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Authors

Ban, Chunmei

Qi, Yue

Wang, Yongqian

et al.

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General Paradigm for Understanding and Preventing Li Dendrite Penetration into Solid Electrolytes. A Proposal

Yue Qi[1]
Chunmei Ban[2]
Stephen J. Harris[3]

[1]Brown University

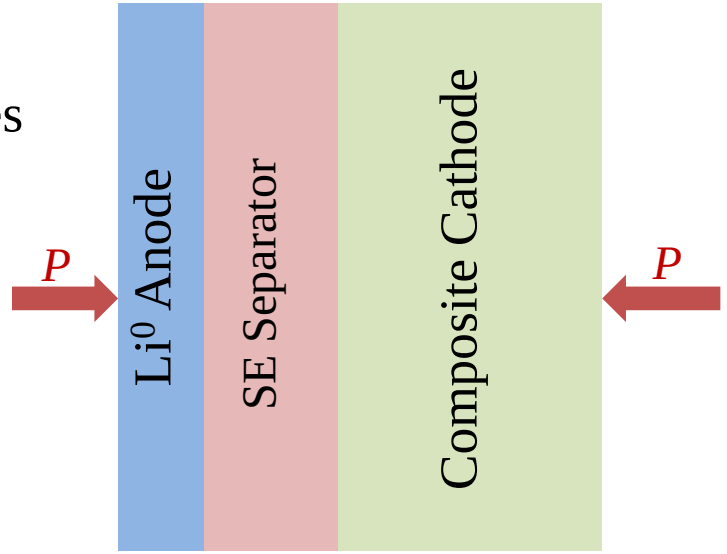
[2]University of Colorado, Boulder

[3]Lawrence Berkeley National Lab, sjharris@lbl.gov

Joule **4**, December 16, 2020, *in press*

The Dream: Solid Electrolytes + Li Metal

- Benefits of SEs
  - Li metal saves mass and volume
    - Large increase in energy density
  - Ceramic electrolytes should block dendrites



Goal: Offer Answers

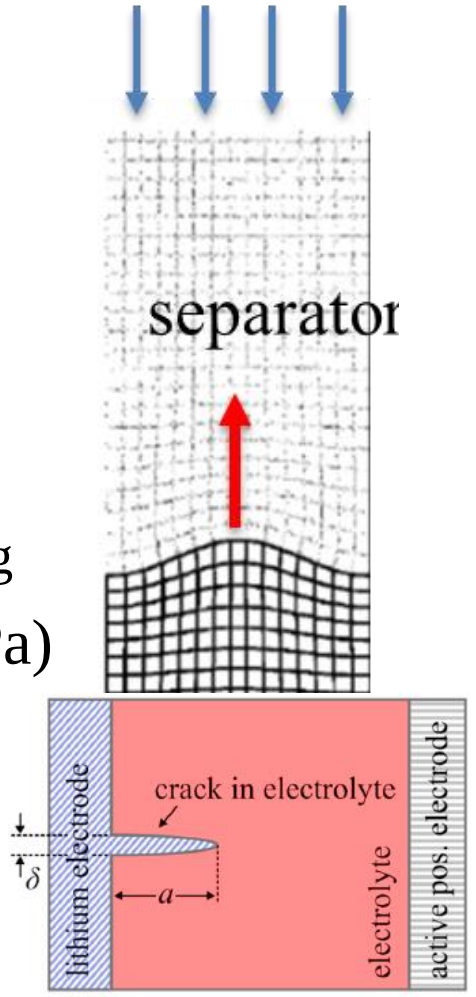
1. How do soft Li dendrites penetrate hard ceramic electrolytes?

2. How do we solve the general dendrite penetration problem for solid electrolytes?

How has the battery field traditionally understood solid-solid contact and dendrite penetration?

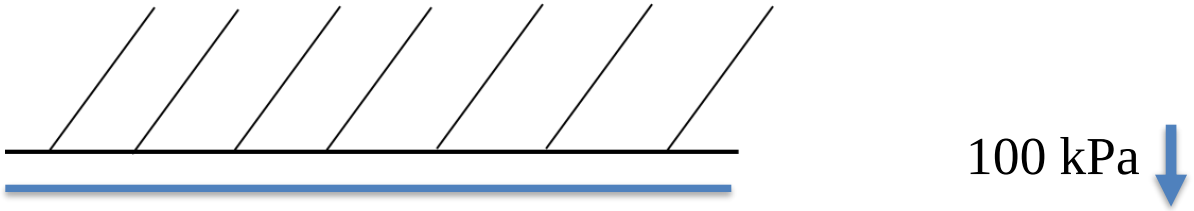
Suppressing Dendrite Penetration

- Monroe-Newman (M-N) model (2003)
  - Suppress dendrite growth mechanically
- Model
  - Conformal contact at a protrusion (proto-dendrite)
  - Fixed flux of Li^+ ions into ~ 10 x 10 μm region
- Competition
  - Transport/electrical lead to dendrite growth
  - Surface energy and stiff separator lead to flattening
- Flattening requires high shear modulus (~ GPa)
- Comments
  - Pressure increases without limit
  - Li yield strength doesn't appear



Contact Between Real Solids

- Engineering surfaces are rough at the μm or sub-μm scale
- Conformal contact is very unusual (unless melted, evaporated)



