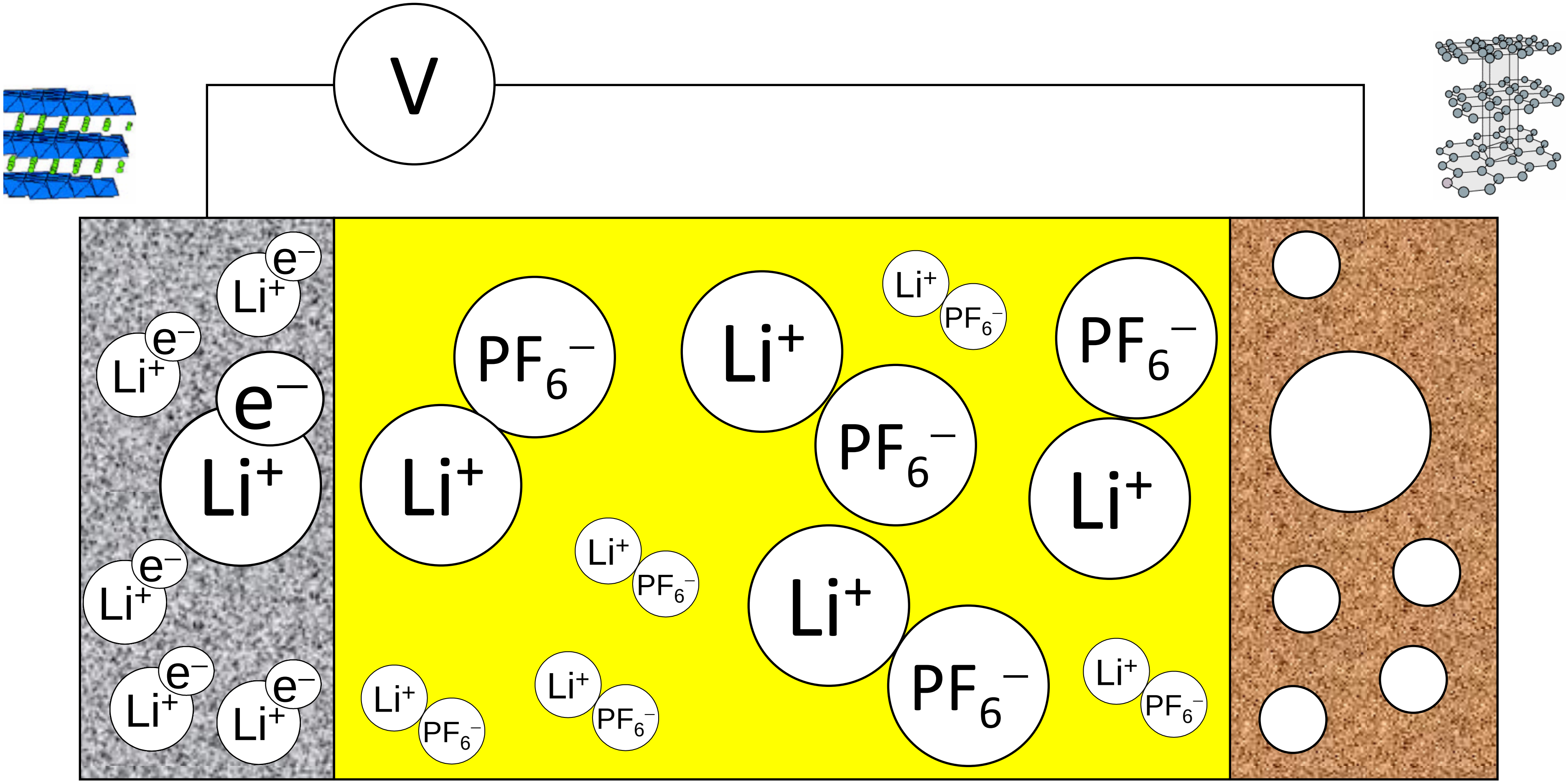
Integrating material properties and Microstructures into Li-ion battery failure modeling

Example: Graphite Anode Deformation during Lithiation

Yue Qi
Chemical Sciences and Materials Systems Lab
General Motors R&D Center
yue.qi@gm.com

In collaborations with:
S. Harris, I. Dutta, A. Timmons, L. Hector, YT Cheng

Charge mechanism (reverse of discharge)



