A cost efficient silicon-carbon based anode material for Li-ion batteries

Results from the SiNODE-project

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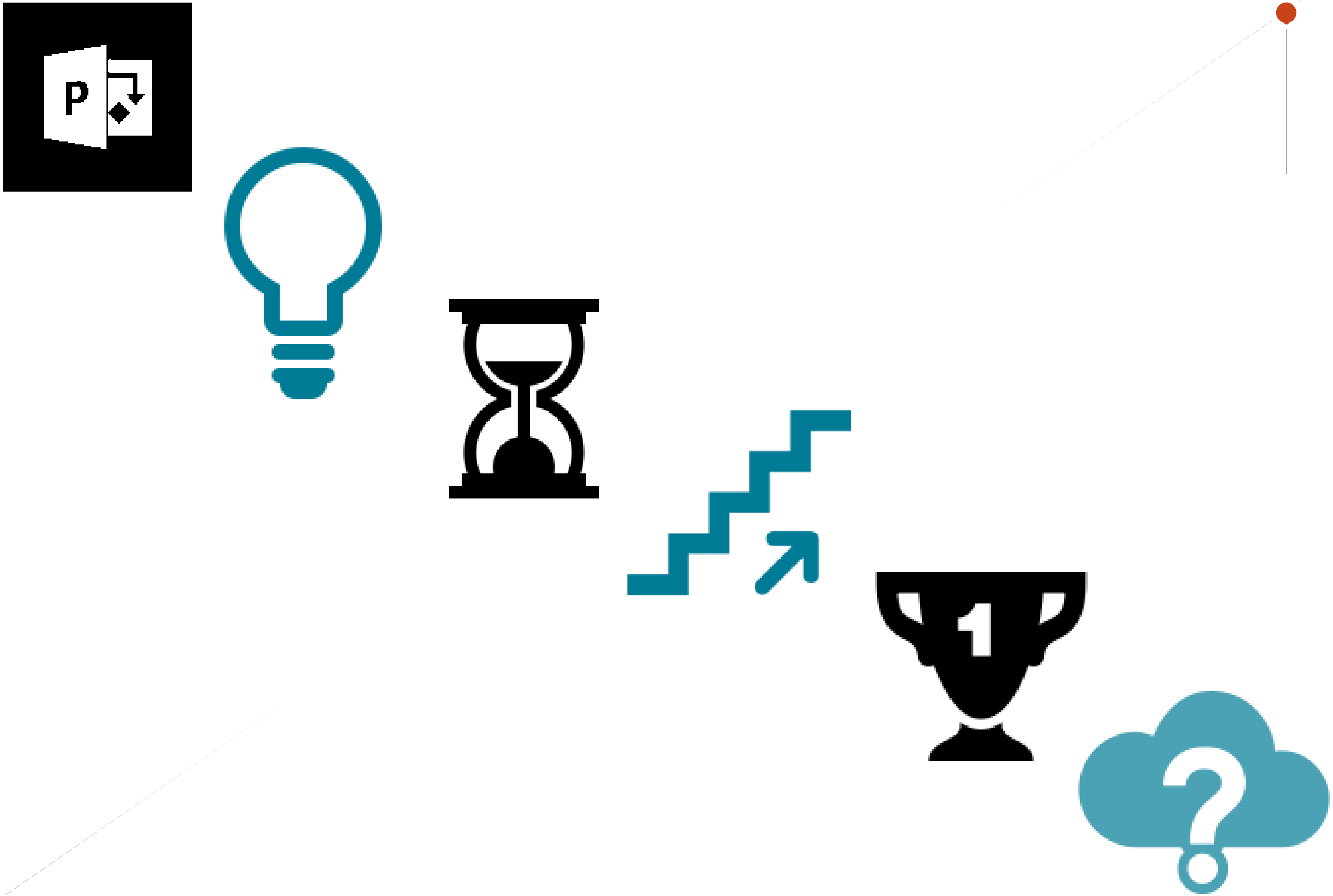


The SiNODE project

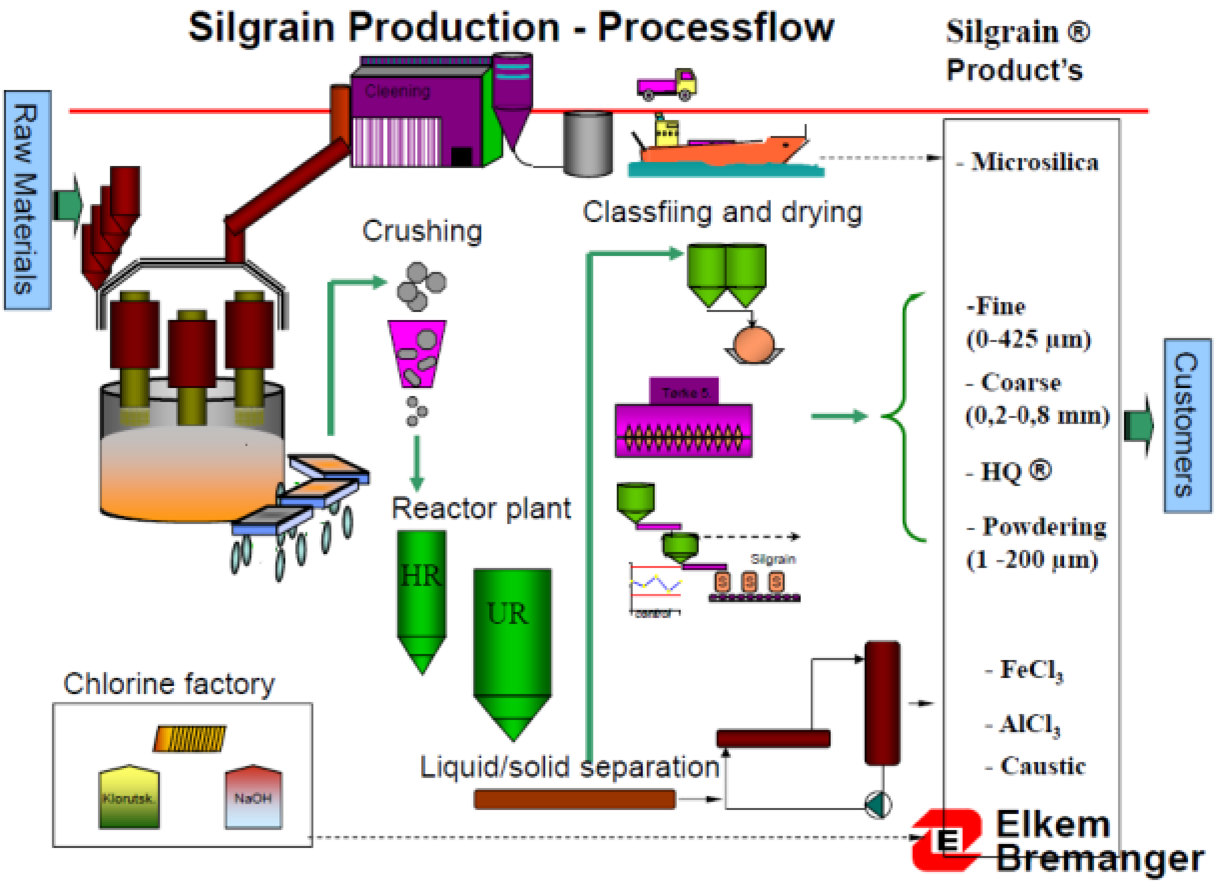
- An IPN project (2012-2015) led by Elkem with SINTEF and IFE

- Financial support from RCN in the BIA-program

- Develop an optimized silicon/carbon composite with Elkem material

Silicon - a Norwegian speciality

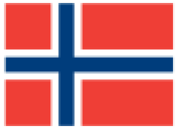
Silicon from Elkem – Silgrain® e-Si



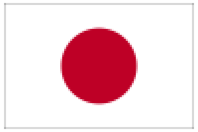
Component	Si	Fe	Al	Ca	Ti
wt%	99.7	0.035	0.035	0.035	0.035

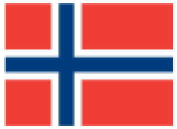
- Elkem Bremanger produces Si metal via patented hydro-metallurgical leaching process called the Silgrain® process
- Silgrain® e-Si is a collection of different Si qualities
- Tailored for Si-based anode material
- Can be adapted to size and shape requirements

