Gas phase synthesis of SiN_x nanoparticles for battery application using a hot-wall reactor

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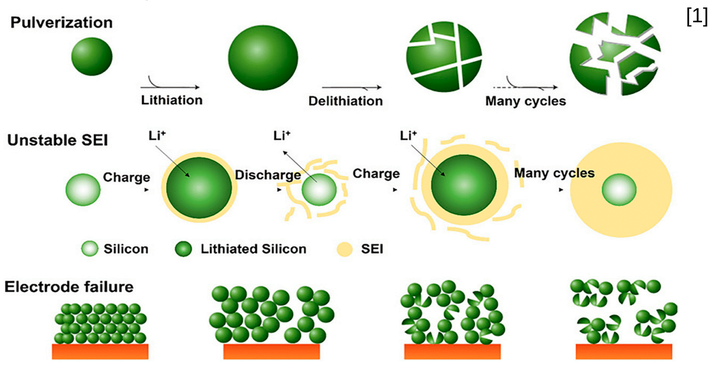
Motivation 1

Stability issues compromise the practical application of silicon as Li-ion battery anode material

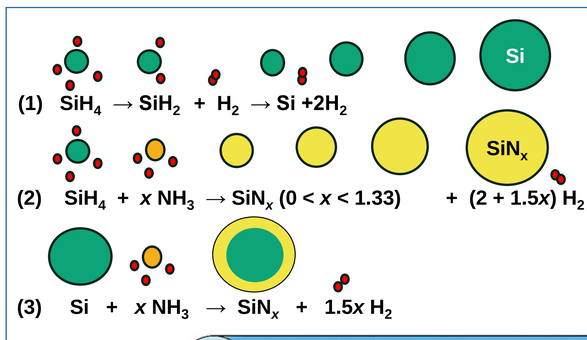


[1]

Conversion type silicon rich silicon nitride (SiN_x) as highly promising alternative to pure silicon with numerous advantages

- Conversion type material forms electrochemically active buffer matrix mitigating structural degradation[2]
- Trades off between cyclic stability, high Coulombic efficiency (CE) and storage capacity
- Tunable properties of SiN_x by adjusting the nitrogen content (*x*)

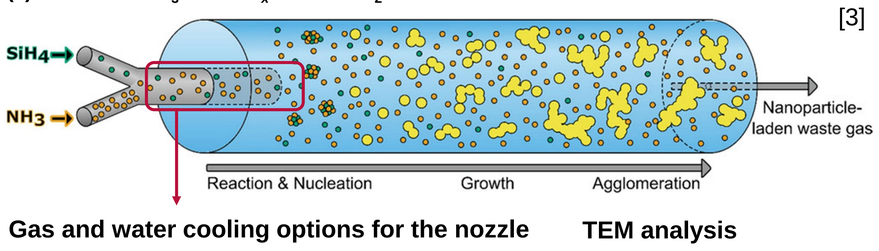
Synthesis: Hot-wall reactor 2



Gas phase Synthesis of SiN_x from SiH_4 and NH_3

- Three thermodynamically favorable reactions
- Reaction (2) is preferred over (3) at high temperatures
- Decomposition of NH_3 is slower than SiH_4 and nucleation of Si (slower than reaction (1))
- Nitrogen rich SiN_x requires NH_3 excess & long residence time

→ **process design required to tune materials properties**



[3]

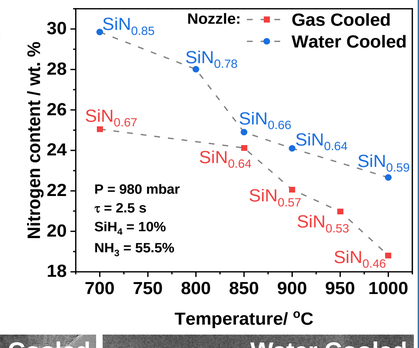
Gas and water cooling options for the nozzle

