Contrasting Stress Evolution During Lithiation and Delithiation of Different Electrode Materials for Thin Film Batteries

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Karlsruhe Institute of Technology: Reiner Mönig, Dominik Kramer

- Why integrated thin film batteries
- High capacity Li-ion electrode materials, mechanical stress and failure:
  - Si and Ge (anode)
  - RuO_2 (cathode)
- Origins and implications of differences

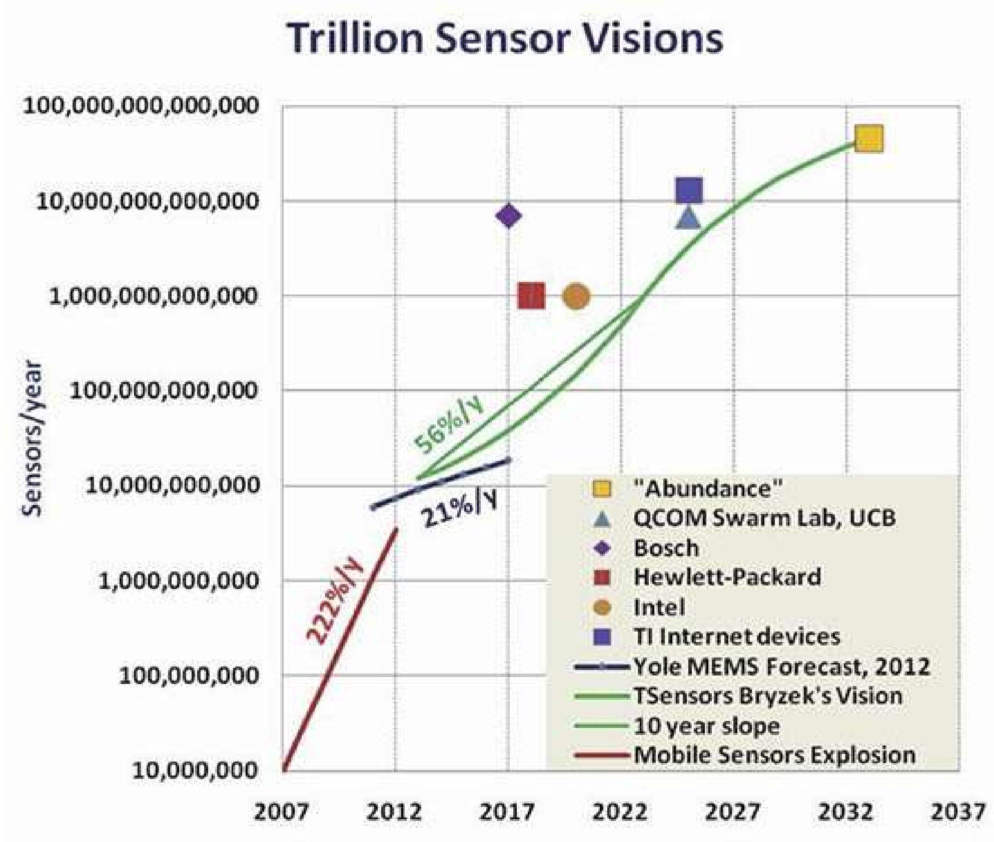
Massachusetts Institute of Technology

* Primary student contributor to work on Ru oxide

MIT MATERIALS RESEARCH LABORATORY

Integrated Thin Film Microbatteries in Microsystems

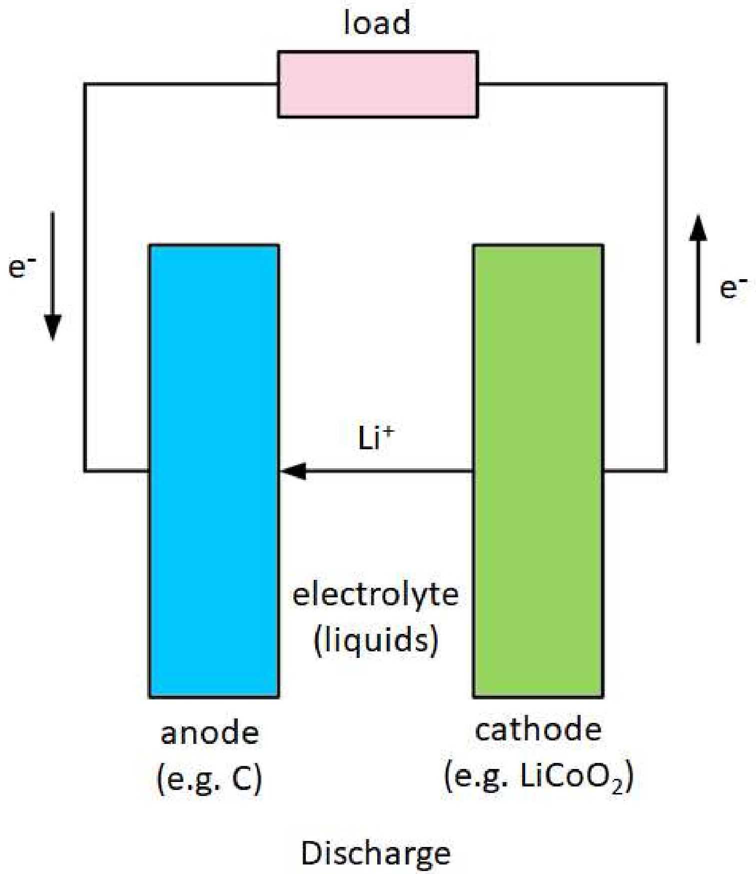
- **Autonomous microsystems:** for the "Internet of Things": integration of energy harvesting, energy storage, Si IC information processing and data storage, sensing devices, and broadcast devices.



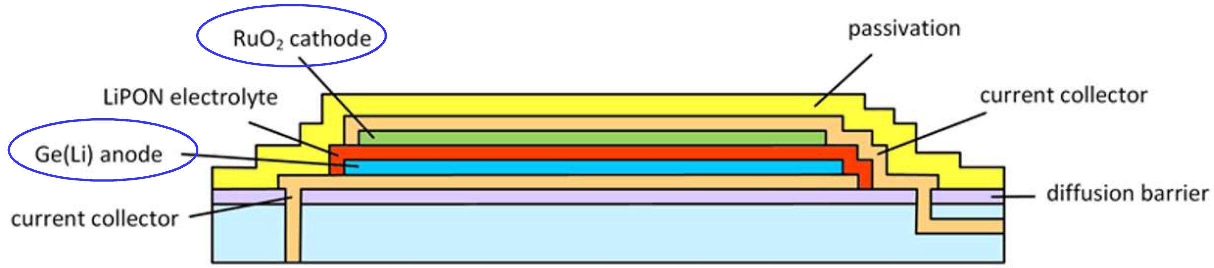
Efficiency, convenience and safety through monitoring health, energy use, transportation, the environment....

Sensors Summit, Stanford University [http://tsensorssummit.org/Resources/TSensors%20Roadmap%20v1.pdf]

Batteries: Mechanisms and Definitions

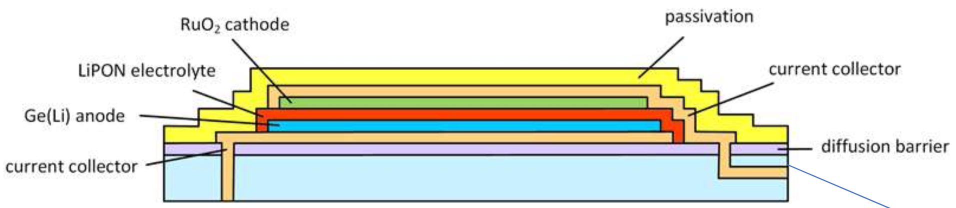


The anode is the negative electrode
during discharge



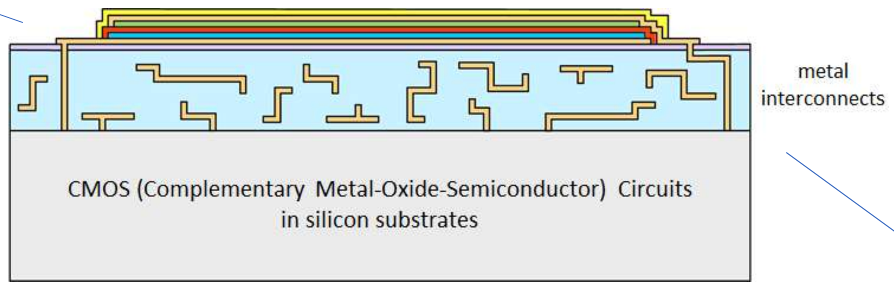
LiPON is a solid state electrolyte

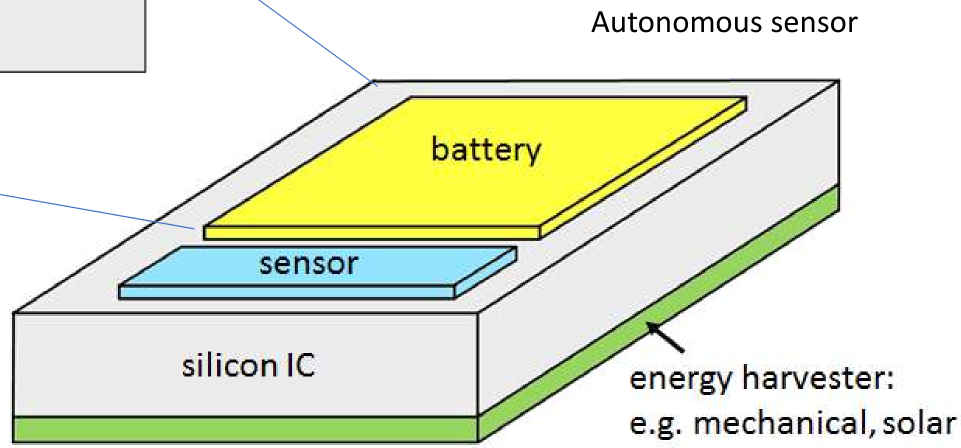
High-Performance Thin Film Batteries Integrated with CMOS Microsystems



Our Goals: New Materials and Processes

- Patterned devices
- **No metallic Li**
- **Room temperature processing**
- **3 to 10X performance improvement**





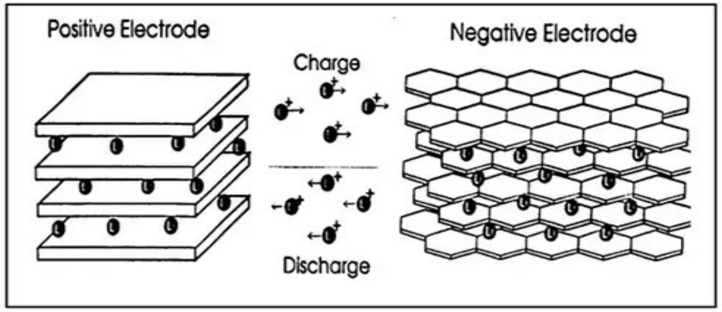
CMOS-compatible Processing and Operation

Autonomous sensors

- fabricated on silicon using conventional processes
- small, low cost

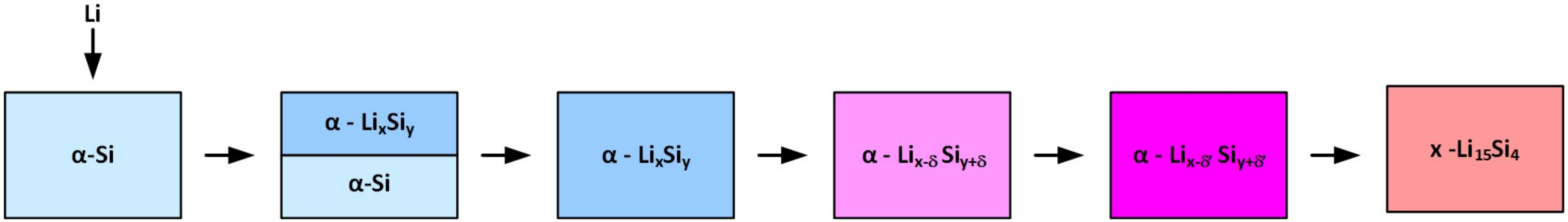
Mechanism of Li Storage in High-capacity Electrodes

Conventional: Intercalation
(e.g. graphite, **400mAh/g)**



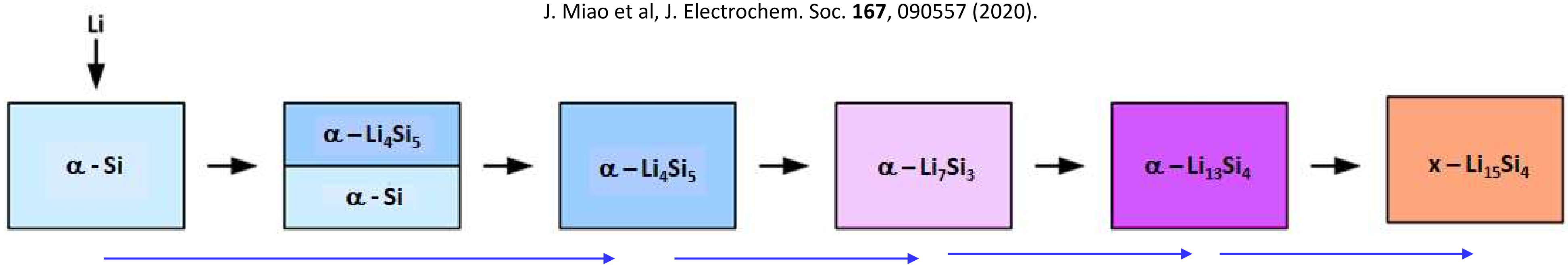
https://www.digikey.com/en/articles/techzone/2016/sep/a-designer-guide-fast-lithium-ion-battery-charging

High capacity: phase transitions (e.g. Si, **3600mAh/g**)



Phase Transition Mechanisms During Lithiation/Delithiation of Si and Ge

J. Miao and C.V. Thompson, J. Electrochem. Soc. **165**, A650 (2018).
J. Miao et al, Phys. Rev. Materials **4**, 043608 (2020).
J. Miao et al, J. Electrochem. Soc. **167**, 090557 (2020).

