The University Of Sheffield.

Magnesiothermic reduction to produce porous silicon for lithium-ion batteries

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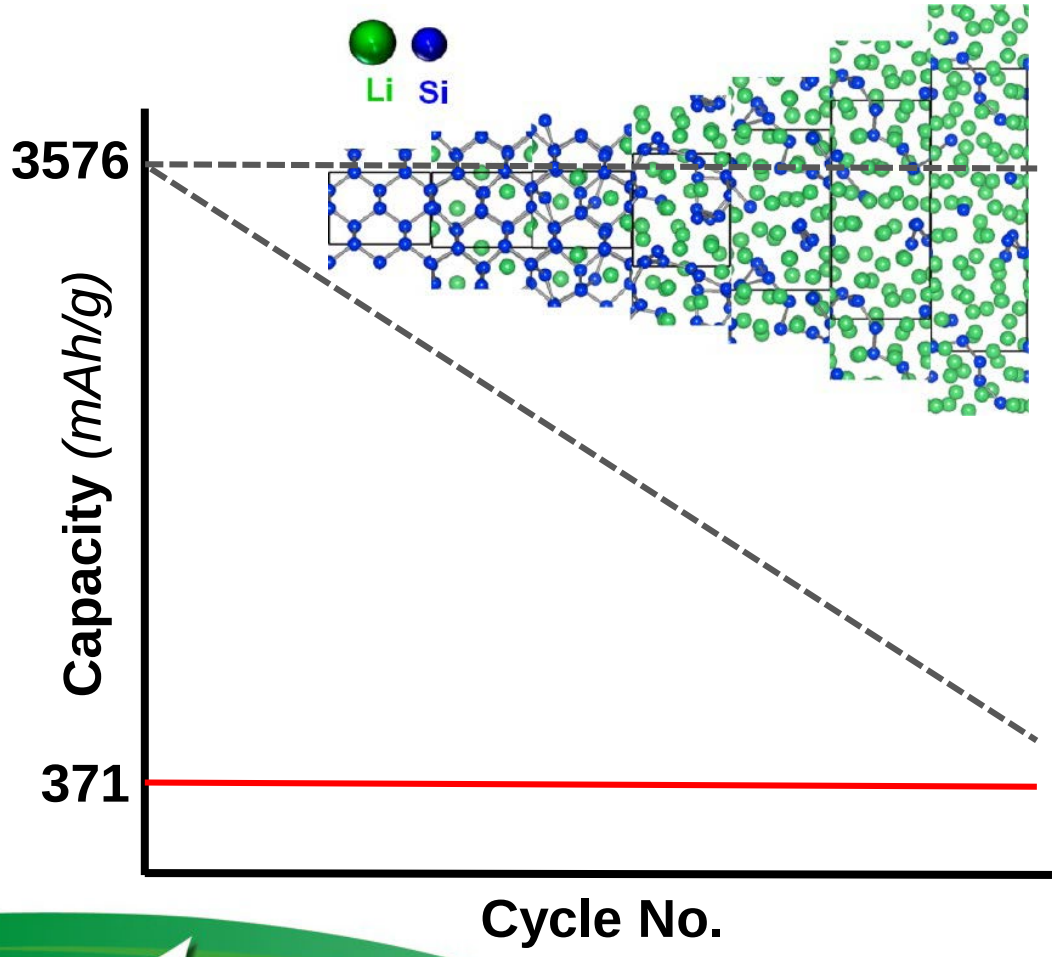
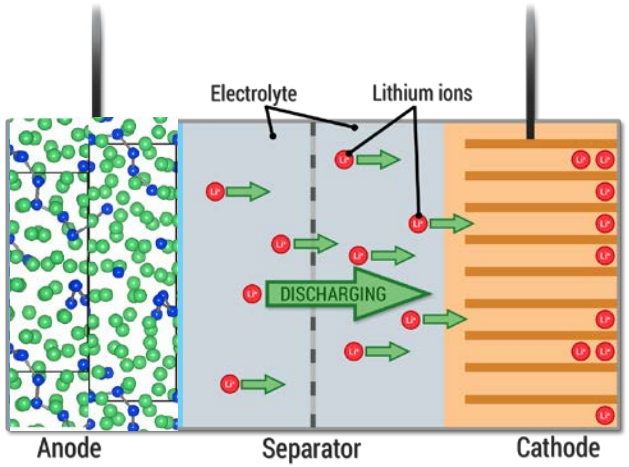
EFNL 249, ACS San Diego, 27/8/19

