Silicon-Graphene Nanocomposite Anodes For Li-ion Batteries

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We develop advanced energy materials to power human innovation.

Our patented silicon-graphene materials enable longer lasting, faster charging batteries to power a range of applications, from wearable devices to electric vehicles.

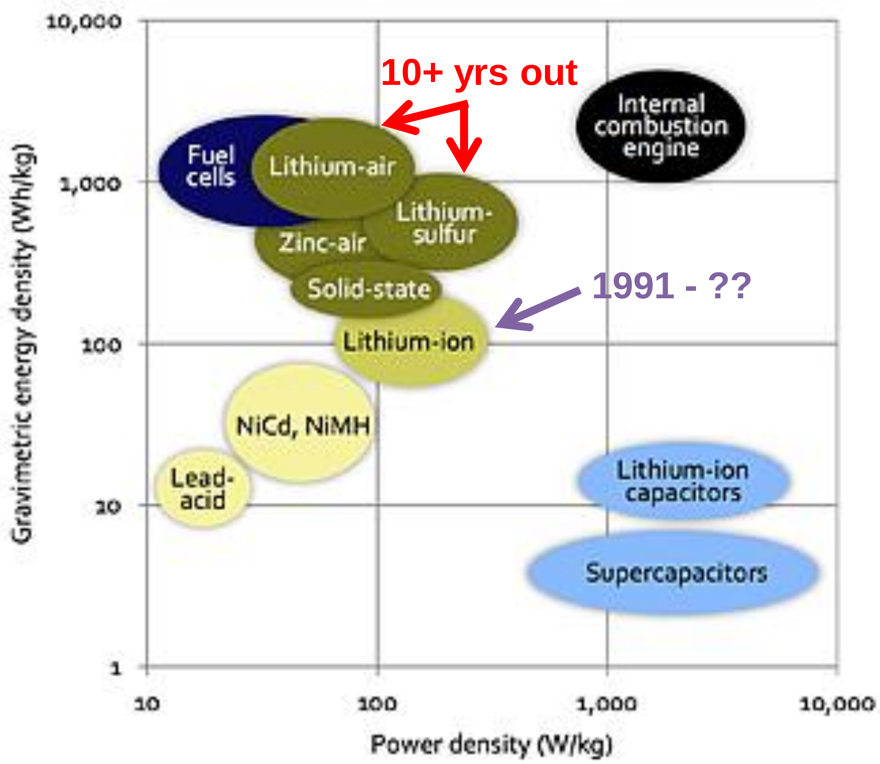
Agenda

- Introduction
- Silicon Background
- Graphene Background
- SiNode Systems Technology
- Silicon-Graphene Technologies
- Conclusions

Introduction

"**It's like a moon shot**… batteries today do not have enough energy per cell, they weigh too much, and they have issues with charging and battery life."

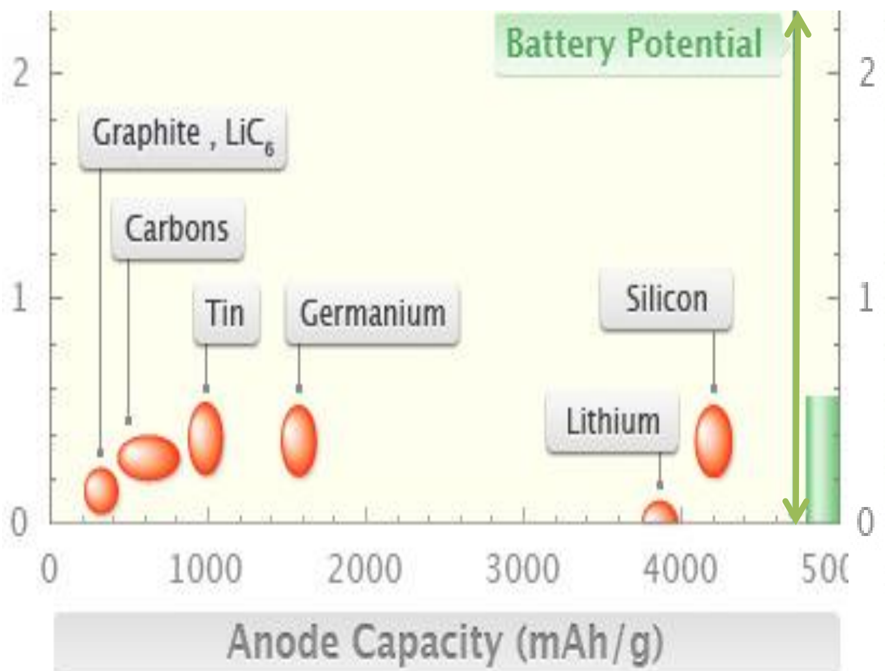
- *Alan Mulally, former CEO of Ford Motor Company*



