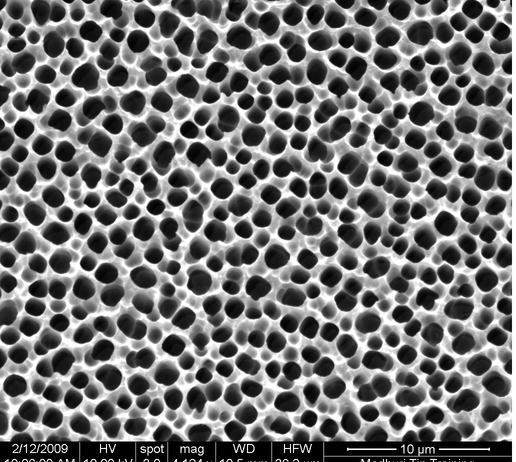

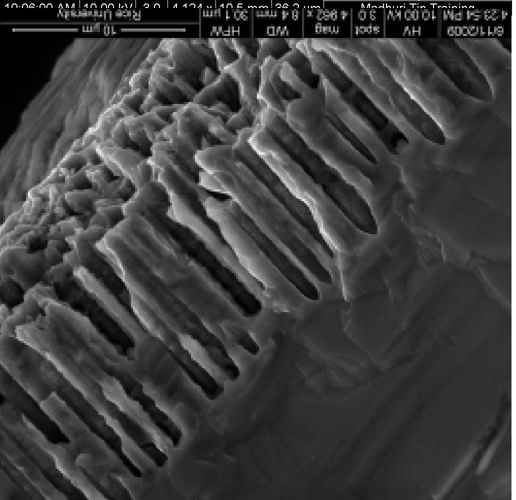

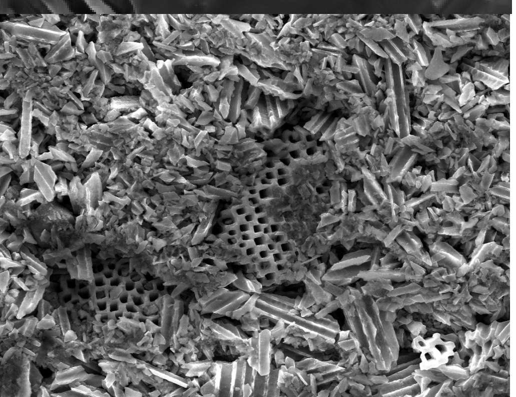

Porous Silicon for high performance energy storage

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Department of Chemical and Biomolecular Engineering
Rice University

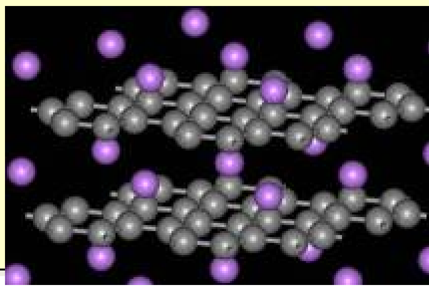
July 29, 2014

Conventional Lithium Ion Battery (LIB)

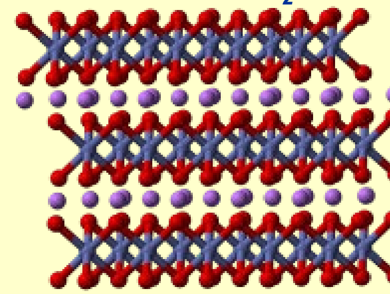
***Electrolyte*: Non-aqueous organic solvent with lithium salts to form lithium ion conductive path.**

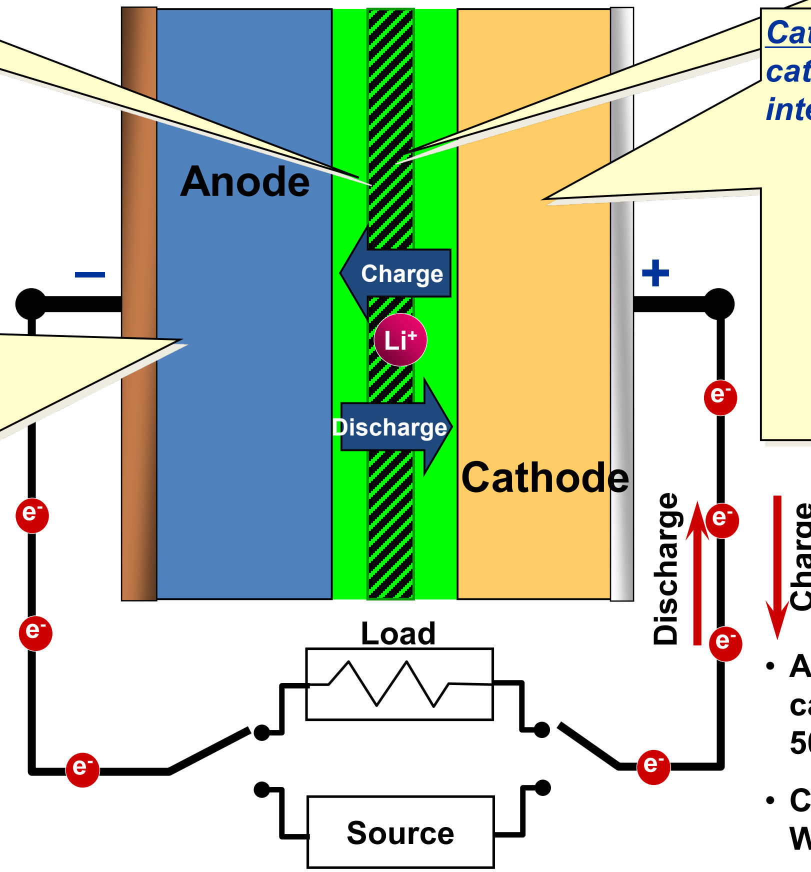
***Separator*: Physical barrier to prevent electrical short circuiting of anode and cathode; porous to electrolyte.**

***Anode*: Based on graphite. Good electron conductor; lithium ions intercalate to form LiC_6. Theoretical capacity 372 mAh/g.**



***Cathode*: Li_xCoO_2 typical cathode material; lithium is intercalated into CoO_2 structure.**





- **Lithium always in 'ion' form – no lithium metal forms during charge or discharge. Critical for safety.**

- **Active materials – anode and cathode typically form about 50% of total cell mass**
- **Current cell performance: 200 Wh/kg.**

(1) Anode is a significant fraction of battery mass.
(2) Higher capacity anodes (mAh/g) = higher capacity batteries (Wh/kg)

Why Silicon for Battery Anodes?