EPSRC Centre for Doctoral Training esa in Energy Storage and its Applications

Silicon vs conventional anode materials



$Li_{3.75}Si$ ($Li_{15}Si_4$)
Gravimetric capacity **3576 mAh/g**
Volumetric capacity **2190 mAh/cm³**

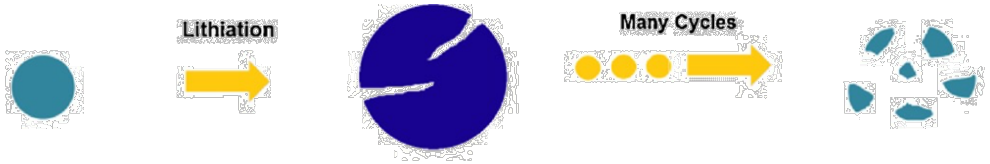


Commercial Graphite **(C_6Li)**
Gravimetric capacity **371 mAh/g**
Volumetric capacity **810 mAh/cm³**

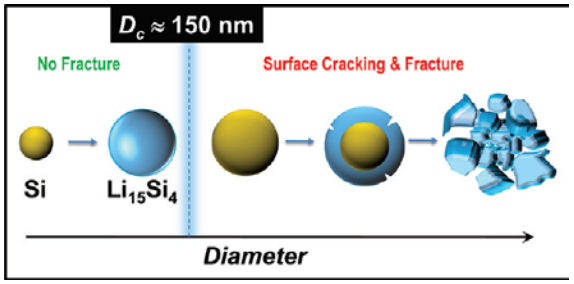
Chan et al, *J. Am. Chem. Soc.* **2012**, *134*, 14362.

Issues with Volume Expansion

Pulverisation

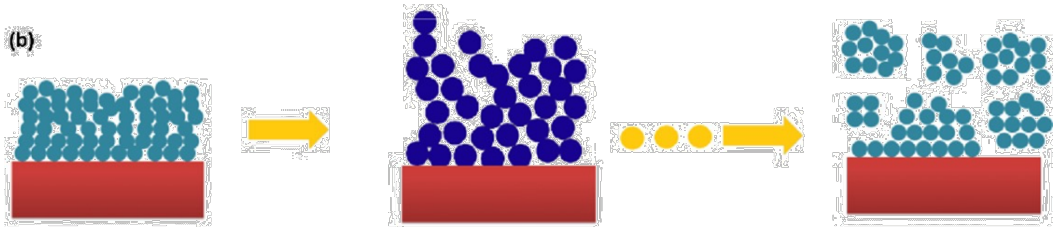


Smaller particle size



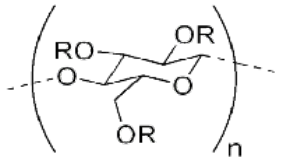
Liu et al, *ACS Nano* **2012**, *6*, 1522.

