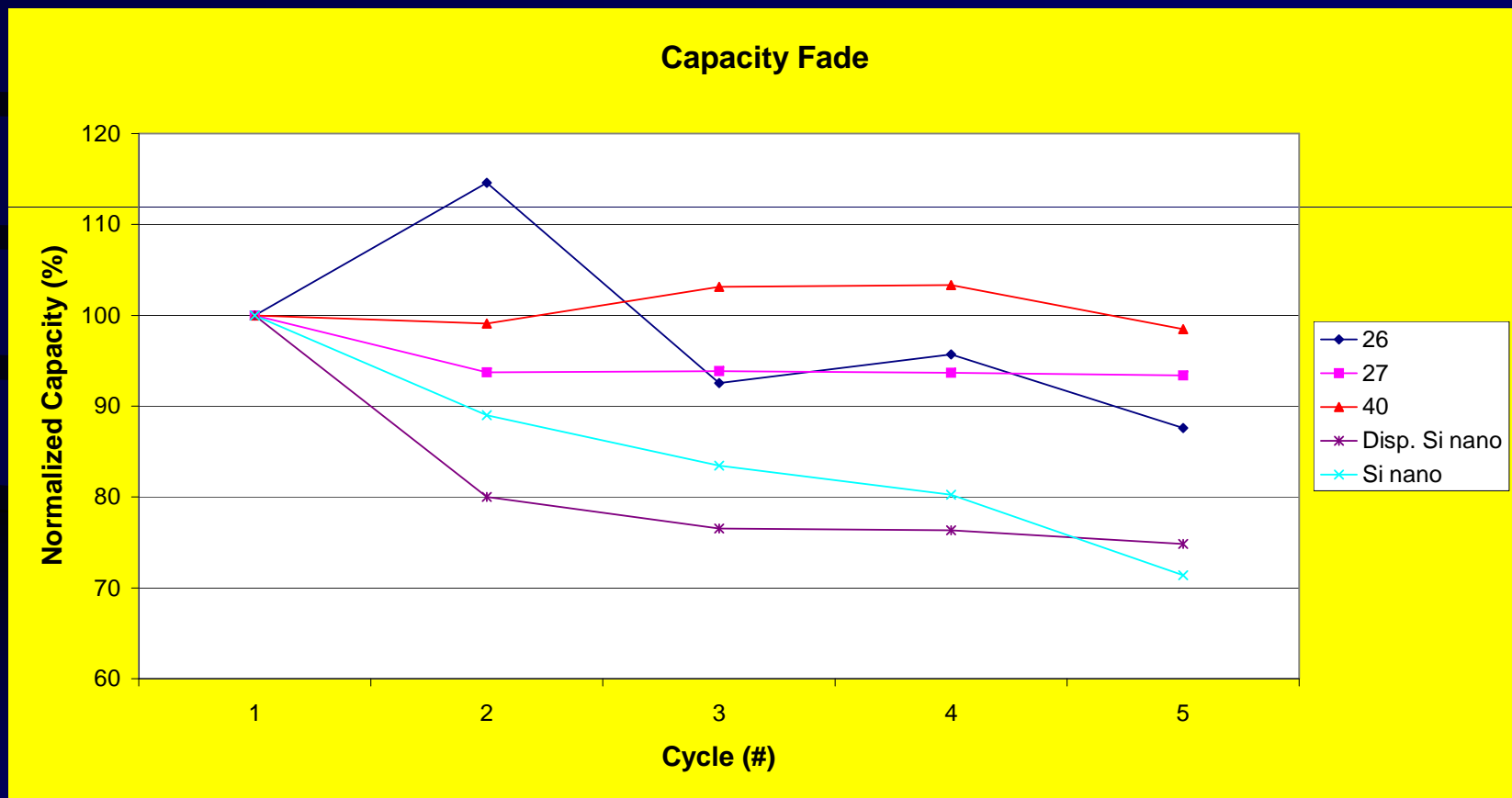
<u>Sample</u>	<u>mAh/g</u>	<u>mAh/ml</u>	<u>Carbon Source</u>	<u>% Si</u>
26	618	147	Type 1	20
27	545	140	Type 1	20
40	656	273	Type 2	20