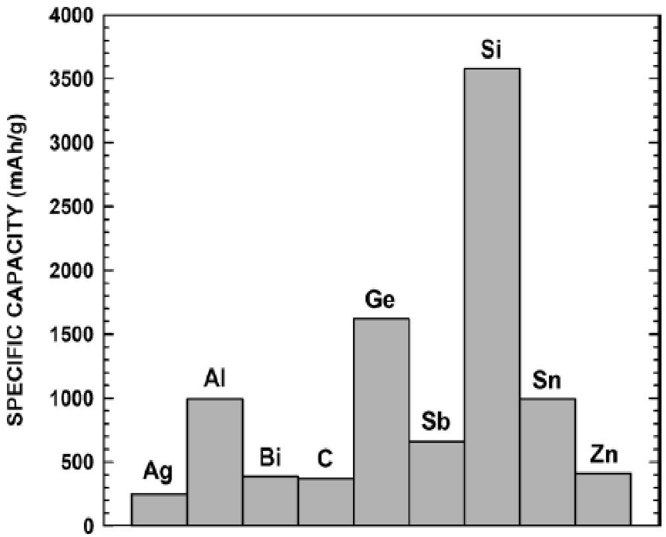


Figure 1. The specific capacity of a number of electrochemically active metal elements.

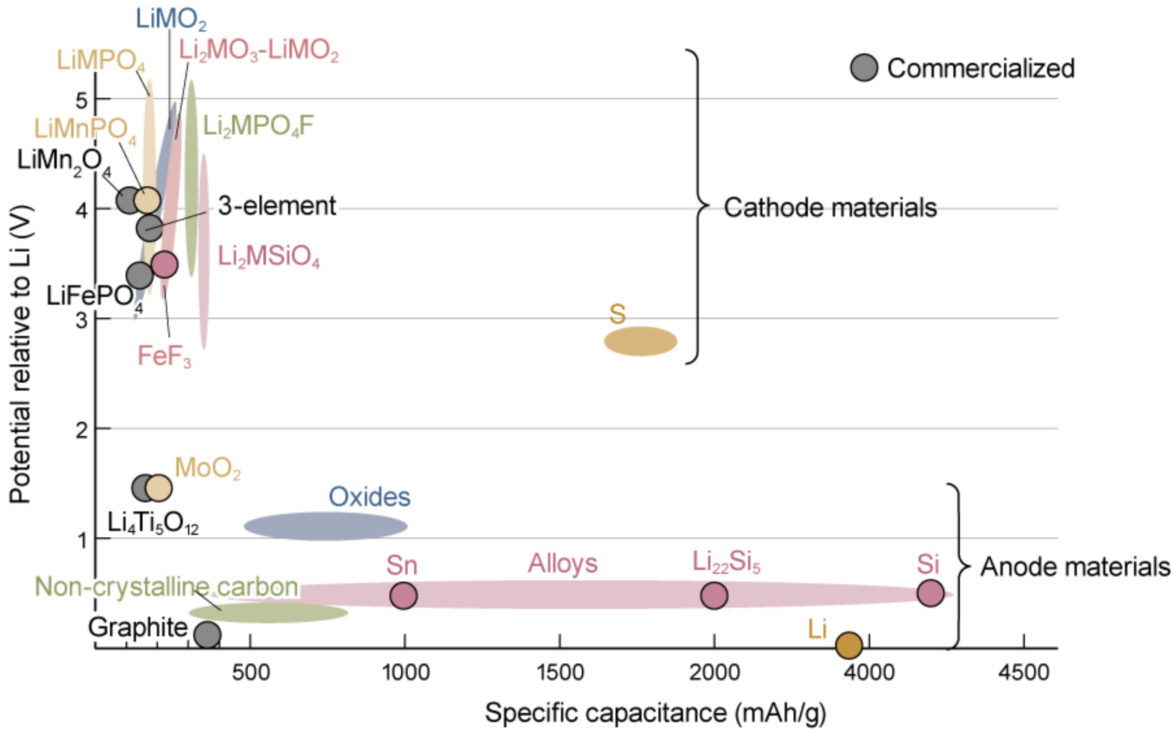
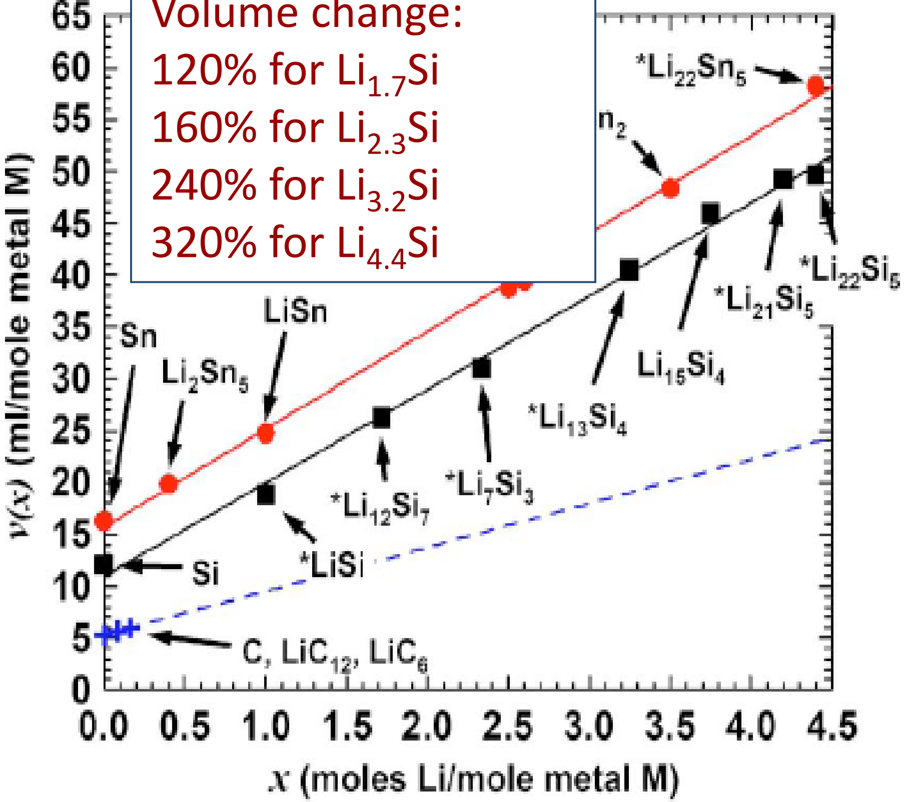