Electrode expansion/ impingement



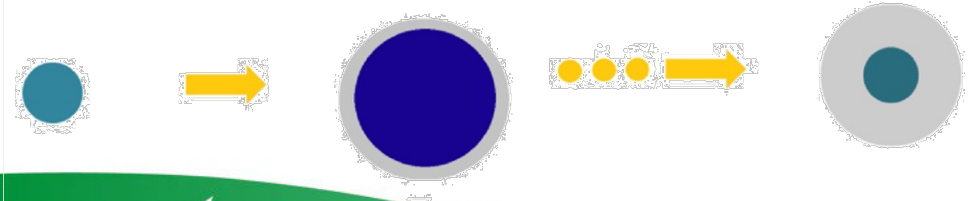
Flexible binders

Carboxymethyl cellulose

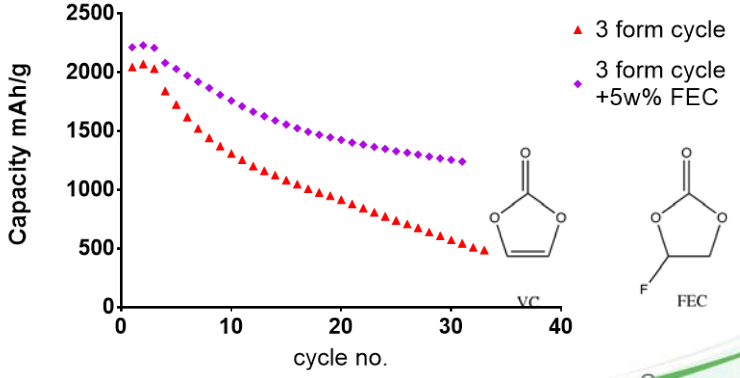


R = H or CH_2CO_2H

Solid Electrolyte Interphase formation



Electrolyte additives



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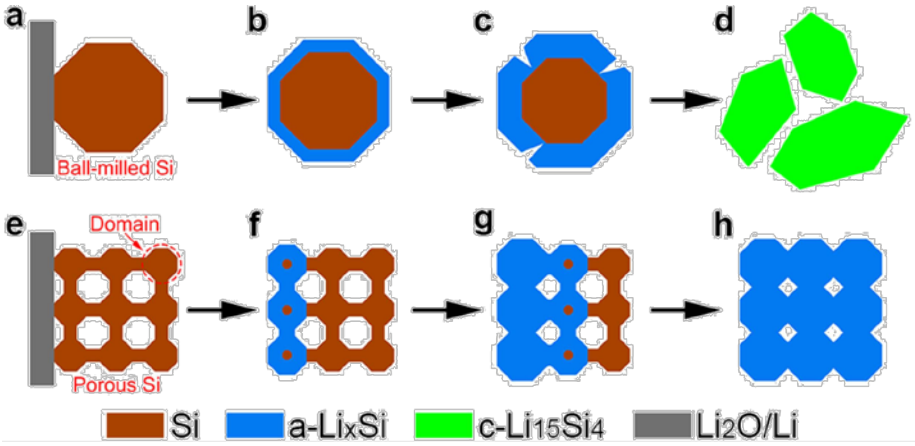
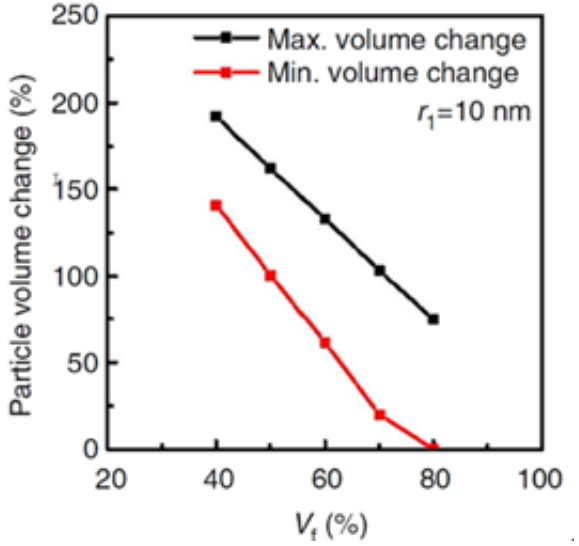
Porous silicon as a solution

- High surface area ⇒ better **accessibility** for electrolyte
- Shorter lithium **diffusion** lengths due to small substructures
- Expansion into own pore volume ⇒ minimum **cracking**
- More favourable **lithiation** behaviour