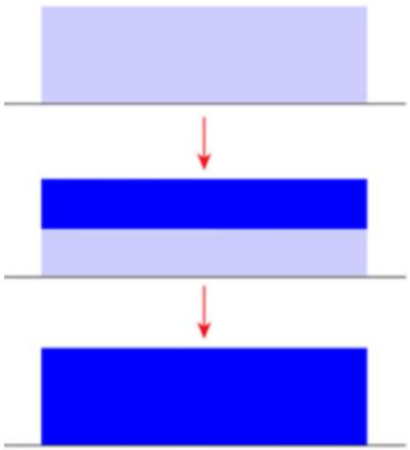


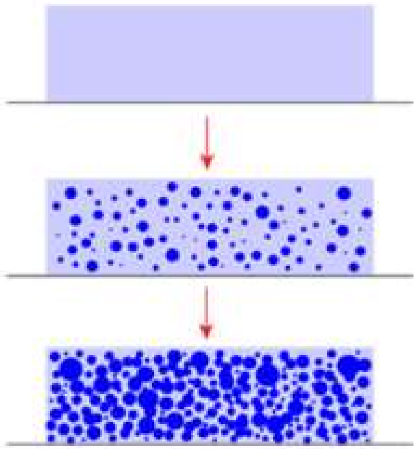
Discontinuous:
Propagation of a planar interface

Discontinuous:
Nucleation and growth

Discontinuous:
Nucleation and growth
(Often not observed in Si films)

1st cycle





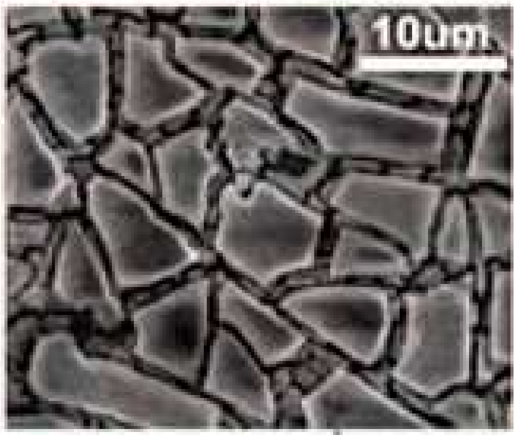
Phase sequence and mechanisms in Si and Ge are the same.

Thin Film Silicon Anodes

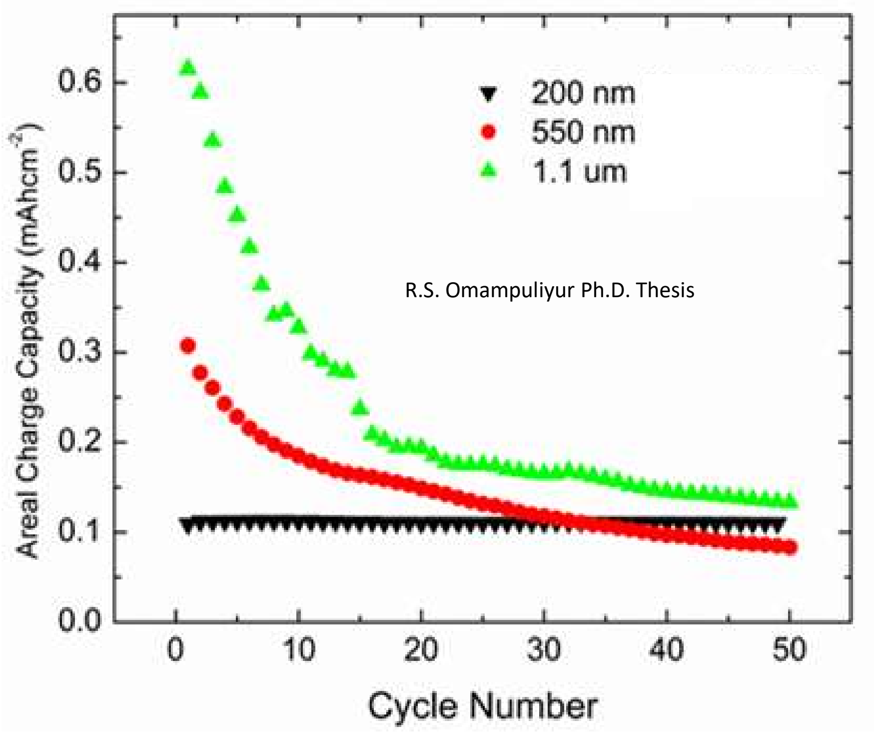
Si has the highest known gravimetric capacity for anode materials, up to 3600mAh/kg (vs. 400mAh/kg for C)

However,

~350% volume change



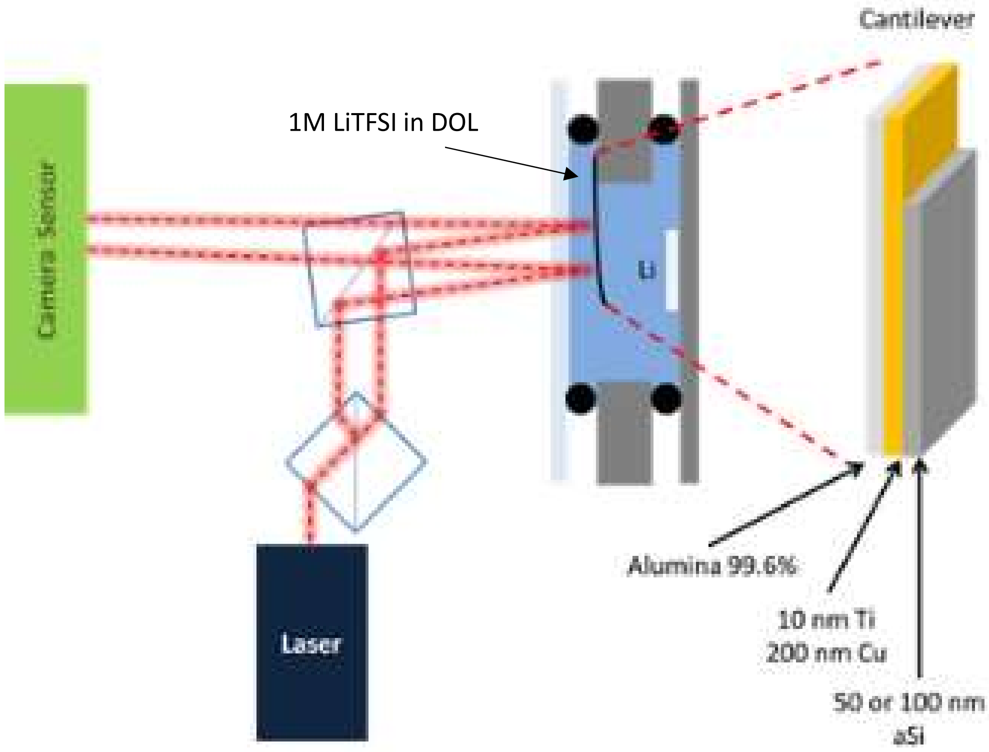
- Cracking under tension during delithiation
- Spalling and pulverization during cycling



LiTFSI in 1,3 Dioxolane (DOL)

Mechanical Stress Evolution During Lithiation and Delithiation of Si and Ge

In situ stress measurements with and without solid electrolyte (LiPON) coatings



Stoney's eqn.

$$\sigma_f h_f = \frac{\tilde{E}_s h_s^2}{6} \kappa$$

σ_f = average stress in the film

h_f = film thickness

$\tilde{E}$ = biaxial modulus of substrate

h_s = substrate thickness

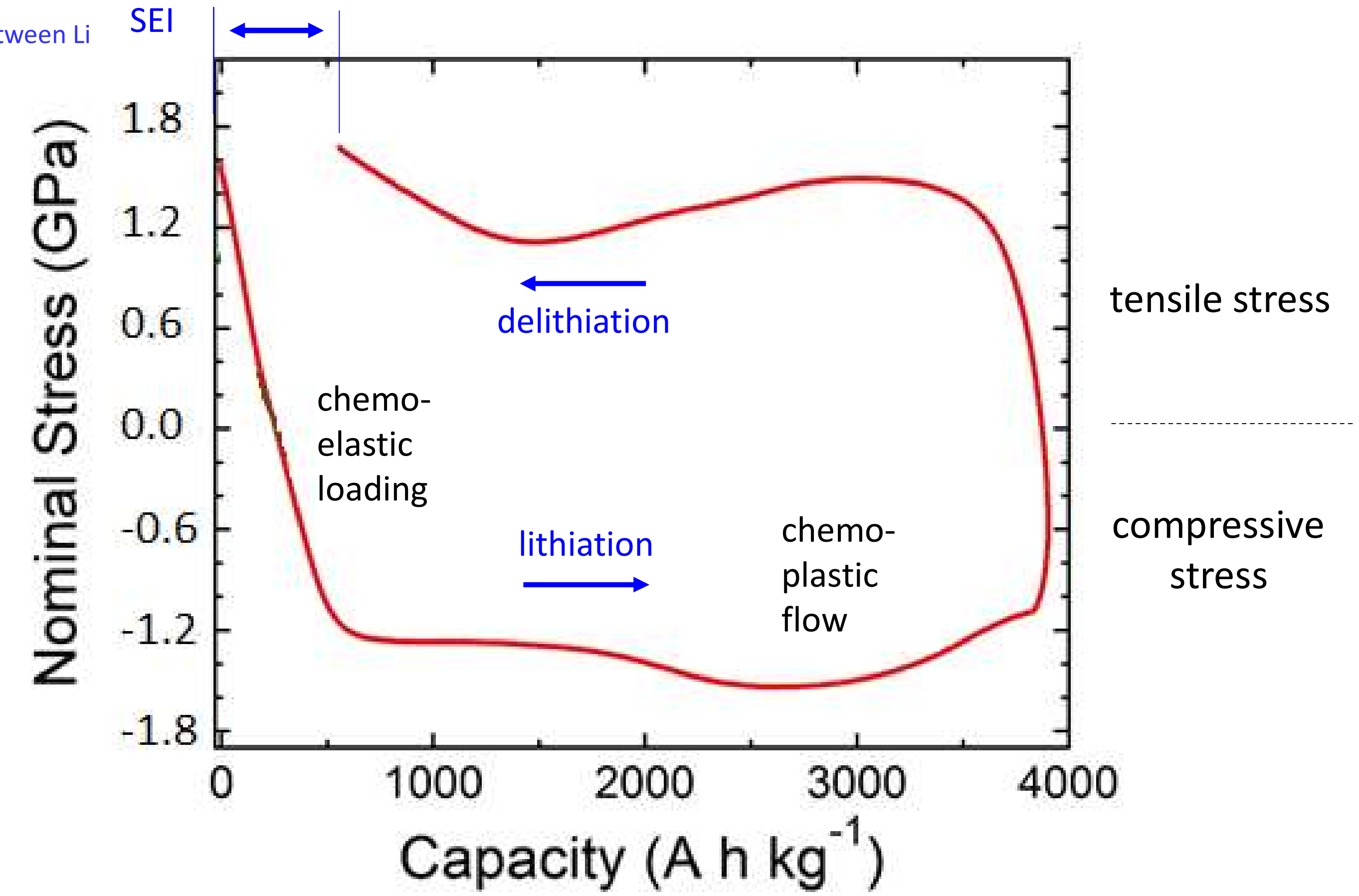
κ = substrate curvature

Collaboration with Reiner Mönig and Dominik Kramer, Karlsruhe Institute of Technology

Mechanical Stress Evolution During Lithiation and Delithiation of Si

Solid Electrolyte Interphase: Irreversible side reaction between Li and the electrolyte and the electrolyte.