Only capacities were about the same

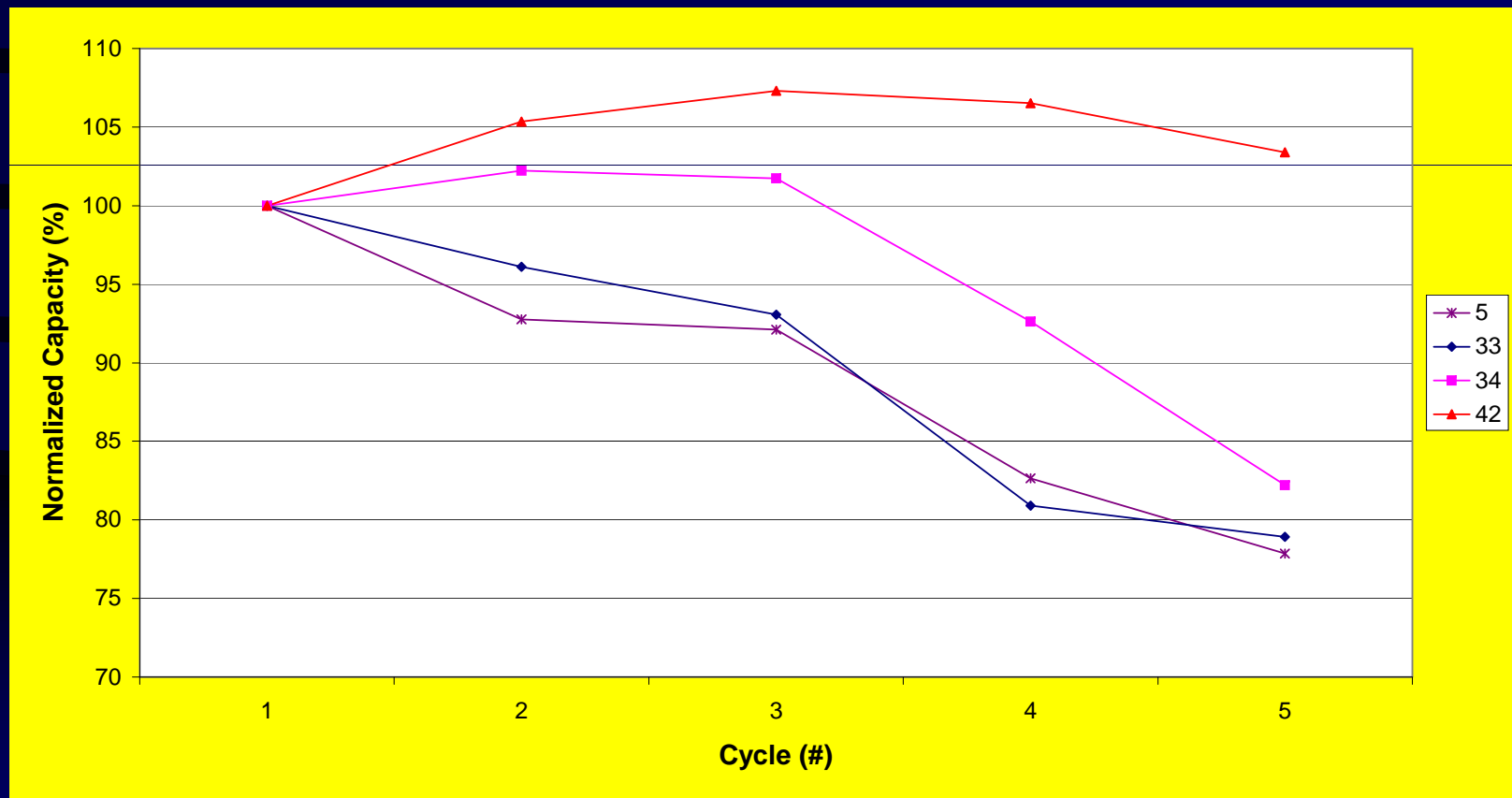
# Carbon Stabilized