Shen et al, *Sci. Rep.*, 2016, **6**, 31334



Li. et al, *Nat. Commun.*, 2014, **5**, 1

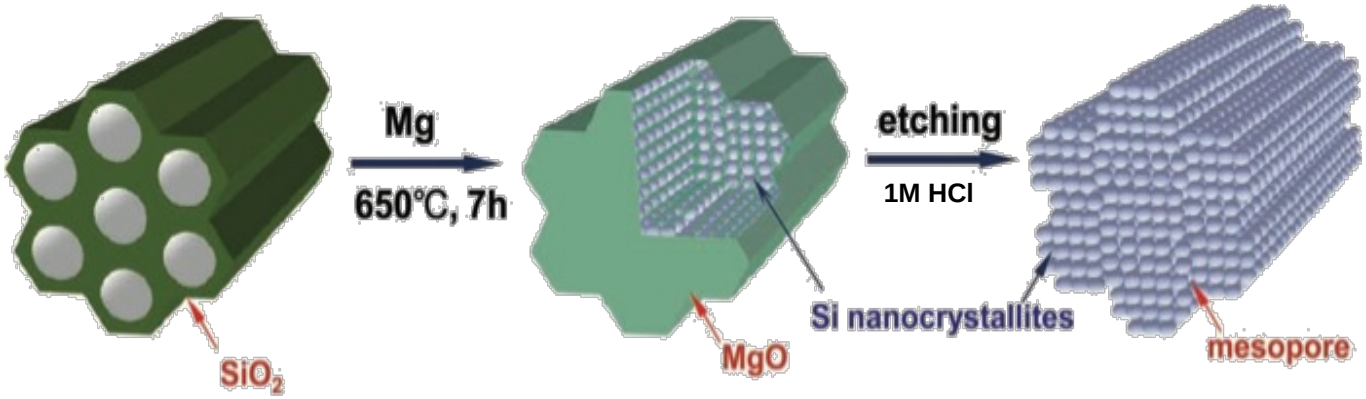
Current Routes to Porous Silicon

- Electroless etching
- Chemical Vapour Deposition
- Electrochemical etching

Most effective for surfaces

For Battery applications, bulk material synthesis routes are needed

Magnesiothermic Reduction for bulk porous silicon production



Good capacities and cyclability:

- 2500 mAh/g for 100s of cycles
  - with <20% capacity loss.

Jia et al. *Adv. Energy Mater.*, 2011, **1**, 1036
Entwistle et al. *J. Mater. Chem. A*, 2018, **6**, 18344

Magnesiothermic Reduction

Missing link: how the reduction process affects the properties and performance of porous silicon?

Solution: A systematic study linking processing-structure-property.

Feedstock → ? → **Process** → ? → **Product**

- Silica sources
- Scalability, availability & cost
- Properties of feedstock
- ……

- *T* and *t*
- C_{silica} : C_{Mg}
- *dT/dt*
- Thermal moderators (NaCl)
- …..

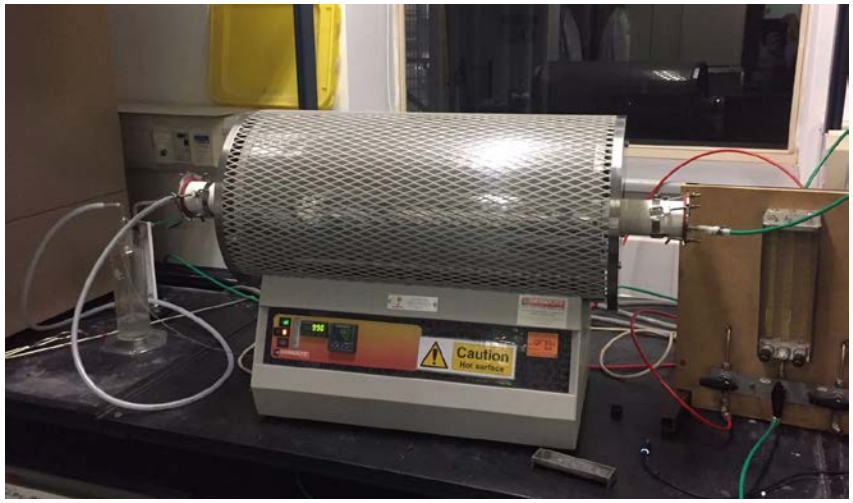
- Yield
- Purity
- Pore structure
- Crystallinity
- ……

Entwistle et al. *J. Mater. Chem. A*, 2018, **6**, 18344

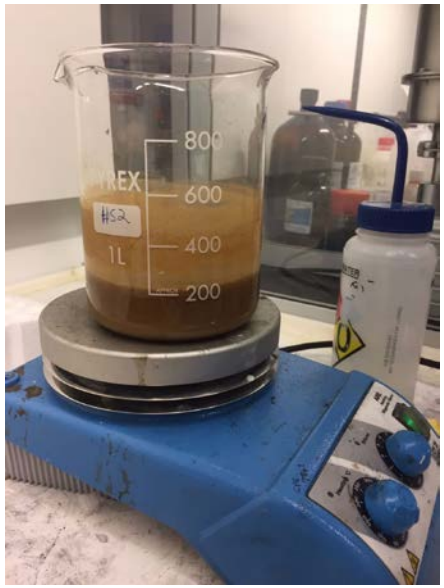
Outline of Magnesiothermic Reaction

$2Mg+SiO_2 \rightarrow 2MgO+Si$

1M HCl



Reduction in a furnace under flowing Ar



Removal of MgO from porous silicon

Curr. Opin. Green Sus. Chem., **12**, 110, 2018.