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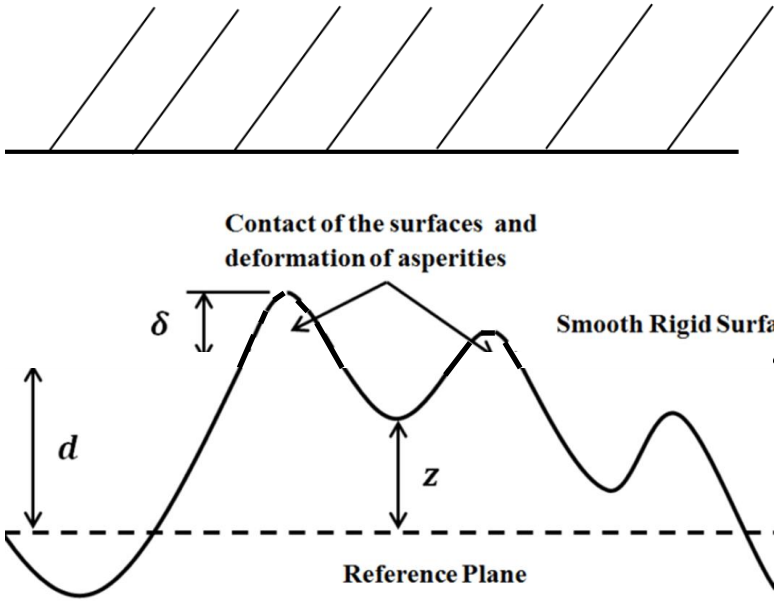
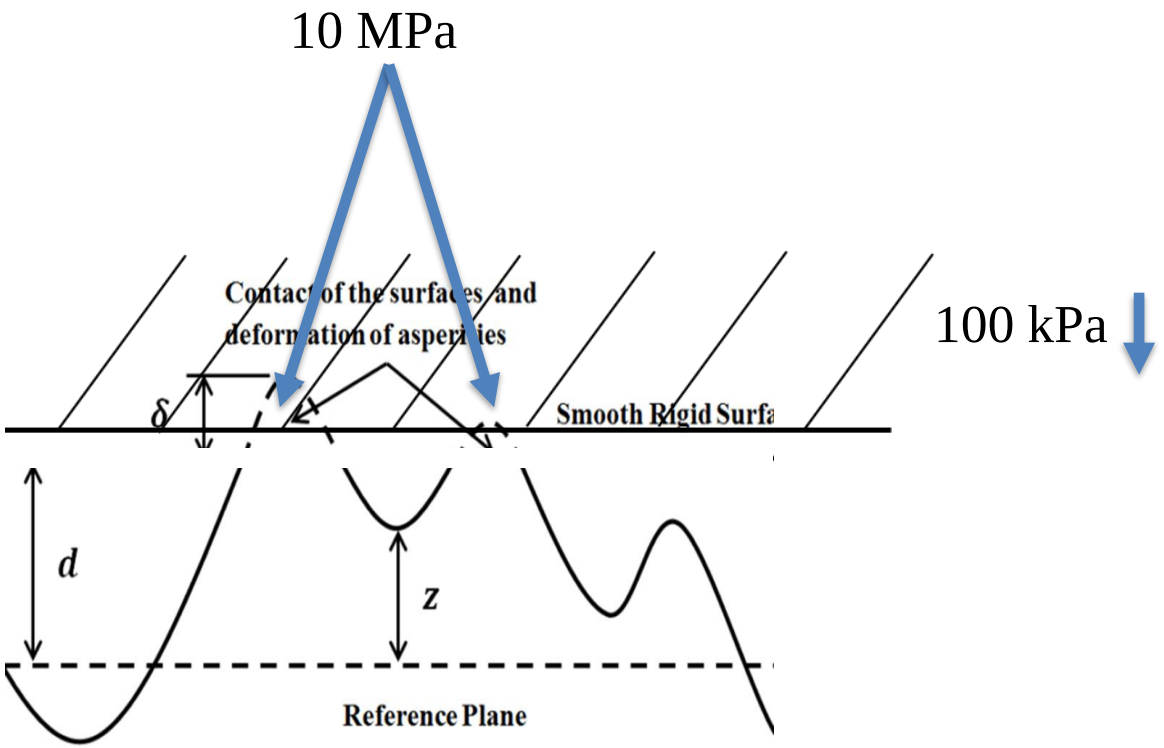


100 kPa

Contact Between Real Solids



The load is carried by 1% of the surface (remainder not in contact)
Yield strength controls contact structure and the maximum possible stress

What is the Yield Strength for Li Metal?

- $\sigma_Y^{indent} \approx 3\sigma_Y^{tension} = H$

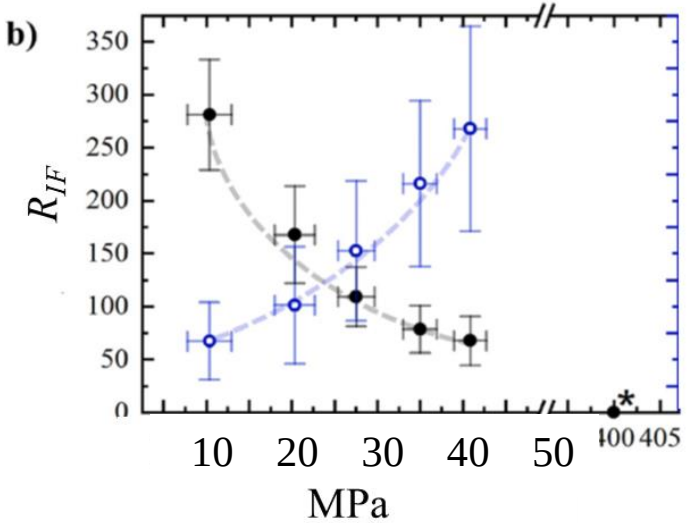
Comparison of uniaxial yield stress Y_0 and identation hardness p (spherical indenter) for fully work-hardened metals (1 GPa ≈ 100 kgf mm^{-2}).

Metal	σ_Y (kgf mm^{-2})	H (kgf mm^{-2})	H/σ_Y
Te–Pb	2·1	6·1	2·9
Aluminium	12·3	34	2·8
Copper	31	88	2·8
Mild steel	77	220	2·9

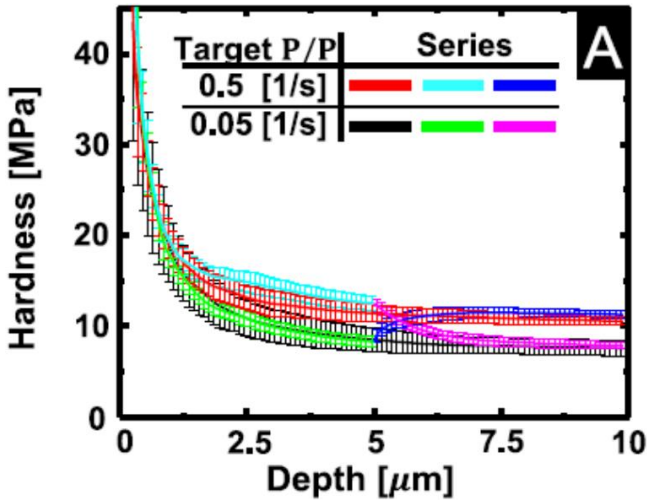
D. Tabor, *PHILOSOPHICAL MAGAZINE A*, 1996, **74**, 1207-1212

- Displaced Li pushes against the bulk
- H is the relevant parameter
- Local pressure $\leq H$
  - If $P_{ext} = H$, surface is fully plastic, conformal contact
    - R_{IF} is minimized