Si Capacity



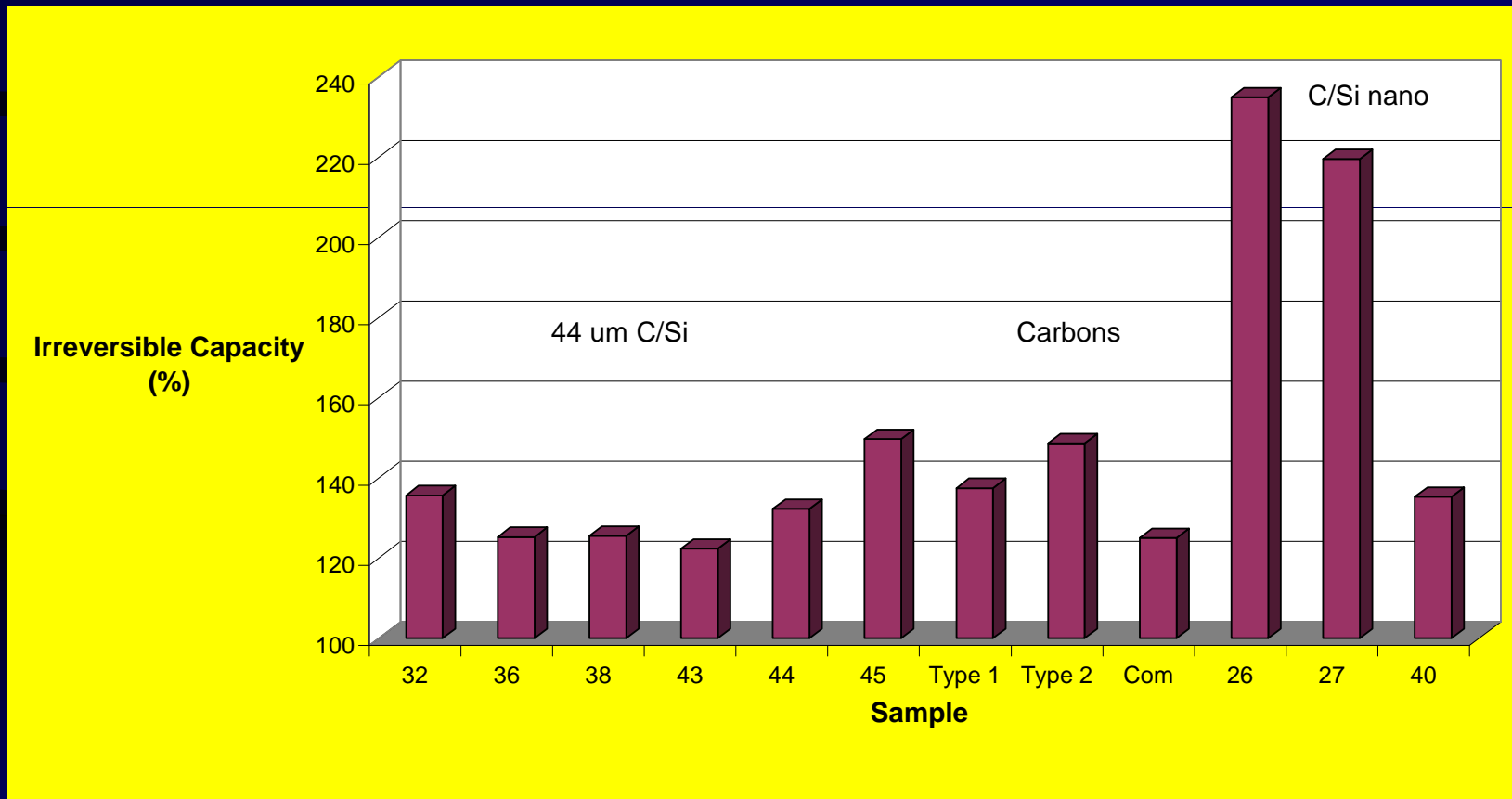
# Carbon Also Stabilized Si-nano