Source: Journal of Power Sources, JM Energy

Motivation for Silicon Anodes

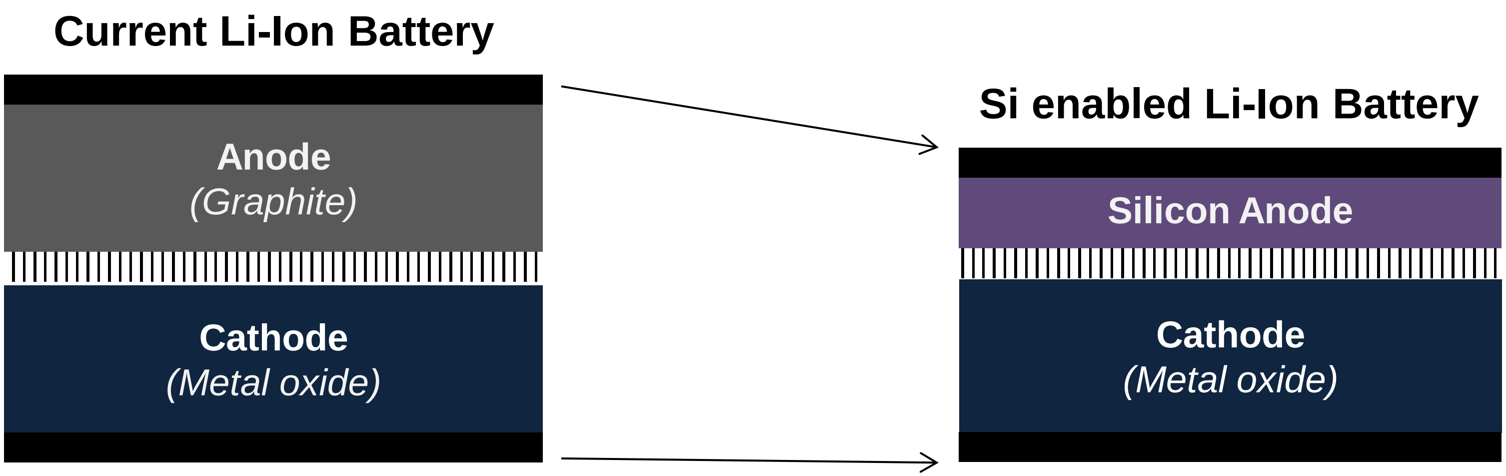
	Graphite	Silicon
Intercalation Reaction	$Li + 6C \leftrightarrow LiC_6$	$4.4Li + Si \leftrightarrow Li_{4.4}Si$
Potential vs Li/Li^+	0.05 V	0.4 V
Gravimetric Capacity	372 mAh/g	4200 mAh/g



- >10x (theoretical) increase in lithium storage capacity
- Vastly abundant
- Environmentally benign
- Well understood from semiconductor industry

Source: Nexeon.co.uk

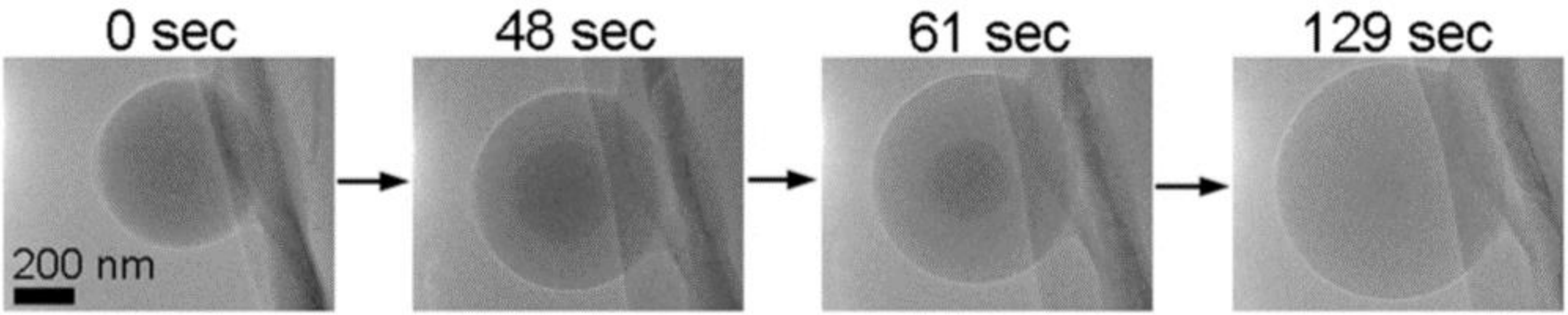
Full Cell Performance Implications



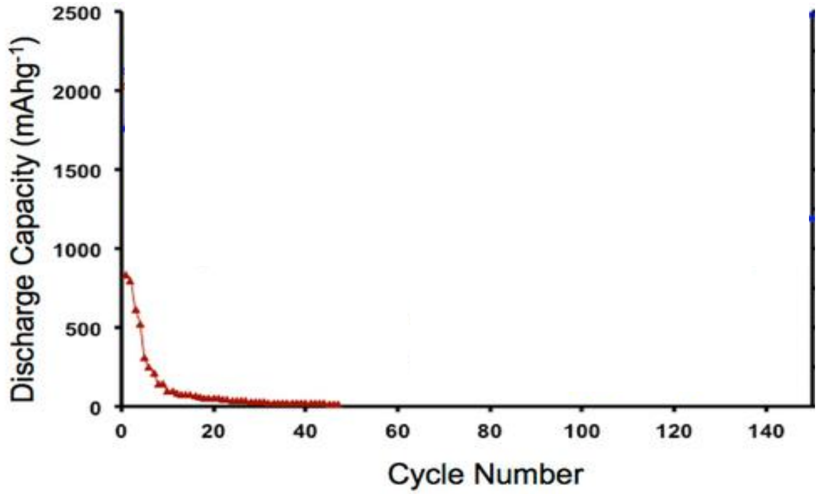
System	mAh/g (AM_{Anode})	mAh/g (AM_{Total})	Capacity Increase
Silicon / NCA	**2000**	**160**	**53%**
Graphite / NCA	370	104	
Silicon / NMC	**2000**	**156**	**46%**
Graphite / NMC	370	107	

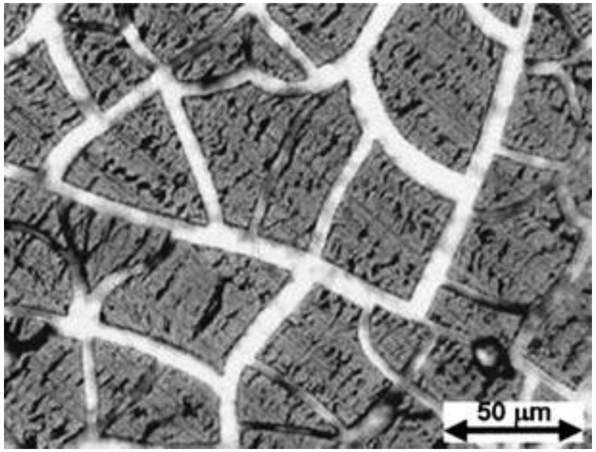
Source: SiNode Systems

Engineering Challenges of Silicon Anodes



- 300% volume expansion upon silicon lithiation
- 10% volume expansion upon graphite lithiation