Value chain for batteries

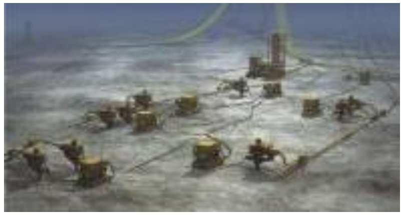


SiNODE





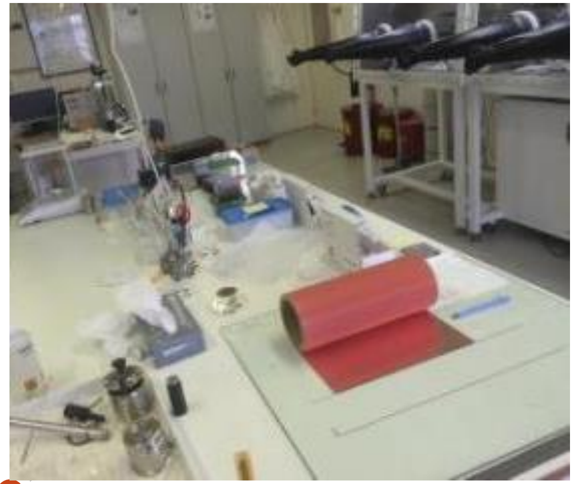
Raw material → Adapted raw material → Batteries → Modules → End-user



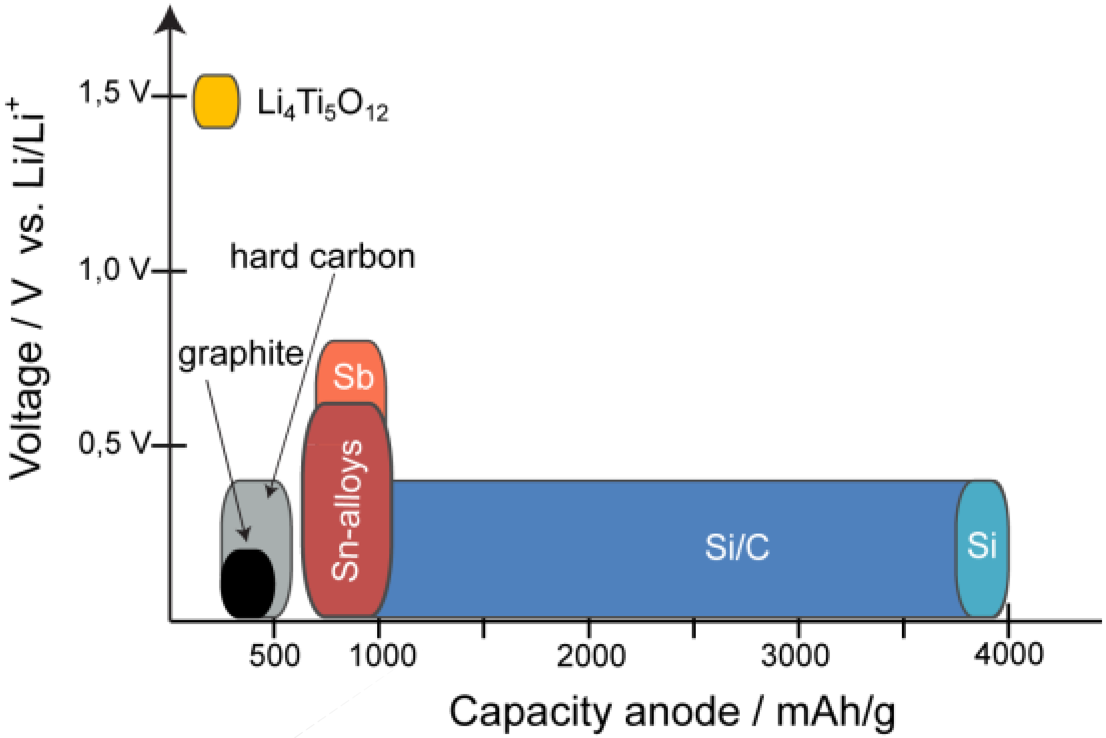
Battery material group and laboratory

- Material synthesis and characterization
  - Slurry mixing:
    - High energy planetary ball milling
    - Planetary centrifugal mixing
  - CVD and coating methods:
    - Tape casting
    - Screen printing
  - Colloidal chemistry
    - rheology, size determination

- Cell preparation and testing
  - Coin cell preparation in inert atmosphere
  - Other cell designs possible
  - 144 test channels < 5 A
  - Electrochemical impedance spectroscopy
  - In-house development of dQ/dV software

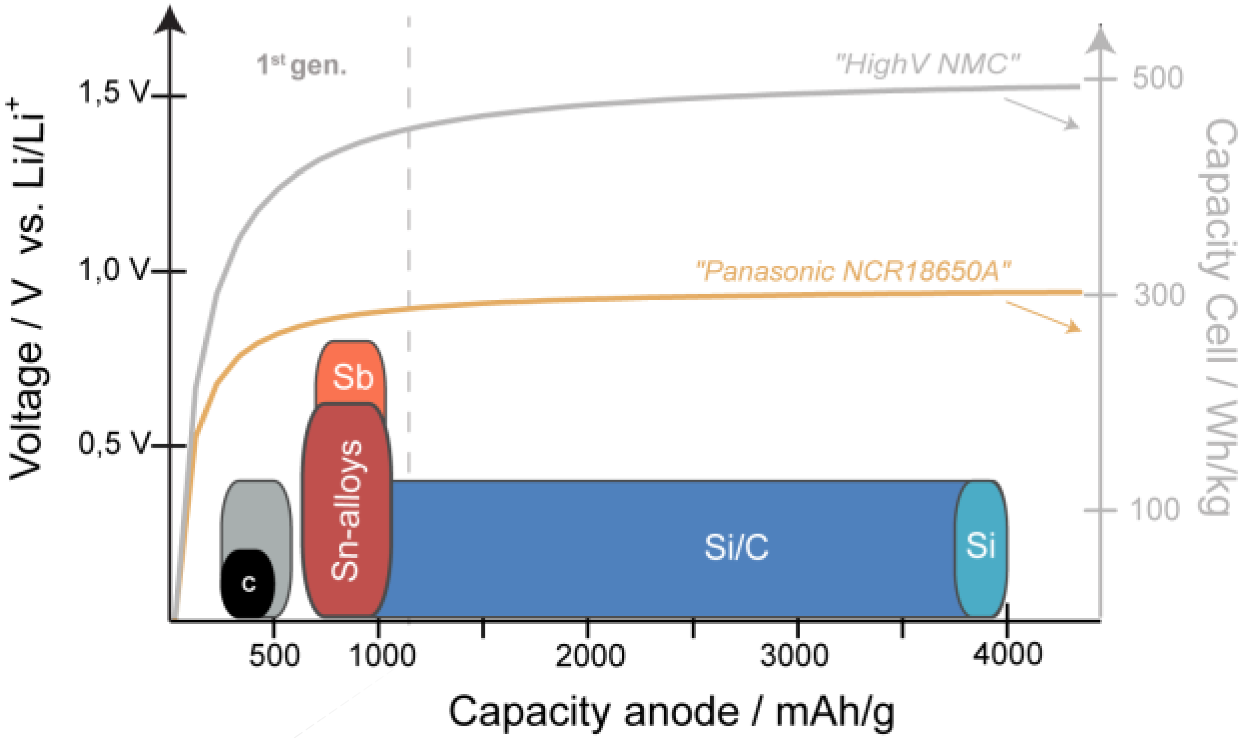


Silicon as an anode material



- Theoretical capacity >> graphite
- Specifications
  - Doping?
  - Morphology?
  - Nanostructuring?
  - Surface treatment?
- Price?