$\sigma_f \, h_f$



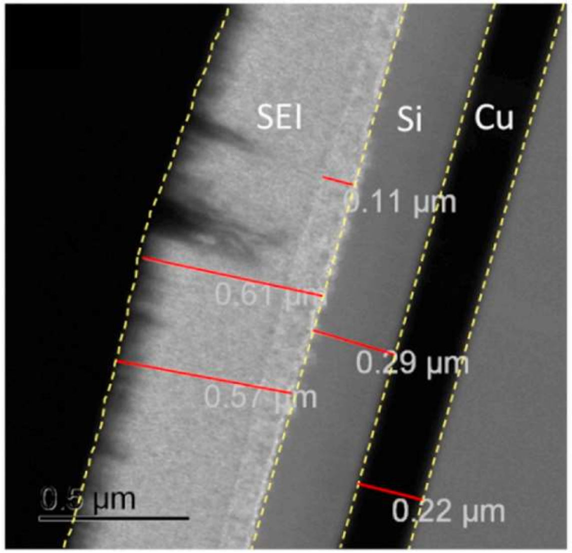
LiTFSI in 1,3 Dioxolane (DOL)

Nominal stress = measured quantity, $\sigma_f \, h_f$, divided by the initial film thickness

Solid Electrolyte Interphase (SEI) Layer

Most electrode materials (anode or cathode) in most liquid electrolytes and salts

- *Irreversibly* form an SEI layer on their surface, that is a
- Result of reaction with the electrolyte and the salt, and that is
- *Composed of a range of organic compounds, insoluble lithium salts and Li-oxides,* and that is
- Dependent on the electrolyte and salt used, and this
- *Consumes some of the electrode material.*

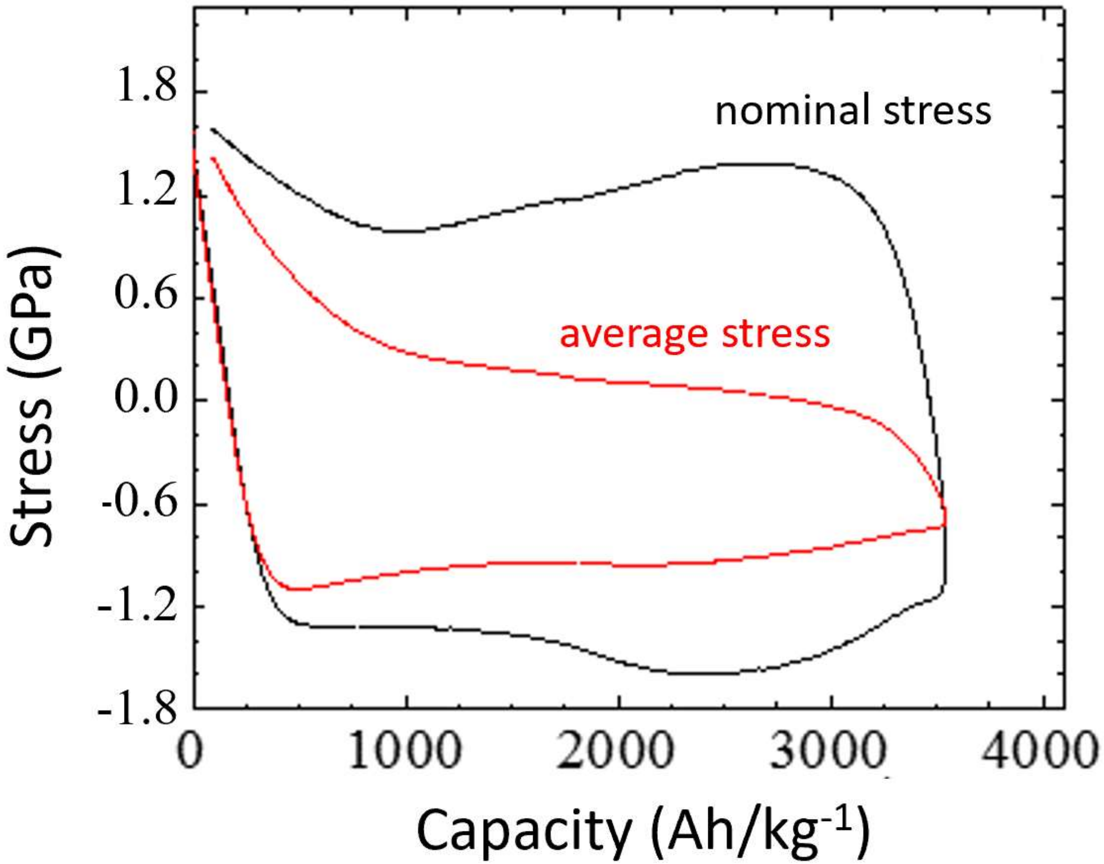


K. Guo, Nano Energy 68, 104257 (2020)

P. Saha et al, Chap.6, Silicon Anode Systems for Lithium-Ion Batteries (2022)

Nominal Stress vs. Average Stress

$$\boldsymbol{\sigma_f h_f} = \frac{\tilde{E}_s h_s^2}{6}\,\kappa$$

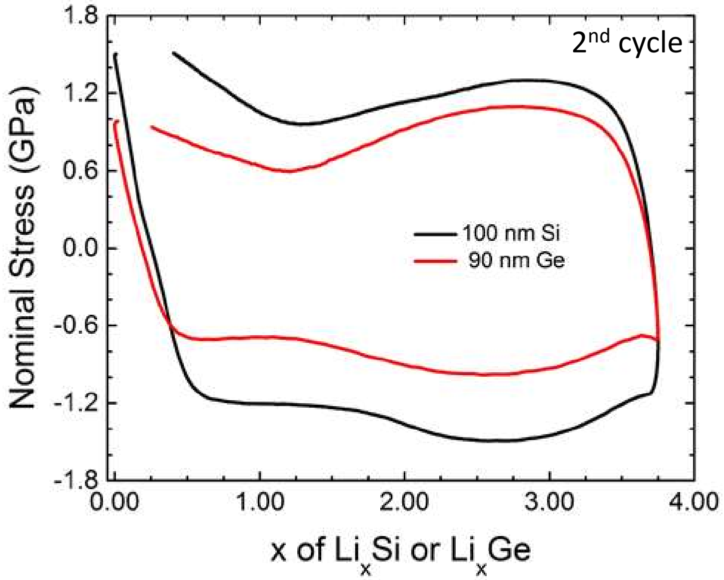


Nominal stress = $\sigma\ h_f$/ (initial film thickness)

Average stress = $\sigma\ h_f$/(estimated film thickness)

Germanium vs. Si

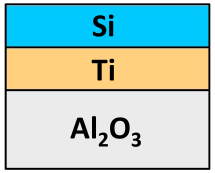
Anode	Theoretical Gravimetric specific capacity (mAh g^{-1})	Theoretical Volumetric specific capacity (mAh $cm^{-2}\mu m^{-1}$)
Si	3576.5	0.83
Ge	1383.7	0.74



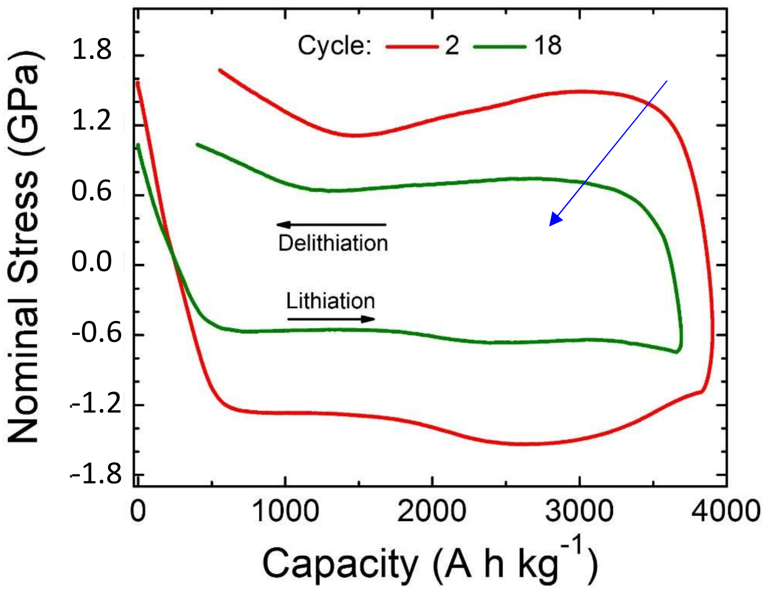
Comparable volumetric specific capacity (what matters in thin film batteries)

- Lower flow stresses, a bit more mechanically robust
- Charges and discharges faster

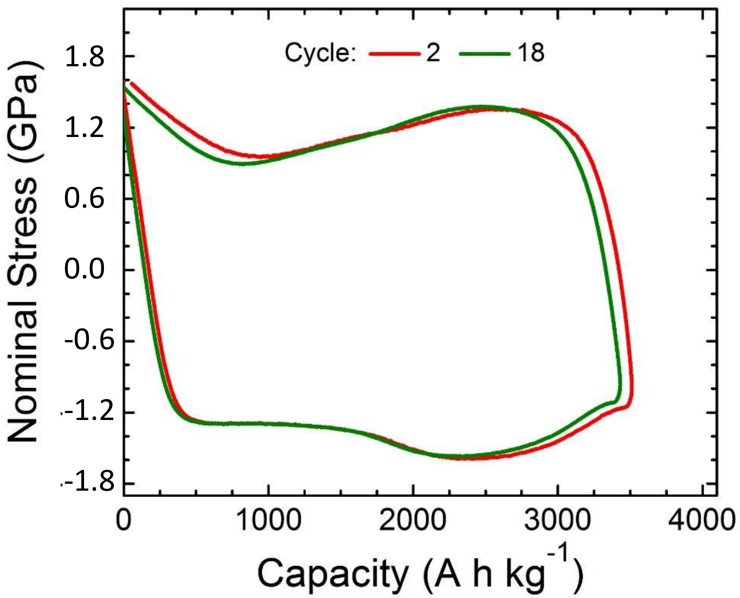
Stress vs. Capacity: Si vs. Silicon/LiPON



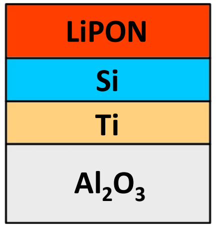
Si without LiPON coating



Si with LiPON coating



h_{Si} = 100nm, h_{LiPON} = 600nm



- LiPON mechanically stabilizes silicon.
- This leads to **improved cyclability**.
- LiPON significantly **reduces** Li loss to **SEI formation**.
- Mechanical and chemical stabilization allows mechanical and electrochemical studies with reproducible structure evolution.