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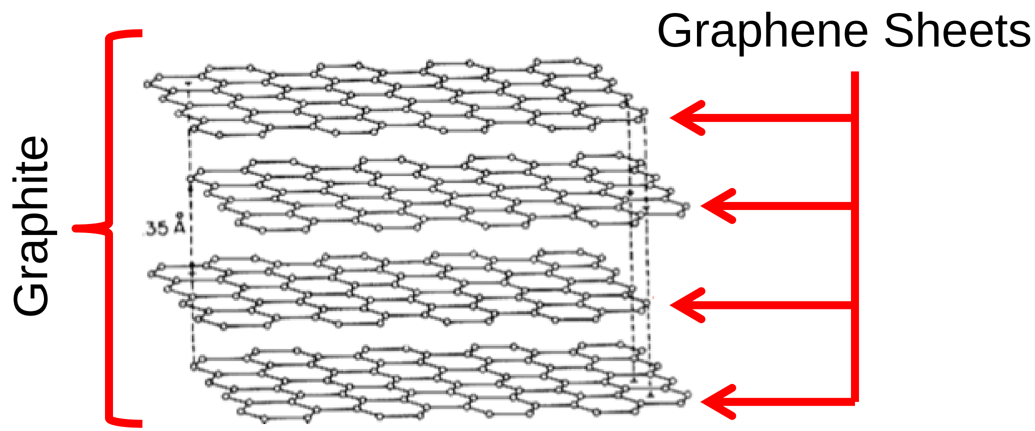
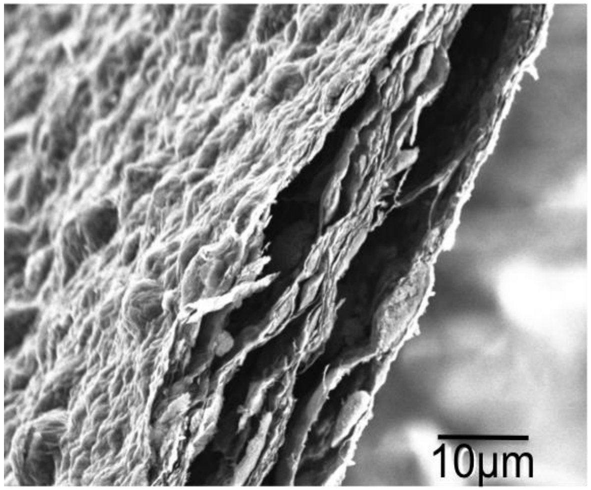
Source: McDowell, et al. Nano Lett, 2013, 13(2), 758-764

Silicon Engineering Strategies

Failure Modes	Mitigants	Challenges
Cracking & Pulverization	Employ nano-Si <100nm	Expensive
Lithium / e-lyte consumption by continuous SEI Growth	Manage SEI with electrolyte additives	SEI is chemically complex and difficult to study
Particle isolation & loss of electrical contact	Conductive coatings & frameworks	Decreases volumetric density

Graphene: The Wonder Material





Properties

- High electron mobility (200,000 $cm^2 V^{-1}s^{-1}$)
- High tensile strength (~140 GPa)
- High thermal conductivity (<5,300 $W m^{-1}k^{-1}$)
- High aspect ratio and surface area (>2600 m^2/g)
- Flexible

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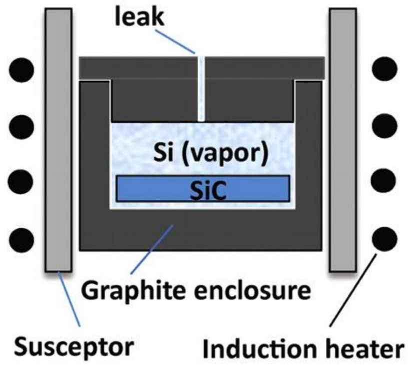
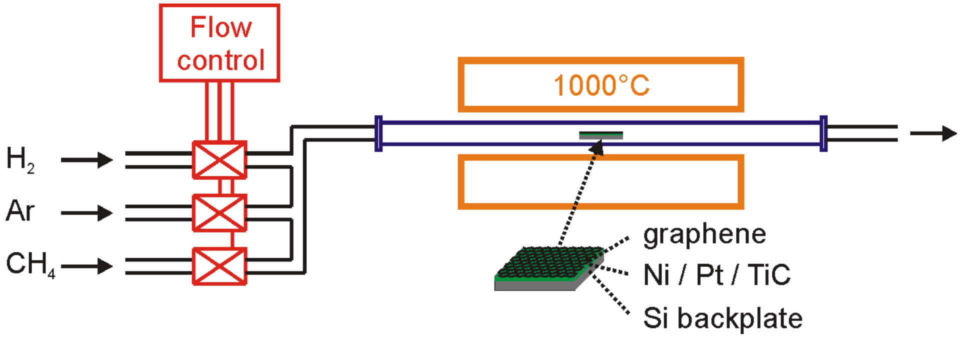
Graphene Manufacturing