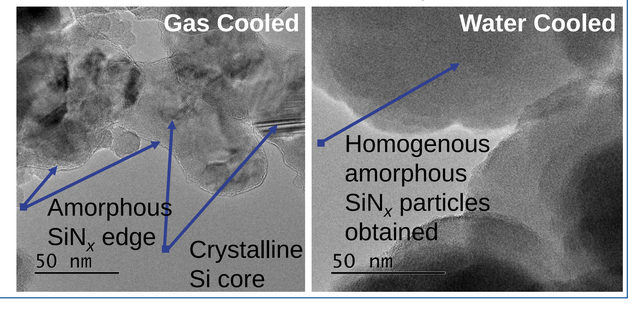
- Gas cooling leaves the nozzle hot enough for reaction (1) to initiate within the nozzle
- Water cooling curbs the early onset of (1) in the nozzle, exposing more SiH_4 to NH_3

TEM analysis

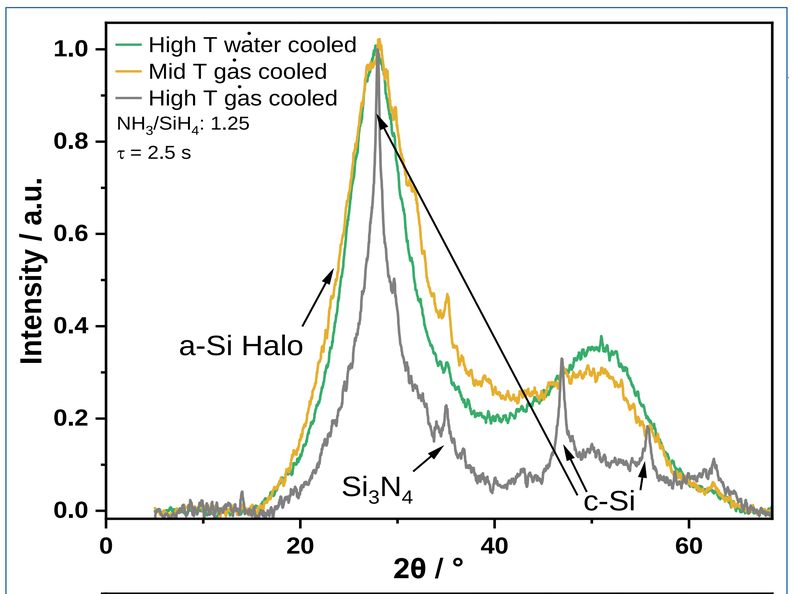
Premature reaction (1) in a gas-cooled nozzle results in core-shell morphology; water cooled nozzle hampers premature reaction (1)

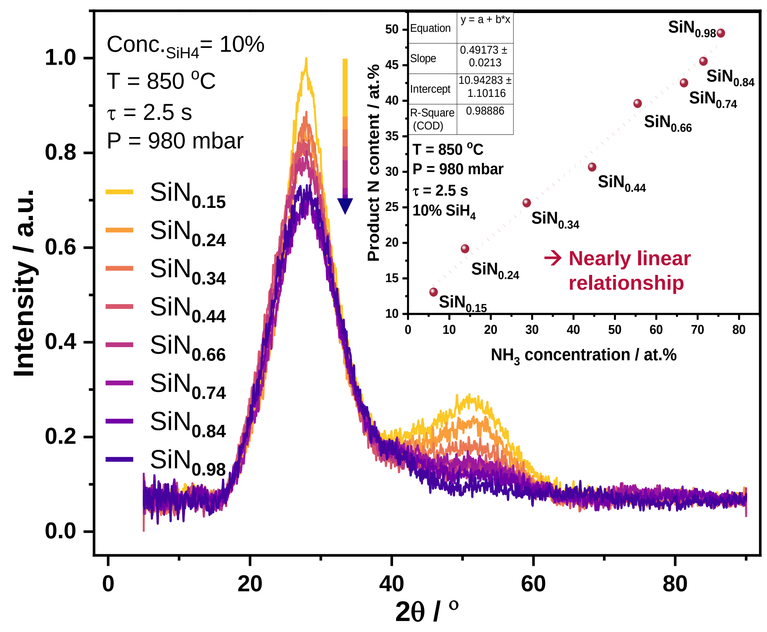
- Higher *x* can be seen in water cooled case for same temperature