High Pressure Reduces Interfacial Resistance



J. Janek *et al*, *ACS Applied Materials & Interfaces* **11** (2019) 14463-14477



M. Pharr, "Mechanical properties of metallic lithium: from nano to bulk scales," *Acta Mat* **186** (2020) 215

$H^{eff} \geq 40$ MPa

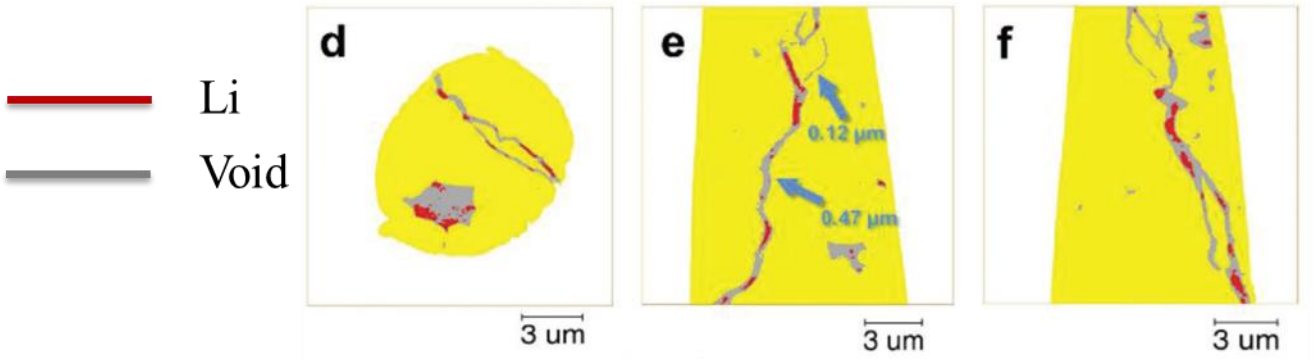
($H^{eff} = 48 \pm 6$ MPa modeling Sakamoto data*)

There is a strong size effect in Li

*Harris et al, *Cell Reports Physical Science* **1**, 100012

Conformal Contact Summary

- Conformal contact should almost never be assumed
  - Conformal contact achieved for $P_{ext} \geq H_{eff} > 40$ MPa
  - But for a large format commercial cell $P_{ext} << H_{eff}$
    - 300 tons stack pressure for 20 cm x 30 cm cell
    - 3 atm stack pressure (QuantumScape) requires 4,000 lb load
- Li flow into gaps keeps hydrostatic pressure below *H*
- Contact usually assumed to be conformal inside cracks
  - Dendrites will be squeezed out at the base high hydrostatic *P* > H



Shearing, *Adv. Funct. Mater.* **2020**, 2007564

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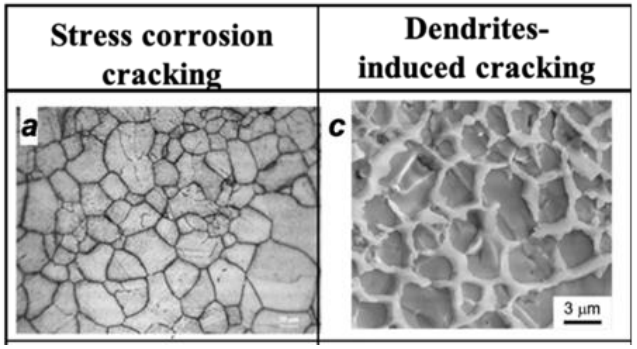
    - 3 atm stack pressure (QuantumScape) requires 4,000 lb load
- Li flow into gaps keeps hydrostatic pressure below *H*
- *P* cannot get near GPa level
- How does something so soft penetrate something so hard?

Understanding Dendrite Penetration

- Reminiscent of Stress Corrosion Cracking/Static Fatigue
  - Salt water (soft, no shear strength) penetrates through steel (hard)



Sakamoto, "Intergranular Li metal propagation through polycrystalline LLZO," *Electrochimica Acta* **223** (2017) 85–91.

Is the Analogy Valid?

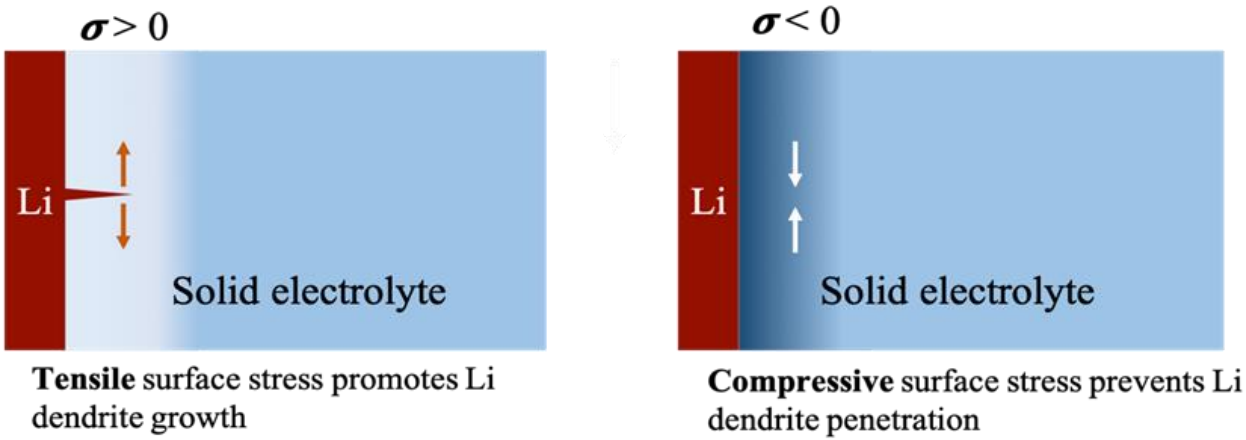
- Require tensile stresses on the surfaces of SEs
  - LLZT prepared by the spark plasma sintering (SPS) technique exhibits a residual tensile stress > 100 MPa*

    * Yamada et al, "Influence of strain on local structure and lithium ionic conduction in garnet-type solid electrolyte," *Journal of Power Sources* **368** (2017) 97.

- SCC and static fatigue are solved problems
  - Can we import these solutions?
  - Will the solution work even if the SCC analogy is wrong?