A. Al-Obeidi, D. Kramer, R. Mönig, and C.V. Thompson, Appl. Phys. Letts **109**, 071902 (2016).

Cathode Materials

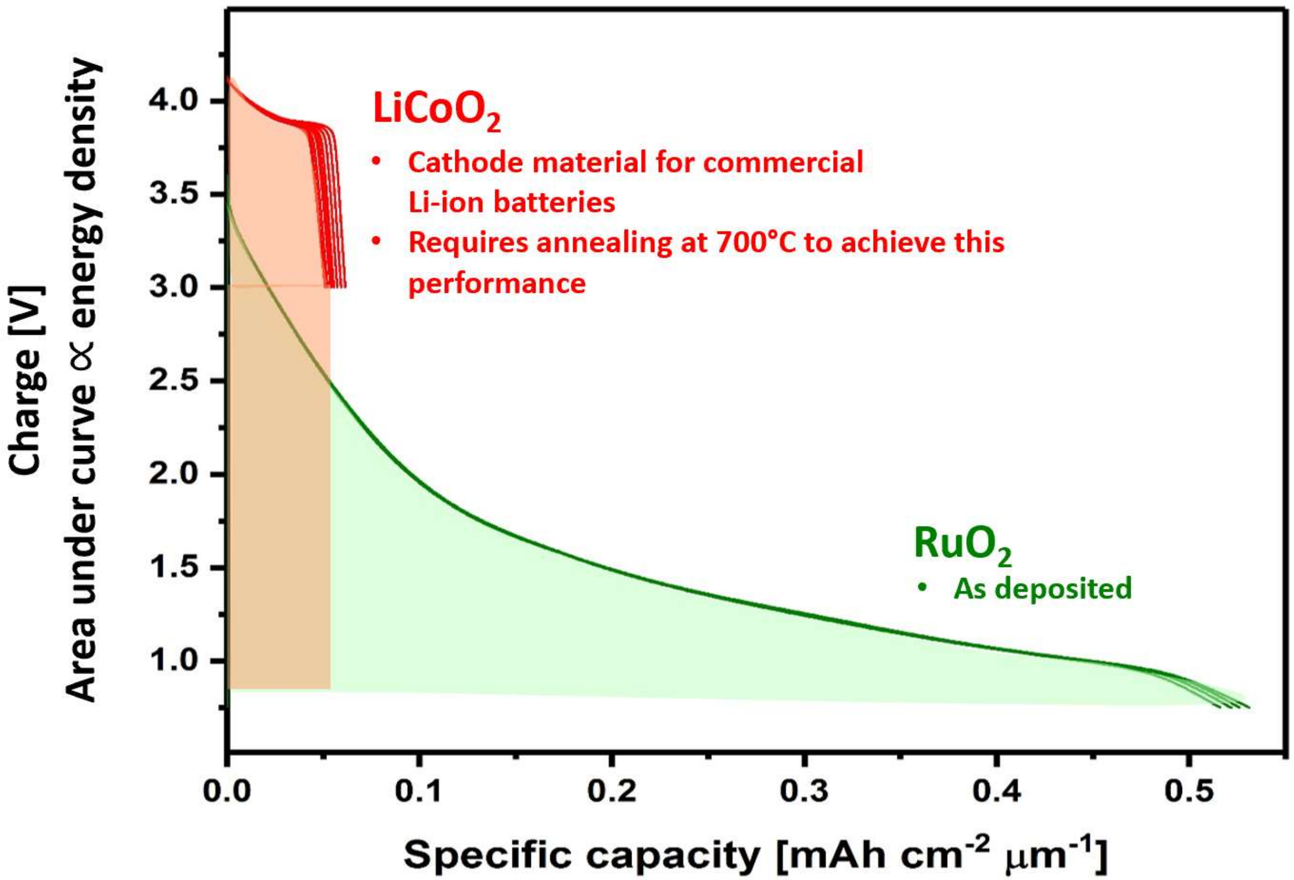
Cathode materials	Voltage vs. Li/Li^+ [V] (1)	Volumetric specific capacity [μAh/cm²μm]	Volumetric specific energy [μWh/cm²μm]
$LiCoO_2$	3.9	64	248
$LiMn_2O_4$	4.0	63	250
$LiNi_{0.5}Mn_{0.5}O_2$	4.0	65	260
RuO_2	2.2	562	1014

C. M. Haynes et al, Ann. Rev. of Chemical and Biomolecular Eng. 3 (2012) 445-471.

- $LiCo_2$ and LMNO films must be deposited or annealed at ≳ 650 °C to have high capacity for Li.
- Deposited RuO_2 has high capacity as deposited at room temperature. This is important for compatibility with CMOS processing.

D. Perego, J.H.S. Teng, X. Wang, Y. Shao-Horn, and C.V. Thompson, Electrochimica Acta **283**, 228 (2018).

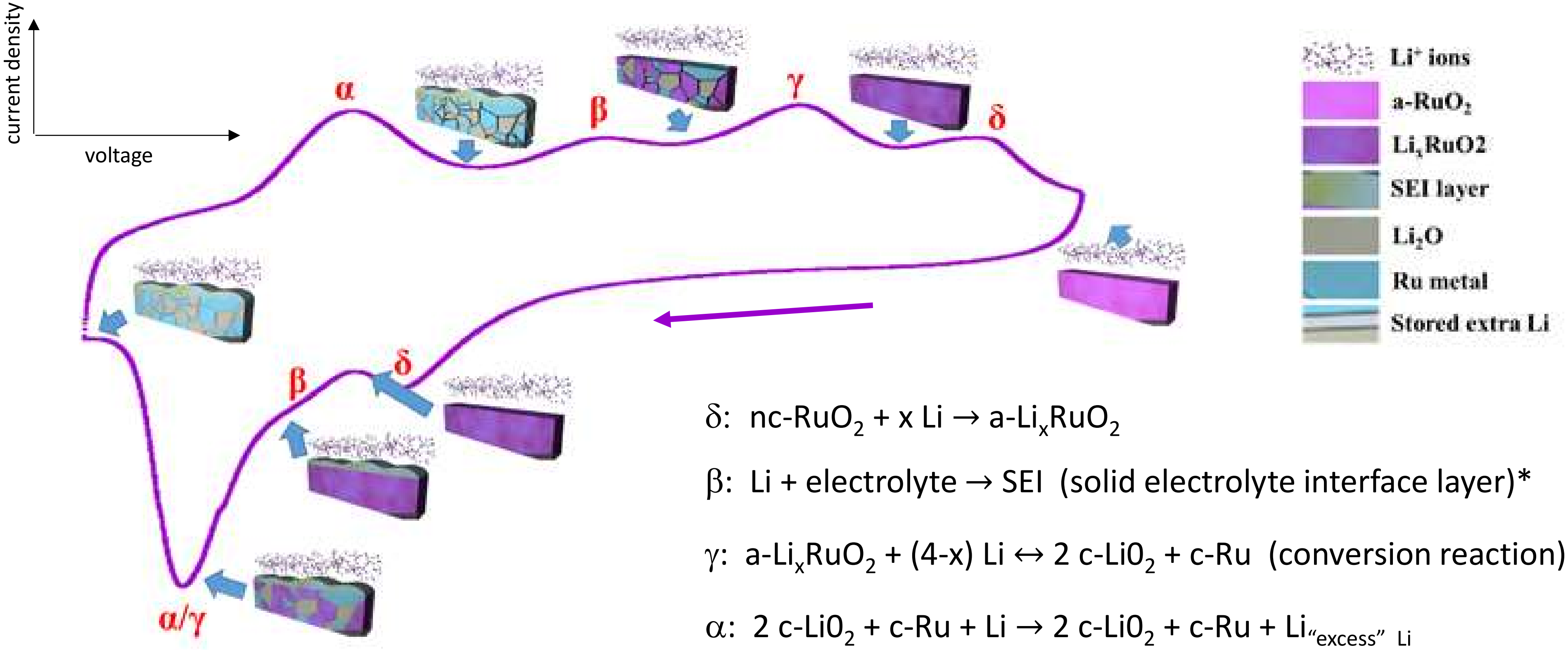
RuO_2 Cathodes: Half Cell Energy Density



- IC's operate at < 1V
- Control circuits are required to step-down the voltage in both cases

- 5x measured volumetric energy density of $LiCoO_2$

Li Storage Mechanisms in RuO_2



δ: nc-RuO_2 + x Li → a-Li_xRuO_2

β: Li + electrolyte → SEI (solid electrolyte interface layer)*

γ: a-Li_xRuO_2 + (4-x) Li ↔ 2 c-$Li0_2$ + c-Ru (conversion reaction)**

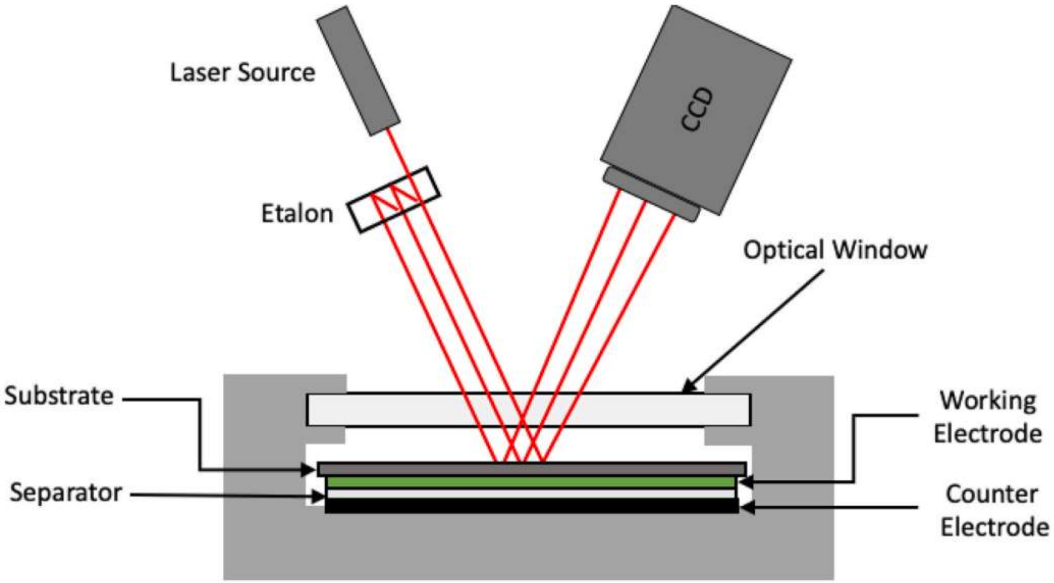
α: 2 c-$Li0_2$ + c-Ru + Li → 2 c-$Li0_2$ + c-Ru + $Li_{\text{“excess” Li}}$

* Forms and disassociates reversibly (very unusual)

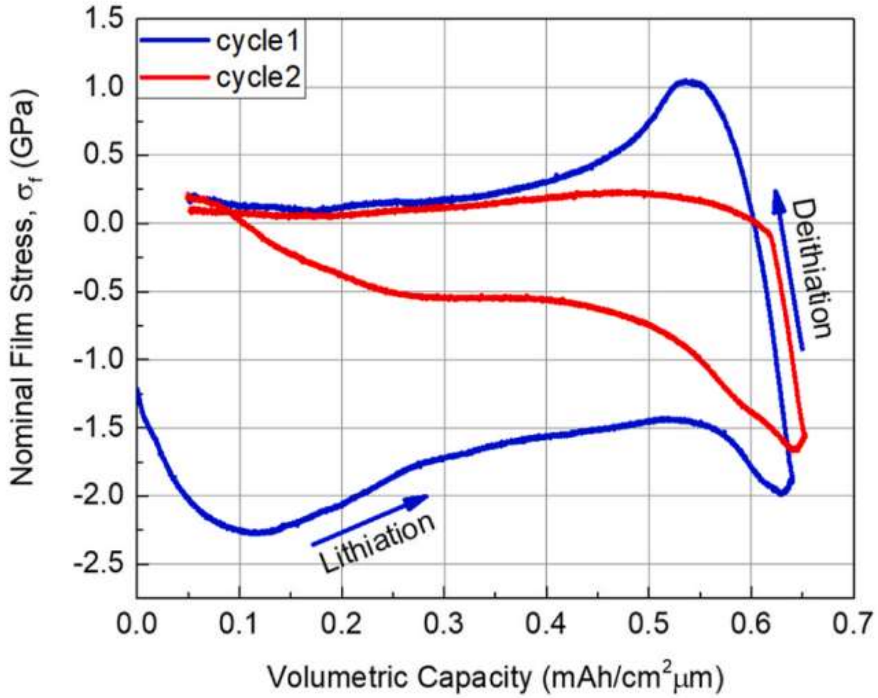
** Slow kinetics limits overall cyclic efficiency

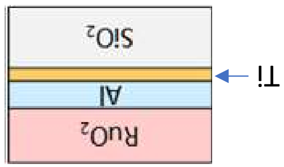
L. Xu and C.V. Thompson, J. Mater. Chem. A **8**, 21872 (2020).