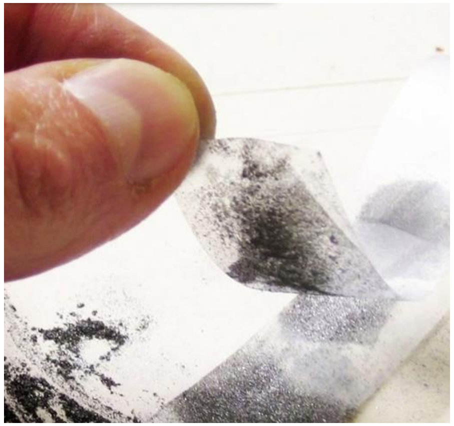
Epitaxial Growth

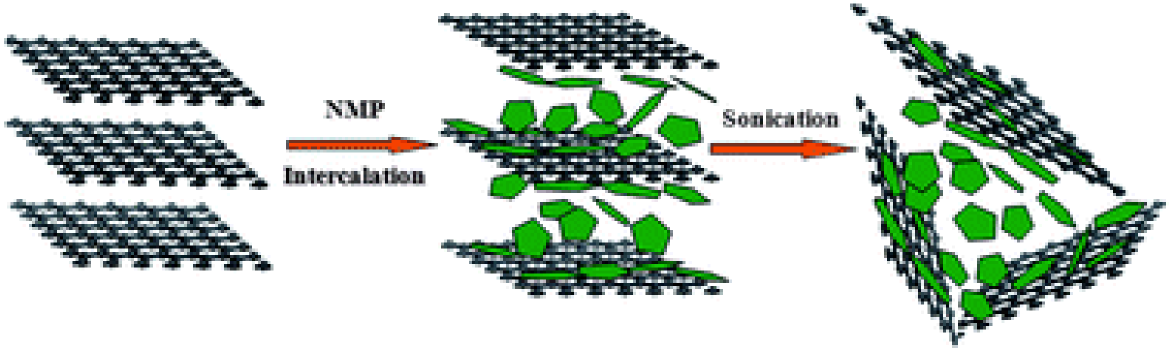


Chemical Vapor Deposition (CVD)



Mechanical / chemical cleavage – scotch tape, ultrasonication, shear mixing



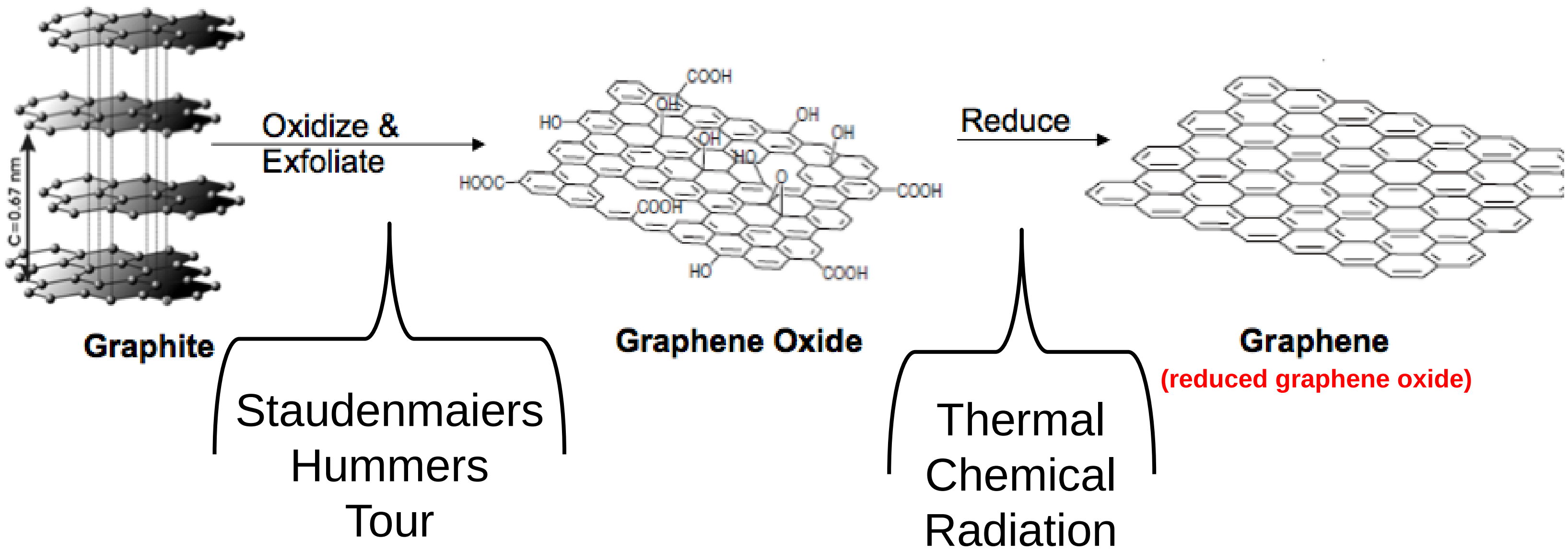


- Often results in multi-layer graphene

Sources: Walt A. de Heer et al. PNAS 2011 108 (41) ; Gong et al, J. mat. Chem., 2012, 22, 16950-16956

Graphene Manufacturing (Cont.)

Graphene Oxide by chemical exfoliation



- Sheet size is dependent on graphite source and post processing
- Oxidation (C/O ratio) is dependent on synthesis method
- Sheet conductance is dependent on quality of reduction step

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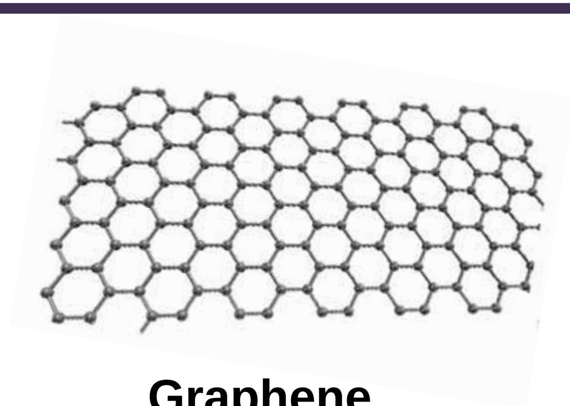
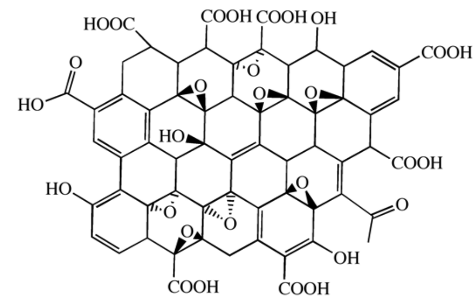
Graphene Vs Graphene Oxide





	Graphene	Graphene-Oxide
Solubility	✗ ▪ Hydrophobic ▪ Requires surfactants ▪ solvent exchange	✓ ▪ Hydrophilic ▪ Readily dispersible in polar solvents
Conductivity	✓ ▪ Inherently conductive	✗ ▪ Requires reduction step