Proposed Solution to Dendrite Penetration

- Put the surface into state of residual compressive stress
  - Residual stress is what remains after external loading is removed
    - Intrinsic property of the material
    - 2-3 orders of magnitude higher than achievable with stack pressure
  - Cracks cannot form and propagate
    - Pre-existing cracks tend to close

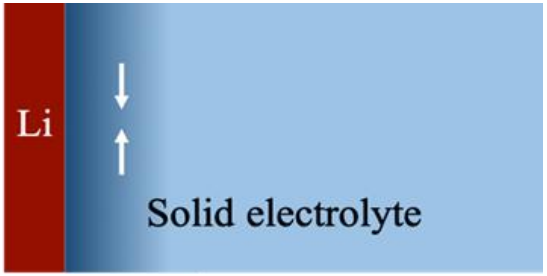


Tensile surface stress promotes Li dendrite growth

Compressive surface stress prevents Li dendrite penetration

Proposed Solution to Dendrite Penetration

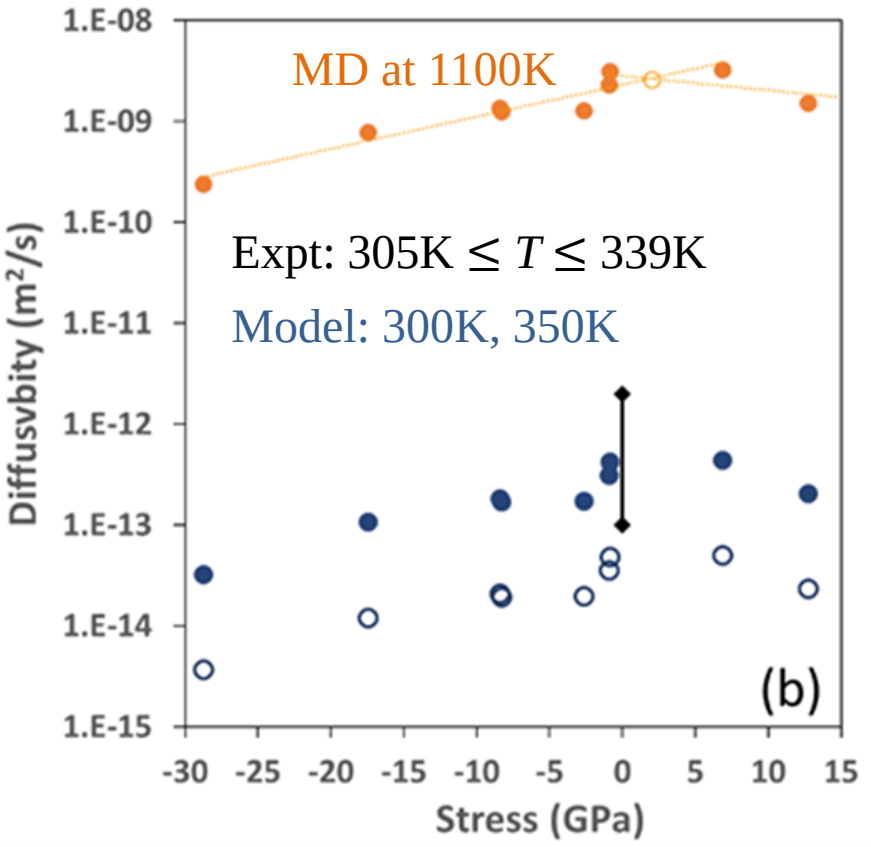
- Surface residual compressive stresses $\lesssim$10 GPa can be put in ceramics
  - Ion exchange: *e.g.*, exchange small Na^+ for larger K^+
    - Monovalent ions are easily exchanged; don't exchange away too much Li^+
  - Ion implantation
    - Control of dopant species, concentration, energy and spatial distribution



Why Won't Ion Implantation Work?

1. Li^+ are immobilized at high residual compressive stresses
   - MD calculations in LLZO

10 GPa compression leads to a modest reduction in Li^+ diffusivity



A periodic cubic cell of $Li_{24}La_{24}Zr_{16}O_{96}$ was simulated using GULP software and implemented in Materials Studio with a force-field including the long-range Coulombic potential, the short-range Buckingham potential, and a core–shell polarizable potential for O atoms. The simulation cell length was varied from 12.4 Å to 13.7 Å, and the mean square displacement (MSD) of Li^+ ions was tracked during NVT (fixed cell) dynamics.

Why Won't Ion Implantation Work?

2. SE will be amorphized in implantation region
   a. Amorphous (glassy) $Li_2SP_2S_5$, 0.3 mS/cm*

* Porz et al, "Mechanism of Lithium Metal Penetration through Inorganic Solid Electrolytes," *Adv. Energy Mater.* **2017**, *7*, 1701003

Why Won't Ion Implantation Work?

3. Residual compressive stress will relax via diffusion
   a. Will implanted ions remain in regions of high stress?
      i. Small monovalent ions are relatively mobile
      ii. Large and/or polyvalent ions are good candidates

Conclusions

- Assumption of GPa-level stresses in Li to explain SE penetration
  - Not likely and not necessary
  - Stress corrosion cracking, operates without external pressures
    - Explains how soft materials can penetrate through hard materials
    - Chemical reactions + high tensile stresses are driving forces
- Solved Problem: Import the solution into the battery field
  - Introduce high residual surface compressive stresses
    - Implantation, ion exchange, other
  - Side benefits
    - Improved fracture toughness for easier handling
    - Implanted surfaces can be less reactive
    - Resist dendrite penetration from the Li surface or from SE bulk

The End

Solution Approach

- Surface deflection

$$u_{ij} = -\sum_{(k,l)\in I_g} K_{|i-k|,|j-l|}\, p_{kl},$$

  - The net deflection produced at each grid node is the sum of the deflections produced at this point by the *N* individual pressures

$$\hat{u}_{ij} = -\hat{K}_{ij}\,\hat{p}_{ij}$$

where $u\hat{}$ and $K\hat{}$ are the Fourier transforms of u_{ij} and K_{ij}. Closed-form analytical expressions are available for the Fourier coefficients $K\hat{}$.

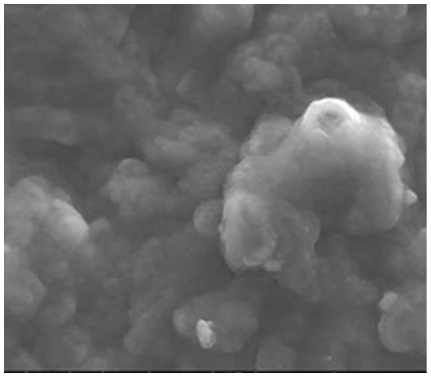
Nodal surface deflections are calculated by applying the inverse 2D Fourier transform to the array of Fourier coefficients. The total cost of the nodal deflection computation using the FFT technique is $O(N \log N)$.

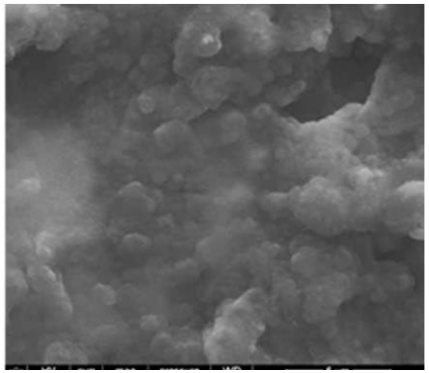
Solution is iterative.