Metal oxide

Electrolyte

Carbon

Cathode is full of lithium when manufactured and at the end of discharge

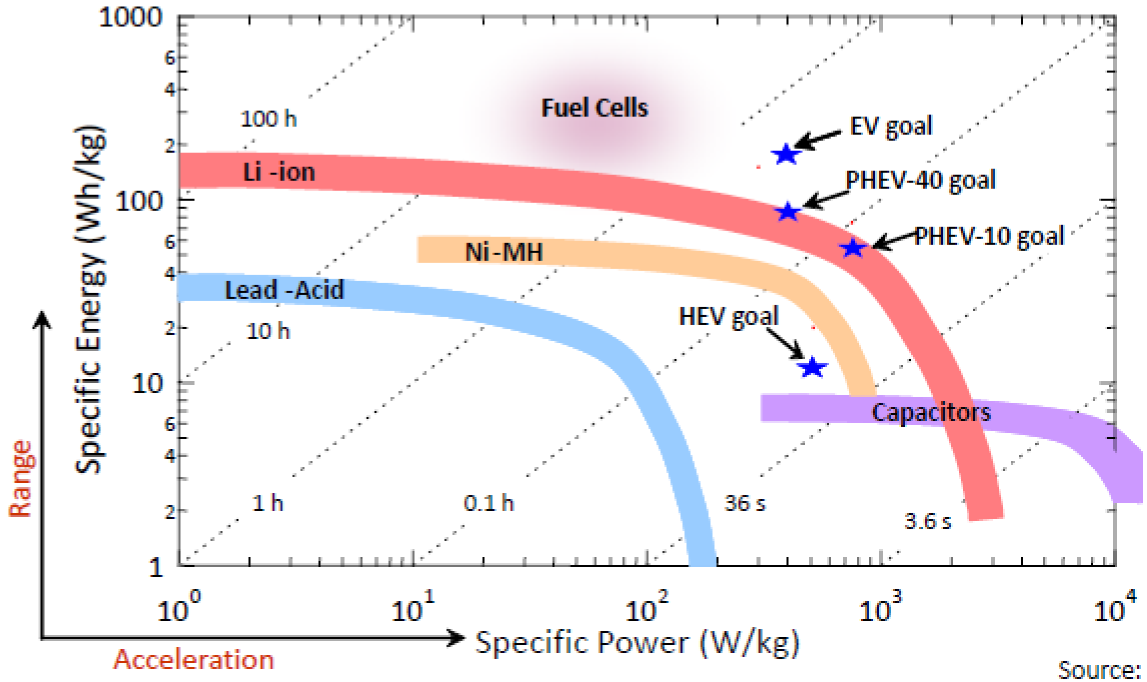
By putting energy into the cell, lithium is forced out of the metal oxide (positive) and into the carbon (negative).

General Needs for Li-ion Batteries

- Simultaneously address these critical challenges
  - **Performance**
    - **low-temperature operation**
    - **energy (capacity X voltage)**
    - **power**
  - **Cost**
    - **Cell (material + manufacture) + other components in the pack**
  - **Life**
    - **Calendar life**
    - **Cycle life**
  - **Abuse tolerance**

These problems are inter-connected, for example: life & cost

Choice of application decides the critical problems to be solved



IC Engine-2500 Wh/kg

EV – Electric Vehicle
HEV – Hybrid-Electric Vehicle
PHEV– Plug-in Hybrid-Electric Vehicle

Source: Product data sheets

- **EV: Need double the energy density of presently available Li batteries**
- **<u>Plug-in hybrid: life and cost</u>**
- **HEV: low-T operation, cost, and abuse tolerance**

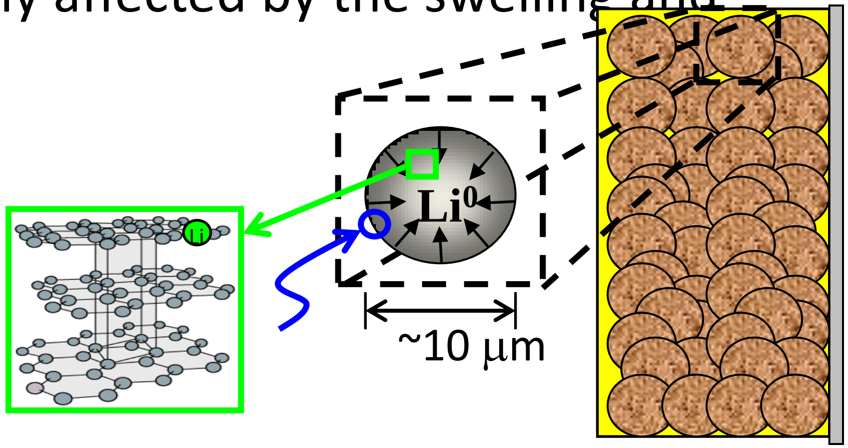
Mechanical Degradation of Graphite Negative Electrode

- During cycling, graphite particles can crack into smaller pieces. The free surface is then covered by SEI, which consumes Li, thus leads to capacity fading.