Measurement of Stress in RuO_2 films



Multibeam Optical Stress Sensor



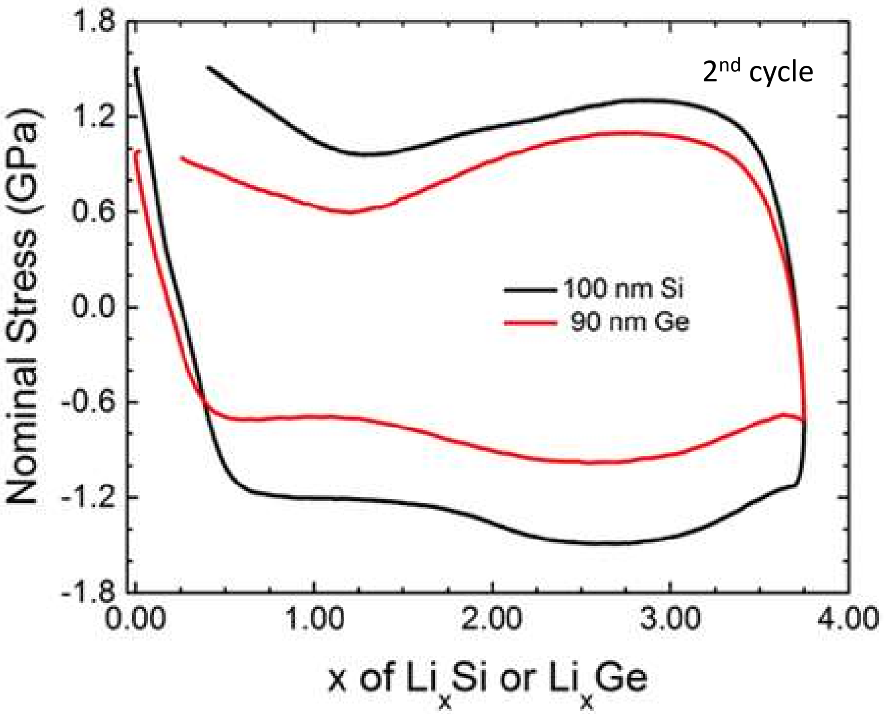


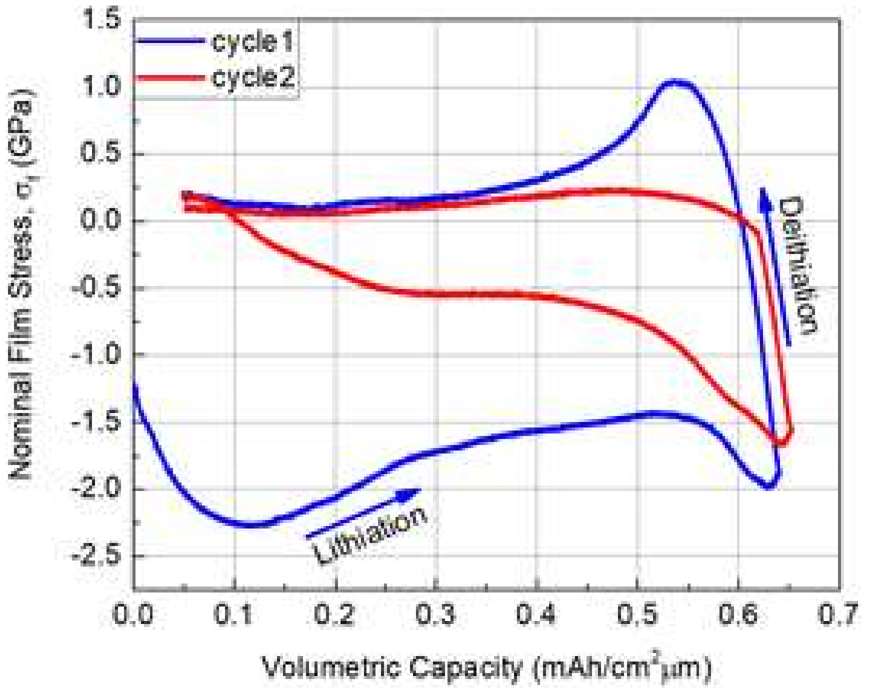
2nd cycle:

- Relatively low compressive stress.
- Very low tensile stress
- Full expected capacity

L. Xu, M. J. Chon, B. Mills, and C. V. Thompson, J. Power Sources **552**, 232260 (2022).

Comparison of Ge and Si with RuO_2



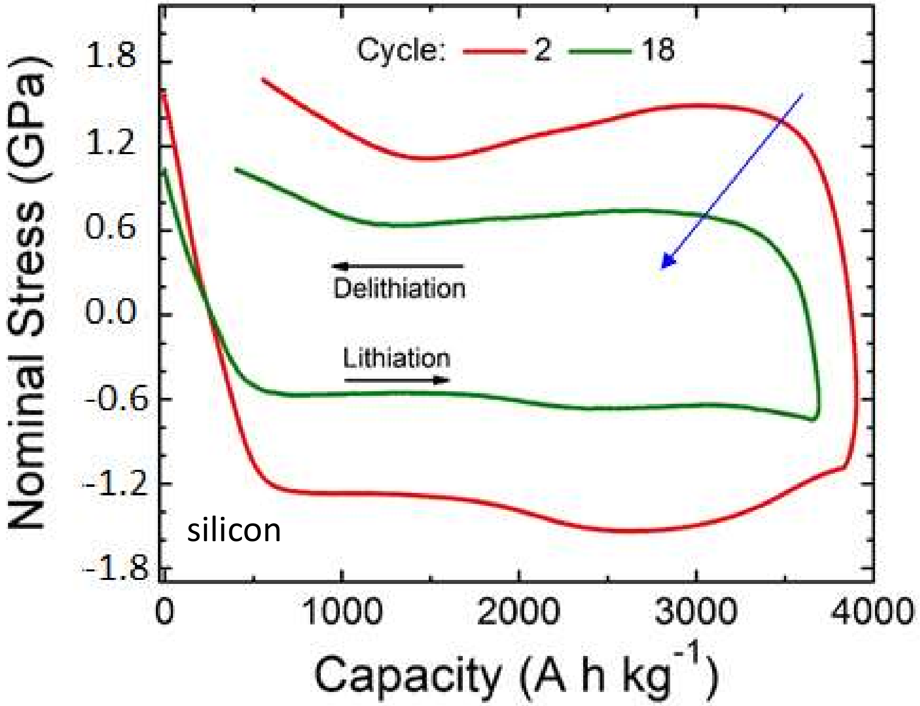


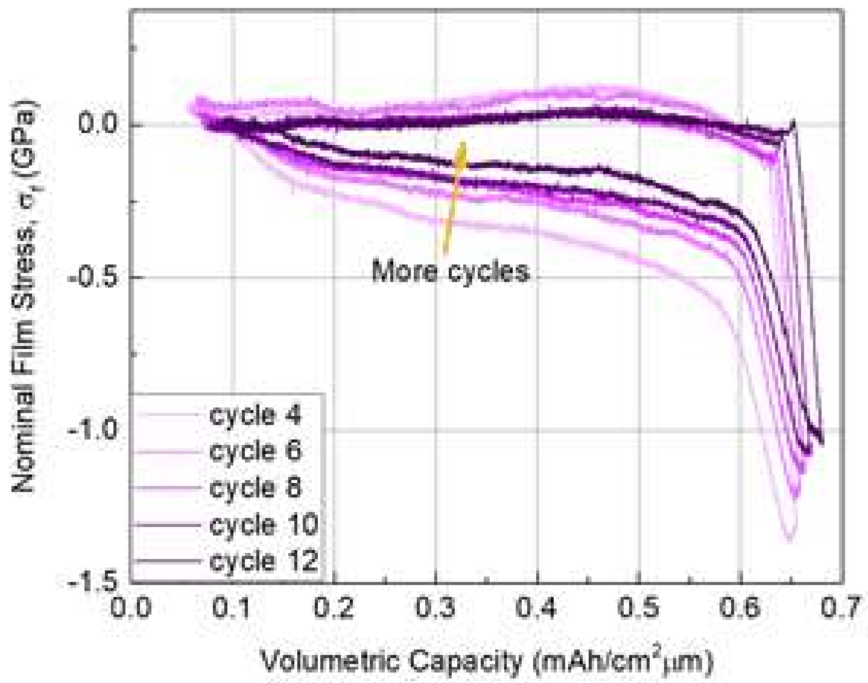
- Tensile stress remains high in second cycle.
- After a chemoelastic regime, the compressive stress is high and stays high.

- Tensile stress is low low in the 2nd cycle
- No clear chemoelastic regime during lithiation. Compressive stress gradually increases

Si : A. Al-Obeidi et al, Appl. Phys. Letts **109**, 071902 (2016). **Ge**: A. Al-Obeidi et al, J. Power Sources 297, 472 (2015); A. Al-Obeidi et al, J. Power Sources 3**06**, 817-825 (2016). RuO_2 (LEES II): L. Xu et al, J. Power Sources **552**, 232260 (2022).

Comparison of Si and Ge with RuO_2



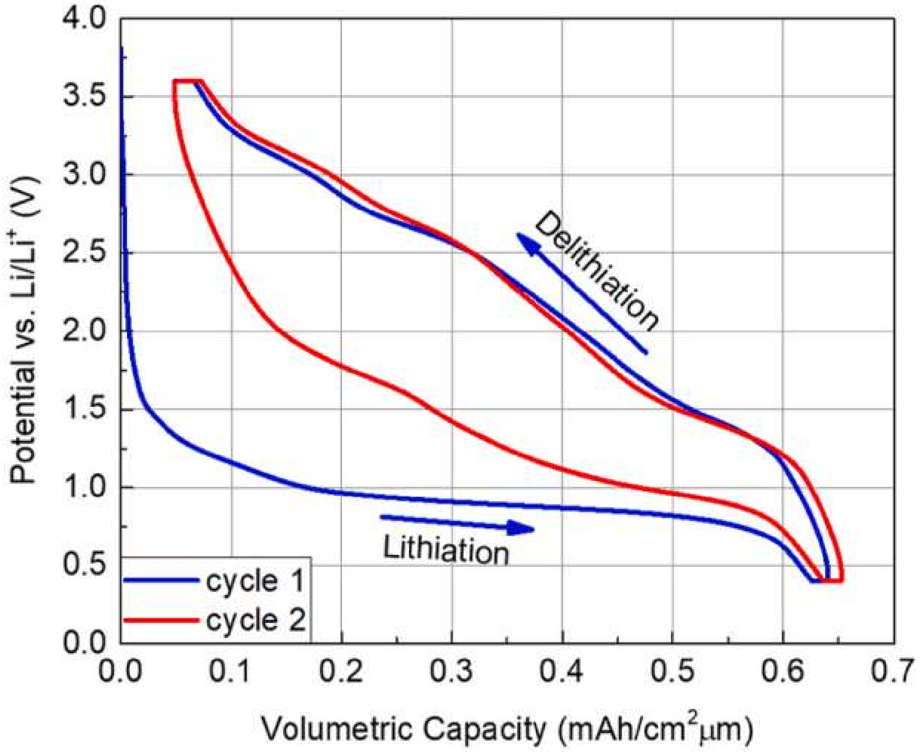


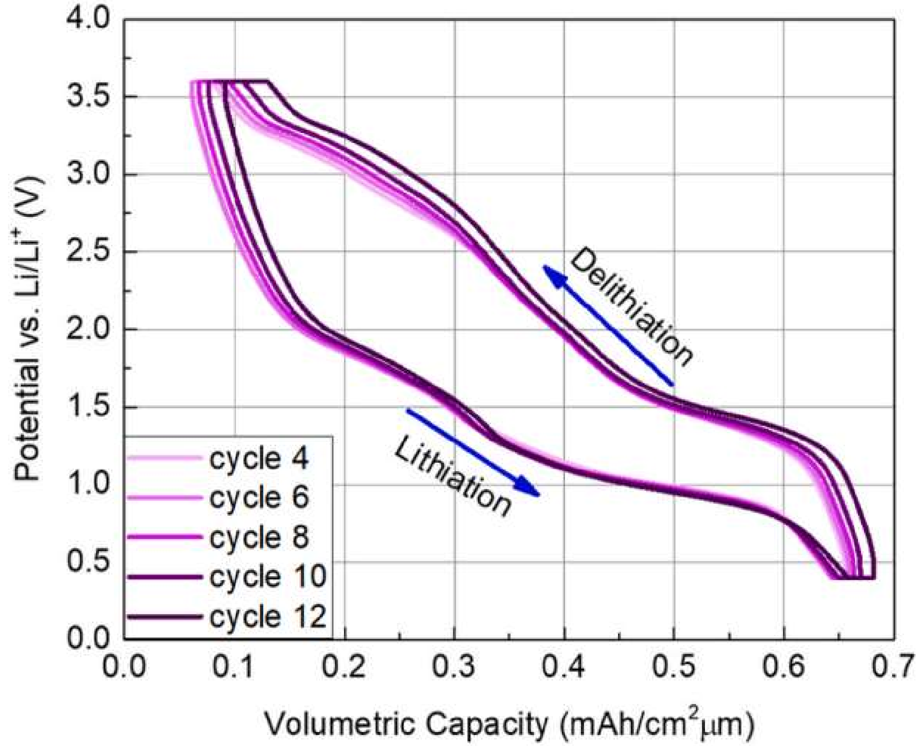
- Tensile and compressive stress remain high.
- Capacity fade due to material loss during cycling.
- Similar results are obtained for Ge

- Tensile stress becomes even lower during cycling
- No significant capacity fade, no loss of material.

Si : A. Al-Obeidi et al, Appl. Phys. Letts **109**, 071902 (2016). **Ge**: A. Al-Obeidi et al, J. Power Sources 297, 472 (2015); A. Al-Obeidi et al, J. Power Sources 3**06**, 817-825 (2016). RuO_2 (LEES II): L. Xu, J. Power Sources **552**, 232260 (2022).