Why Won't Ion Implantation Work?

4. Implantation changes the local chemistry
   a. Possible solutions
      i. Local implantation concentrations $\lesssim 1\%$
      ii. Implantation thickness $10 - 1{,}000$ nm
      iii. Find ions that do not interfere with ion transport

LLZO Morphology



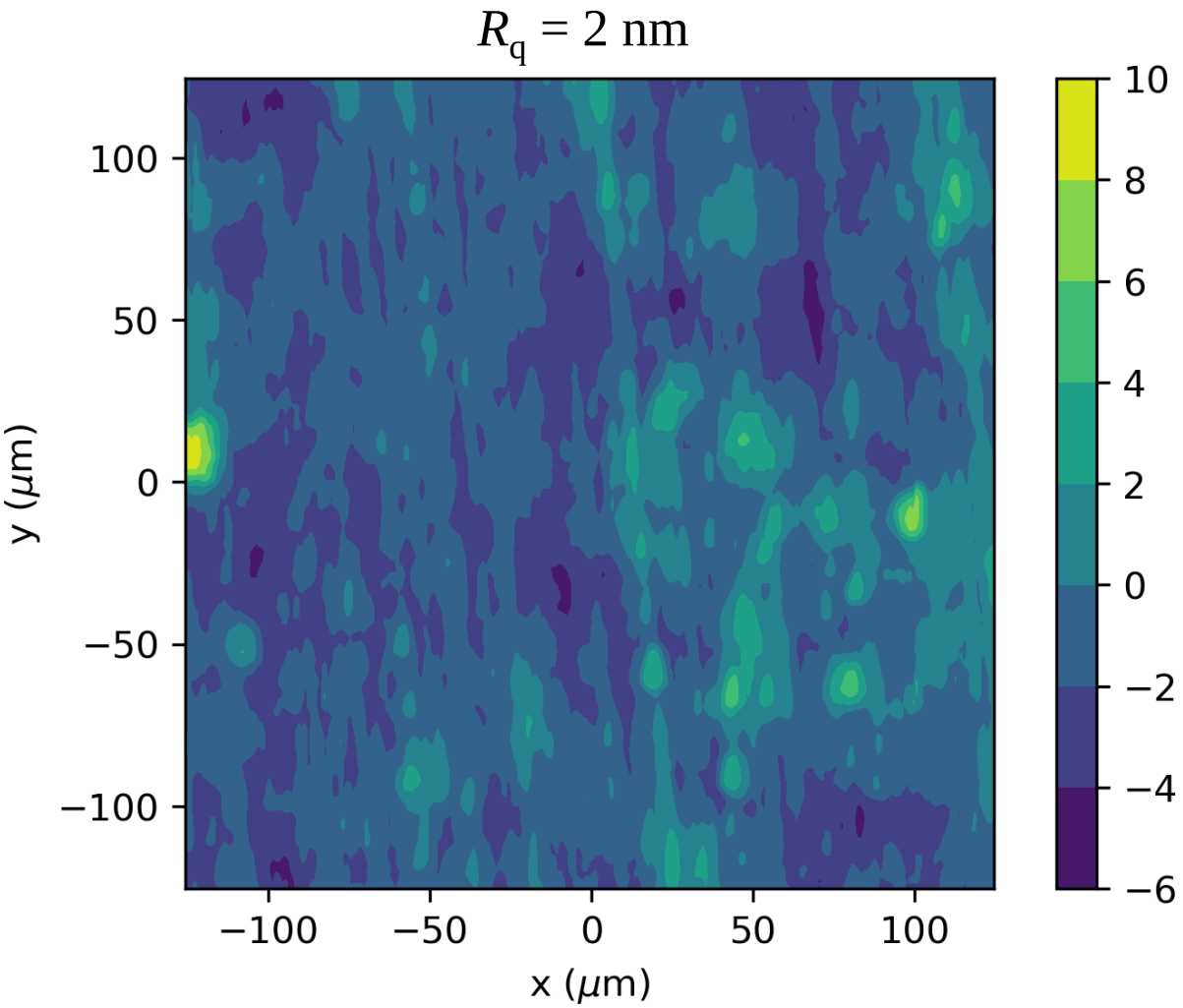


5 μm

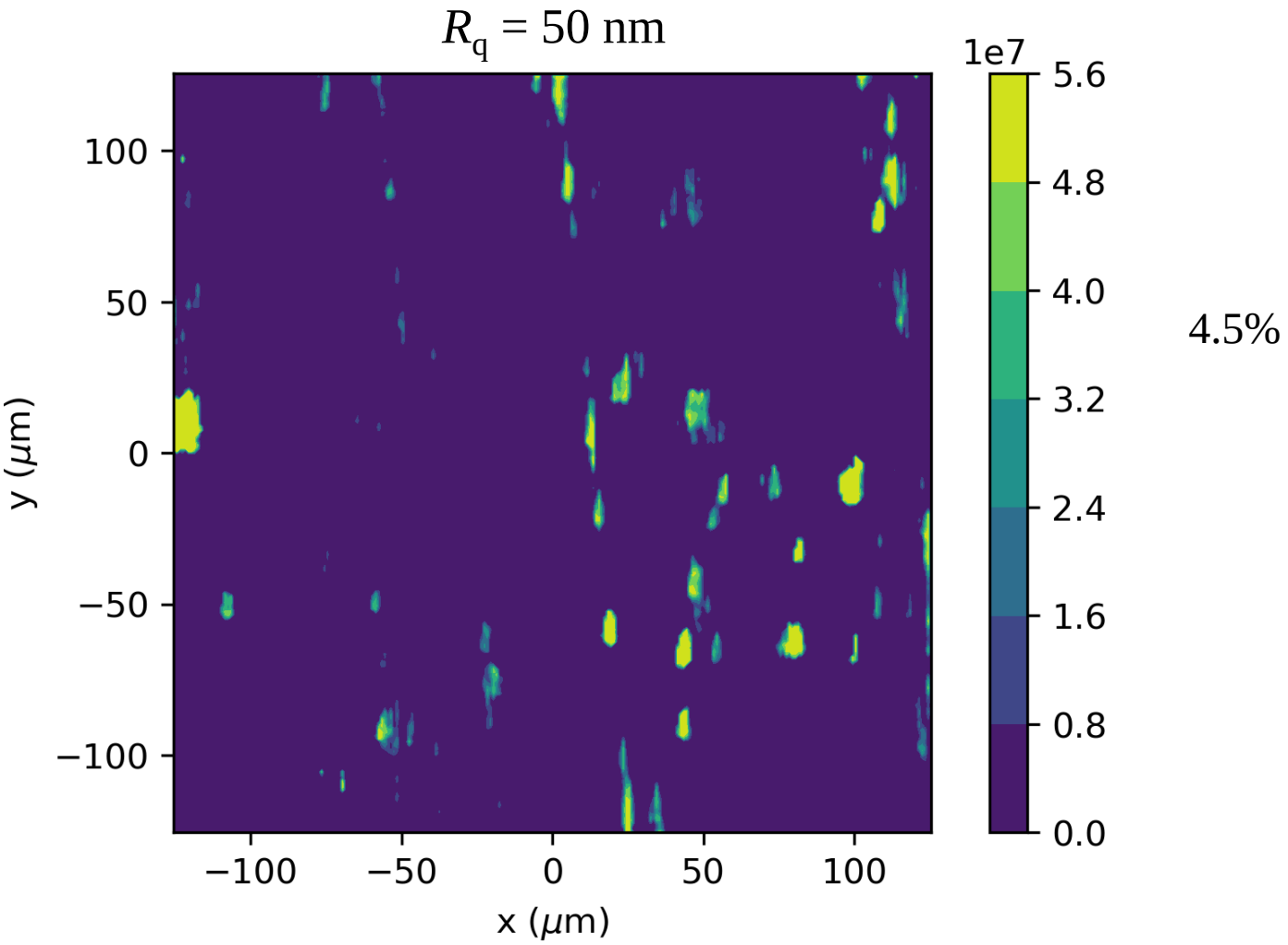
$$\mu_v = \int_{-\infty}^{\infty} z^v p(z)\, dz$$