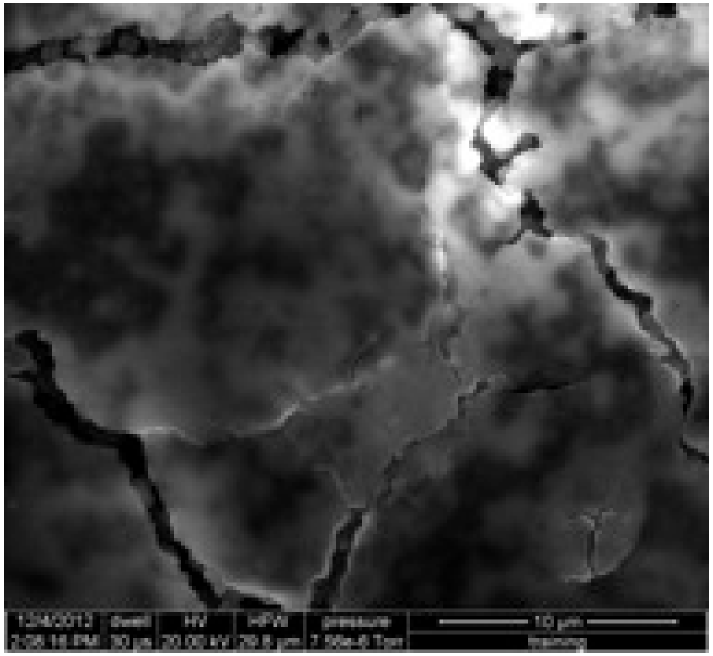
Diagram by Nikkei Electronics

Silicon has the largest lithium specific capacity of any known anode material

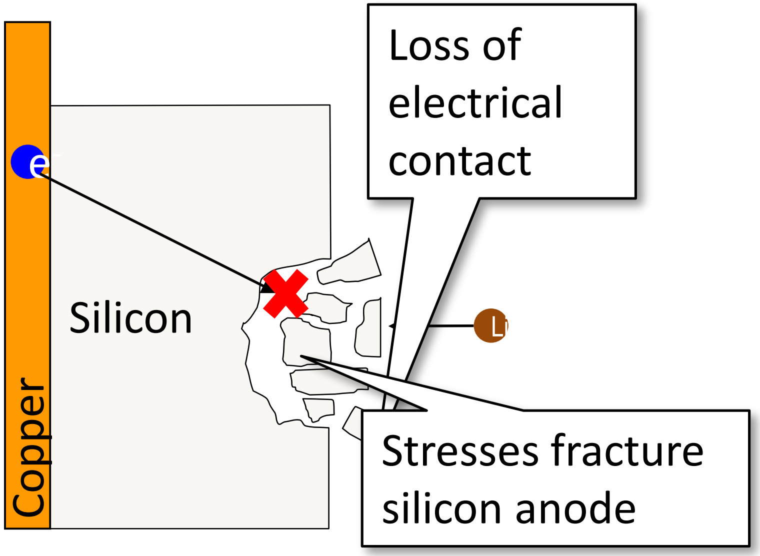
Why Hasn't Silicon Been Used Already?

Volume change:
120% for $Li_{1.7}Si$
160% for $Li_{2.3}Si$
240% for $Li_{3.2}Si$
320% for $Li_{4.4}Si$





Silicon had poor cycle life because volume expansion results in material and electrode structure degradation



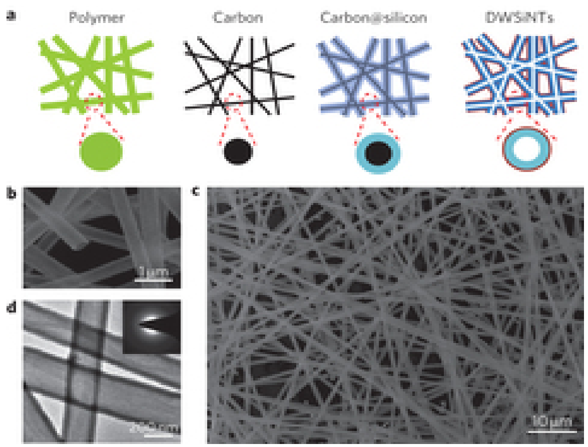
Existing Approaches: Nanotechnology for Lithium Ion Batteries

LETTERS | nature nanotechnology

PUBLISHED ONLINE: 25 MARCH 2012 | DOI: 10.1038/NNANO.2012.35

Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control

Hui Wu[1§], Gerentt Chan[2‡], Jang Wook Choi[1†], Ill Ryu[1], Yan Yao[1], Matthew T. McDowell[1], Seok Woo Lee[1], Ariel Jackson[1], Yuan Yang[1], Liangbing Hu[1] and Yi Cui[1,3]*



Super-Charging Lithium Batteries

Technology Review PUBLISHED BY MIT

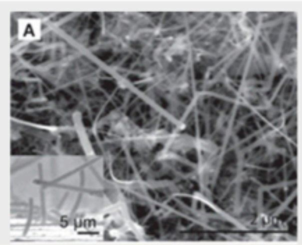
Nanowire electrodes could improve the performance of electric vehicles.

By Peter Fairley

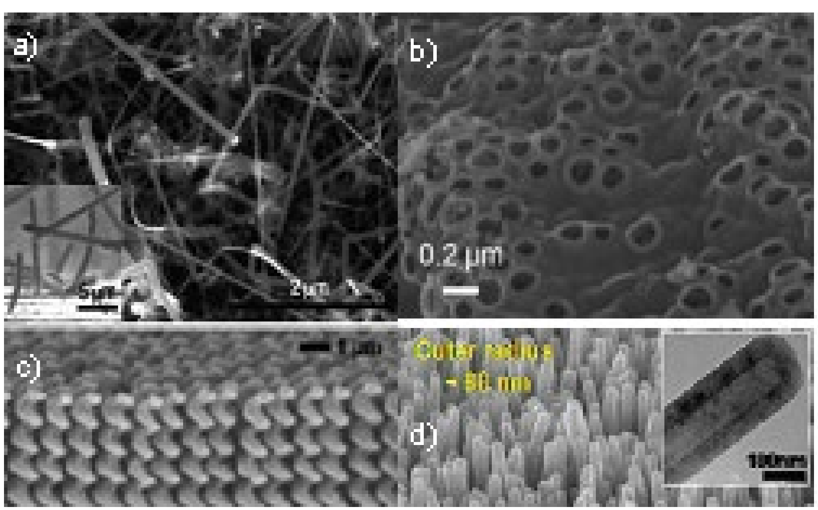
FRIDAY, JANUARY 04, 2008

E-mail Audio » Print Favorite Share »

Existing lithium batteries can enable battery-powered electrical vehicles to travel hundreds of miles on a charge, prompting a race among major automakers to demonstrate that the batteries are safe and durable enough for mass marketing. Battery developers, meanwhile, continue to push lithium performance. Last month, Stanford University materials scientists unveiled a nanowire electrode that could more than triple lithium batteries' energy storage capacity and improve their safety.



The development, reported in the scientific journal *Nature Nanotechnology*, stems from the labs of nanowire innovator Yi Cui and battery expert Robert Huggins at Stanford's Materials Science and Engineering Department. The researchers show that nanowires of silicon just a few atoms across can function as high-capacity electrodes, absorbing and releasing about 10 times more lithium ions than the graphite electrodes that are commonly used today.