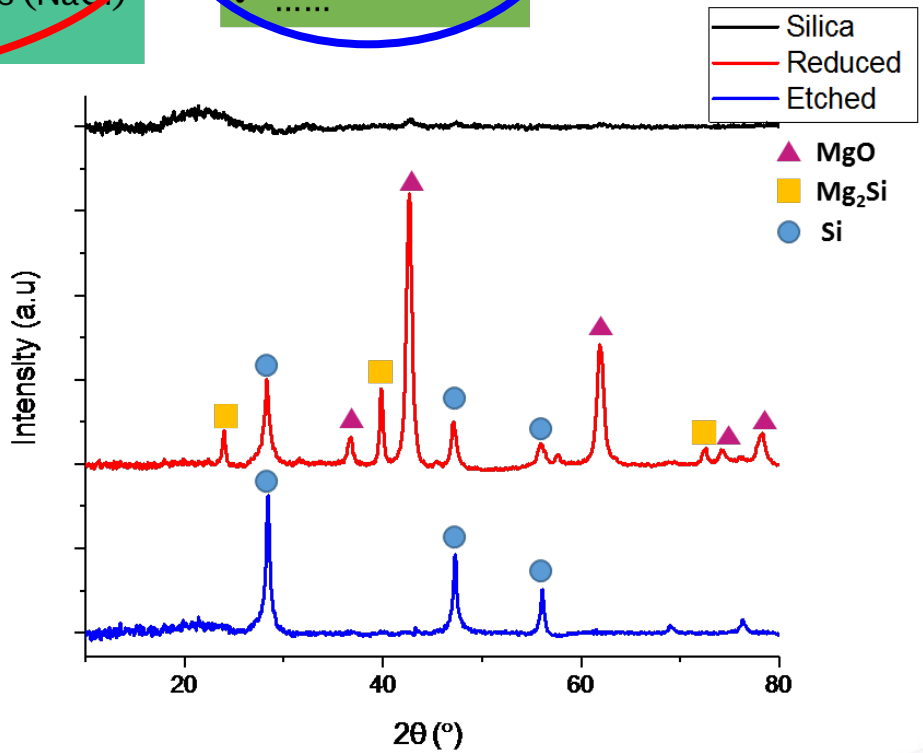
Studying the process

To be varied

Feedstock	Process	Product
• Silica sources • Scalability, availability & cost • Properties of feedstock •	• T and t • $C_{silica} : C_{Mg}$ • dT/dt • Thermal moderators (NaCl) •	• Yield • Purity • Pore structure • Crystallinity • .....