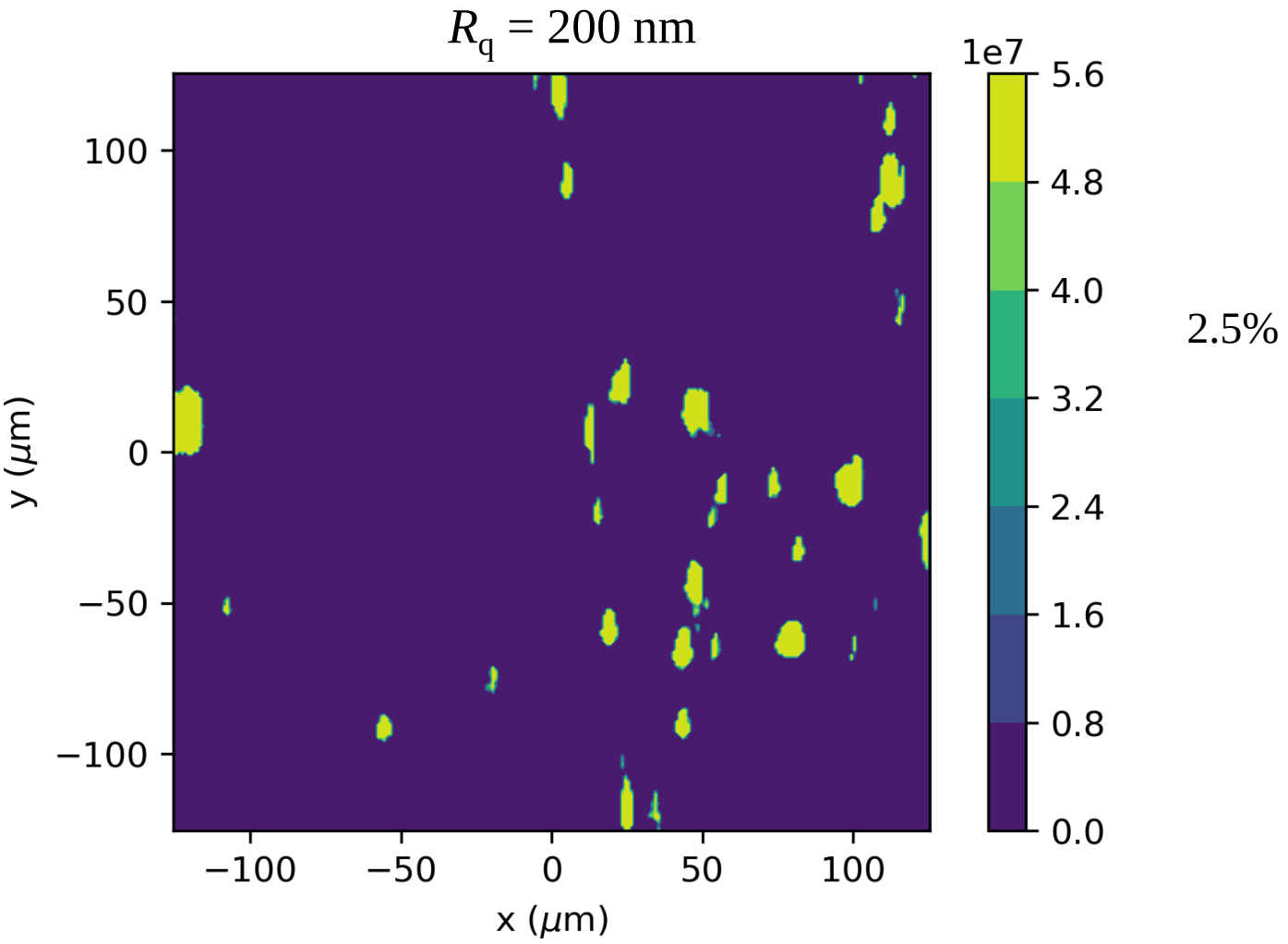
$$R_q = \sqrt{\mu_2}$$

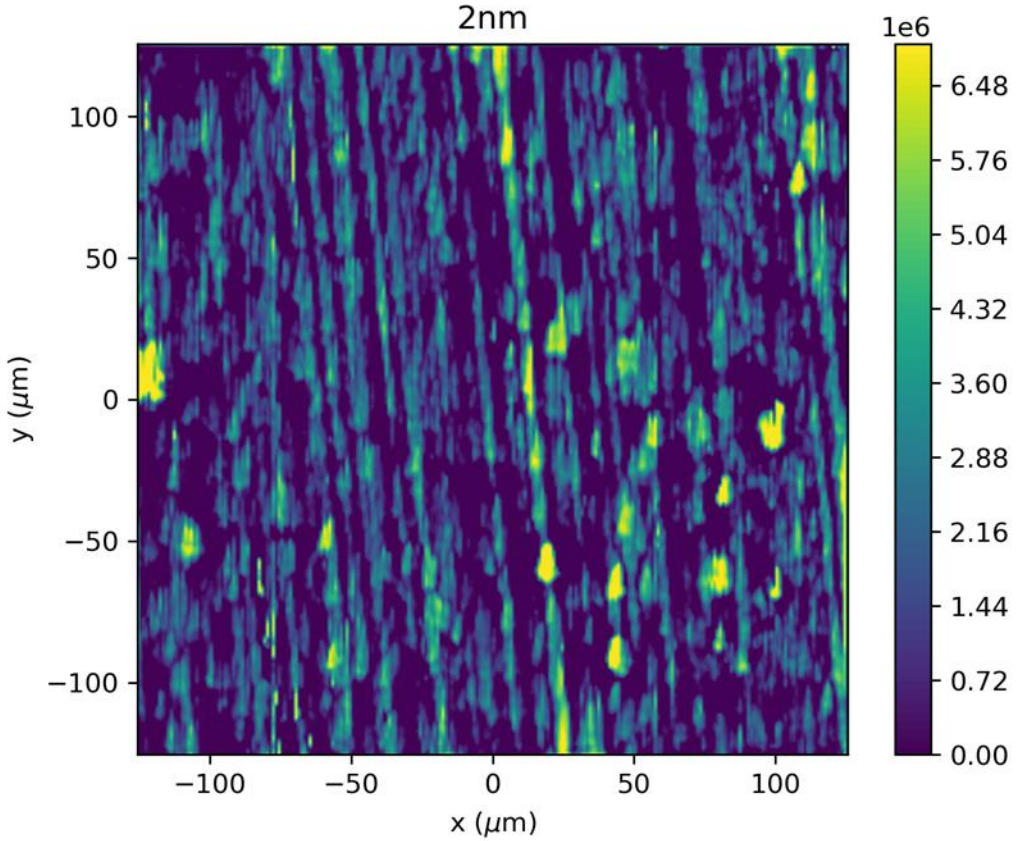
Assumed Surface Profile

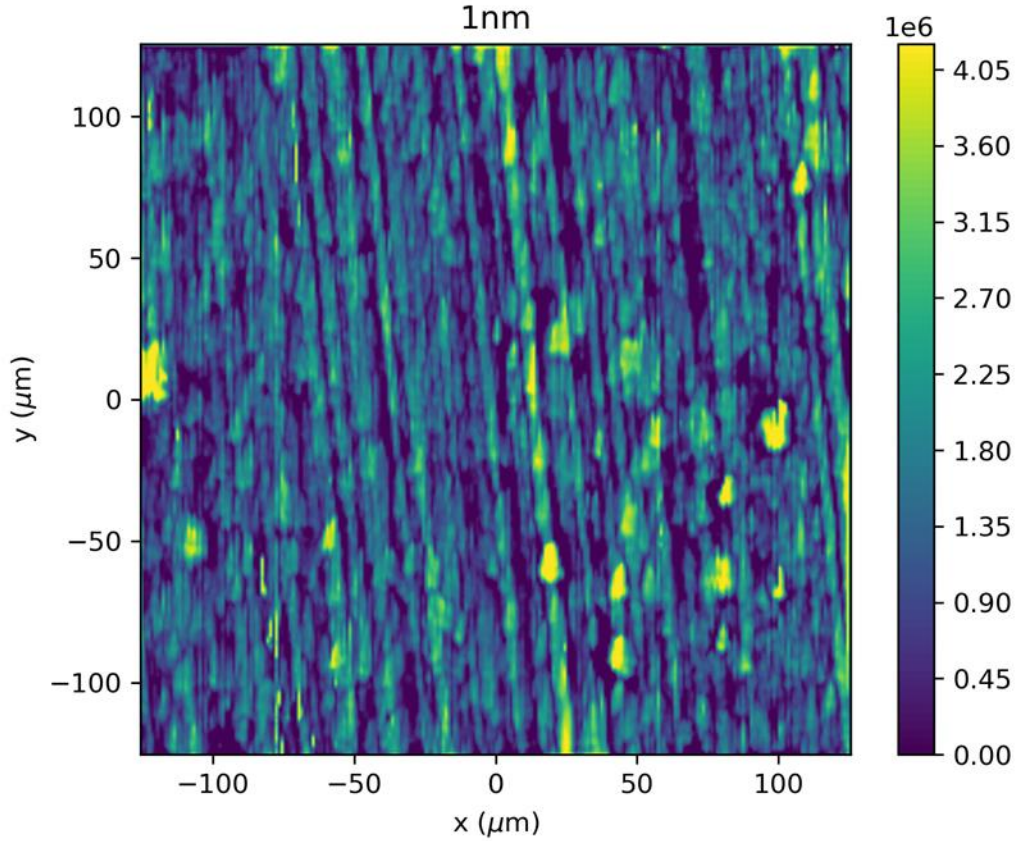


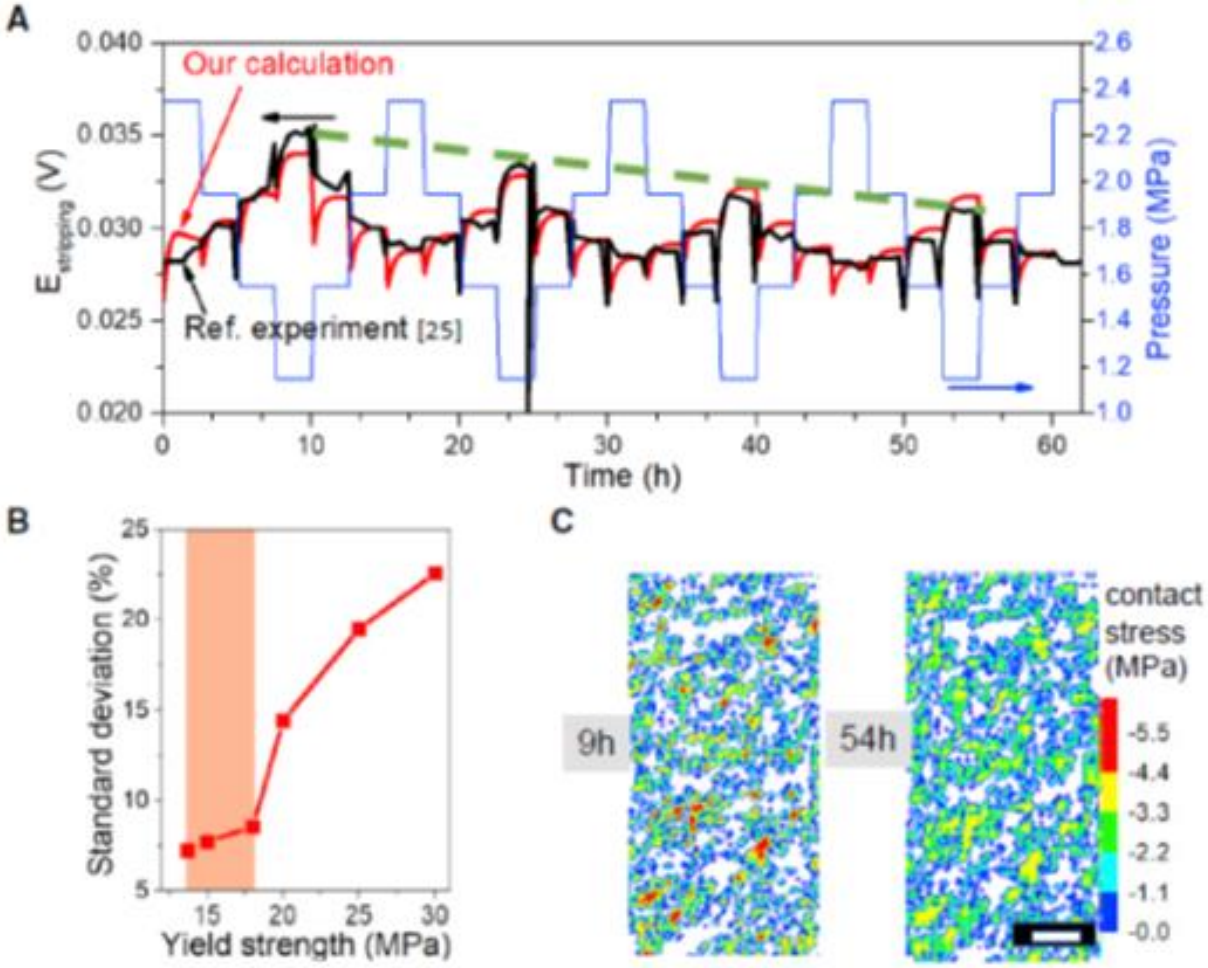
Contact Stress Map 2MPa



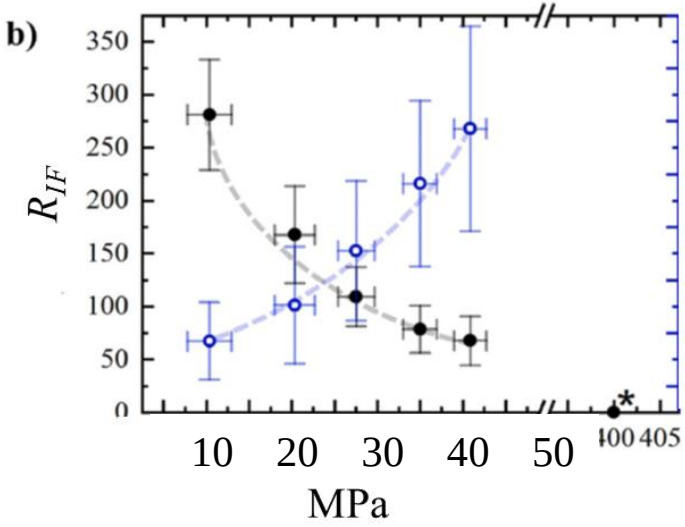

R_q = 200 nm
1e7
5.6
4.8
4.0
3.2
2.4
1.6
0.8
0.0
100
50
0
−50
−100
y (μm)
−100
−50
0
50
100
x (μm)