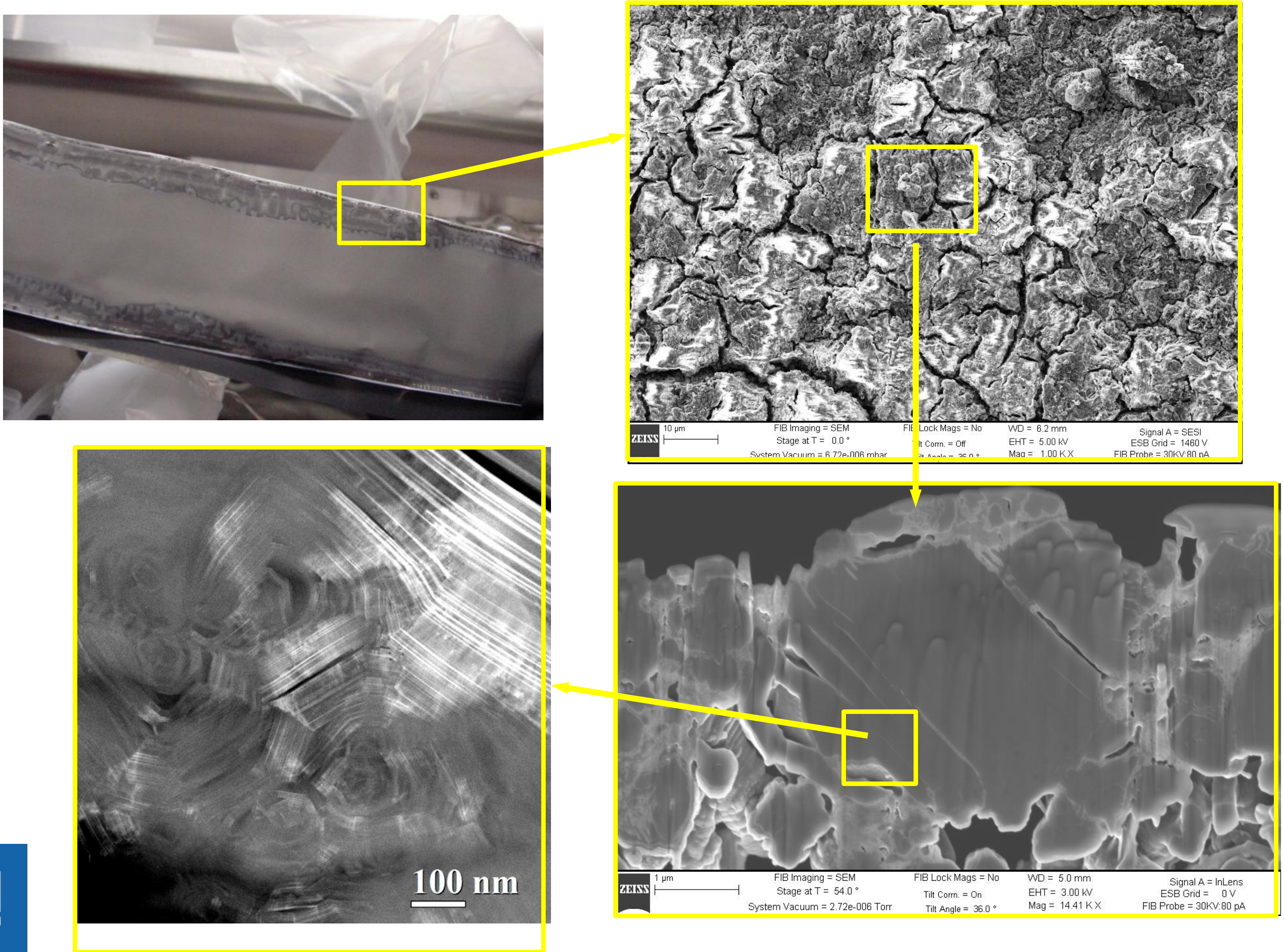
- The swelling and shrinking of graphite particles can also lead to decohesion of the electrode from the current collector, to failure of the binder, and to movement of conductive carbon, all of which reduce connectivity

  → loss of active materials and loss of capacity

- Packing of graphite particles with different geometries will influence whether or not porosity is significantly affected by the swelling and shrinking of graphite particles.