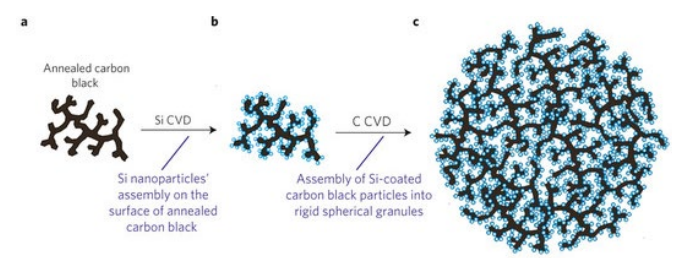


nature materials | ARTICLES

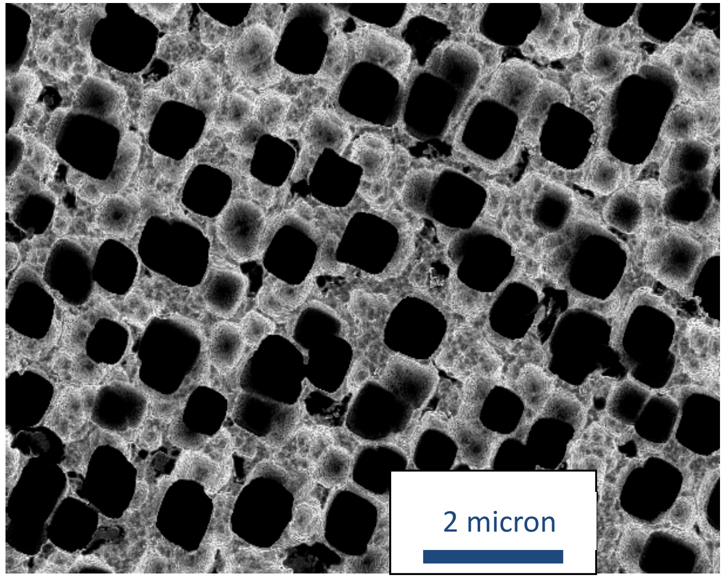
PUBLISHED ONLINE: 14 MARCH 2010 | DOI: 10.1038/NMAT2725

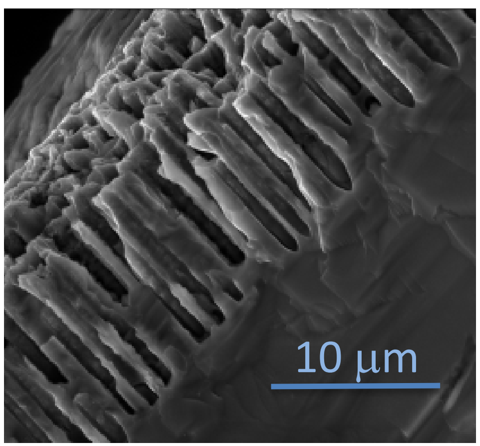
High-performance lithium-ion anodes using a hierarchical bottom-up approach

A. Magasinki[1], P. Dixon[1], B. Hertzberg[1], A. Kvit[2], J. Ayala[3] and G. Yushin[1,4]*

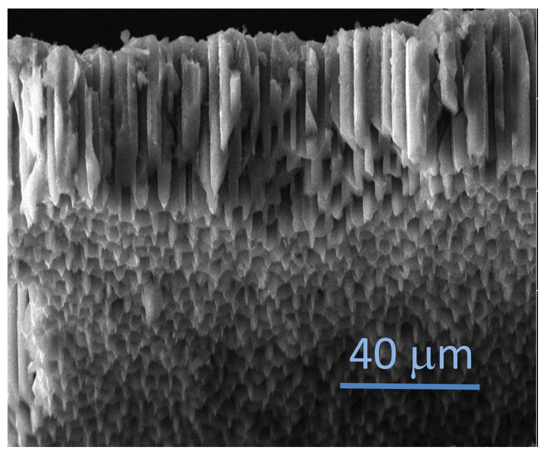


Our Approach

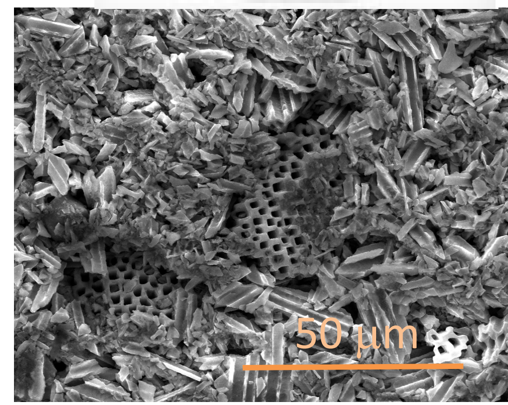




Gold-Coated
Porous Silicon Film



Lift-off Porous Silicon
Films



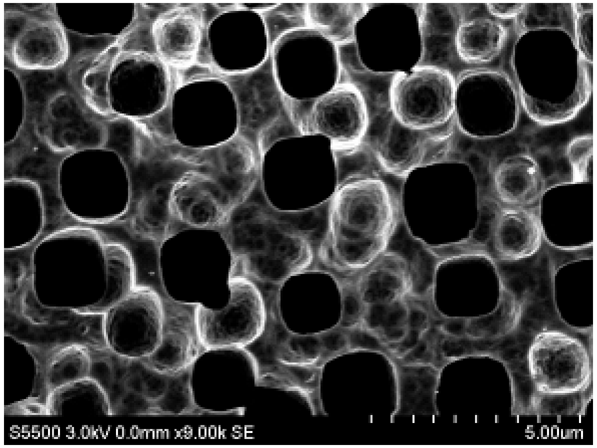
Macroporous Silicon
Particulates

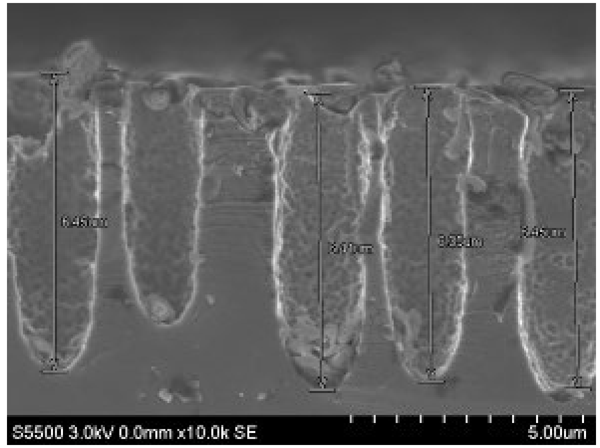
Journal of Power Sources, 205 pp 426-432 (2012).

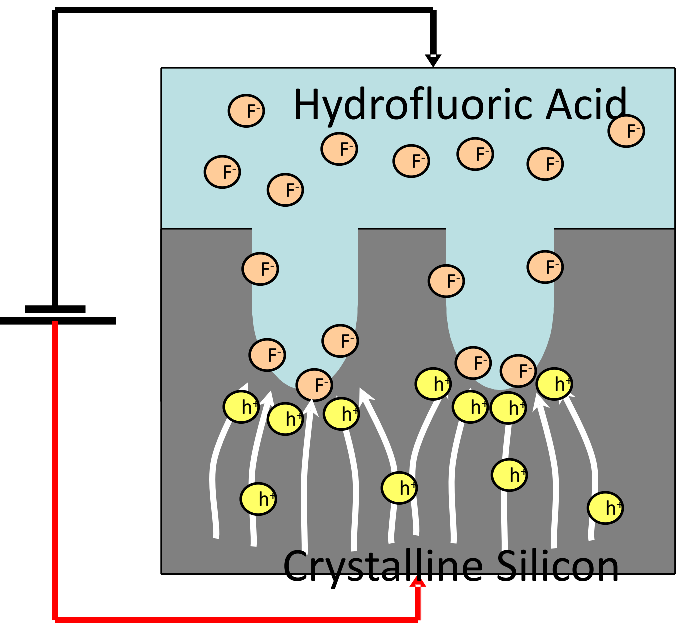
Chemistry of Materials (2012), 24(15) pp 2998-3003 (2012).