2.5%

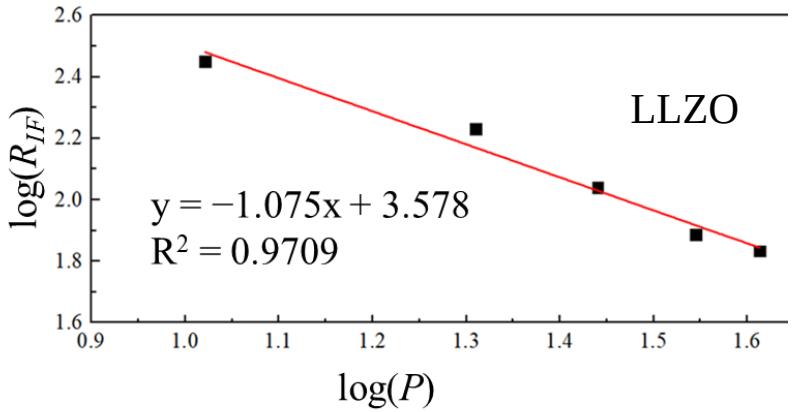

2nm
1e6
6.48
5.76
5.04
4.32
3.60
2.88
2.16
1.44
0.72
0.00
100
50
0
−50
−100
y (μm)
−100
−50
0
50
100
x (μm)


1nm
1e6
4.05
3.60
3.15
2.70
2.25
1.80
1.35
0.90
0.45
0.00
100
50
0
−50
−100
y (μm)
−100
−50
0
50
100
x (μm)


A
Our calculation
Ref. experiment [25]
$E_{stripping}$ (V)
Pressure (MPa)
Time (h)
B
Standard deviation (%)