Cracking of Graphite Negative Electrode



Analyses comprehending both electrochemistry and solid mechanics

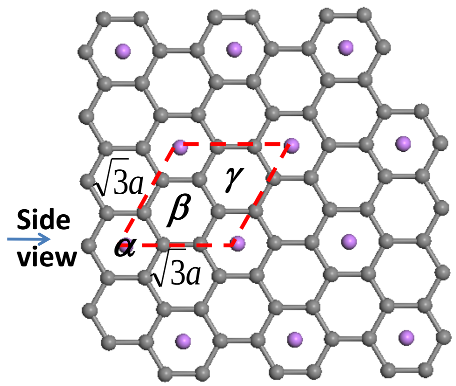
electrochemistry → Li concentration gradient

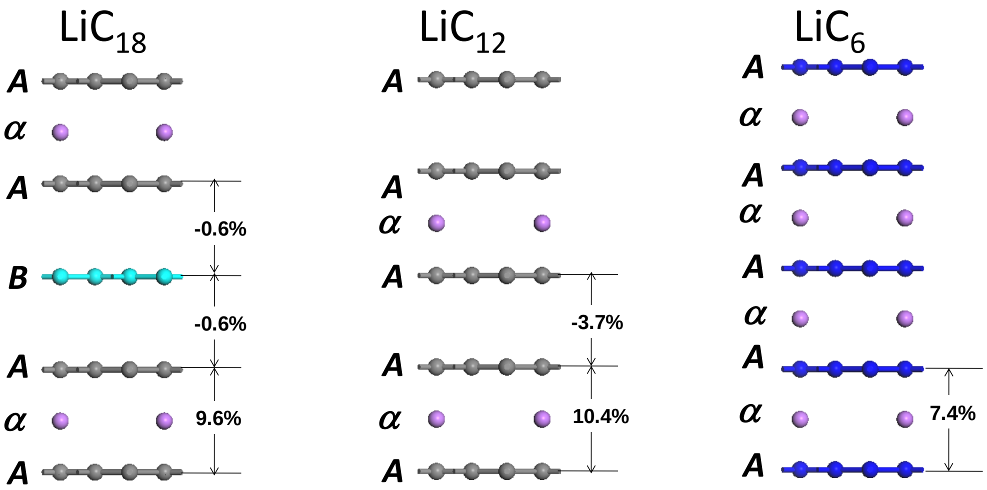
→ volume change → solid mechanics

- R. A. Huggins and W. D. Nix, Ionics 6, 57 (2000)
- R. E. García, Y-M. Chiang, W. C. Carter, P. Limthongkul, and C. M. Bishop, J. Electrochem. Soc. 152, A255 (2005).
- J. Christensen and J. Newman, J. Electrochem. Soc. 153, A1019 (2006).
- J. Christensen and J. Newman, J. Solid State Electrochem. 10, 293 (2006).
- X. Zhang, W. Shyy, and A. M. Sastry, J. Electrochem. Soc. 154, A910 (2007).
- X. Zhang, A. M. Sastry, and W. Shyy, J. Electrochem. Soc. 155, A542 (2008).
- YT. Cheng and MW Verbrugge, *J. Appl. Phys.,* 104, 083521 (2008)
- M. W. Verbrugge, Y-T. Cheng, The Electrochemical Society Transactions 16 (2008) 127.
- …..

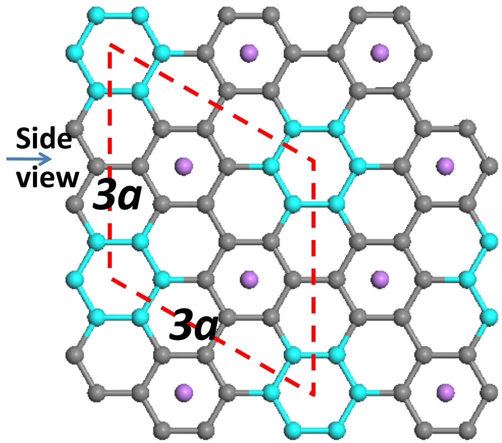
How materials change? Microstructure? Validation?