Incorporation into anode material is determined by synthesis route

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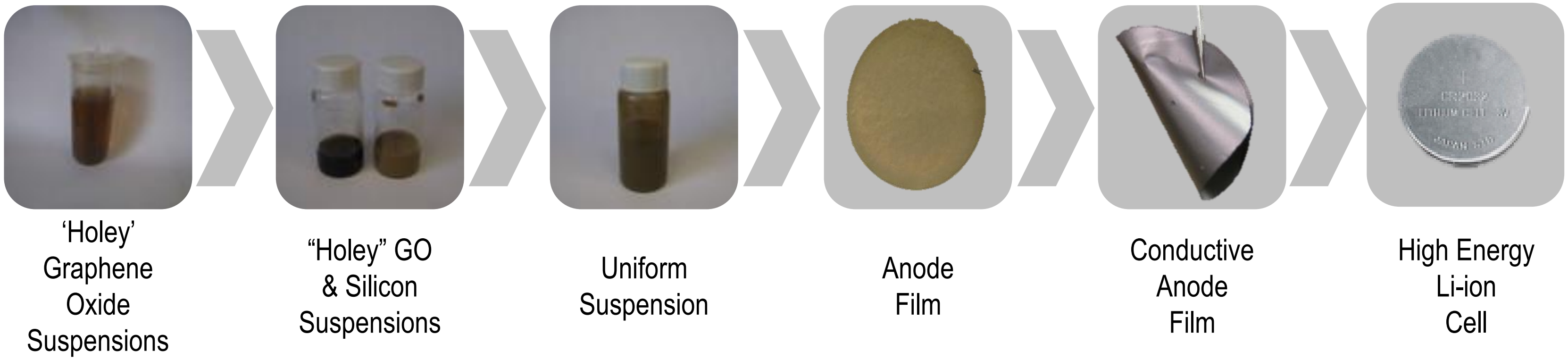
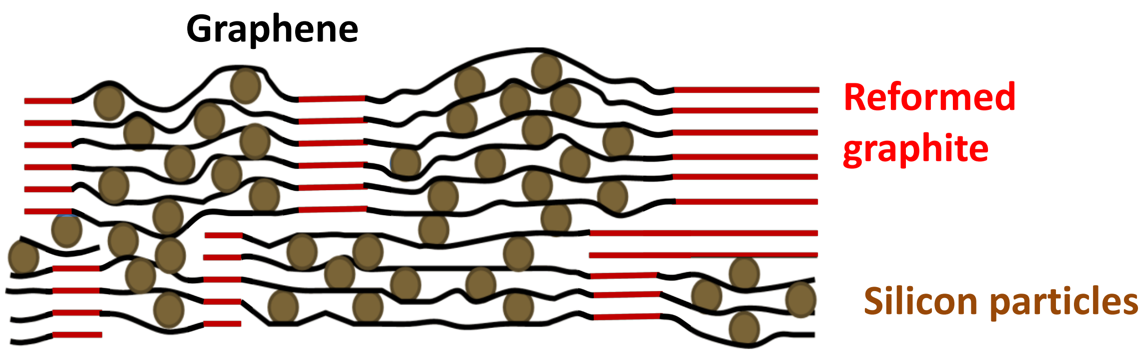
SiNode Graphene Scafolding Anode





- Patented “holey graphene” enables rapid Li-ion diffusion
- Flexibility, high electronic conductivity, and mechanical durability
- Accommodate volumetric strain in composite materials
- Processing techniques allow for self-supporting graphene anodes

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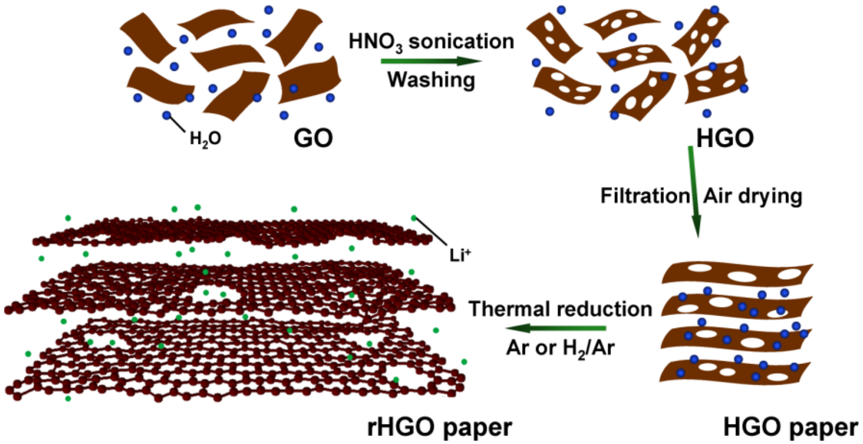
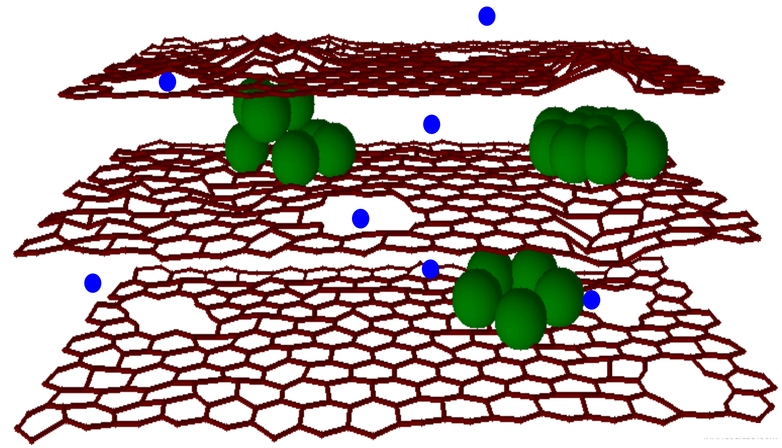
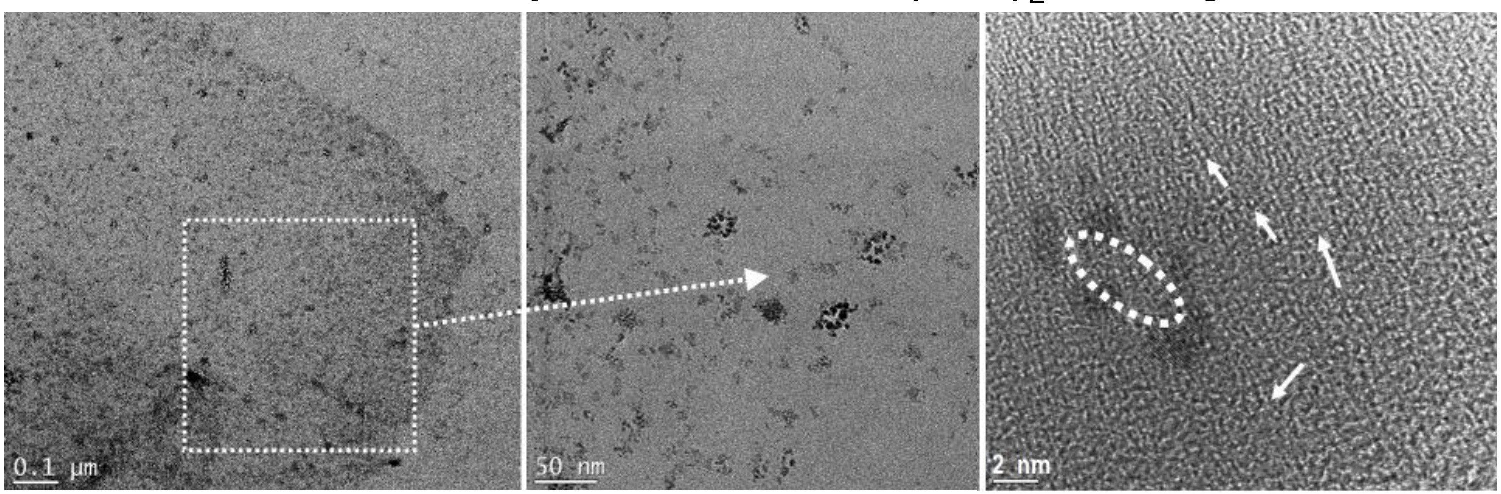
Formation of 'Holey' Graphene Oxide