Yield strength (MPa)
C
9h
54h
contact stress (MPa)
-5.5
-4.4
-3.3
-2.2
-1.1
-0.0

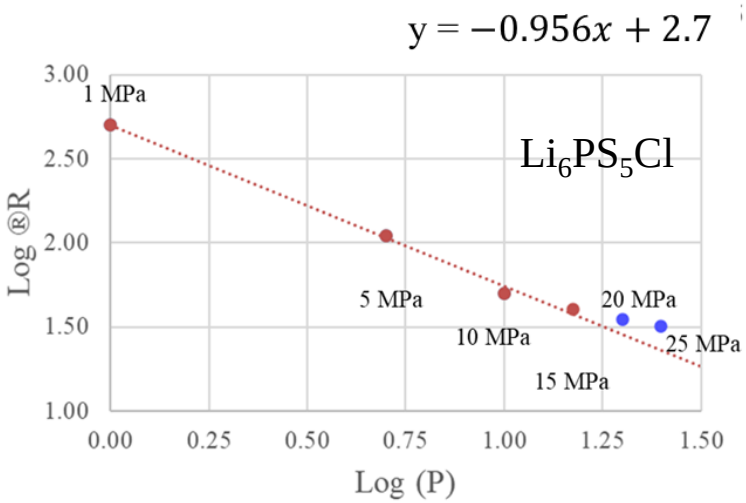
High Pressure Reduces Interfacial Resistance





J. Janek *et al*, *ACS Applied Materials & Interfaces* **11** (2019) 14463-14477

$H \geq 40$ MPa



Contact area fraction ~ P

At 1 MPa, contact ≈ 2.5%

S. Meng *et al*, *Adv Energ Mat* **10**, 1903253 (2020)