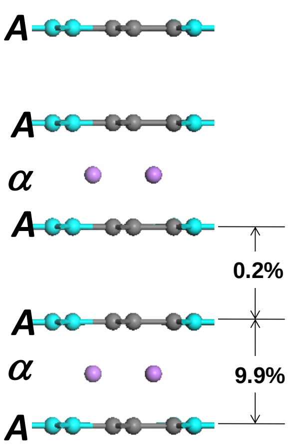
Atomic Charges in Li-GIC Structures





stage-3 LiC_{18}





dilute stage-2 LiC_{18}

● **Li**, with +0.8*e*

● **C**, with -0.14*e*

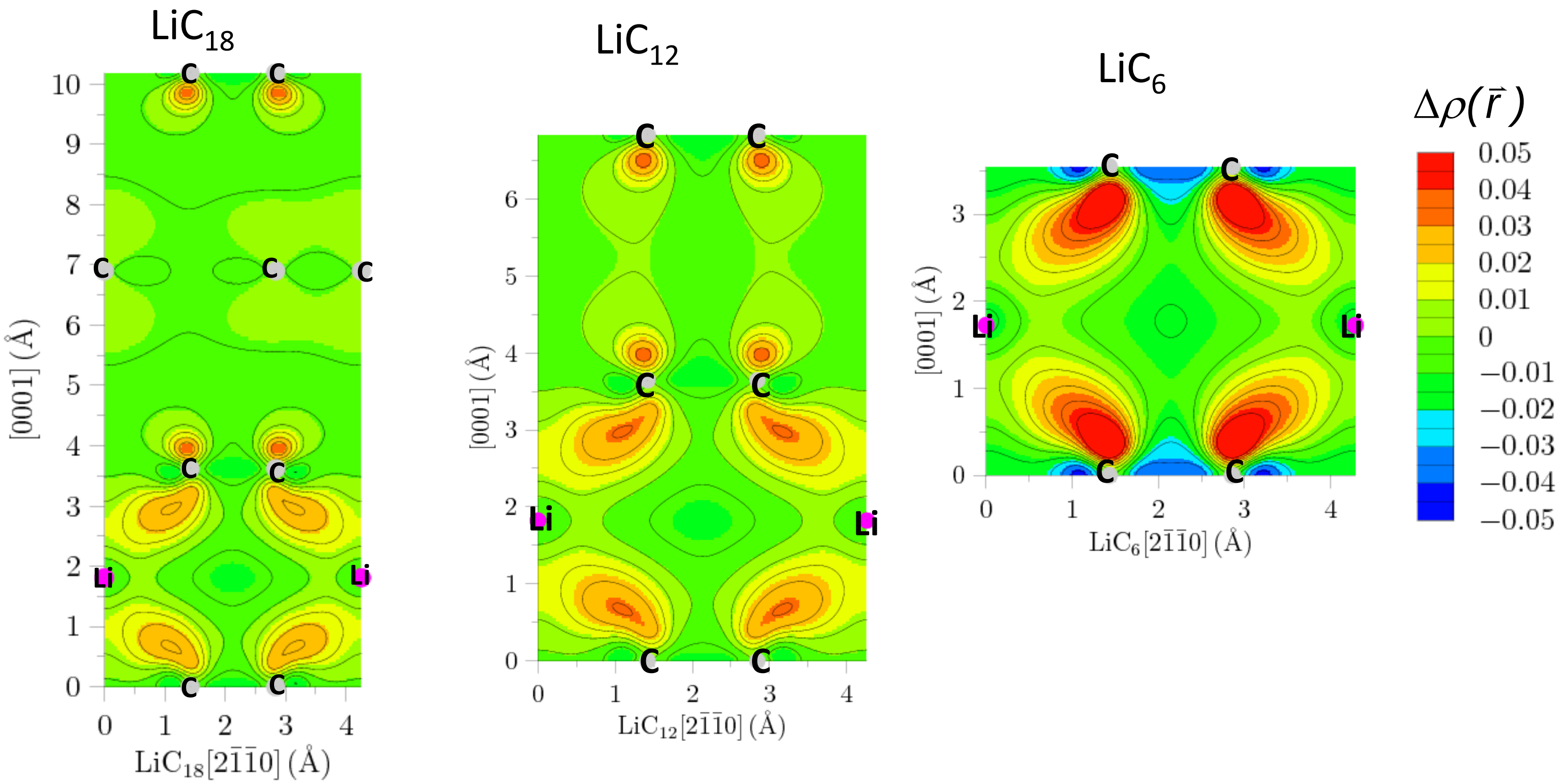
● **C**, with -0.06~-0.07*e*

● **C**, with 0~-0.01e

Li insertion reaction in graphite (S is the site for Li^+)

$$Li^+ + e^- + S \Leftrightarrow [Li^+ - S^-]$$

Atomic Bonding in Li-GIC



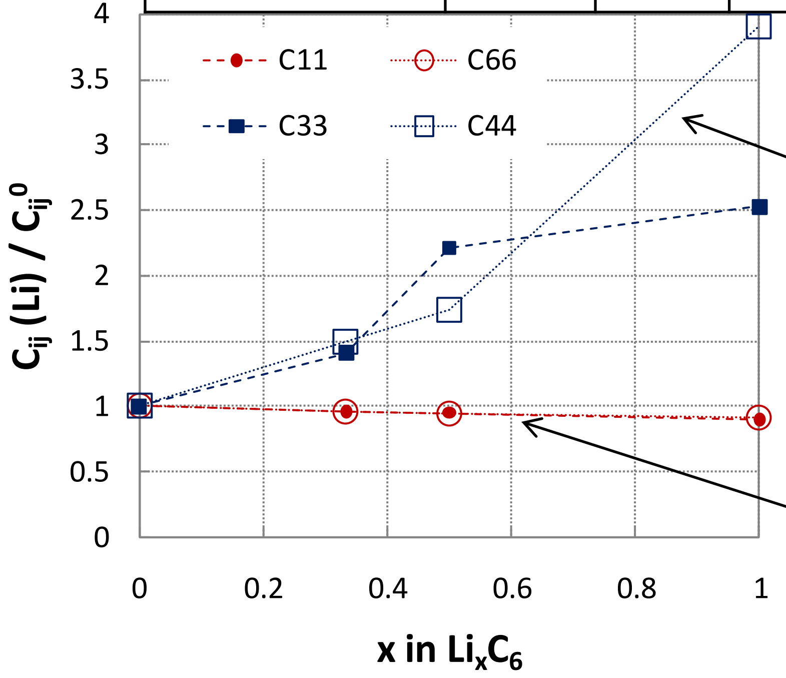
Inter-layer bonding: The ionized Li and the C-ring above and below it form a strong cation-π interaction → **Stronger**