Scientific Reports (2012) 2-795.

Porous Silicon Fabrication

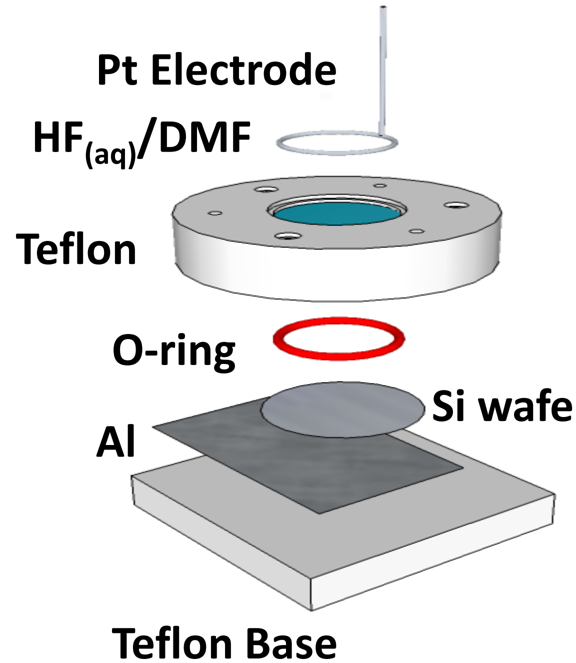






Process variables:

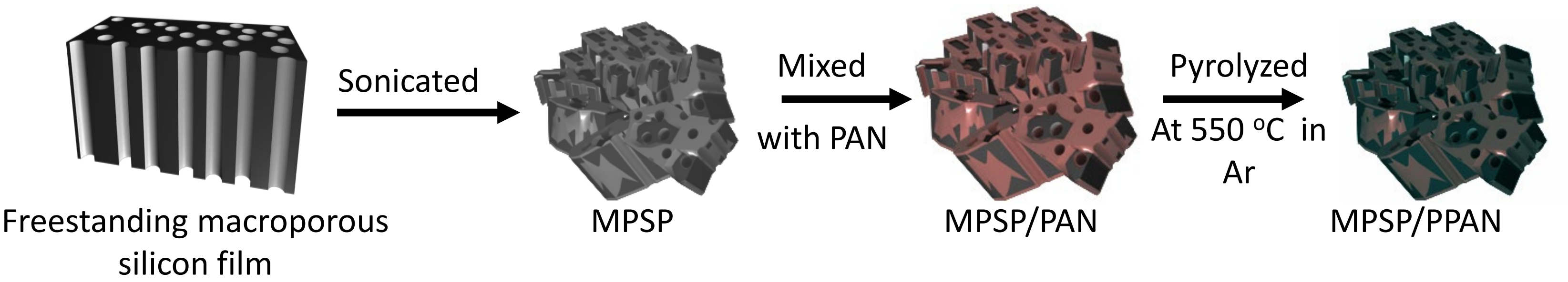
- **Electrolyte (HF) concentration**
- **Current density**
- **Silicon doping type & density**
- **Temperature**

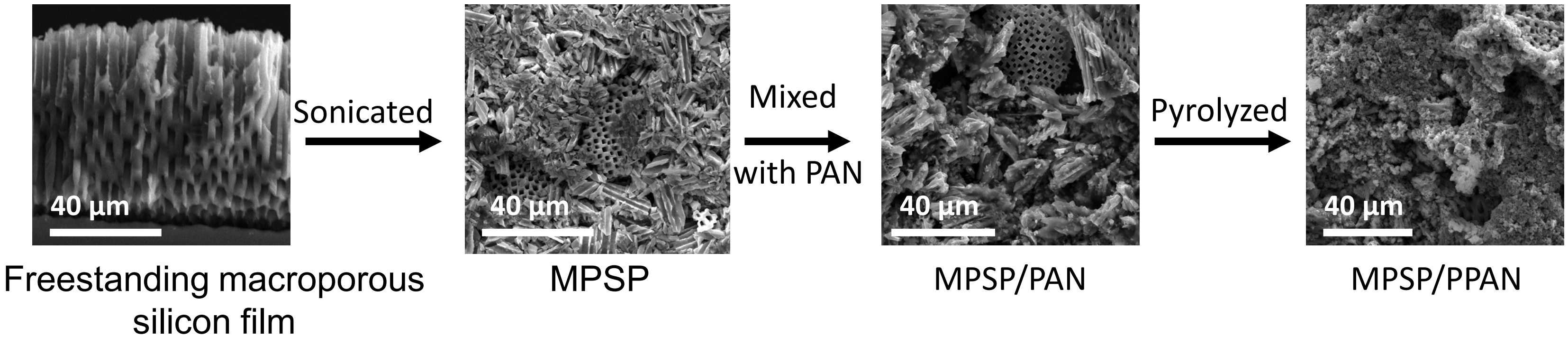


Potential to leverage silicon wafer processing infrastructure

Fabrication process simpler and will be lower cost than other proposed nanostructured silicon anodes