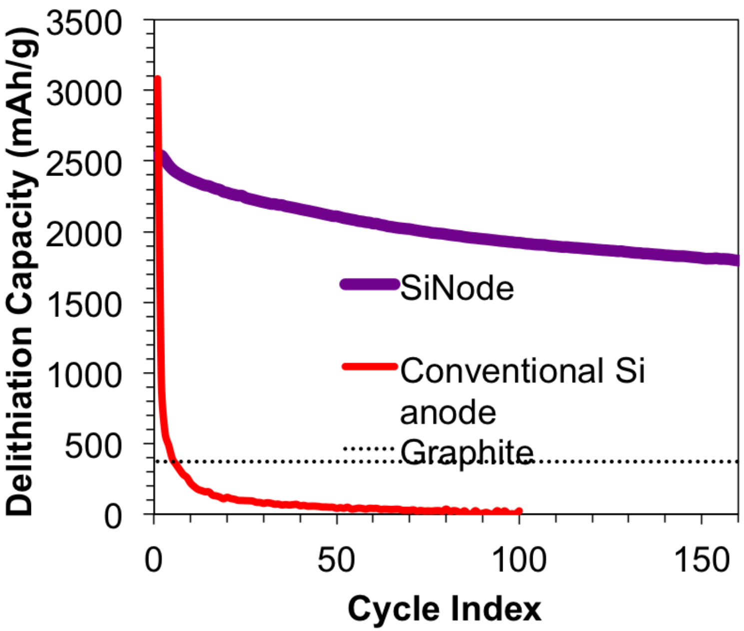


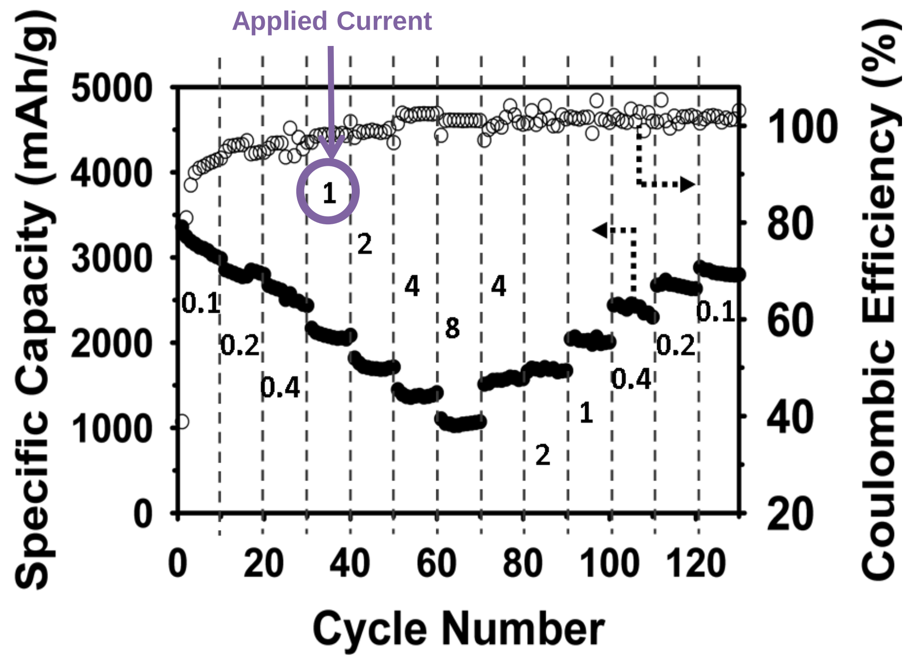


Pore Confirmation by HRTEM and Pd(OAc)$_2$ staining



SiNode Half cell performance & rate performance

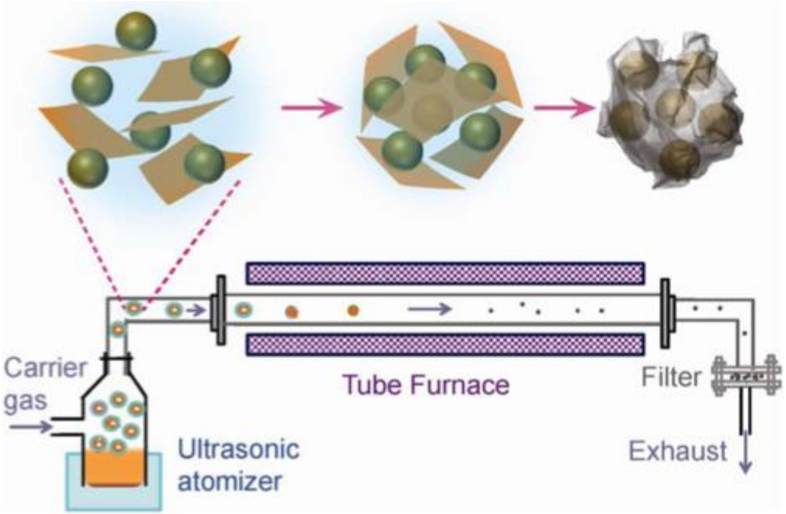


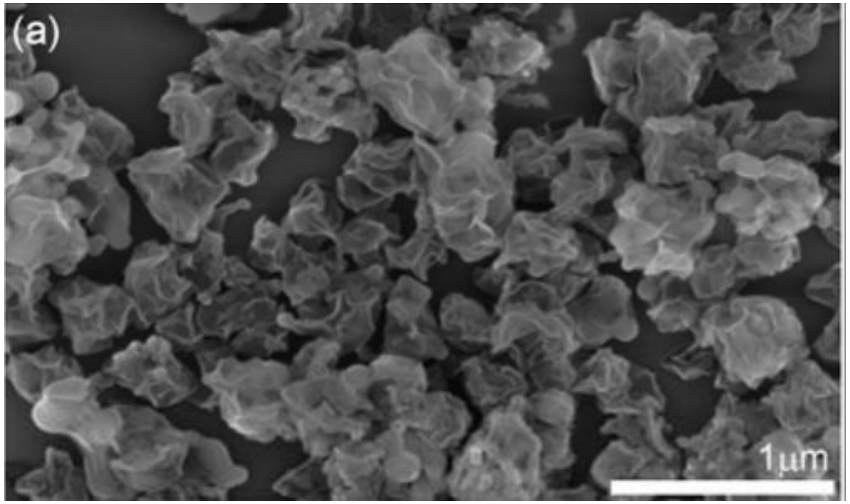


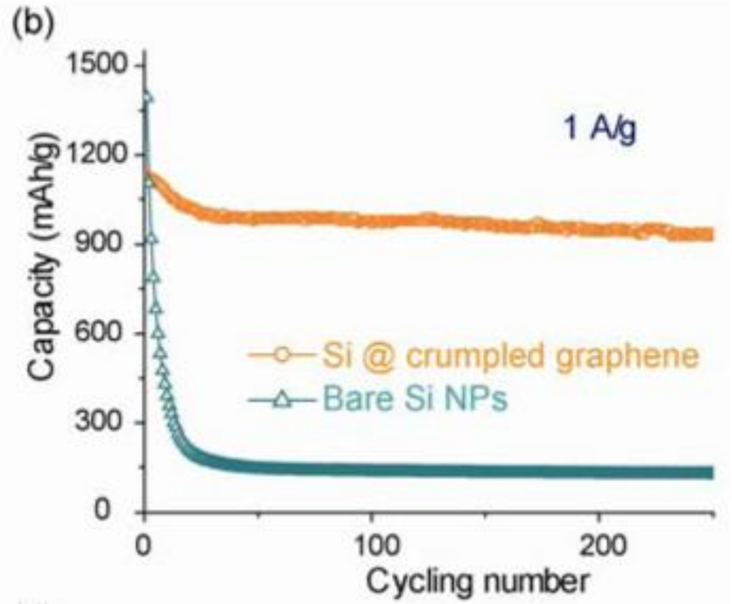
- 1^{st} cycle efficiency of 87%
- 100+ cycles to 80% capacity retention
- High rate capabilities: 1000 mAh/g @ 8 A/g

Source: Zhao, Et al., Adv. En. Mat. 2011, 1, 1079-1084

Crumpled Graphene – Silicon Anodes







- Capillary assisted assembly
- 250 cycles to 80% IC
- 73% initial CE

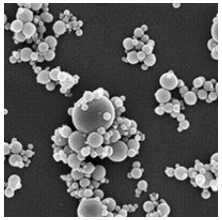
Lou et al., Phys Chem Letters, 2012, 3, 1824-1829