Intra-layer bonding: Excess electrons fill the anti-π bonding orbitals in graphite, and in-plane σ-bonds loss electrons → **Weaker**

Elastic Properties Changes for Single Crystals

DFT predicted

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
Graphite	**1104.8**	**203.9**	**-2.5**	**30.9**	**5.6**	**450.45**
stage-3 LiC_{18}	**1058.1**	**194.8**	**-2.5**	**43.4**	**8.4**	**431.65**
LiC_{12}	**1047.7**	**191.9**	**-5.9**	**68.3**	**9.7**	**427.9**
LiC_6	**988.6**	**170.6**	**2.1**	**78.0**	**21.9**	**409**



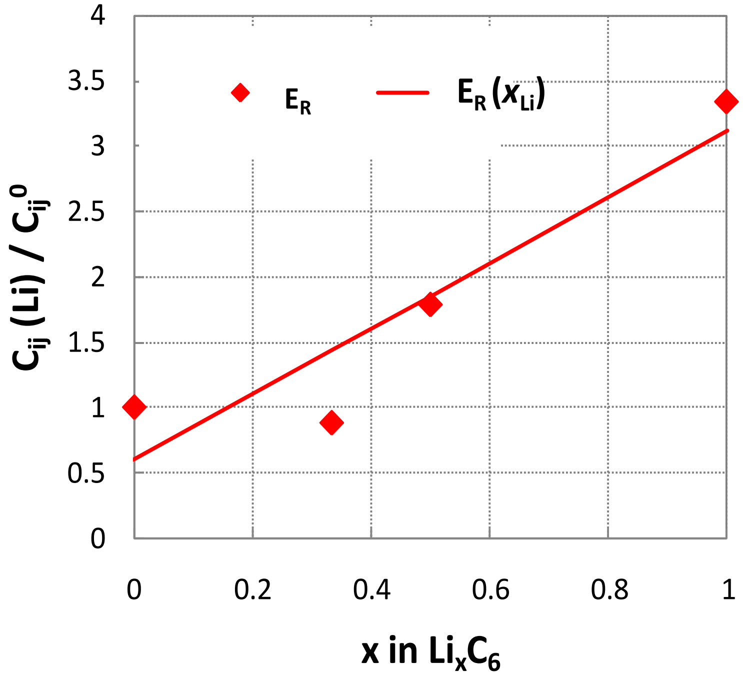
Inter-layer bonding: stronger

Intra-layer bonding: weaker

[Y. Qi, H. Guo, L. Hector, A. Timmons, J. Electrochemical Society, 157 (5) A558 (2010)]

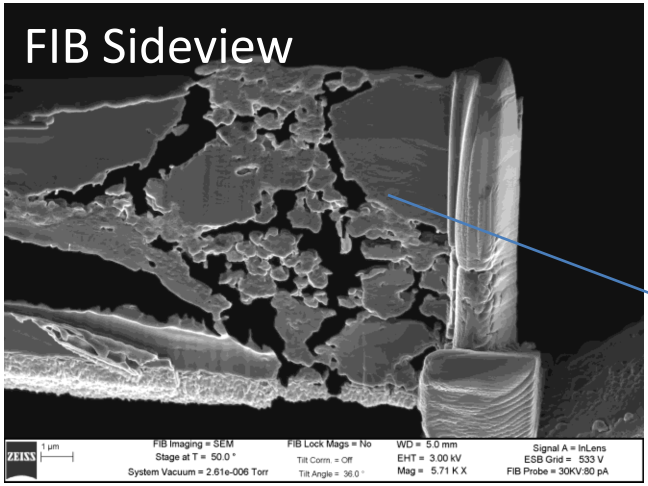
Averaged Elastic Properties for Polycrystals