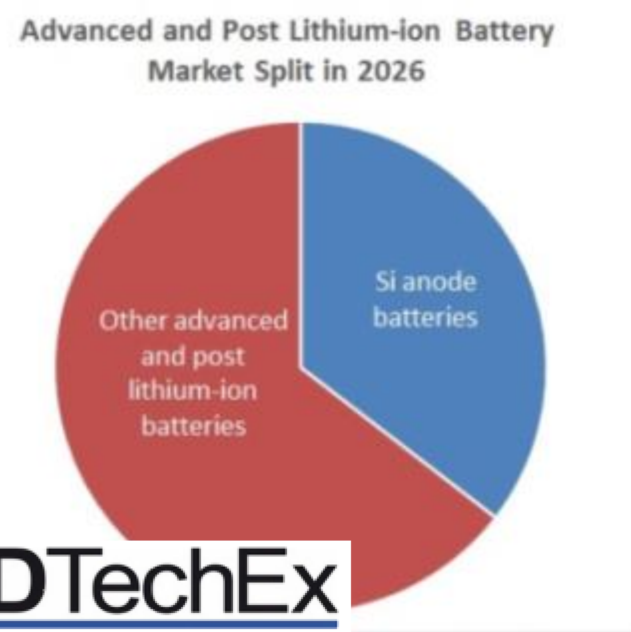
Silicon as an anode material



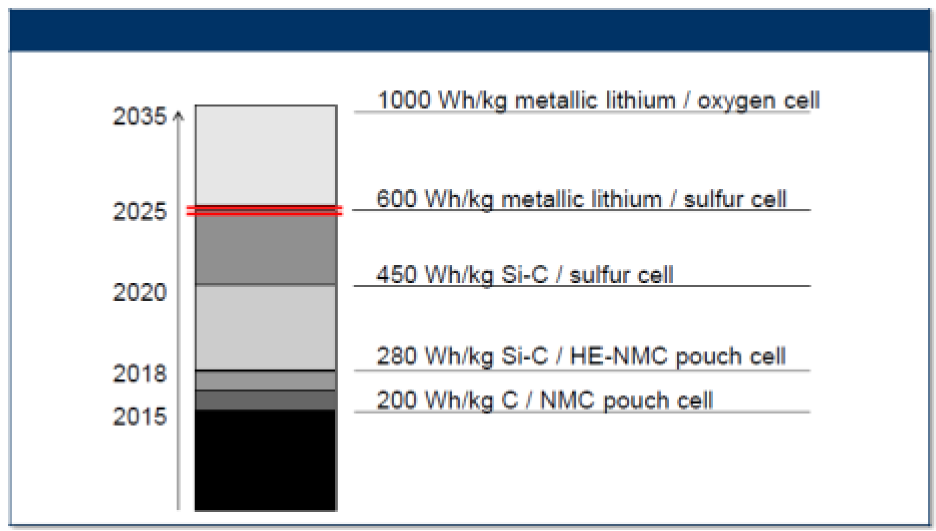
- Large gain from graphite → 1000 mAh/g
- Minimal gain from 1000 → 4000 mAh/g

Si anodes on the official roadmaps

> "This is just sort of a baby step in the direction of using silicon in the anode," Elon Musk said during the call. "We're still primarily using synthetic graphite, but over time we'll be increasing silicon in the anode."

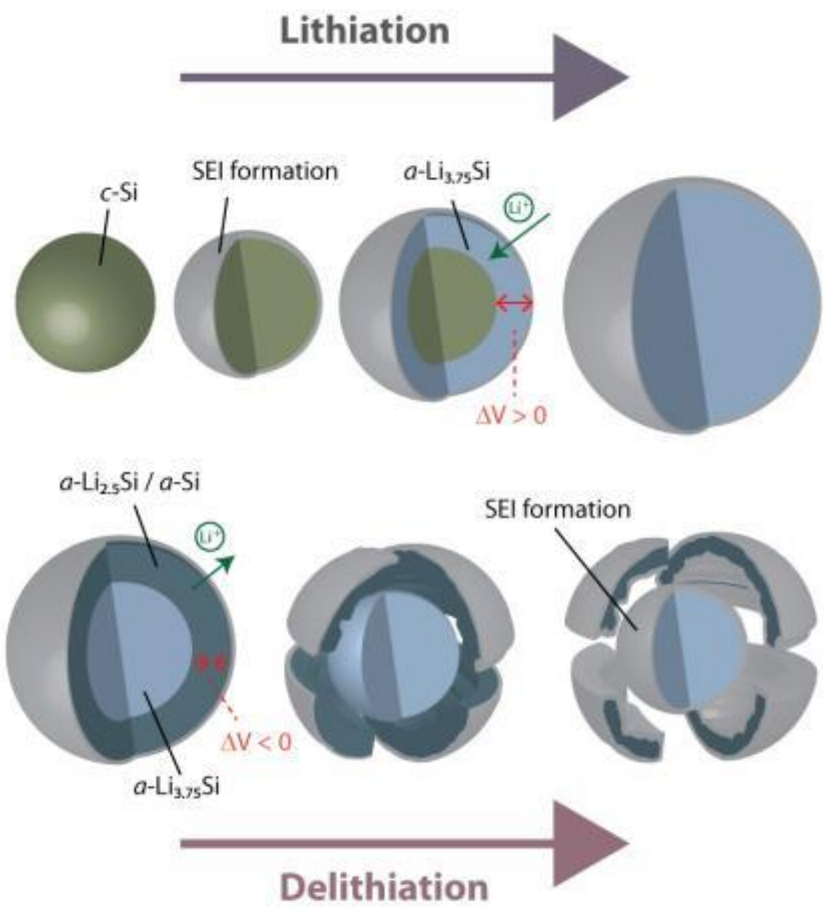


Technology steps of battery cells



http://fortune.com/2015/07/22/teslas-cheaper-car/
http://www.electricvehiclesresearch.com/articles/8732/silicon-anode-batteries-the-holy-grail

Challenges with Si as anode material



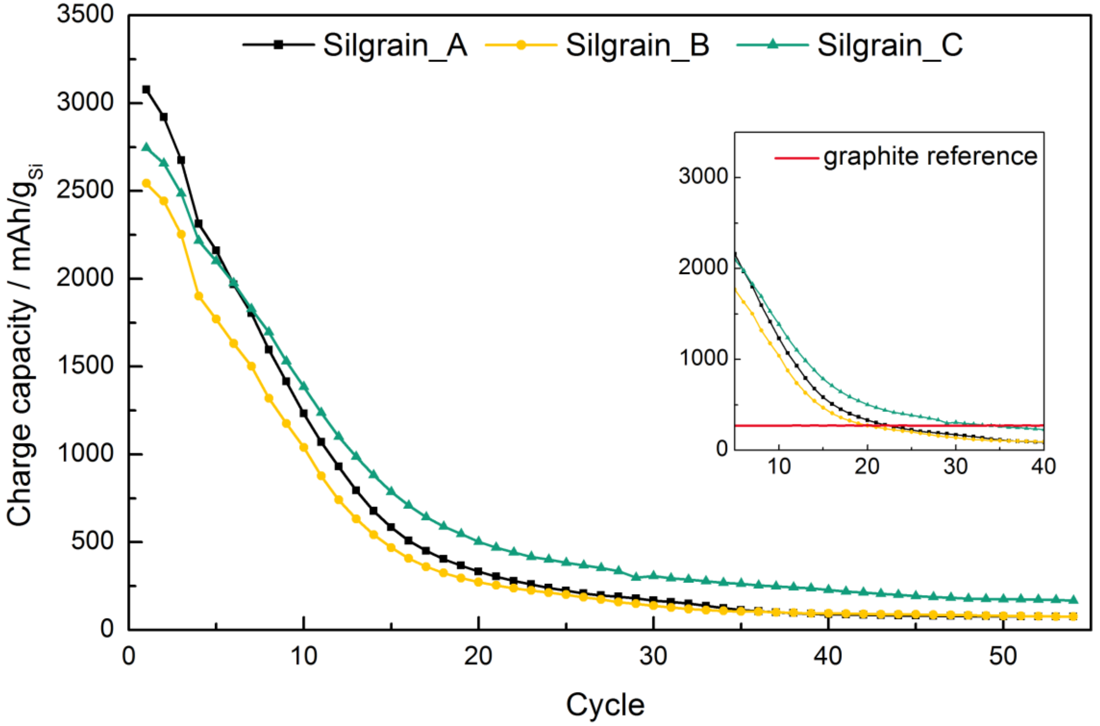
- Huge expansion of Si (> 280 %) when Li goes into the structure
  - Particle cracking
  - Re-formation of SEI
  - Poor cycling abilities
  - Contact issues to current collector / between the Si particles
  - Increased system resistance

«Can't we just test it…?»