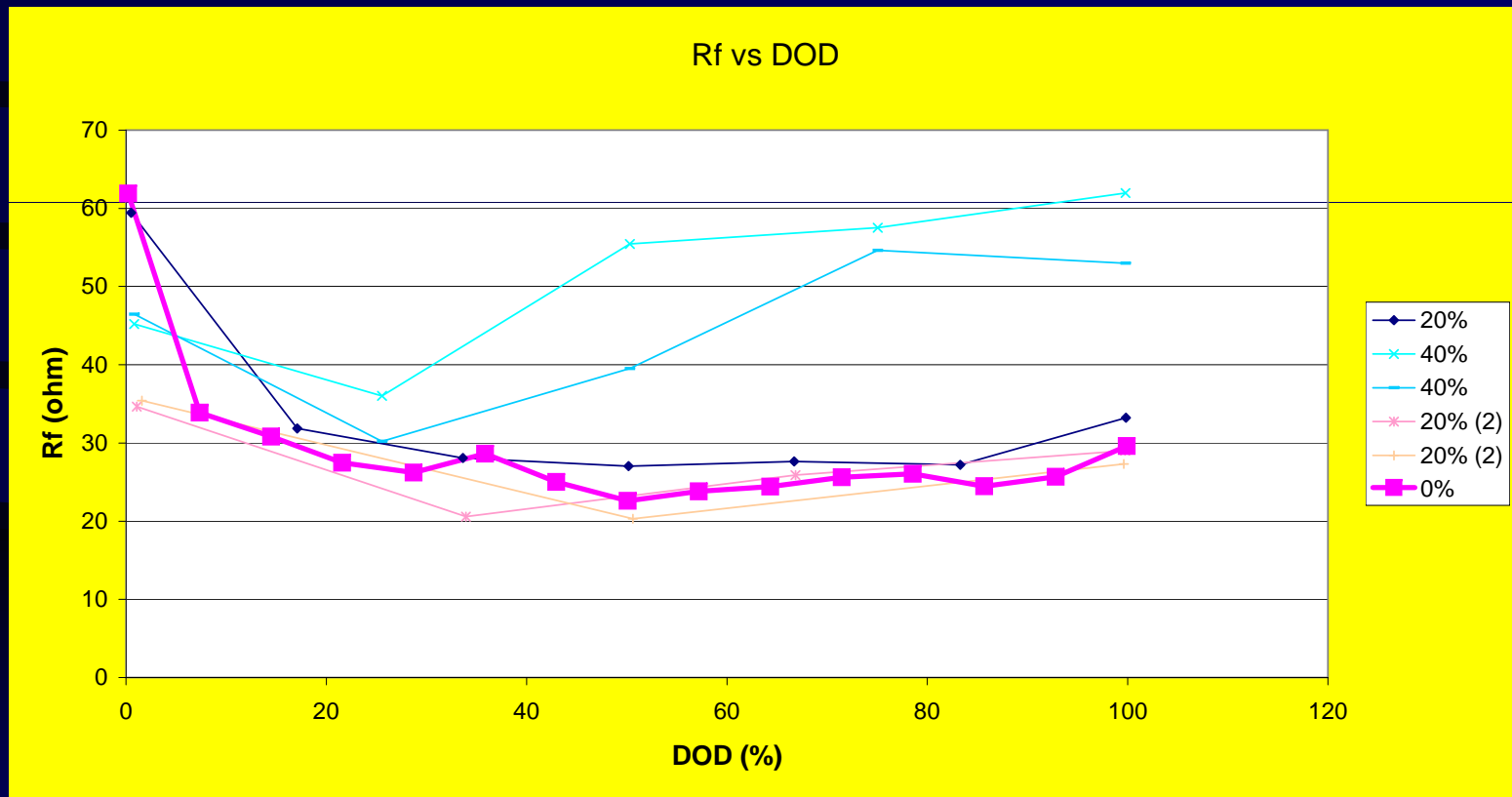
# Type 2 Carbon Has Better Capacity Fade Than Type 1