Graphene coated silicon

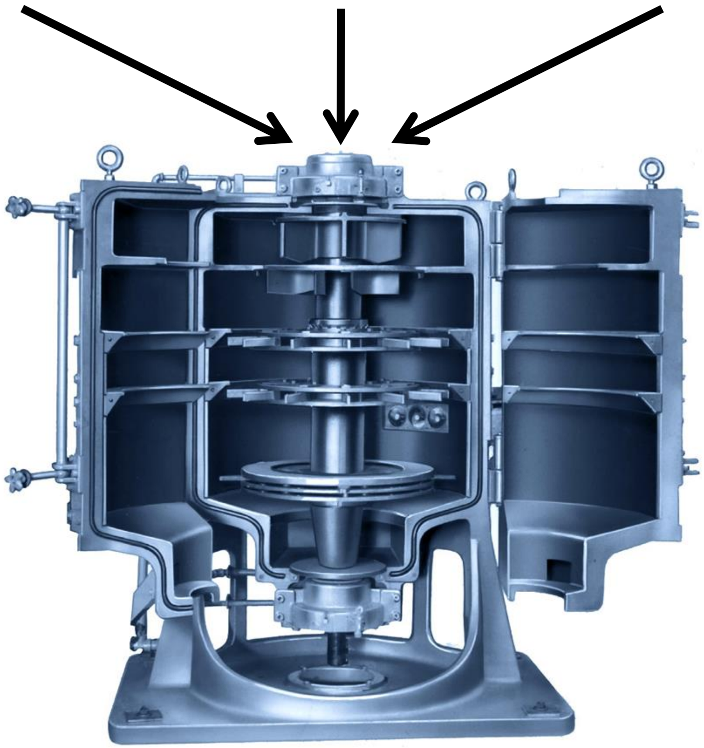
Dry Mill Manufacturing

Natural flake graphite

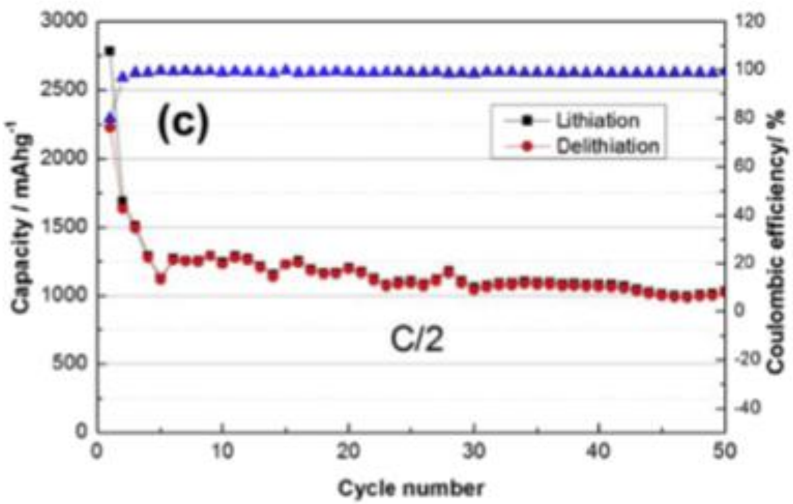
Thermoplastic milling media



Active Material (Si)

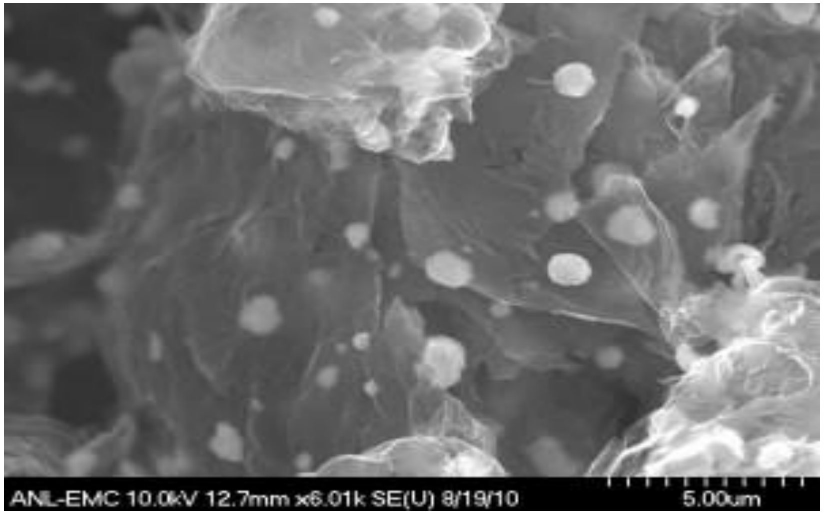


- Low cost
- Lower quality graphene (<100 nm flakes)
- High initial losses (45% in first 6 cycles)

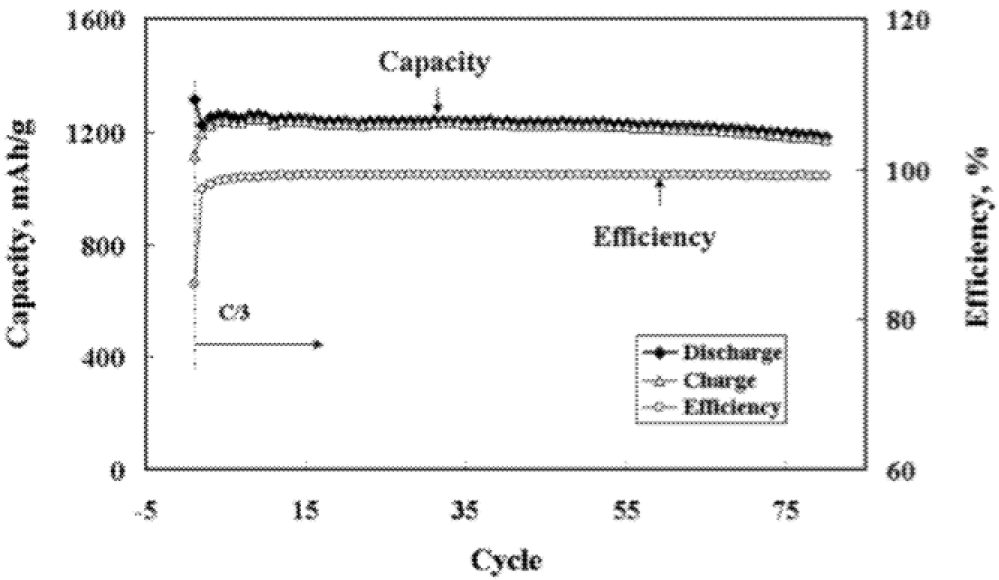


KwangSup E. Et al, Jpowsour, 249 (2014) 118-124

CVD silicon-graphene Anodes



Deposition of silicon nanoparticles onto graphene by silane decomposition



- Highly uniform deposition of silicon
- Powder form factor
- Requires CVD processing

Source: Amine, assignee. Patent US 2012/0282527. 8 Nov. 2012. Print.

Conclusions

- Graphene is an ideal material for improving silicon anode performance

- Challenges
  - Electrolyte optimization & SEI management
  - Cost vs performance of numerous graphene form factors
  - Full-cell Integration: 1st cycle losses, cell-balancing, pack level swelling

- Silicon anode will be crucial for maximizing the potential of traditional Li-ion chemistry – just a matter of when!

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