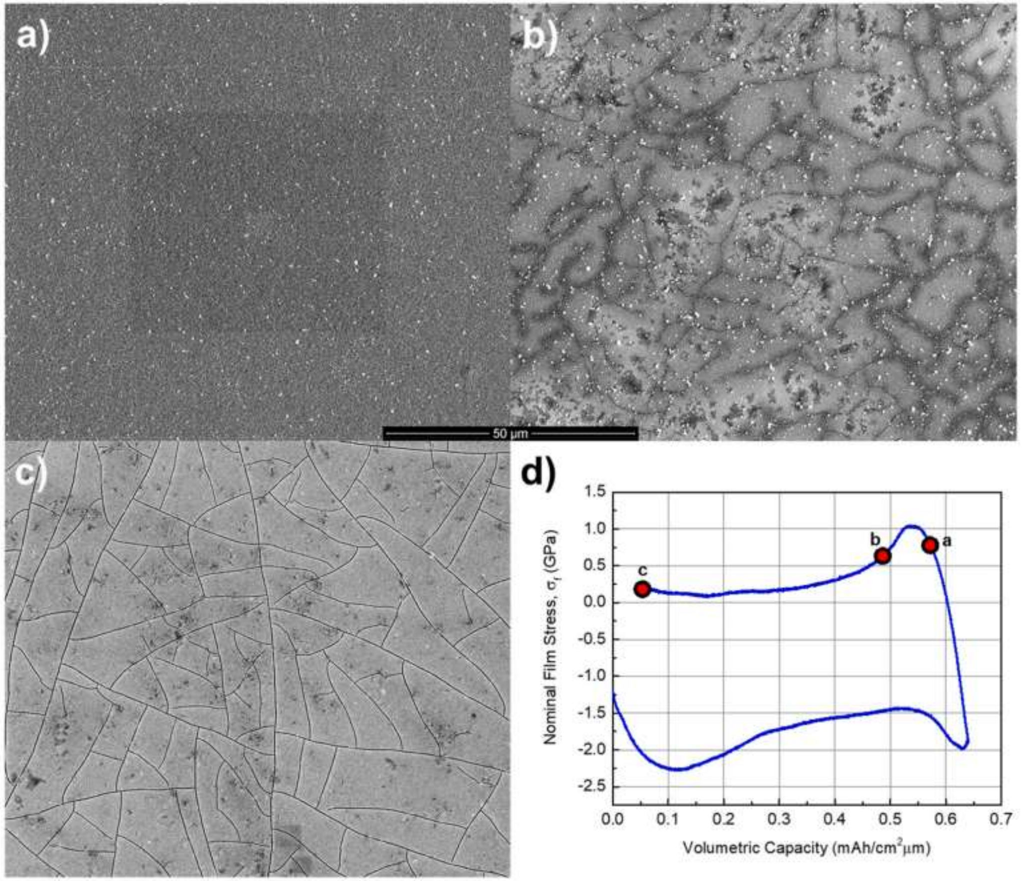
Capacity-Voltage Curves for Ru





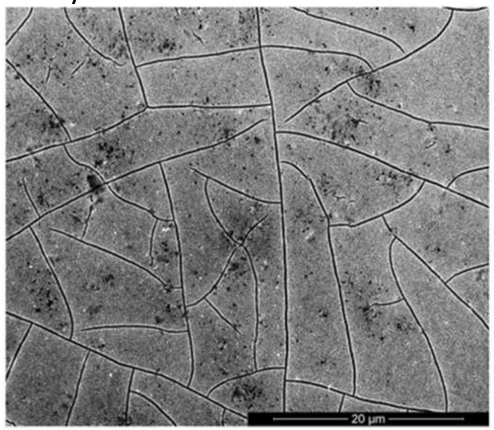
- Volumetric capacity is given by the area within the red curve (left) and purple curves right.
- The volumetric capacity minimally changes (no significant material loss)
- In other experiments, cycling with minimal capacity loss (fade) was observed over hundreds of cycles

Cracks

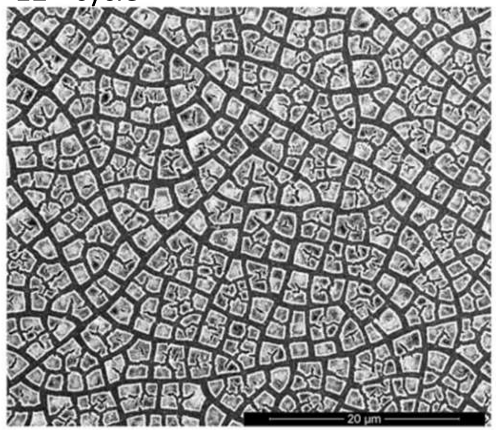


Cracking occurs during the first cycle at about 1 GPa.

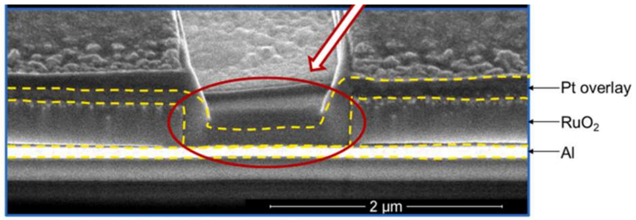
1st cycle



12th cycle



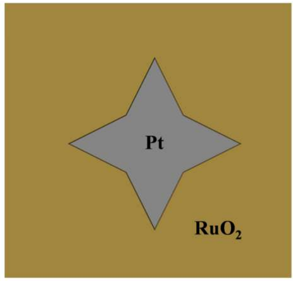
- Cracking continues to a characteristic spacing
- No loss of material.

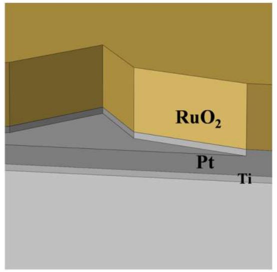


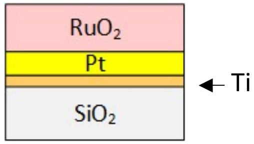
- Cracks are wide.
- They mostly close during relithiation.

Controlling Cracking

Lithographically patterned arrays of notched holes to initiate and control cracking.

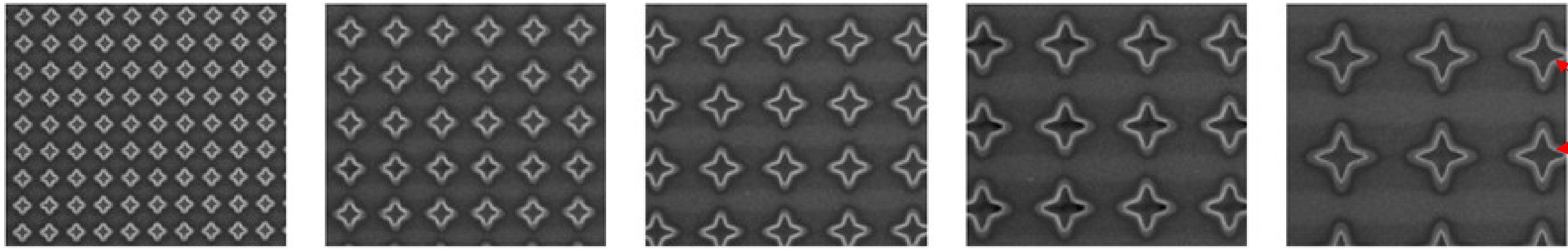




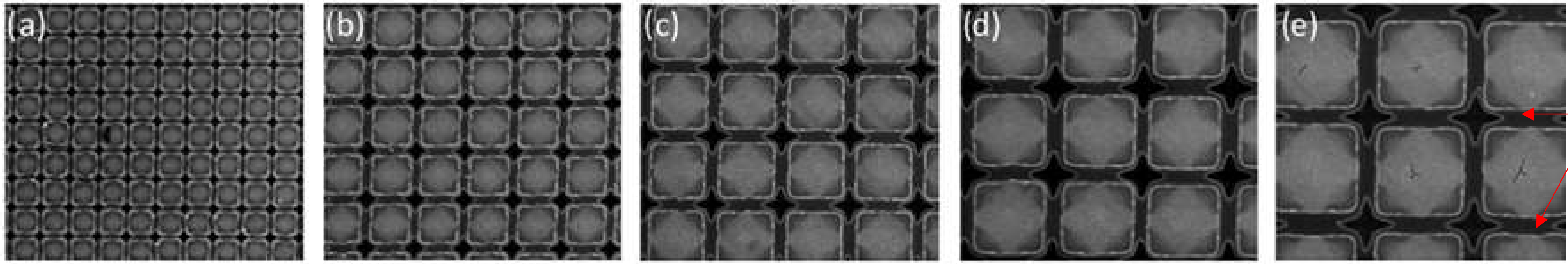


3 µm 5 µm 7 µm 9 µm 11 µm

Spacing of hole centers.



Patterned holes.

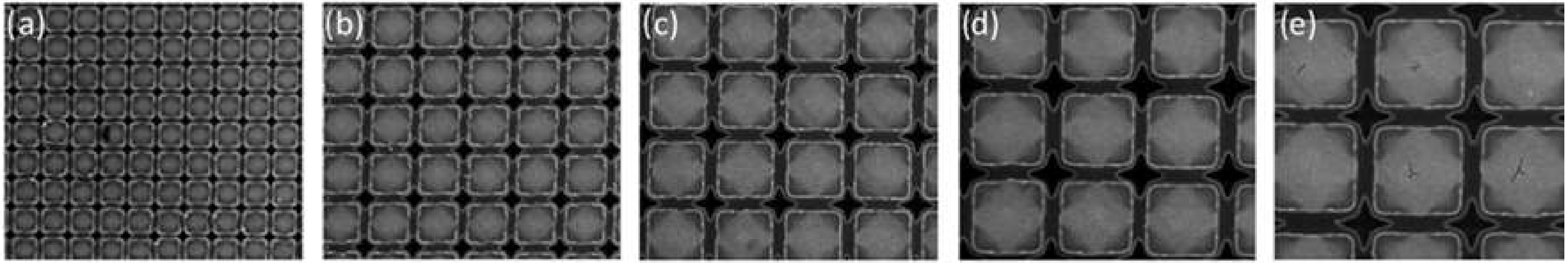


Wide regular cracks form during first delithiation.

After lithiation and delithiation.