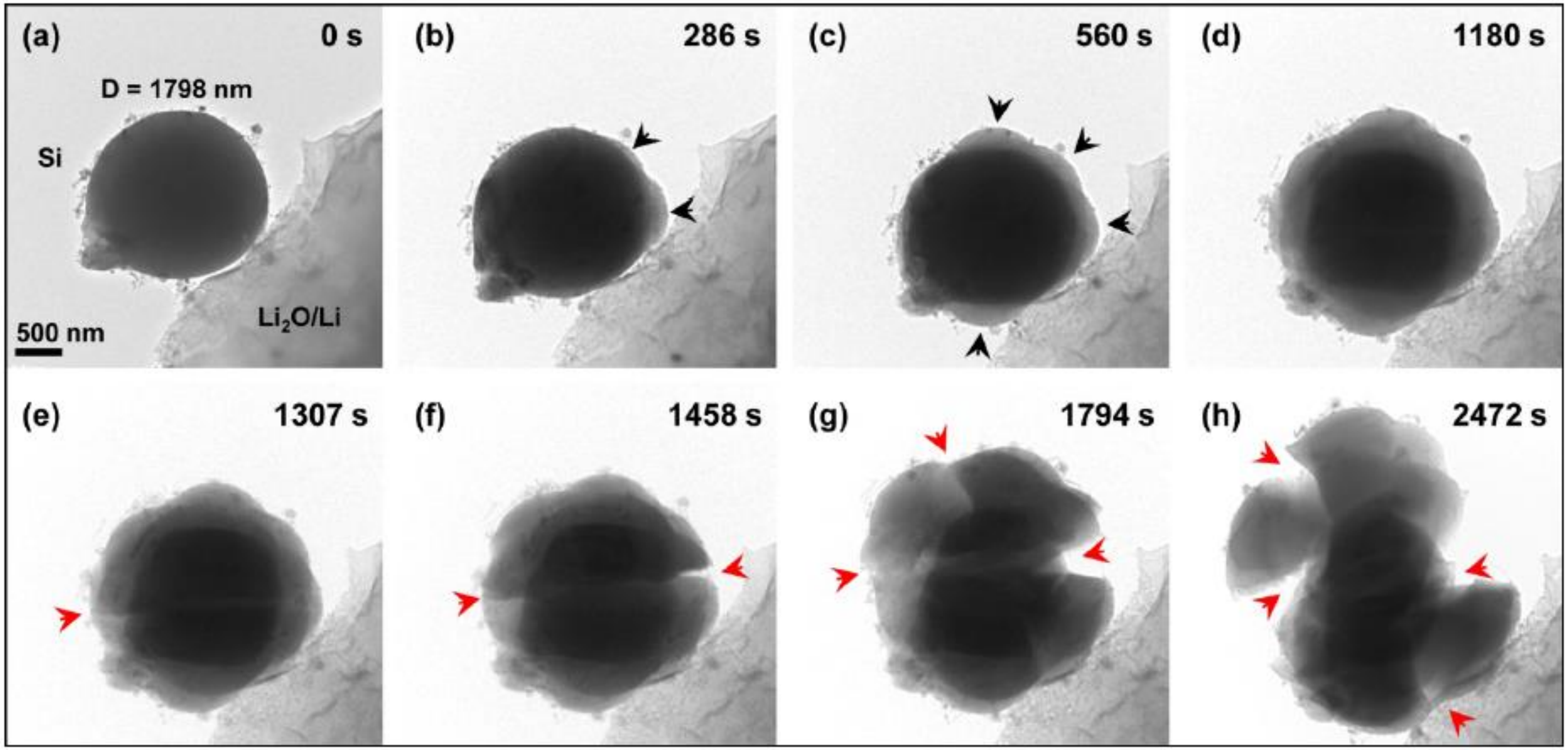
Cycle performance:

- Reach full capacity (1st cycle)
- Immediate capacity reduction
- Within 20 cycles, worse than graphite anodes

- Issues with composite needed to be resolved before Si could be optimized



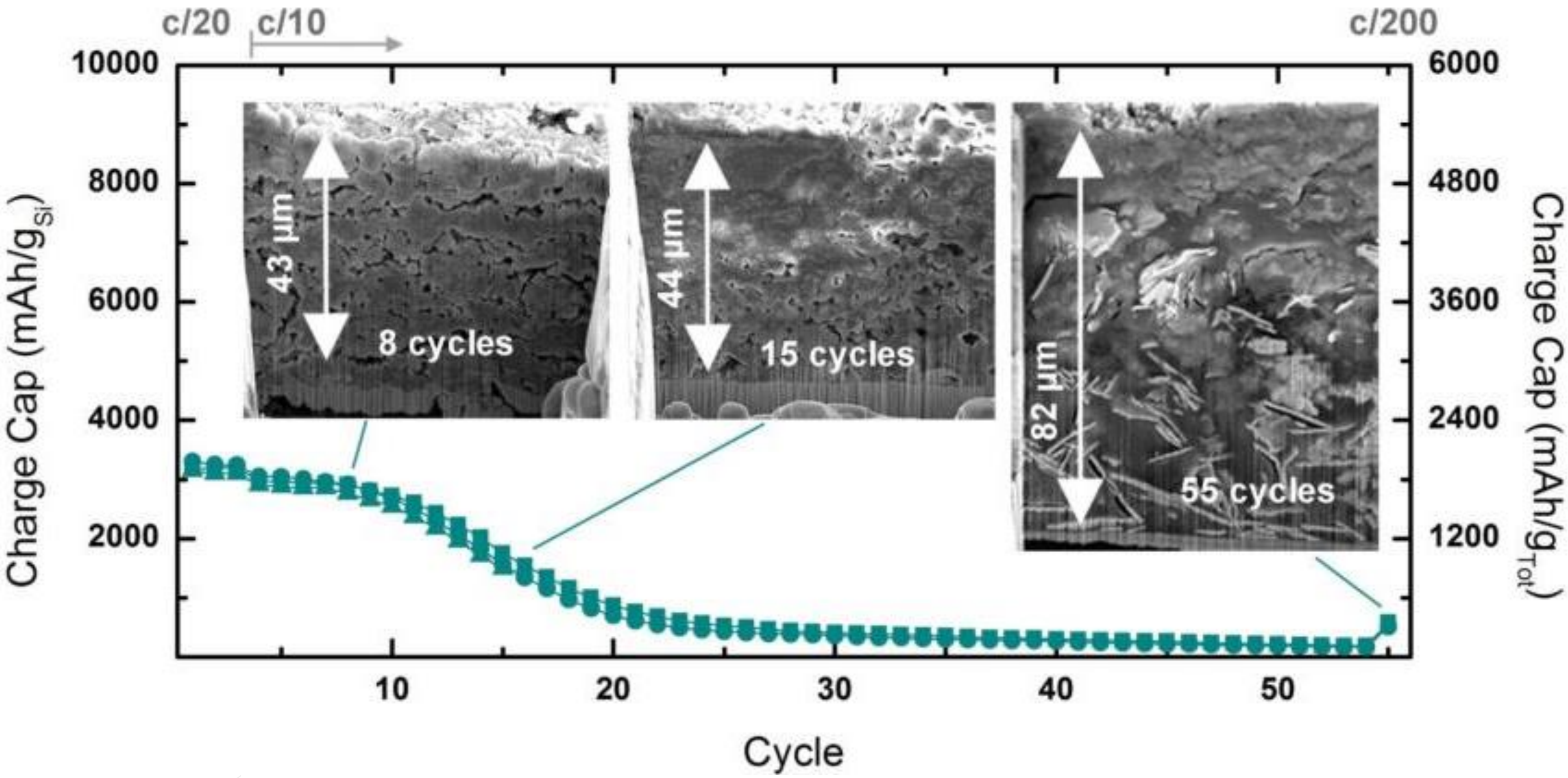
Si cracking (lessons from literature)



- Outer layer is first lithiated, afterwards middle region. Outer region cannot expand further and starts to crack.
- Need small particles