To be measured

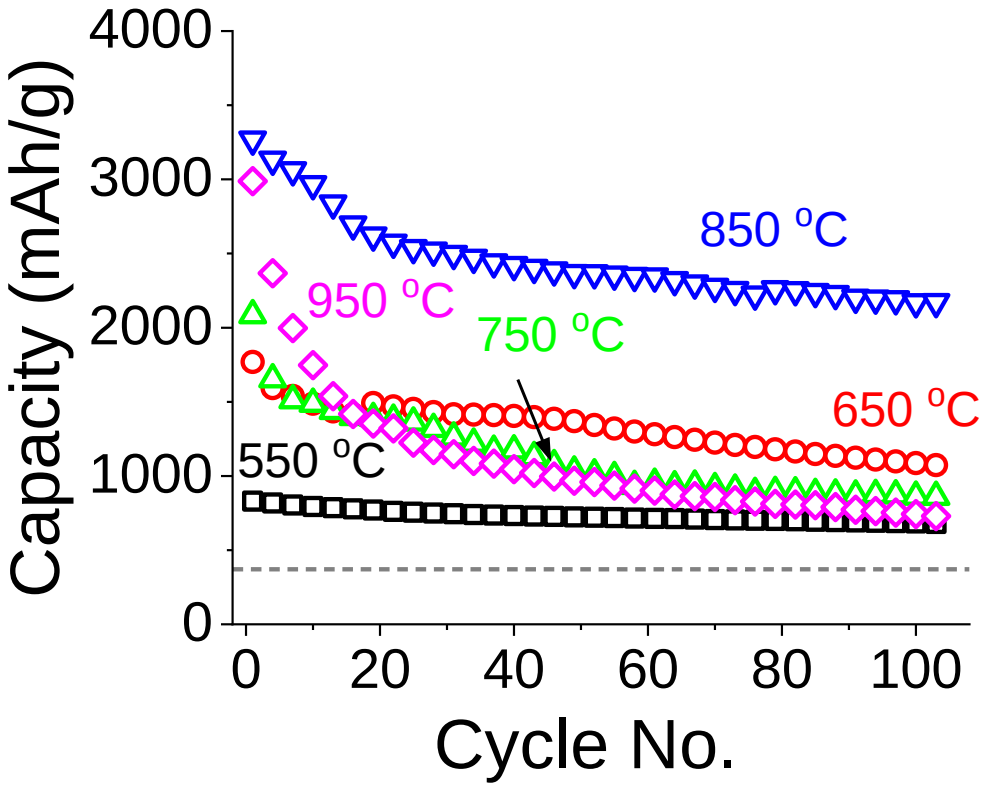
- X-ray diffraction (XRD)
- Thermal Gravimetric Analysis (TGA)
- N_2 Porosimetry (surface area and pore sizes)



*Publication *Currently Under Review.*

Anode Performance

- The capacity retention is very good for some of these samples.
- ↑ T leads to ↑ capacity (due to high purity).



- Porosity is key for extended cycle life span.

t ≈ 1h,
Mg:SiO_2 ≈ 2.25
T ≈ 850°C

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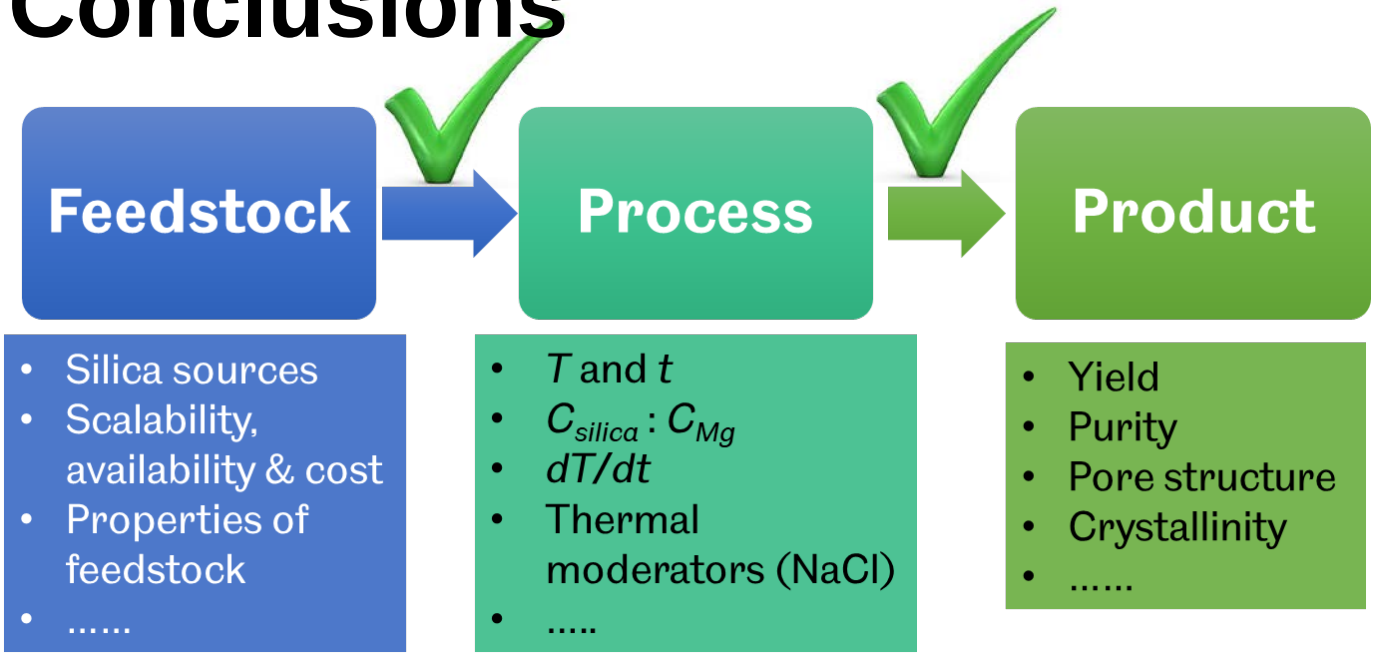
Conclusions