L. Xu and C.V. Thompson, ACS Appl. Nano Mater. 4, 13700 (2021)

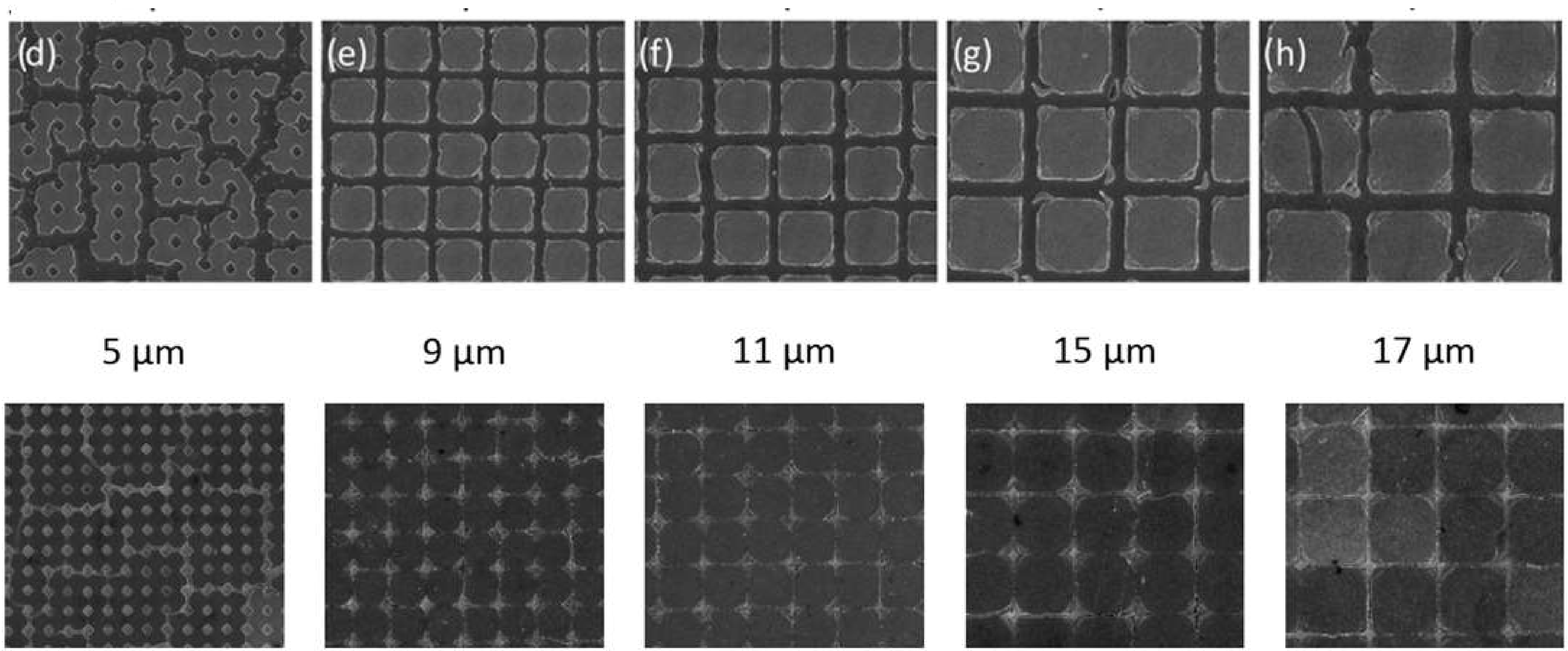
Cracks Reversibly Open and Close



3 µm | 5 µm | 7 µm | 9 µm | 11 µm

250 nm thick, after 10 cycles

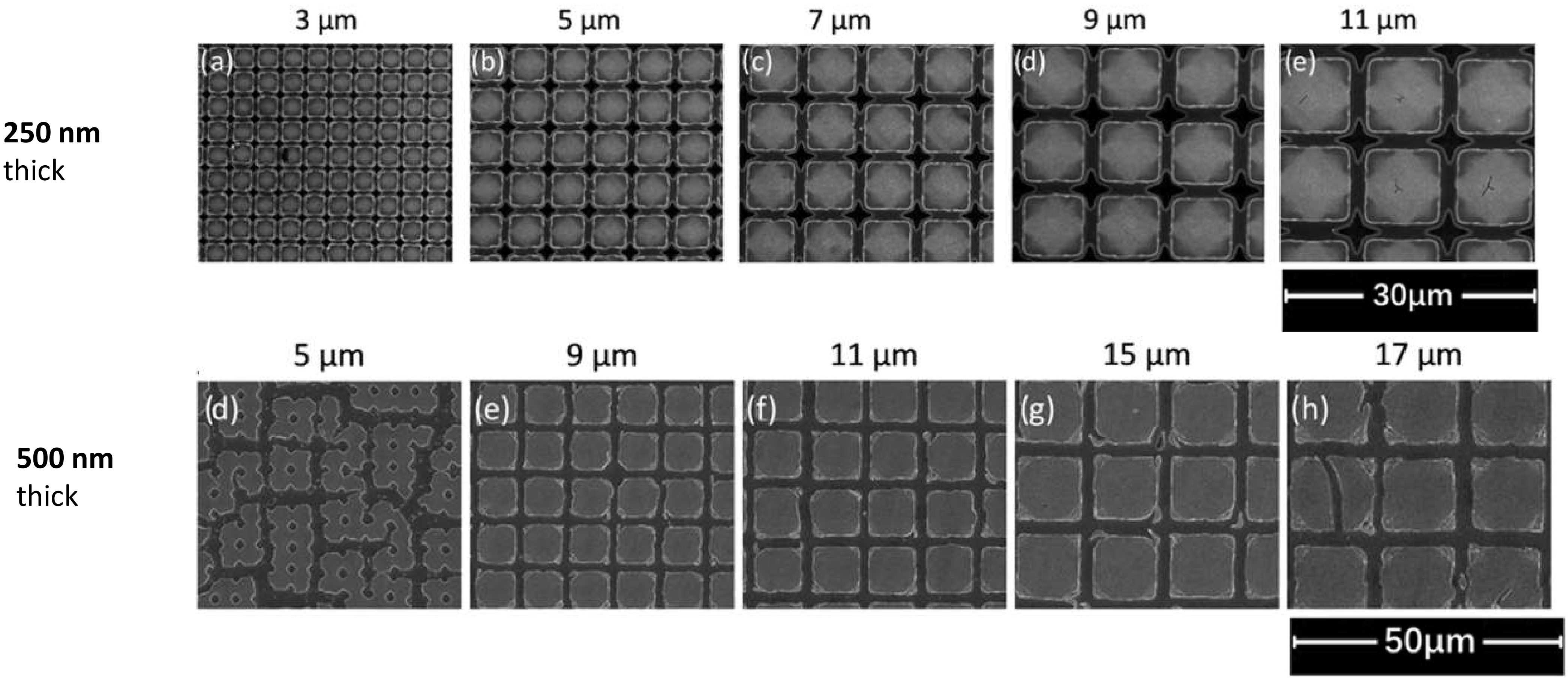
Cracks Reversibly Open and Close



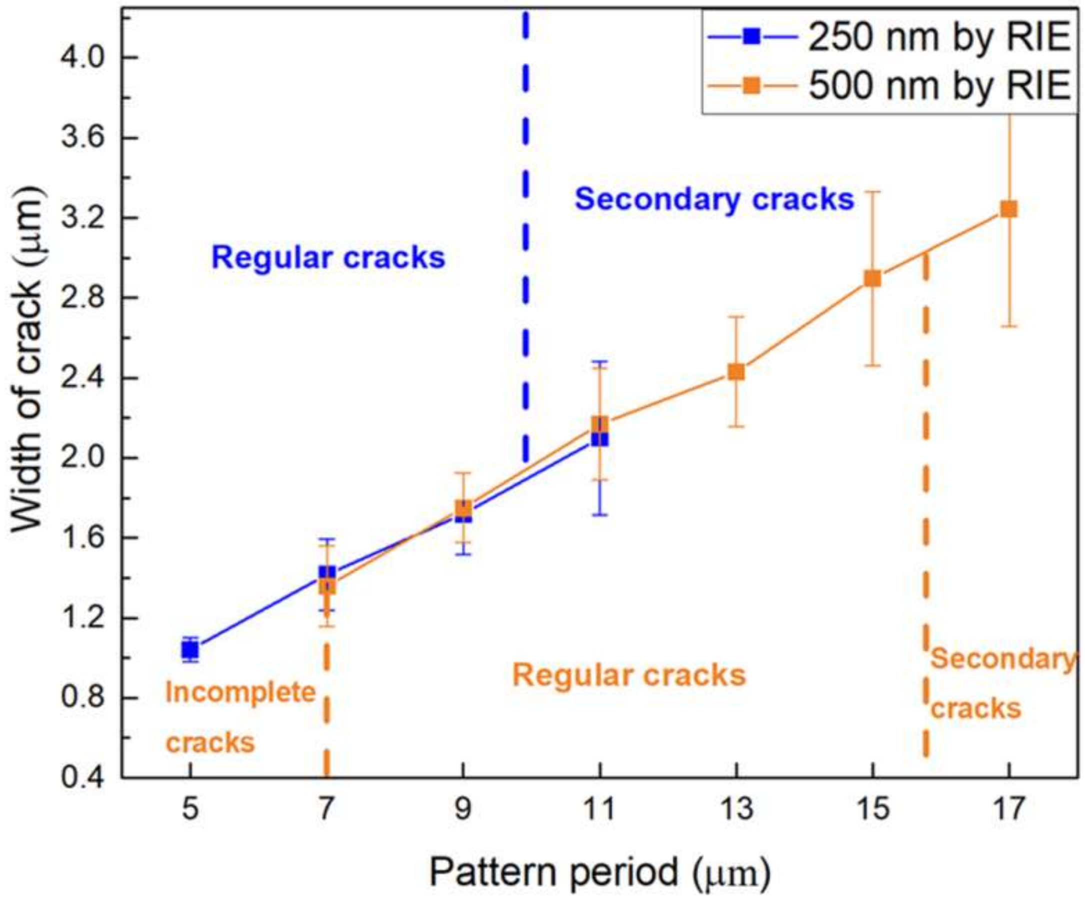
500nm thick, after 10 cycles

(different magnifications)

Limits on Crack Control



Comparison of 250 nm and 500 nm Thick Films



- The crack width scales with the patch period.
- The crack width as a function of patch period is independent of film thickness.
- The limiting patch size to avoid secondary cracking is 500 nm.

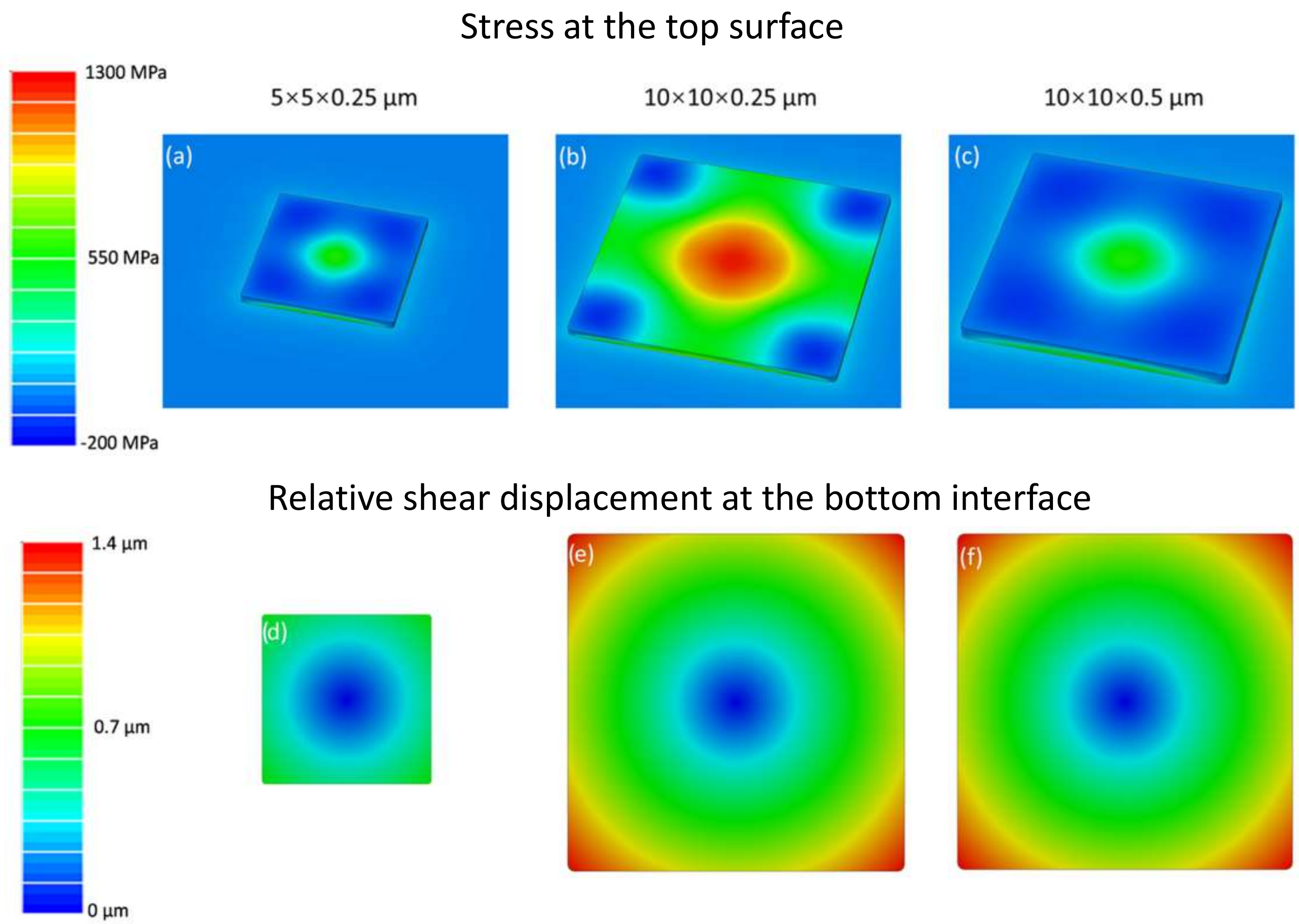
Finite Element Analysis

Following a treatment by Haftbarandan and Gao*, we adopt a rigid-perfectly plastic cohesive zone model and assume that:

Stress is elastically accommodated at the edge up to a limit: the interfacial sliding strength τ_0 (τ_0 was set at 75 MPa).

A constant shear traction force of the same value is then maintained after the elastic limit is reached.

*H. Haftbaradaran, X. Xiao, M.W. Verbrugge, M. W., and H.J. Gao, J. Power Sources 206, 357 (2012).

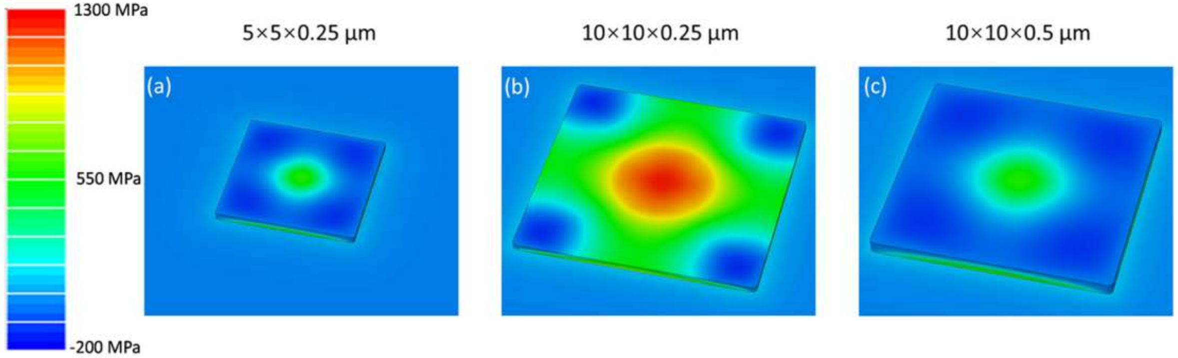


Finite Element Analysis

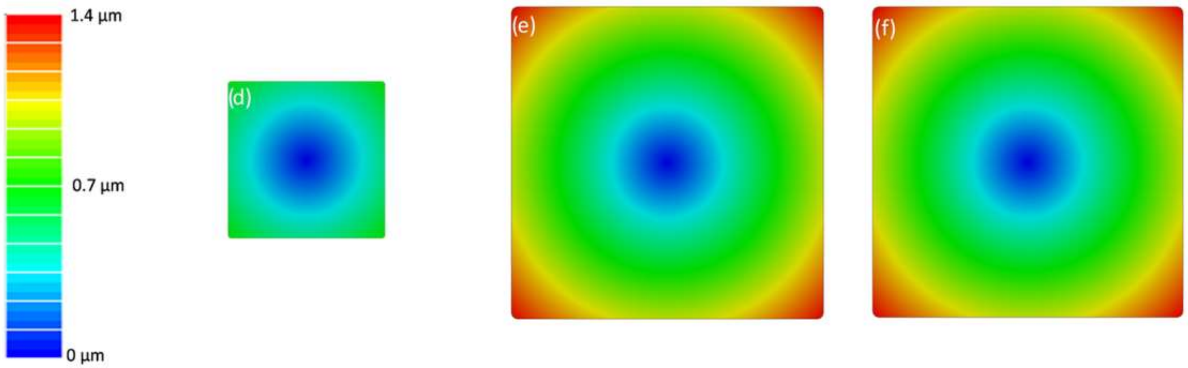
The displacement at the center of all patches is zero. The *maximum stress in the 10 x 10 μm patches is reduced by half in the thicker patch*. *Secondary cracks will form at larger patch sizes for thicker patches*. Consistent with observations.