Porous Silicon Particulates MPSP Fabrication

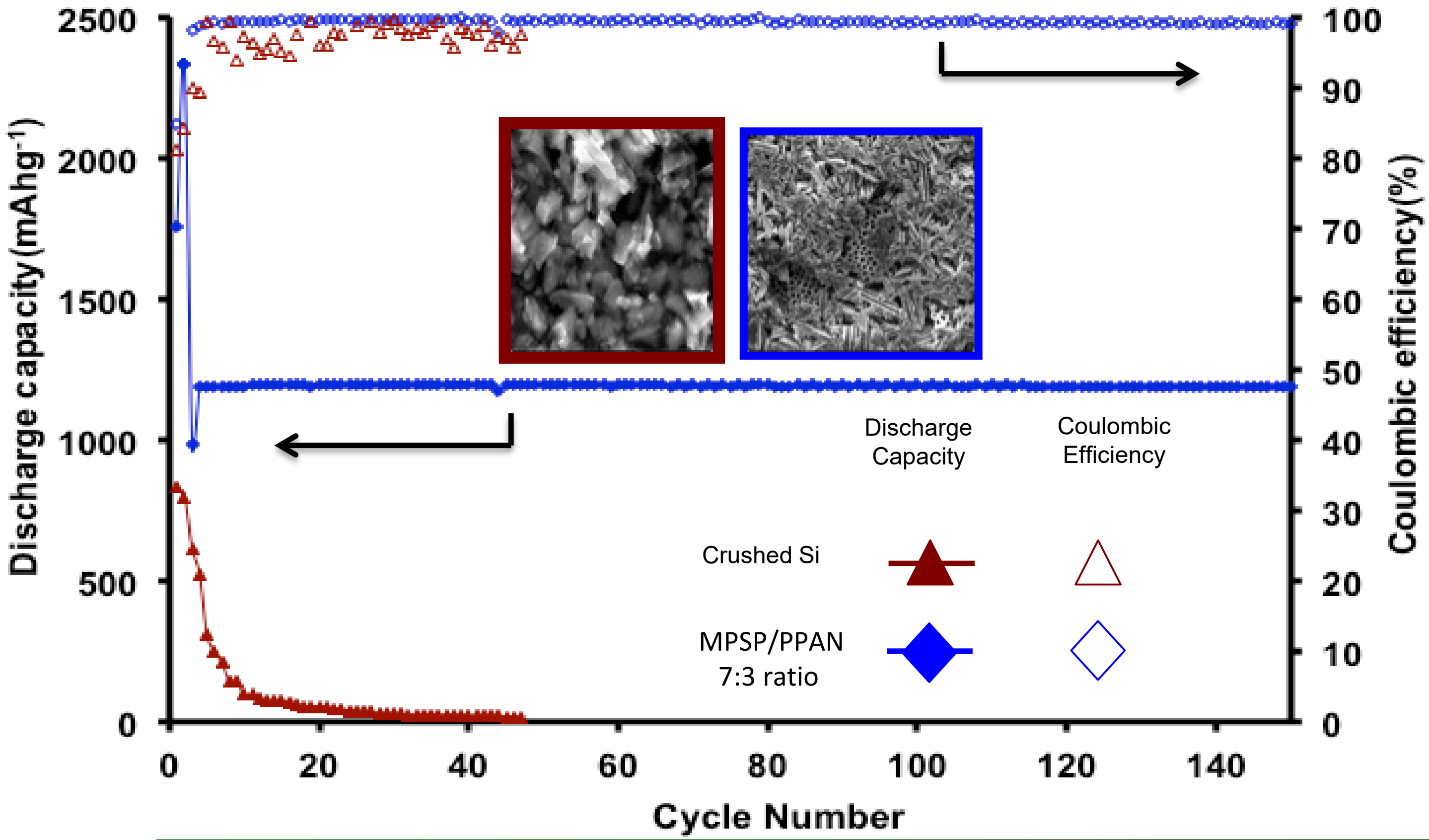




- Macroporous silicon particulates (MPSP) can be fabricated from porous silicon films
- MPSP can be combined with PAN and pyrolyzed to form an anode

Thakur, M., Isaacson, M., Sinsabaugh, S., Wong, M.S., Biswal, S.L., " Inexpensive method for producing macroporous silicon particulates (MPSPs) with pyrolyzed polyacrylonitrile for lithium ion batteries," *Scientific Reports*, Nov 1, 2012

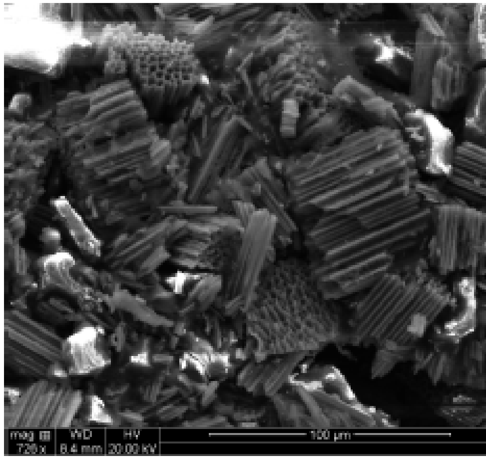
MSPS/PPAN vs. Crushed Si

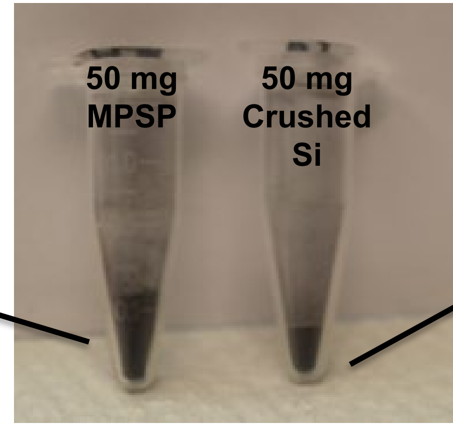


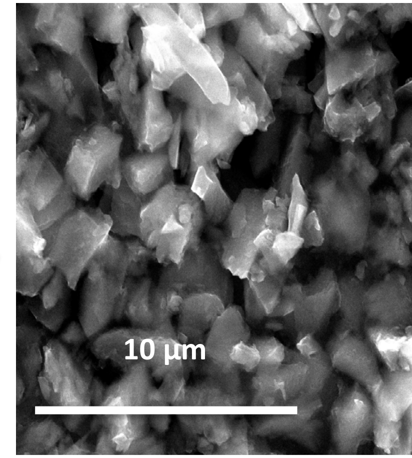
•For the 70:30 silicon/PPAN ratio, the crushed silicon particulates failed within ten cycles while the MPSP remained stable for over one hundred cycles

•Porosity is needed for successful performance

Property: Porosity!