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T ≈ 850°C

*Publication *Currently Under Review. 09_2019*

Future work

- Optimise the porous silicon for high capacity and stable cycle life
- Techno-economic feasibility of magnesiothermic reduction
- Partnering with industry for large scale manufacturing.

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Acknowledgments

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in Energy Storage and its Applications

EPSRC
Engineering and Physical Sciences Research Council

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Thank you

Application of magnesiothermic reduction of silica to produce porous silicon for lithium-ion batteries

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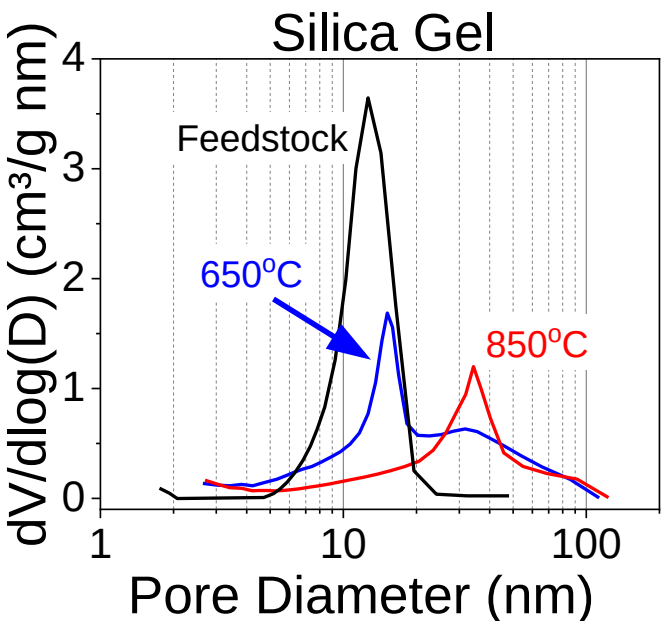
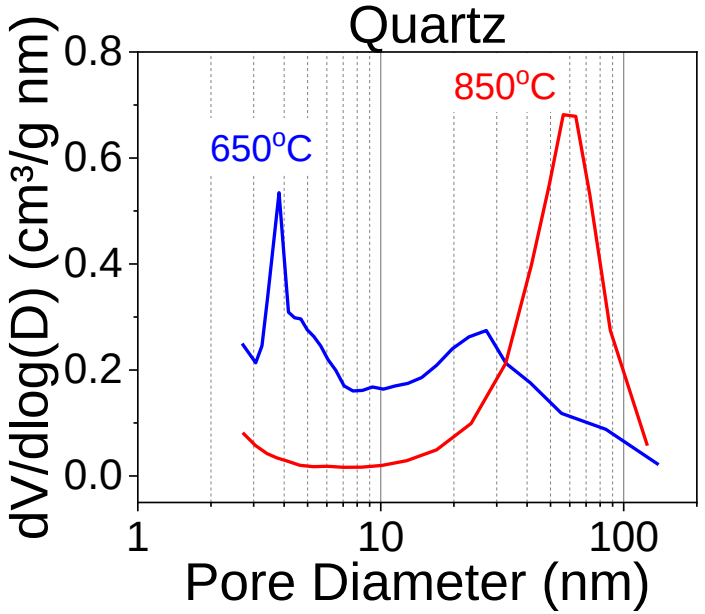
4. Feedstock….