X.H.Liu et al, ACS Nano, 2012, 6 (2), p.1522-1531

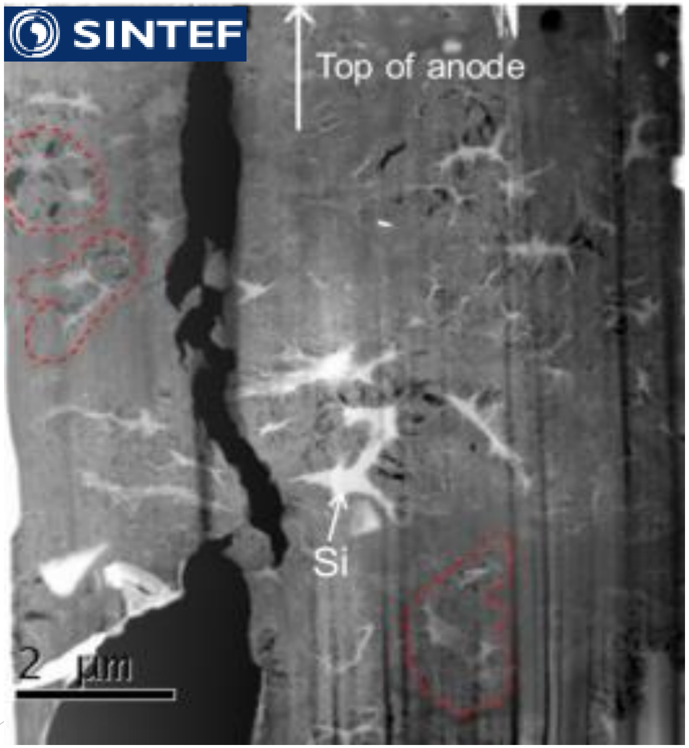
Silicon-‘migration’

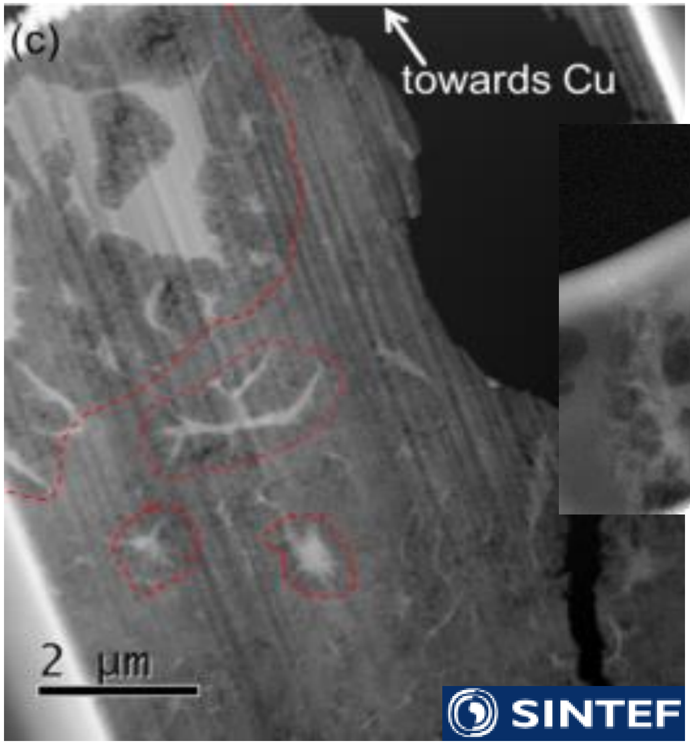


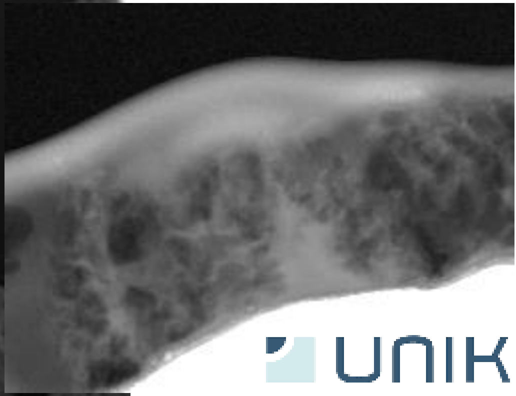
- Large increase in thickness (expansion of Si not reversible)
- Si seems to move with cycling. Accumulation of Si in upper region (closer to electrolyte)

Silicon «dendrites»

- After cycling, an electrochemical sintering and a dendrite structure is seen in the Si particles
- Si remains where Li is drawn out
- Red circle – indication of a fully lithiated particle



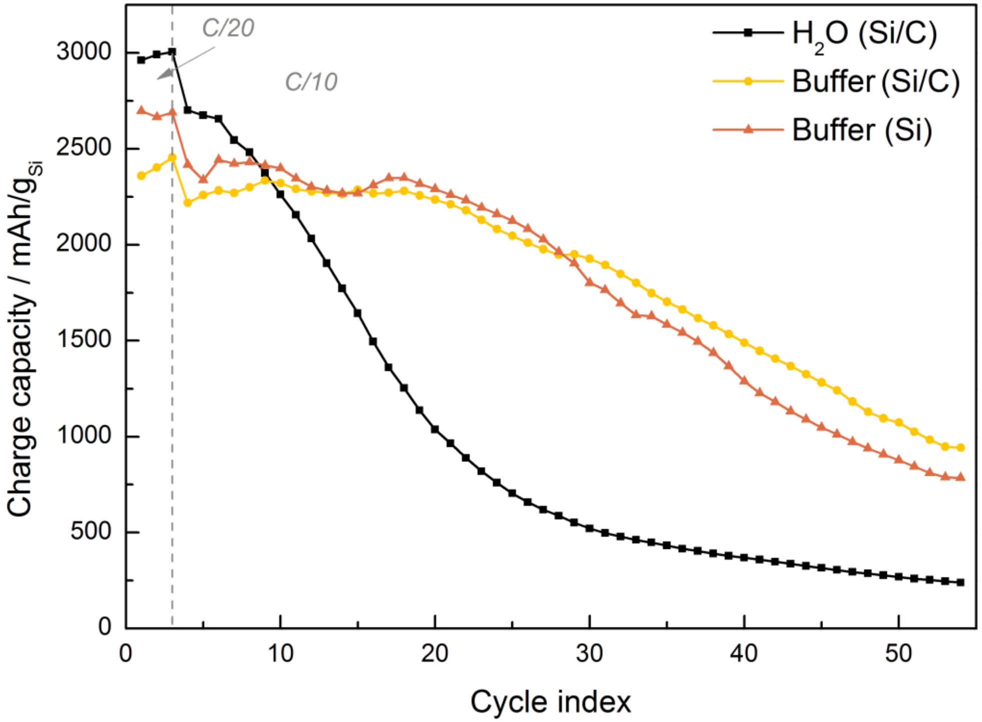




UNIK

Buffer as solvent

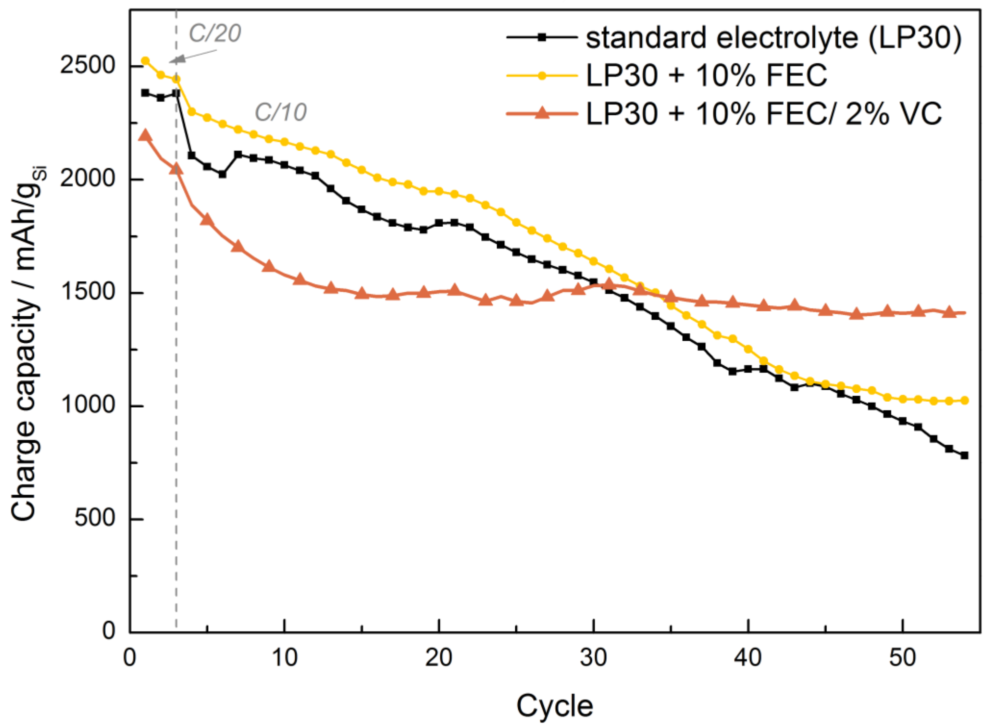
- Carboxymethyl cellulose (CMC) was used as a standard binder
  - Water soluble
- Large improvement by using buffer (pH 3) as solvent
- The low pH promotes covalent bonding of CMC
- Improved cycle life



