Porous Silicon for high performance energy storage

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Conventional Lithium Ion Battery (LIB)

- **Anode**: Based on graphite. Good electron conductor; lithium ions intercalate to form LiC₆. Theoretical capacity 372 mAh/g.

- **Cathode**: LiₓCoO₂ typical cathode material; lithium is intercalated into CoO₂ structure.

- **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.

- 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?

Silicon has the largest lithium specific capacity of any known anode material.
Why Hasn’t Silicon Been Used Already?

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

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

Loss of electrical contact

Stresses fracture silicon anode
**Existing Approaches: Nanotechnology for Lithium Ion Batteries**

**Super-Charging Lithium Batteries**

Nanowire electrodes could improve the performance of electric vehicles.

By Peter Fairley

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.

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

A. Magasinski¹, P. Dixon¹, B. Hertzberg¹, A. Kvit¹, J. Ayala¹ and G. Yushin¹,⁴*
Our Approach

Gold-Coated Porous Silicon Film

Lift-off Porous Silicon Films

Macroporous Silicon Particulates

Porous Silicon Fabrication

Process variables:
- Electrolyte (HF) concentration
- Current density
- Silicon doping type & density
- Temperature

Fabrication process simpler and will be lower cost than other proposed nanostructured silicon anodes
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 m²/g*

- **50 mg MPSP**
- **50 mg Crushed Si**

- **10 µm**

- **0.7 m²/g**

- **BET analysis shows a surface area of 47 m²/g, significantly more than crushed silicon (or 100 nm silicon nanoparticles)**
- **Porous structure remains after pulverization**
How Much PPAN?

Theoretical Capacity

- Mass Ratio of MPSP:PPAN
  - 9:1: 3221 mAh/g
  - 3:2: 2147 mAh/g
  - 4:1: 2863 mAh/g
  - 7:3: 2504 mAh/g

Cycle Number

Discharge Capacity (mAh/g)

Coulombic Efficiency (%)
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/1cm²

- 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.

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