2 Feedstocks: mesoporous silica and non-porous quartz

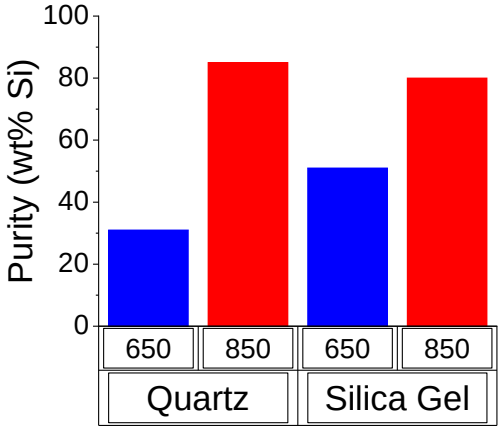
2 Ts for Reduction: 650 and 850 ºC

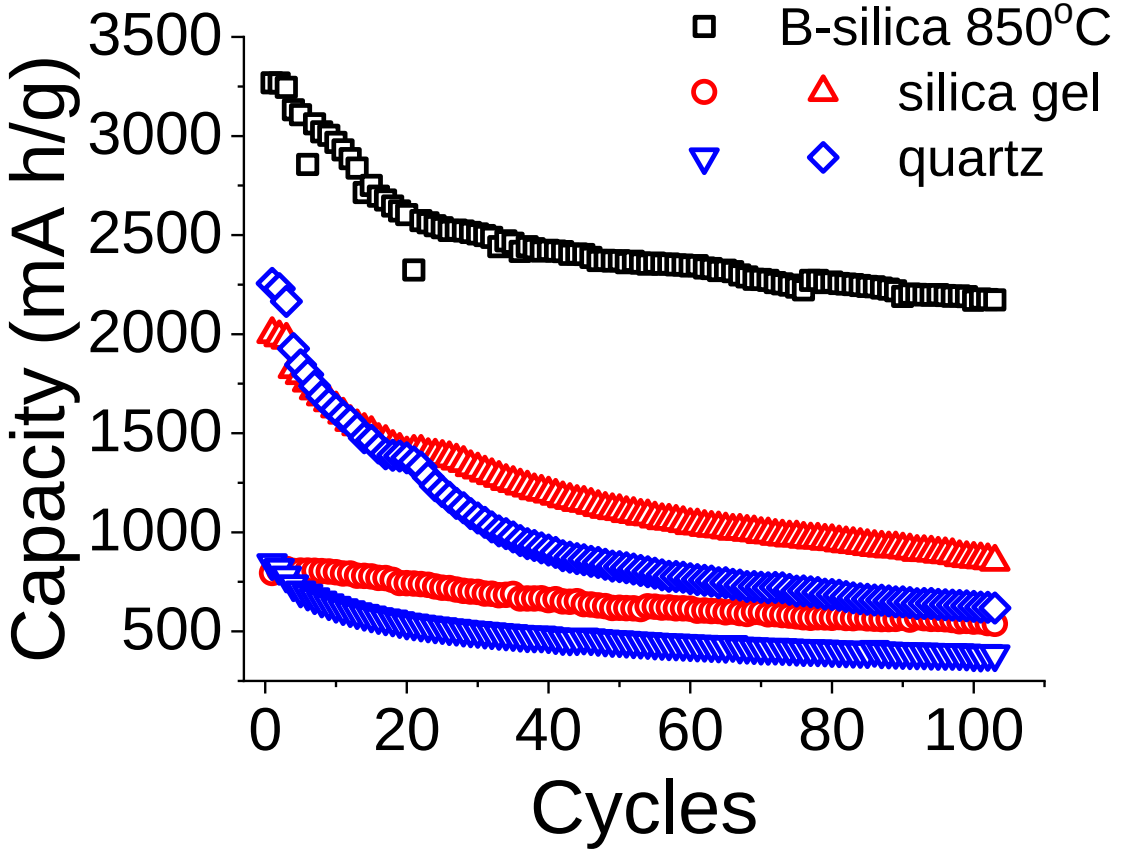




- Analysis of pore evolution is new.
- Porosity was introduced into non porous quartz.

….4. Feedstock


Purity (wt% Si)
100
80
60
40
20
0
650
850
650
850
Quartz
Silica Gel


B-silica 850°C
silica gel
quartz
Capacity (mA h/g)
3500
3000
2500
2000
1500
1000
500
0
20
40
60
80
100
Cycles