D. Mazouzi et al., Journal of Power Sources, 220 (2012)

Additives to control SEI formation

- Electrolyte additives help the formation of protective coating
  - Stabilizes the SEI
  - Decompose prior to main electrolyte components
  - Form robust, protective film
- Testing various additives:
  - Fluoroethylene carbonate (FEC)
  - Vinylene carbonate (VC)
- Our results:
  - Stabilizes cycling performance
  - Dependent on the Si used

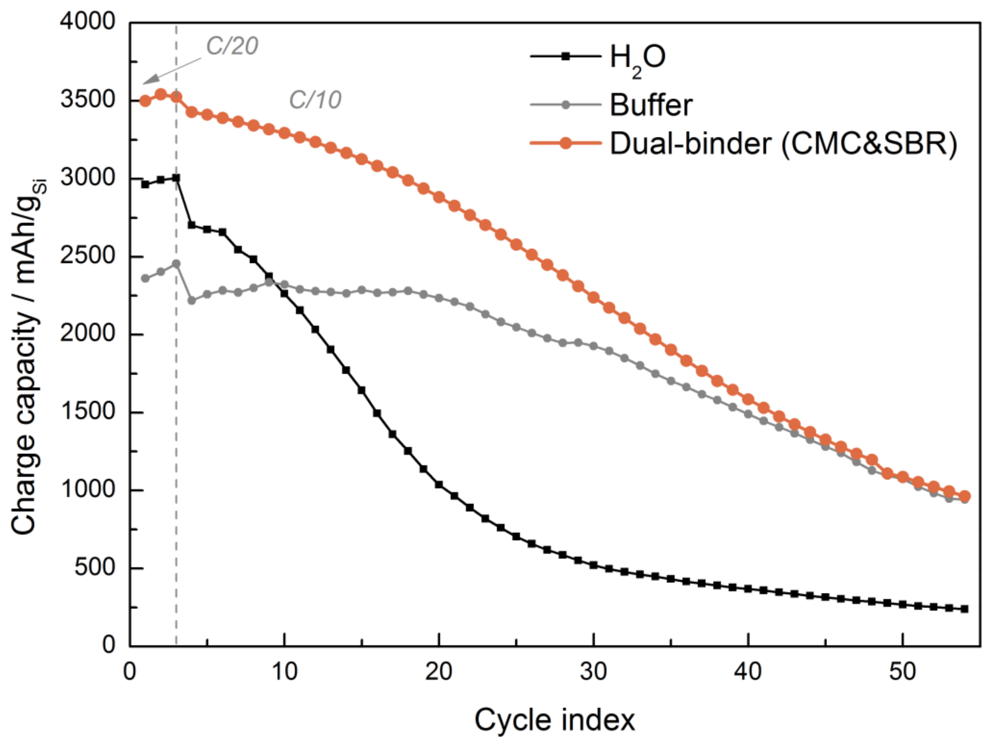


N.-S. Choi et al. / J. Power Sources 161 (2006) 1254–1259
L. Chen et al. J. Power Sources, 174 (2007), pp. 538–543

Binder improvements

- Using a dual-binder
  - Styrene-butadiene rubber (SBR) to improve adhesion to current collector
  - Carboxymethyl cellulose (CMC) is effective thickening agent

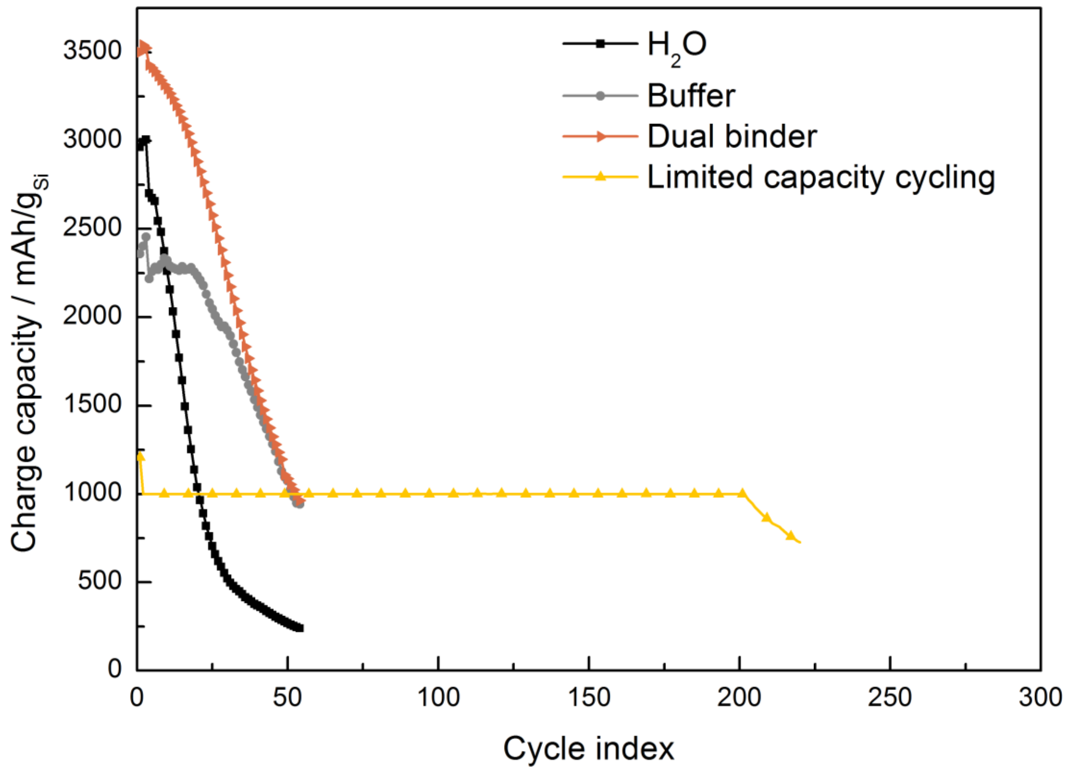
- Changes lead to minor improvements in cycle performance