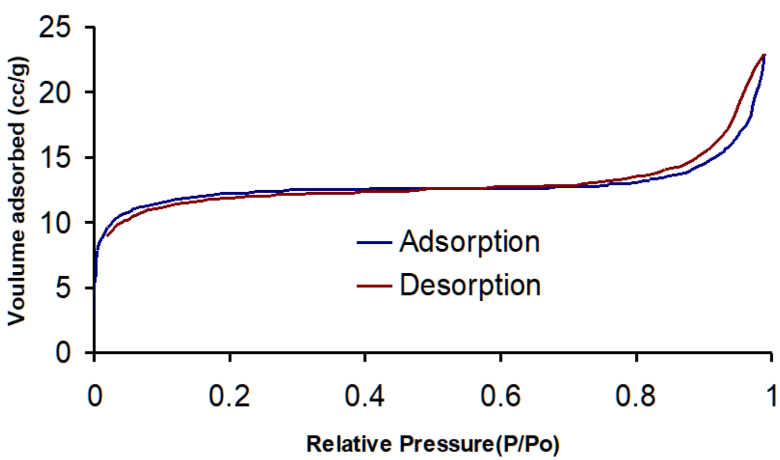






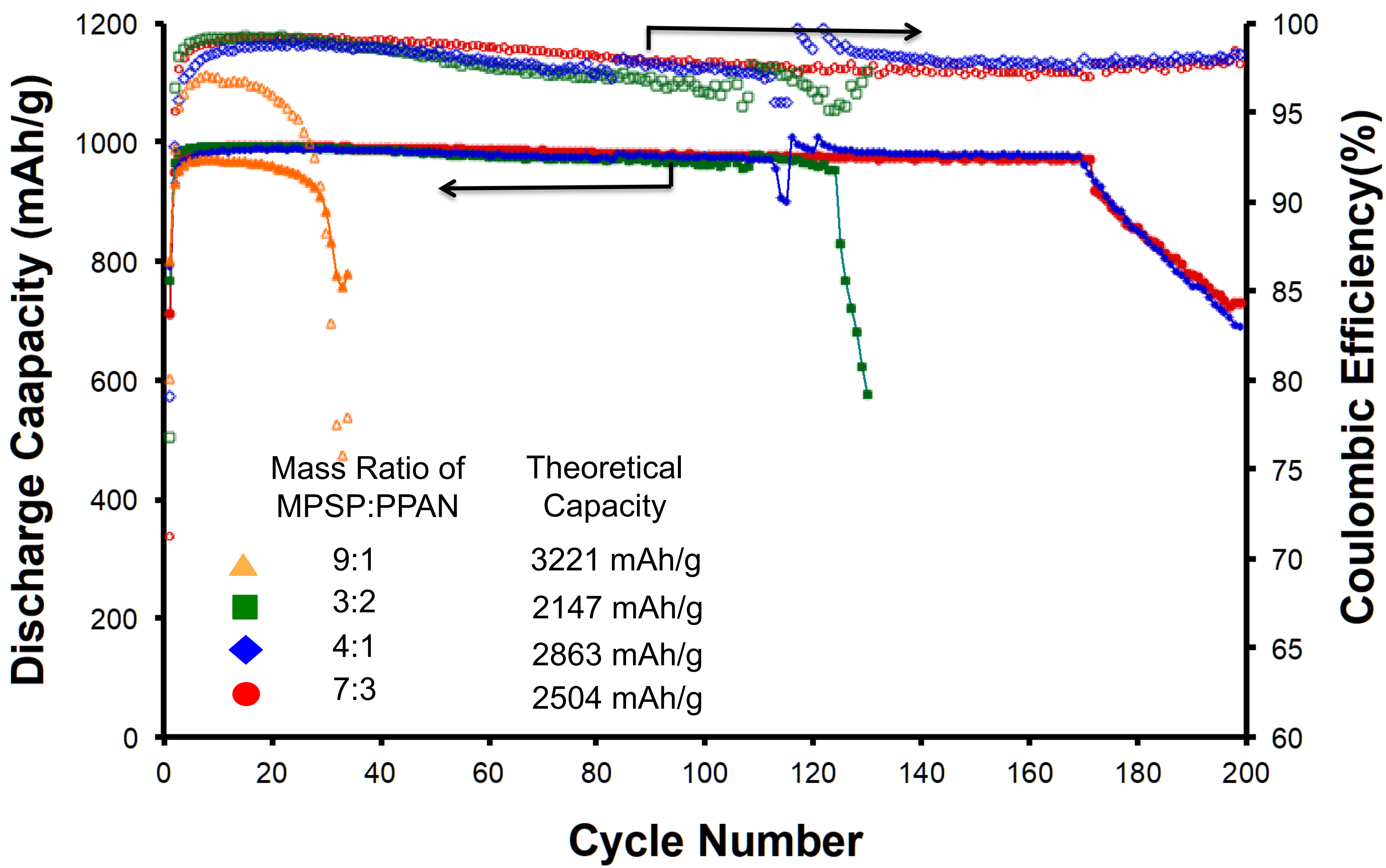
47 m^2/g

0.7 m^2/g

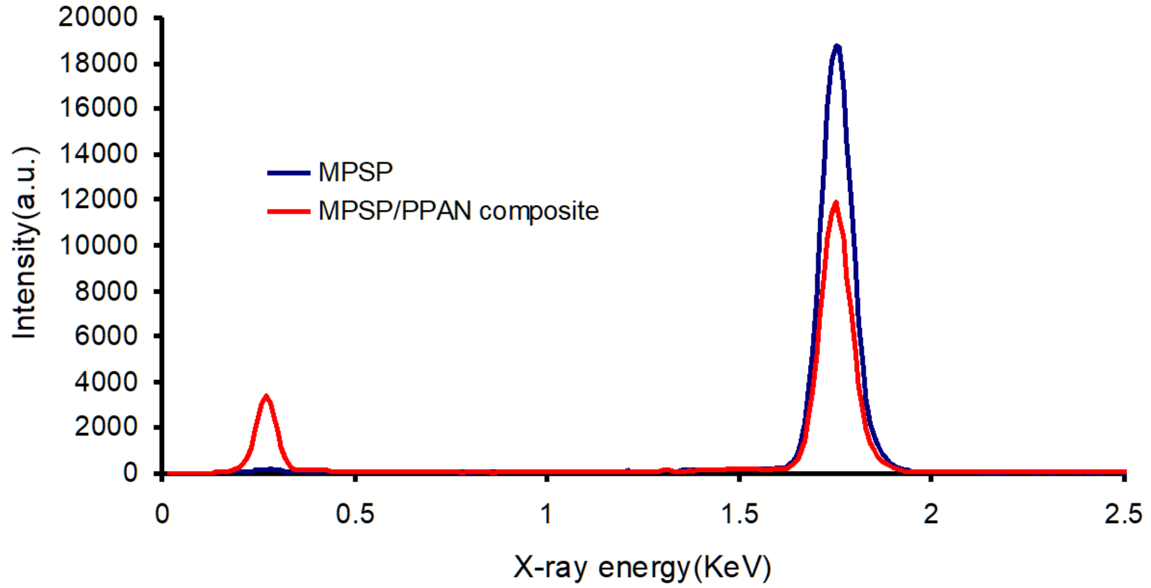


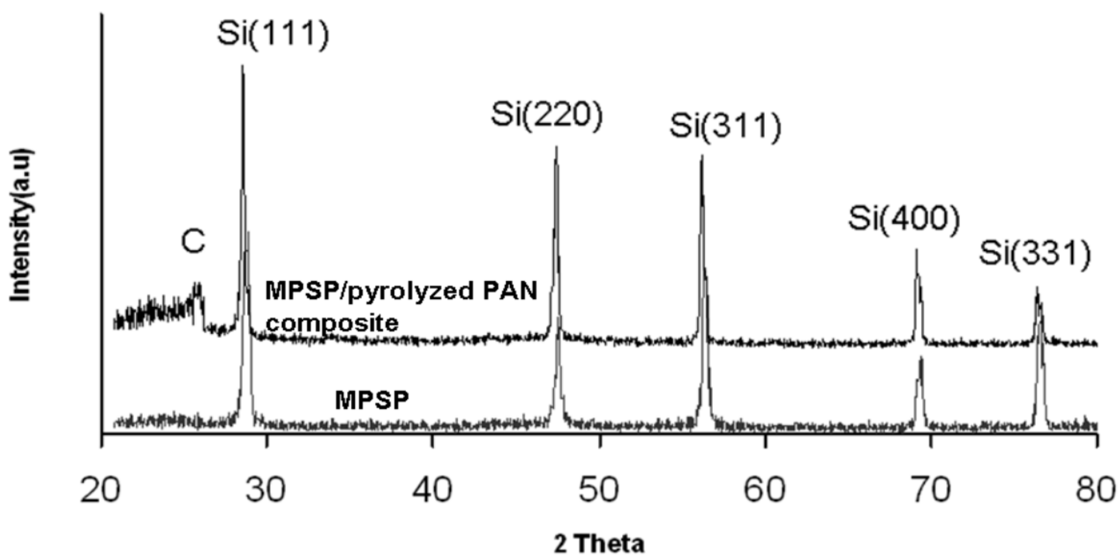
- BET analysis shows a surface area of 47 m^2/g, significantly more than crushed silicon (or 100 nm silicon nanoparticles)
- Porous structure remains after pulverization

How Much PPAN?