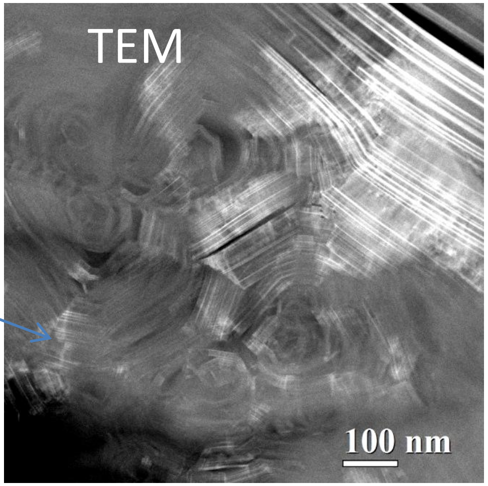
	Reuss average E_R	Reuss average μ
Graphite	**32.47**	**0.31522**
stage-3 LiC_{18}	**28.57**	**0.39**
LiC_{12}	**58.06**	**0.34**
LiC_6	**108.67**	**0.24**



Young's Modulus increases with Li concentration / SOC

$$E_R(x_{Li}) = 19.25 + 82.23x_{Li}$$

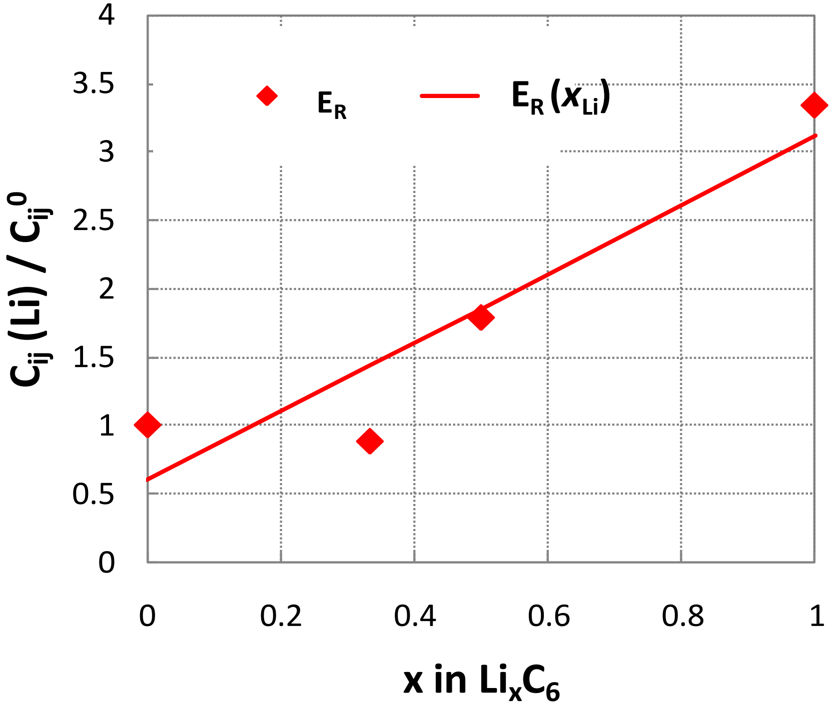




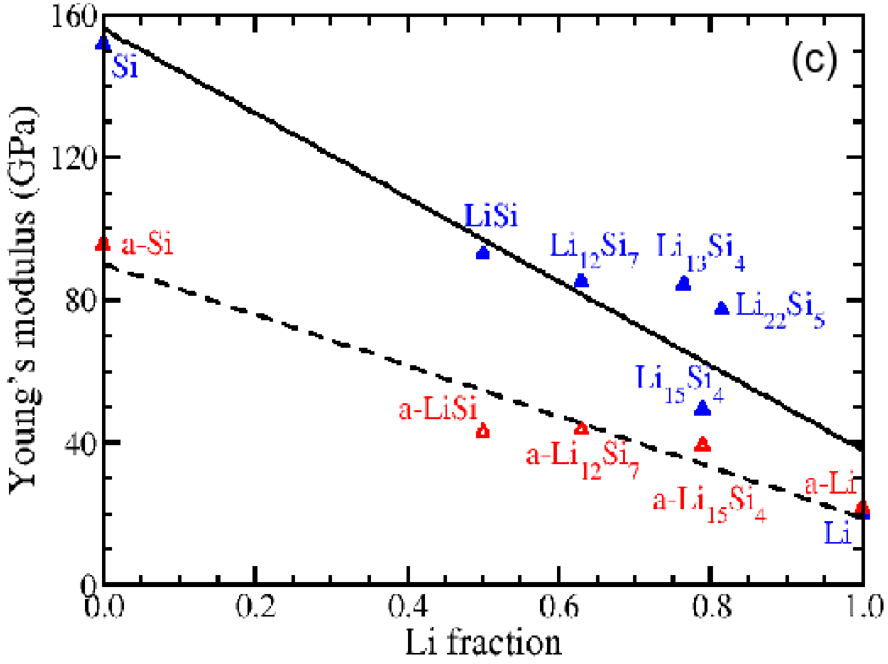
Lithiation induced hardening and softening