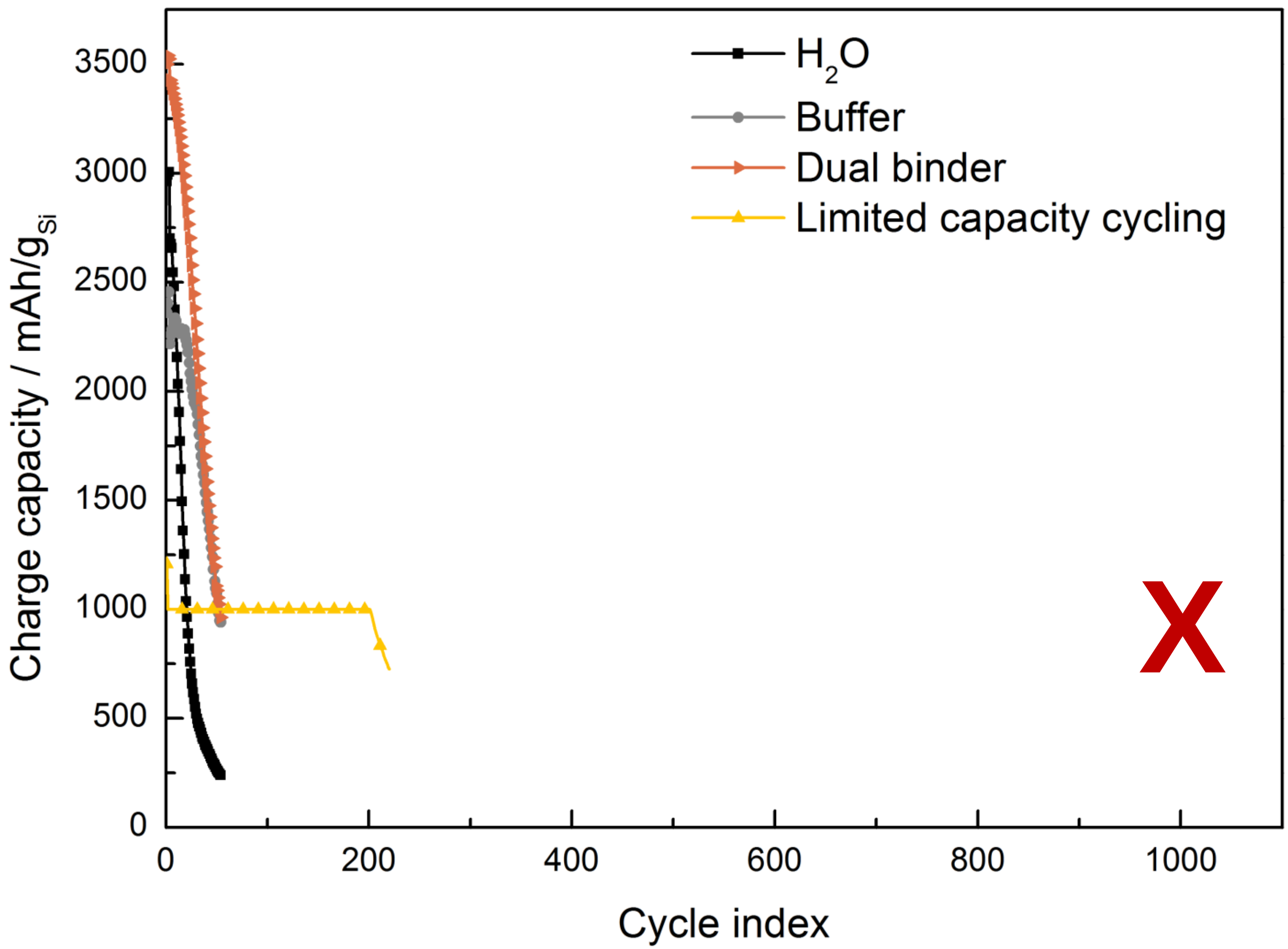
R. Zhang et al., Journal of Power Sources, 285 (2015)

Cycling with limited capacity

- By limiting the capacity taken from Si, the expansion can be reduced
- Capacity set to 1000 mAh/g_{Si}, end-voltage is fluctuating
- Anode can be cycled longer due to less stress on the electrode

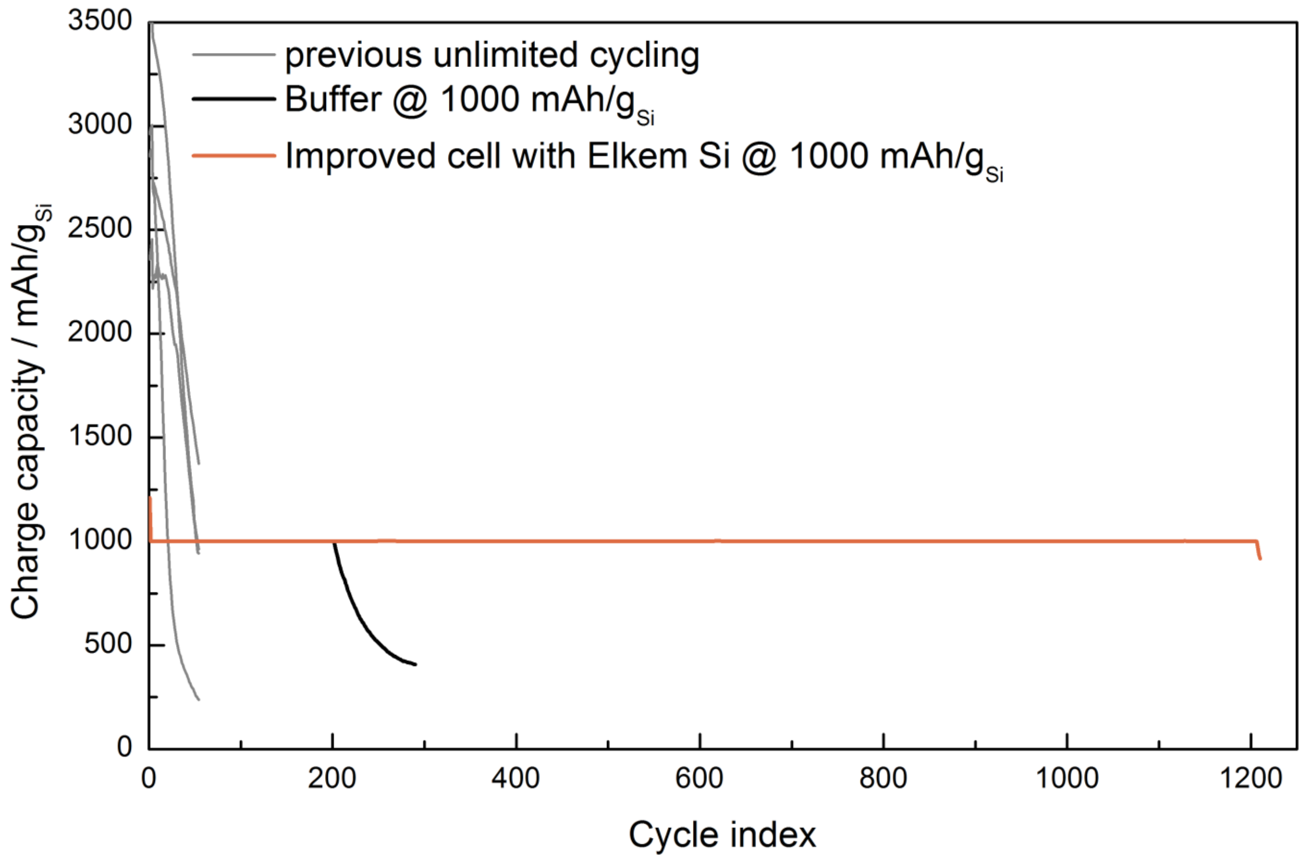


How to increase cycle number?