# Irreversible Capacities are Variable, but Encouraging

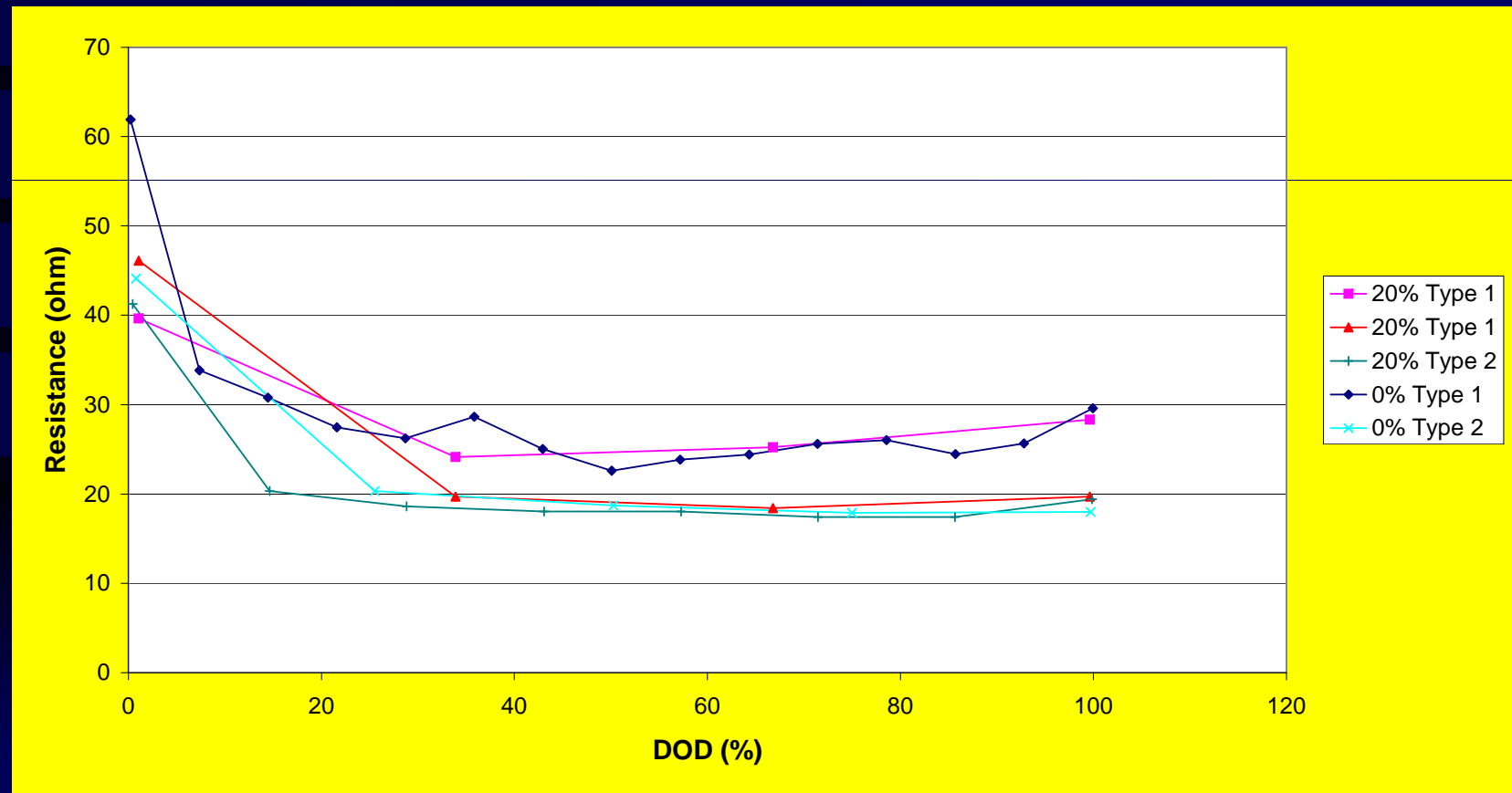


# Power is Dependent on Loading Level of Si



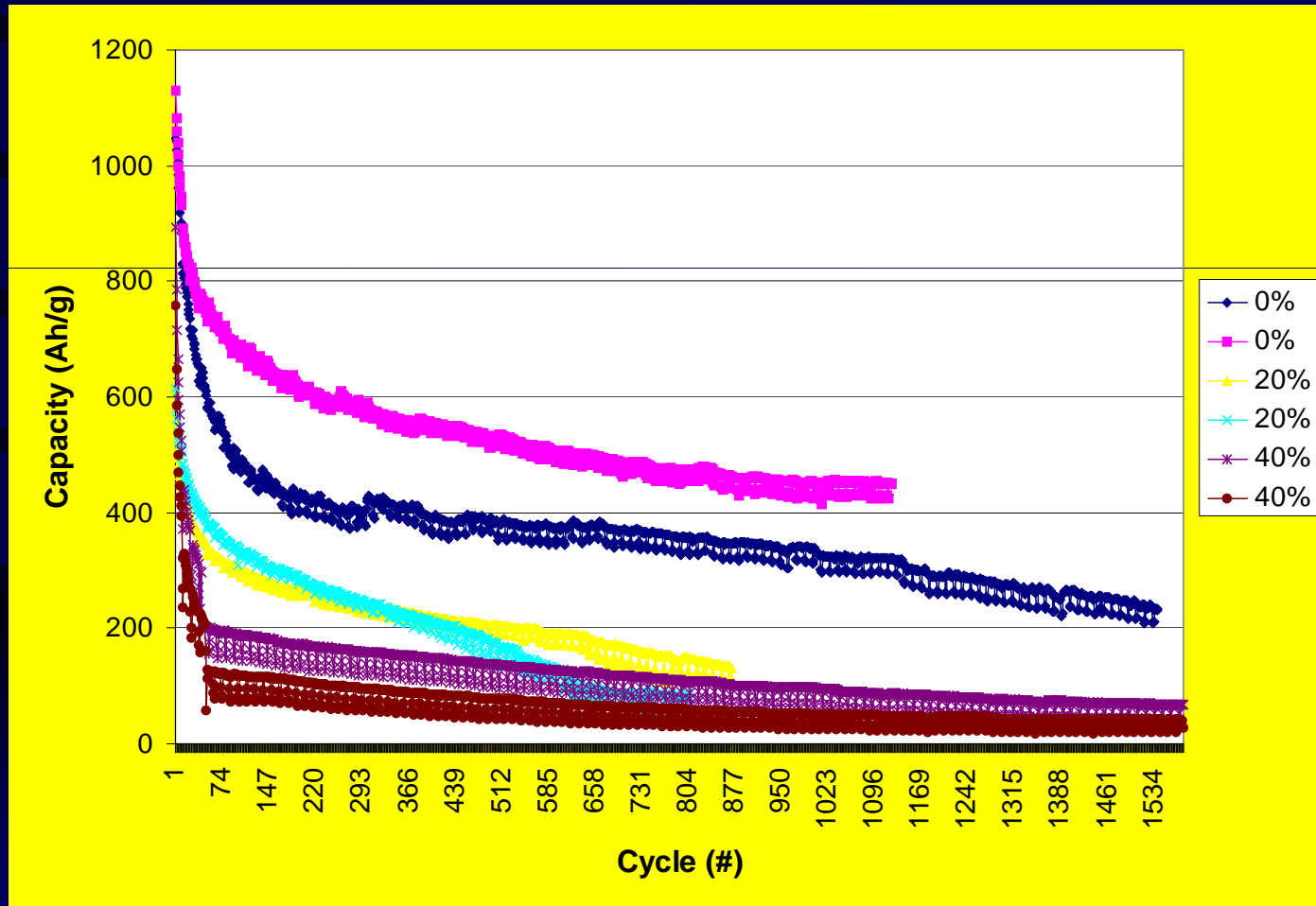
C/44 um Si

# Type 2 Carbon Also Slightly Better for Power



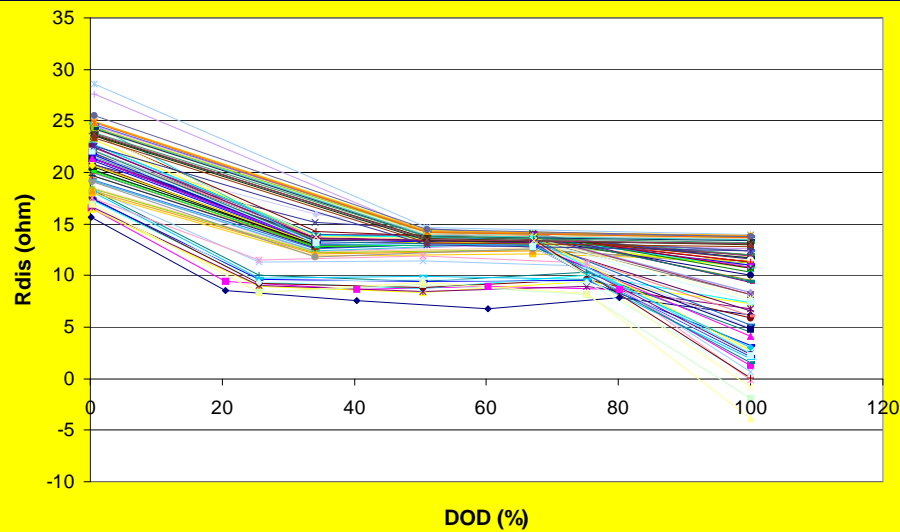
C/Si nano

# Cycle Life Will Be Focus of Future Effort

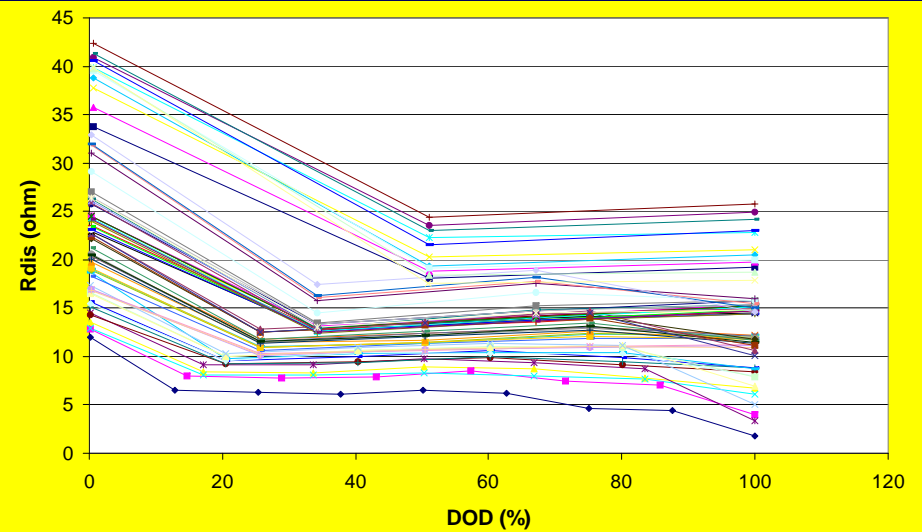


# Resistance Increase Not Excessive

0% Si



20% Si



# Economic Analysis Favors Larger Particle Size Si

	44 um Si <u>(\$/kg)</u>	Nano Si <u>(\$/kg)</u>
<b>Materials Cost</b>	8.2	202.4
<b>Production Cost</b>	17.7	211.9

# Future Effort

- Optimize firing temperature and conditions
- Obtain better dispersion of Si particles in sugar precursors
- Evaluate Si particles size between 44 um and Nano (performance vs. economics)
- Evaluate carbon coatings to deactivate surface activity and extend life
- Scale up production to pilot plant (kg) levels
- Produce commercial prototype cells for delivery and test

**Thanks to NASA JSC for Funding**

**NASA Phase I SBIR**

**Contract #: NNX09CE58P**

**COTR: Judy Jeevarajan**

**Thank You for Your Interest**