Nanocomposites as next-generation anode materials for lithium ion batteries

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The need for storage

Sparks fly
Battery electric vehicles, worldwide

Battery cost, €/kWh

Penetration, %

FORECAST

New forecast

Old forecast

Source: Exane BNP Paribas; UBS

Who gets the bill?
California, net electricity-load requirement*
Typical spring day, gigawatts

An increase of 10.9GW over three hours (February 1st 2016)

Source: California ISO

*Demand minus renewable generation

First Solar among investors in Younicos’ US$50 million energy storage ‘land grab’
Our focus: silicon-based anodes

Inexpensive, sustainable, abundant, non-toxic

<table>
<thead>
<tr>
<th>Materials</th>
<th>Li</th>
<th>C</th>
<th>Li₄Ti₃O₁₂</th>
<th>Si</th>
<th>Sn</th>
<th>Sb</th>
<th>Al</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g cm⁻³)</td>
<td>0.53</td>
<td>2.25</td>
<td>3.5</td>
<td>2.33</td>
<td>7.29</td>
<td>6.7</td>
<td>2.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Lithiated phase</td>
<td>Li</td>
<td>LiC₆</td>
<td>Li₂Ti₅O₁₂</td>
<td>Li₄Si</td>
<td>Li₄Sb</td>
<td>Li₃Al</td>
<td>Li₃Mg</td>
<td></td>
</tr>
<tr>
<td>Theoretical specific capacity (mAh g⁻¹)</td>
<td>3862</td>
<td>372</td>
<td>175</td>
<td>4200</td>
<td>994</td>
<td>660</td>
<td>993</td>
<td>3350</td>
</tr>
<tr>
<td>Theoretical charge density (mAh cm⁻³)</td>
<td>2047</td>
<td>837</td>
<td>613</td>
<td>9786</td>
<td>7246</td>
<td>4422</td>
<td>2681</td>
<td>4355</td>
</tr>
<tr>
<td>Volume change (%)</td>
<td>100</td>
<td>12</td>
<td>1</td>
<td>320</td>
<td>260</td>
<td>200</td>
<td>96</td>
<td>100</td>
</tr>
<tr>
<td>Potential vs. Li (V)</td>
<td>0</td>
<td>0.05</td>
<td>1.6</td>
<td>0.4</td>
<td>0.6</td>
<td>0.9</td>
<td>0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

![Weight Percent Silicon](image_url)

![Temperature Chart](image_url)
Our focus: silicon-based anodes

Our focus: silicon-based anodes

\[ \sim 300\% \text{ volume expansion} \] during lithium insertion --- pulverization and fast capacity fading of the material.

Critical size = 150 nm

Nanotechnology to the rescue

Use nanoparticles and all problems will be solved?

Poor electrical conductivity

Need a very robust contact to a current collector

Too much surface area leads to large capacity loss in first cycle (SEI formation)

SEI is unstable because of volume change during cycling

Nanotechnology to the rescue

- Need a composite, typically silicon-carbon
- Advanced designs – tight control of structural parameters

Our contribution: Si-Sn-C composites

Why adding tin?
- Low electrical conductivity of Si is a major problem
- Tin is conductive and also has good capacity


Good capacity
Excellent rate capability
Our contribution: Si-Sn-C composites

Working hypothesis: Sn addition improves performance of Si-based anodes

Si nanoparticles + SnCl2 + Polyvinylpyrrolidone (PVP) in ethanol

Coat onto copper foil + Anneal in argon 700°C
Our contribution: Si-Sn-C composites

Materials characterization

- XRD indicates presence of both silicon and tin crystals
- Tin nucleates from SnCl₂ during thermal decomposition of polymer
Our contribution: Si-Sn-C composites

Materials characterization

- TEM – High res TEM confirm that the big particles are silicon and the small ones are tin
- High angle annular dark field and elemental scan further support this conclusion
- Tin content is low (<10% by weight). Most tin is lost during thermal decomposition process (high vapor pressure)
Our contribution: Si-Sn-C composites

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- TEM – High res TEM confirm that the big particles are silicon and the small ones are tin
- High angle annular dark field and elemental scan further support this conclusion
- Tin content is low (<10% by weight). Most tin is lost during thermal decomposition process (high vapor pressure)
- Carbon surrounds/wraps the structure
Our contribution: Si-Sn-C composites

Half-cell performance

- Both Si and Sn are electrochemically active
Our contribution: Si-Sn-C composites

Half-cell performance

- Both Si and Sn are electrochemically active
- Vast improvement compared to control-structure without tin
- Note that tin content is low (2.2% by weight)
- First cycle CE 81% on a highly porous structure
Our contribution: Si-Sn-C composites

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• Good rate capability
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Why does it work so well?

- Substantial decrease in anode impedance
- This is achieved with a very small tin addition
Summary

Silicon-tin-carbon composites have been realized using off-the-shelf components.
Production protocol is simple (mix-and-bake).

Pros: minor tin addition is highly beneficial.
Cons: parameter space is now significantly larger.

Pros: it is very likely that this structure is far from optimal.

About silicon nanoparticle synthesis

- Vacuum (but not UHV) process
- Large reaction volume
About silicon nanoparticle synthesis

From problem to opportunity

About silicon nanoparticle synthesis

- Remarkably simple - reproducible
- High precursor utilization – high production rate
- Easy to scale – large volume plasmas are easy to make

SiH$_4$ or SiCl$_4$

1 gram/hour of <10 nm Si crystals at the lab scale

>80% precursor utilization rate (SiH$_4$-to-NP)

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3M - NTFA