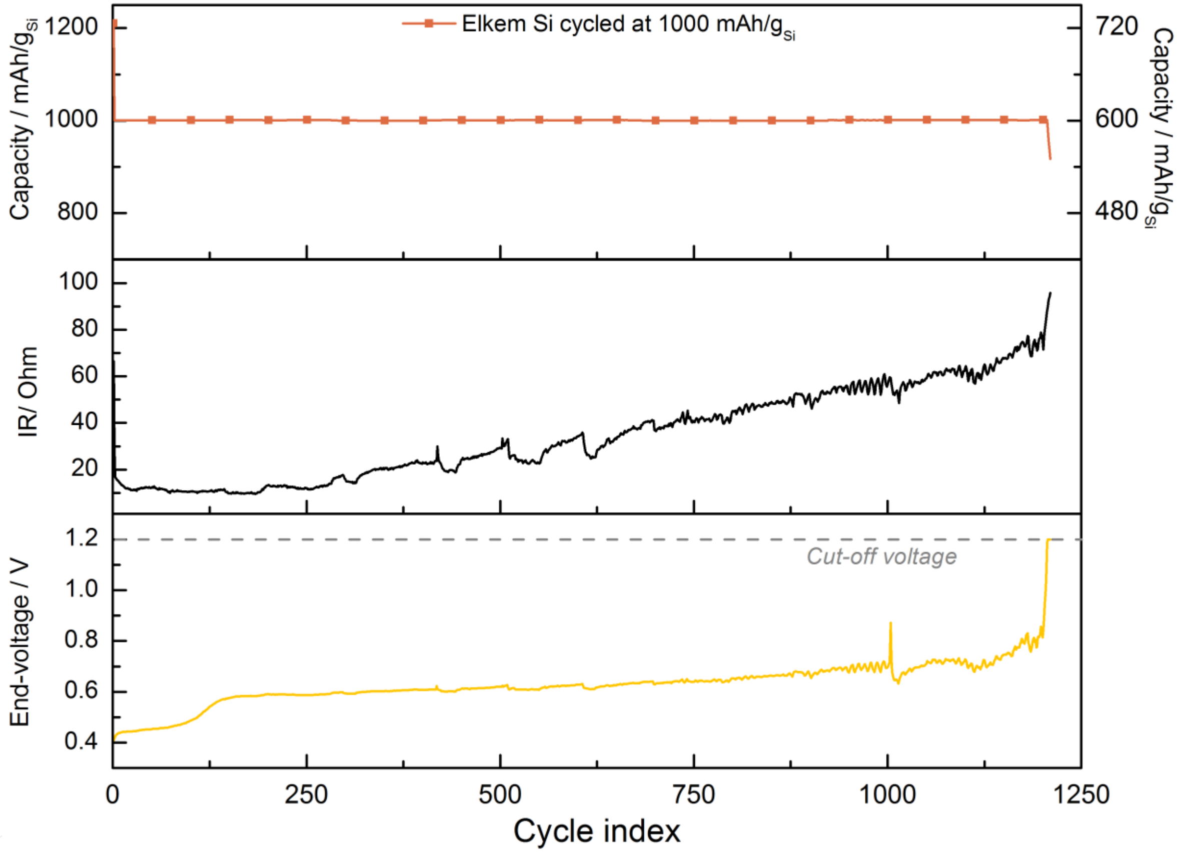


SiNODE breakthrough

- By combining the right improvement steps:
  - 1200 cycles
  - 1000 mAh/g_{Si}



What do we learn from 1200 cycles?

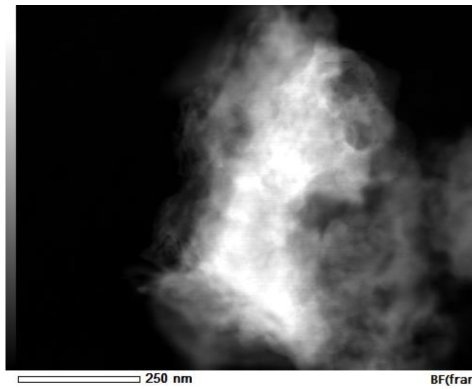


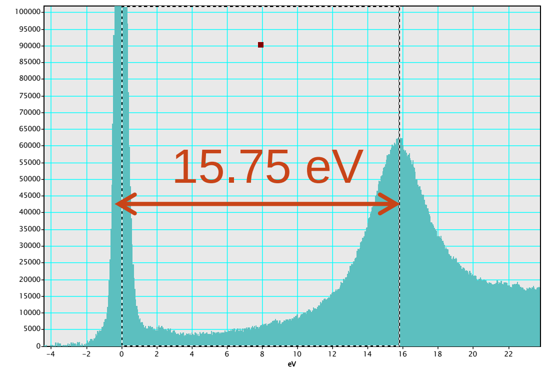
- Need to examine the degradation mechanisms happening while cycling
  - Monitor the internal resistance (IR) and the increasing end-voltage
  - Relate to differential capacity plot

What do we learn from 1200 cycle

Delithiated Si particle | HAADF STEM | Plasmon energy | Composition

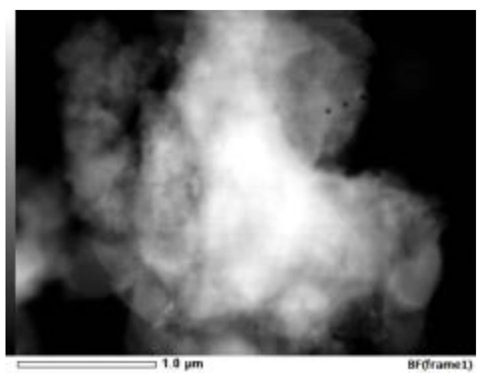
1

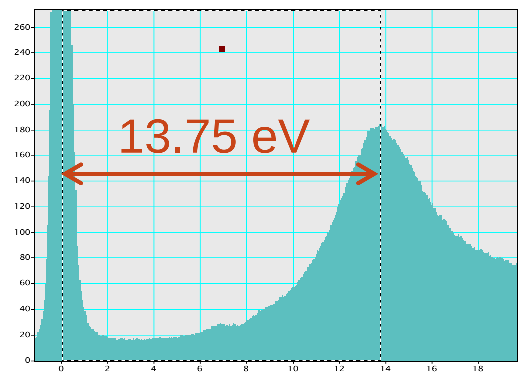




$Li_{0.5\text{-}1.0}Si$

2





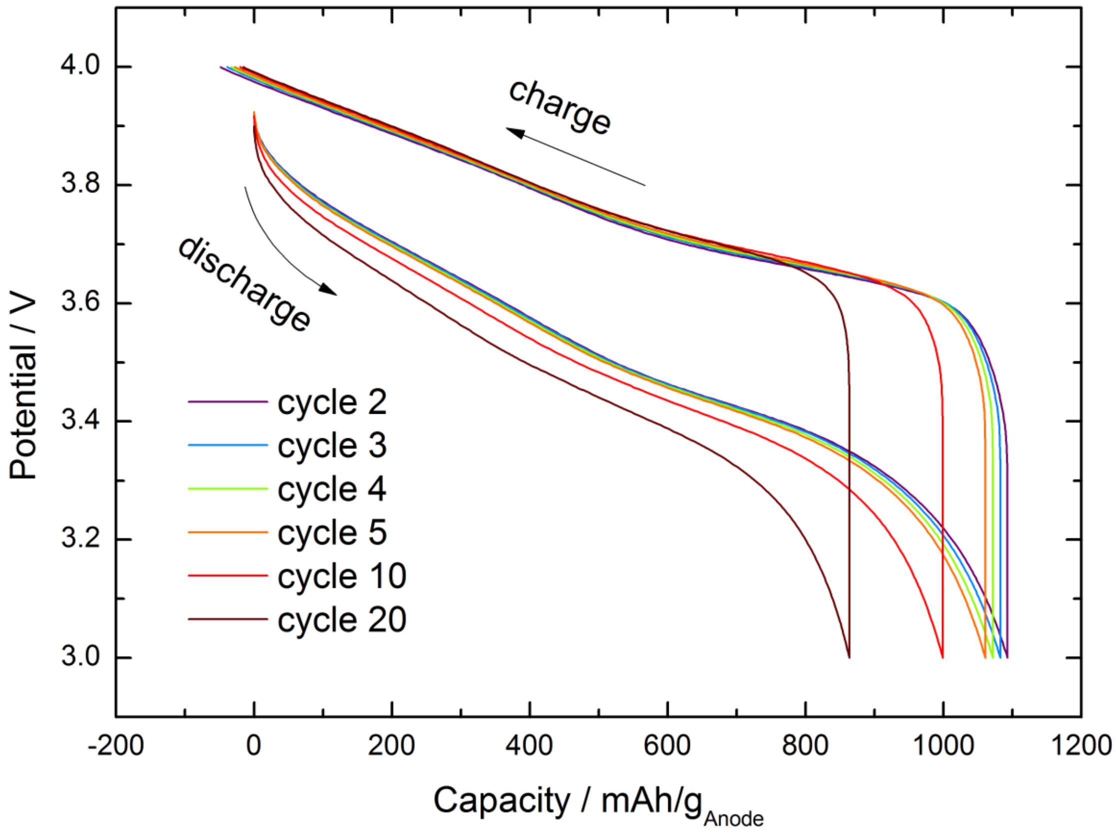
$Li_{2.3}Si$

Li_xSi		E_p (eV)
Si	(x = 0)	16.7
$Li_{12}Si_7$	(x = 1.7)	14.2
Li_7Si_3	(x = 2.3)	13.8
$Li_{13}Si_4$	(x = 3.3)	12.8
$Li_{22}Si_5$	(x = 4.4)	12.7
Li		7.5

- Inhomogeneous lithiation
- Composition of lithiated Si varies

The next challenge: full cell testing

- Realistic amount of Li and electrolyte
- Suitability with commercial cathodes
- Resolve slow degradation and lithium trapping issue



Silgrain® coupled with commercial LCO

Thank you for the attention!

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EDS analysis of Si migration