The *displacement at the edge is proportional to size of the patch* and *does not change significantly with film thickness*. Consistent with observations.

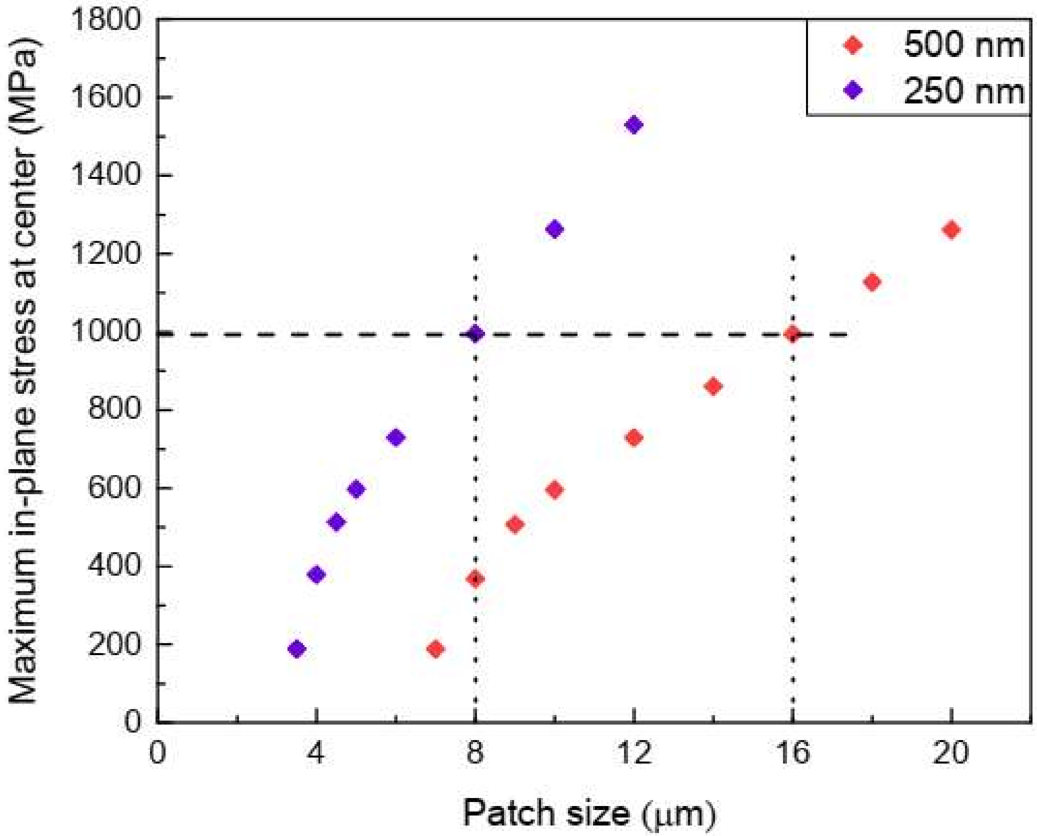
Stress at the top surface



Relative shear displacement at the bottom interface



The Interfacial Sliding Strength τ_0



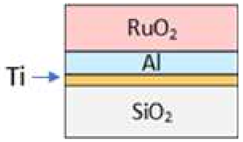
The fracture stress is about 1GaP, based on in situ stress measurements.

The observed limiting patch size is well approximated for τ_0= 75 MPa.

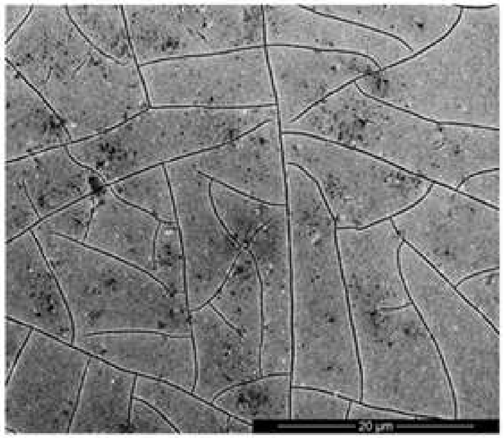
(Metals on mica $\tau_0 \approx$ 40 Mpa.)

Effects of Current Collector?

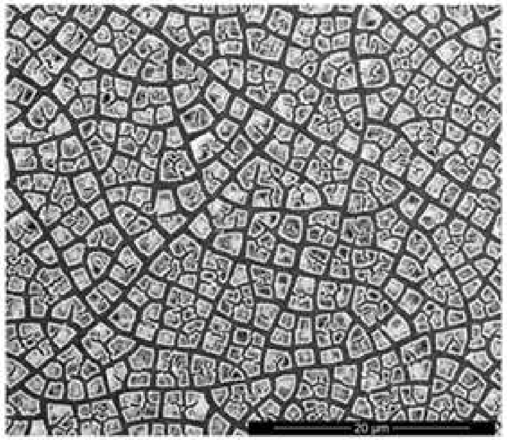
in-situ stress measurements



1^{st} cycle

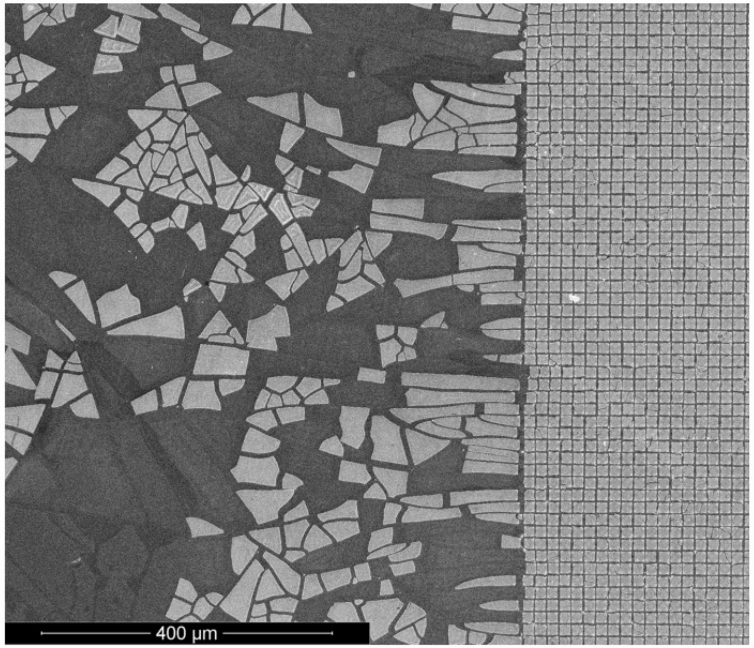


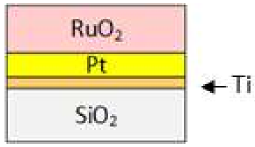
12^{th} cycle



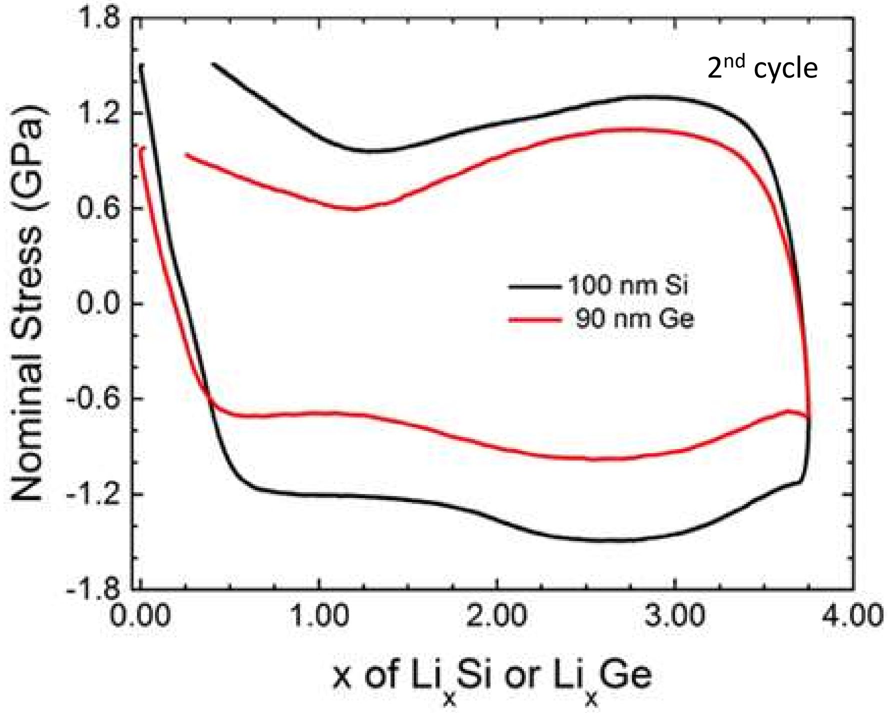
notched holes

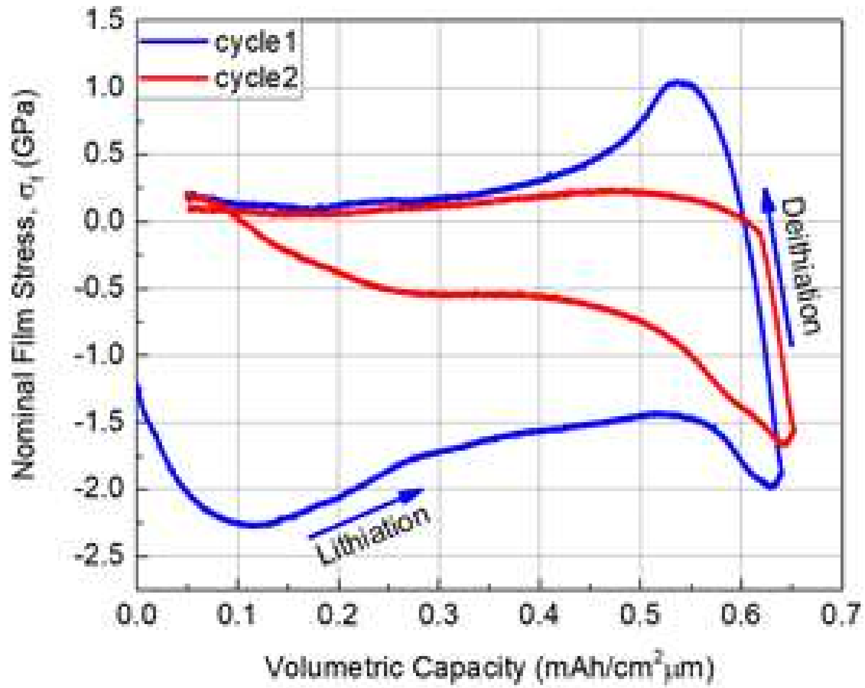
10^{th} cycle





Comparison of Ge and Si with RuO_2 Revisited





Hypothesis:

- The SEI layer suppresses sliding for Si and Ge, so they plastically flow at a high tensile stress during delithiation.
- Once cracks have formed, sliding keeps tensile loading low in RuO_2 during delithiation.
- During lithiation, a stress gradient develops and applies a downward force, leading to higher traction.
- Impingement causes a sudden rise at the end.

Summary

- Li-ion battery electrodes with a high capacity to store Li undergo large volume changes during lithiation and delithiation.
- This leads to mechanical stresses that can lead to pulverization and performance degradation and eventual failure.
- Thin film electrodes thicken and are put in compression during lithiation, and are put under tension and eventually crack during delithiation.
- Whether cracking leads to failure depends on the:
  - Effects of the SEI layer (if there is one)
  - Character of the interface with the current collector: adhesion and interfacial sliding strength.