XRD analysis 3

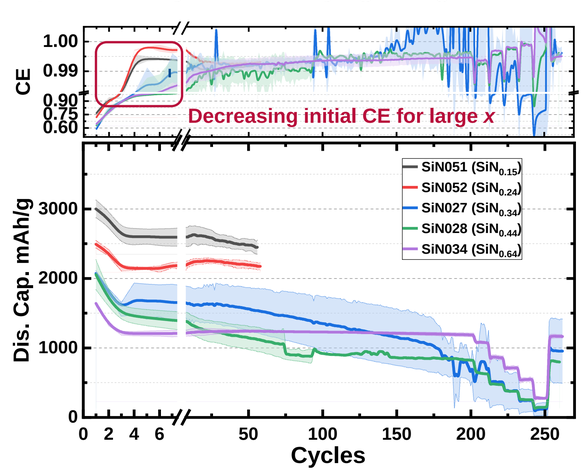




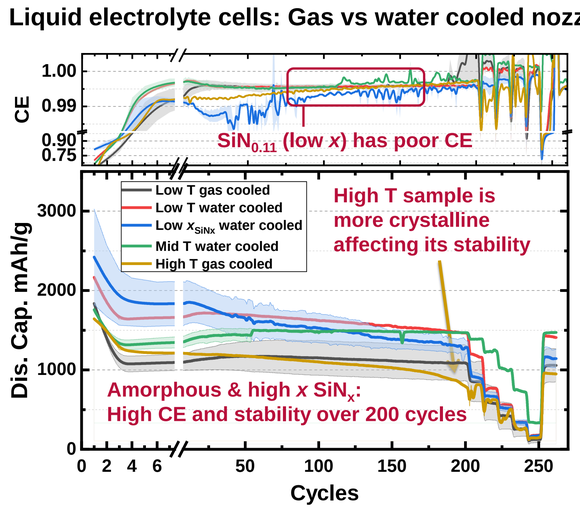
- High T, and midpoint sample shows crystalline phases of Si and Si_3N_4
- Crystalline peaks not prominent in high T water cooled sample
- No crystallinity at all for compositions with $x > 0.15$
- Decreasing crystallinity with increasing concentration of NH_3

Half-cell testing in liquid electrolyte 4

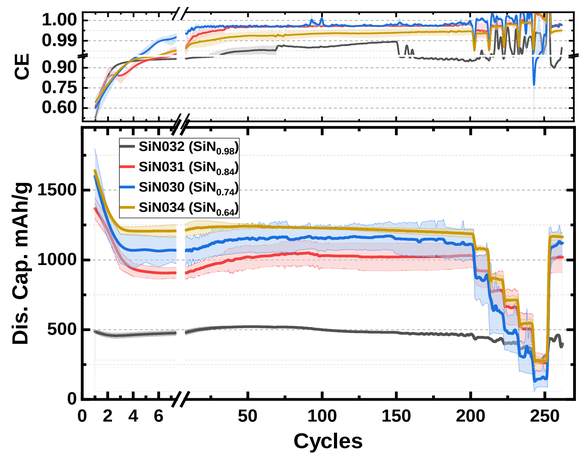
Liquid electrolyte cells: Varying nitrogen content