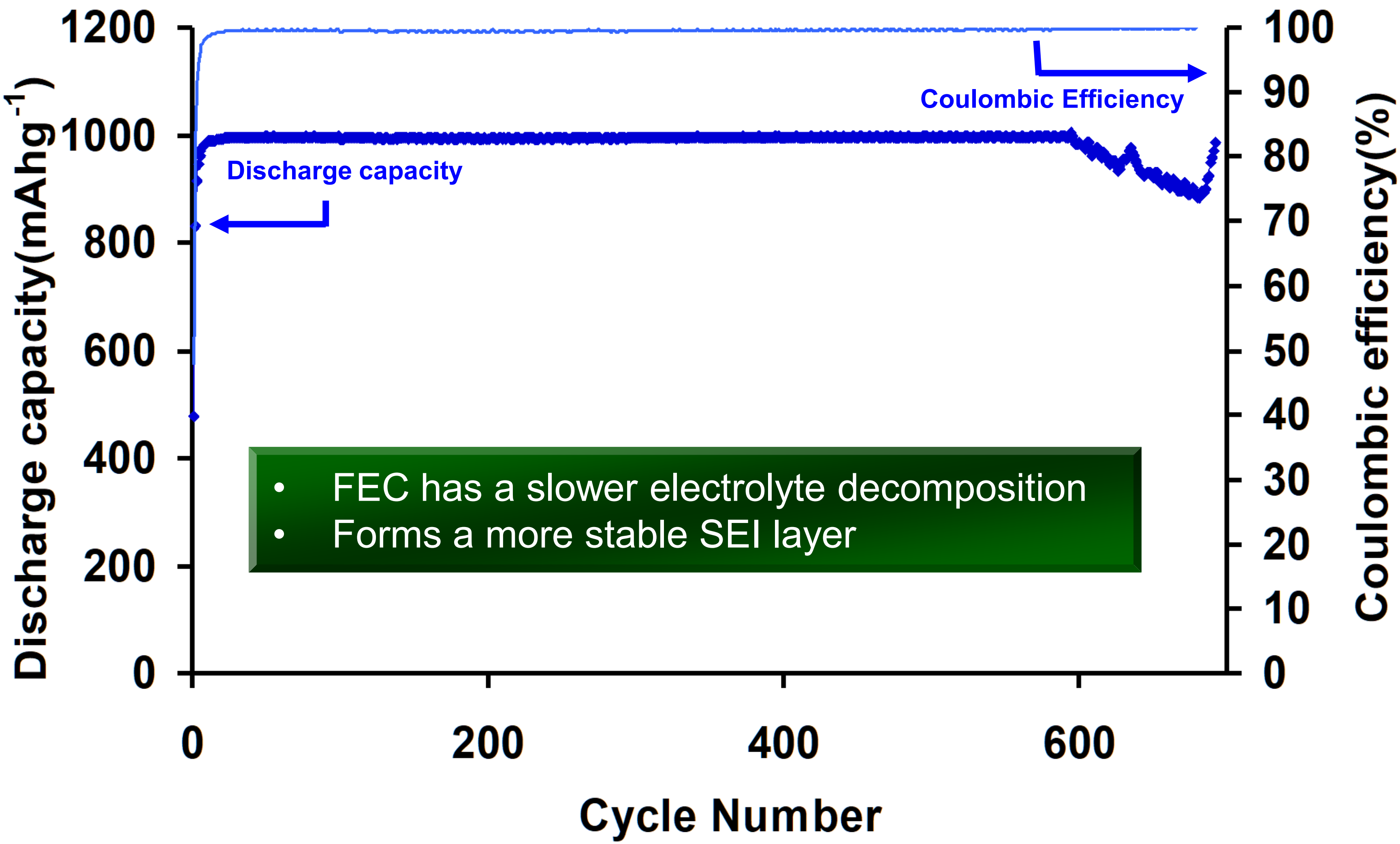
Pyrolyzed PAN does not change Si structure





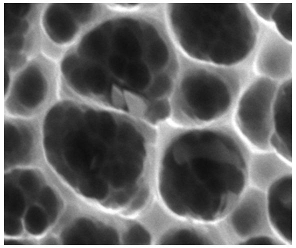
Using a Fluorinated (FEC) Electrolyte with 7:3 MPSP/Si Composite

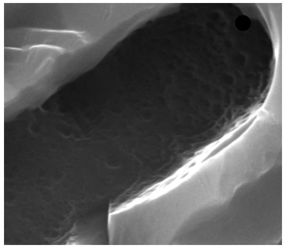
Mass per unit area of MPSP/PPAN = 1.5mg/1cm^2



- FEC has a slower electrolyte decomposition
- Forms a more stable SEI layer

Summary





- Macroporous silicon particulates (MPSP) provide an inexpensive method for generating silicon with a high surface area to volume ratio.

Acknowledgements

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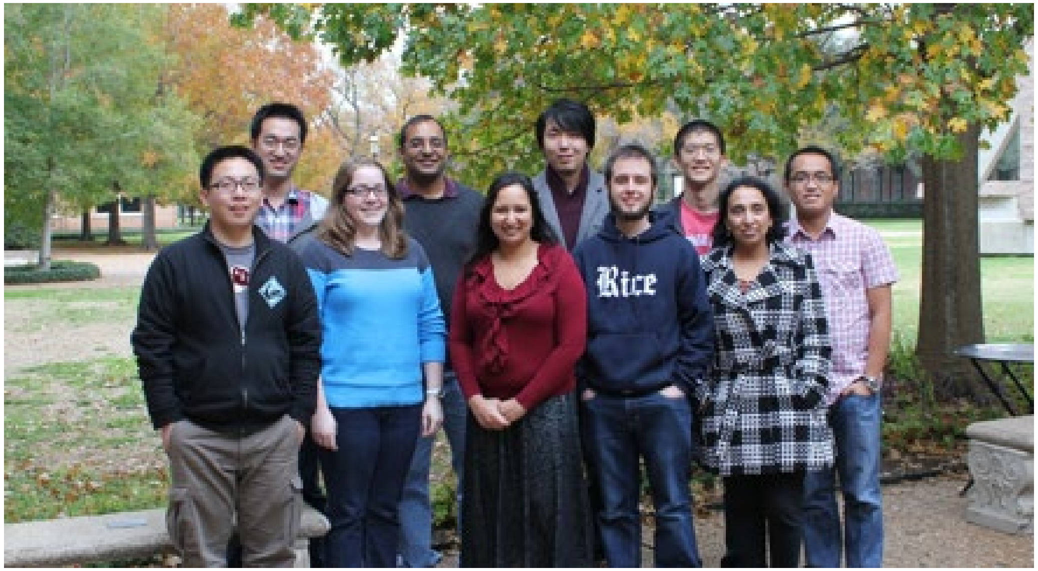

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