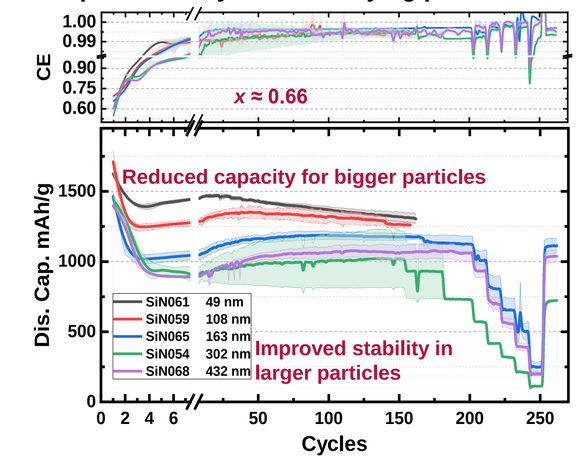
Liquid electrolyte cells: Gas vs water cooled nozzle



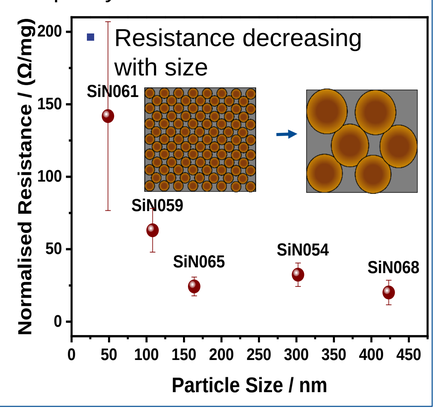
- The c-$Li_{15}Si_4$ phase which irreversibly reacts with the electrolytes and is detrimental to the Coulombic efficiency, is suppressed with higher *x*
- Buffer matrix formed from SiN_x composed of various lithium nitridosilicates and Li_3N, allows for a multi-phase lithiation



Liquid electrolyte cells: Varying particle size

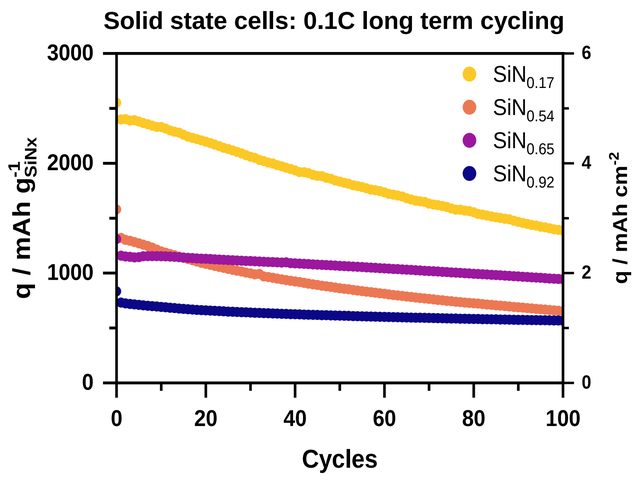


- Lithiation of core is difficult in larger particles decreasing their specific capacity

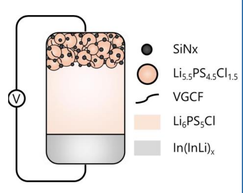


Half-cell testing in solid electrolyte 5

Solid state cells: 0.1C long term cycling



Schematic of the solid state cell



- Capacity fade with rising *x* due to less silicon in material
- High *x* also has less initial CE due to matrix phase formation
- Stability is rising with *x*
- Optimum composition around $x = 0.6$ to 0.8

Conclusions 6

- Particle composition, size and morphology can be adjusted to use cases in a scaled up synthesis of upto 1 kg per hour
- SiN_x: High stability, CE, and rate performance can be achieved for slightly less capacity compared to pure silicon
- Performance of material in solid state cells is comparable to the liquid electrolyte cells
- Even high *x* cells ($SiN_{0.84}$) retains a capacity of 1000 $mAhg^{-1}$ with CE > 99.5% and over 200 cycles in a liquid electrolyte cell.

Acknowledgements 7

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