$$E=E_0+k*c$$

Li-Graphite

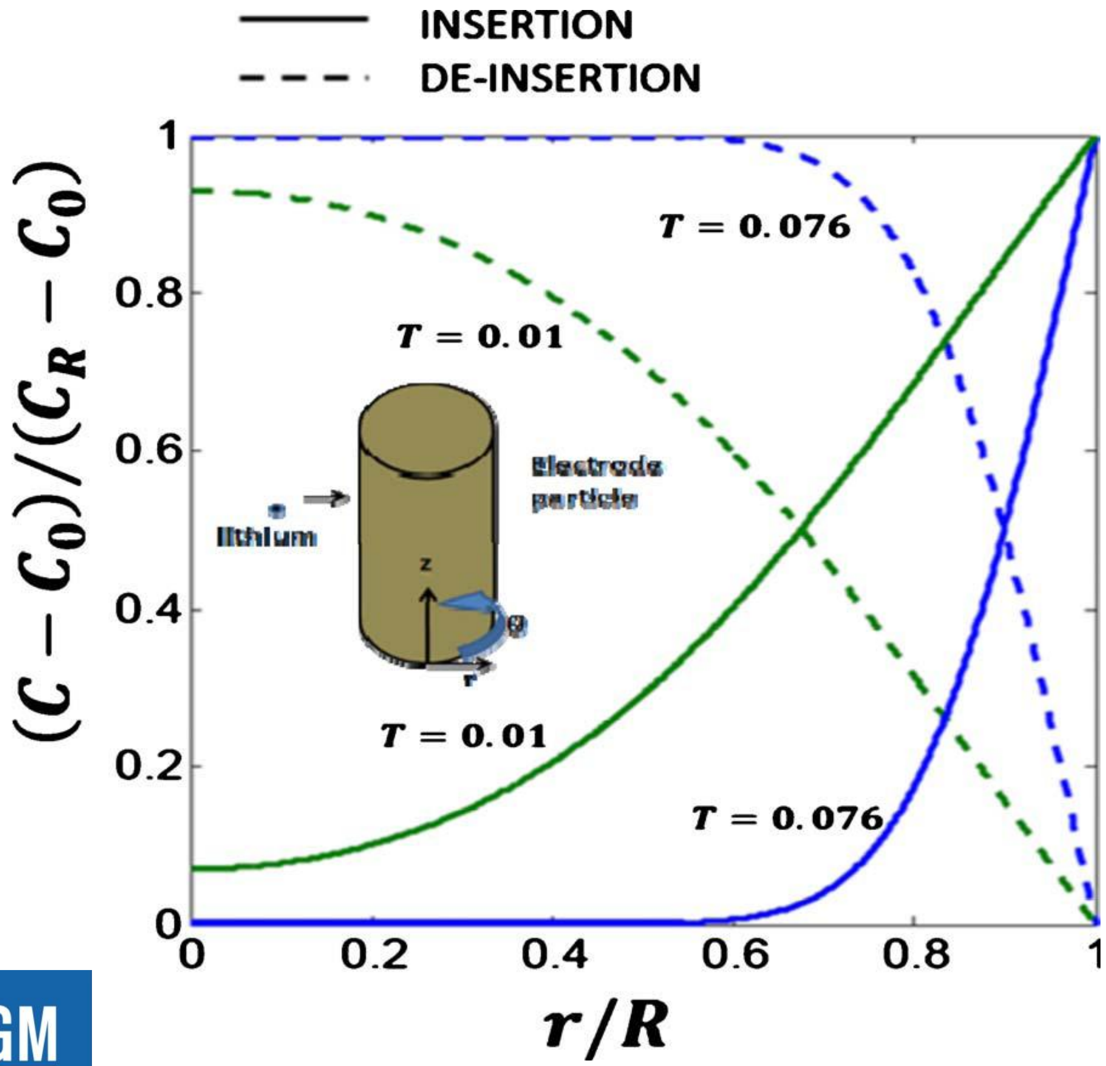


Li-Si (crystal and amorphous)



[Y. Qi, H. Guo, L. G. Hector and A. Timmons, Journal of The Electrochemical Society , 157, A558-A566 (2010).]
[V. B. Shenoy, P. Johari, Y. Qi, **J. Power Sources**, 195, 6825 (2010)]

Resolve the DIS for a solid particle with E(SOC)



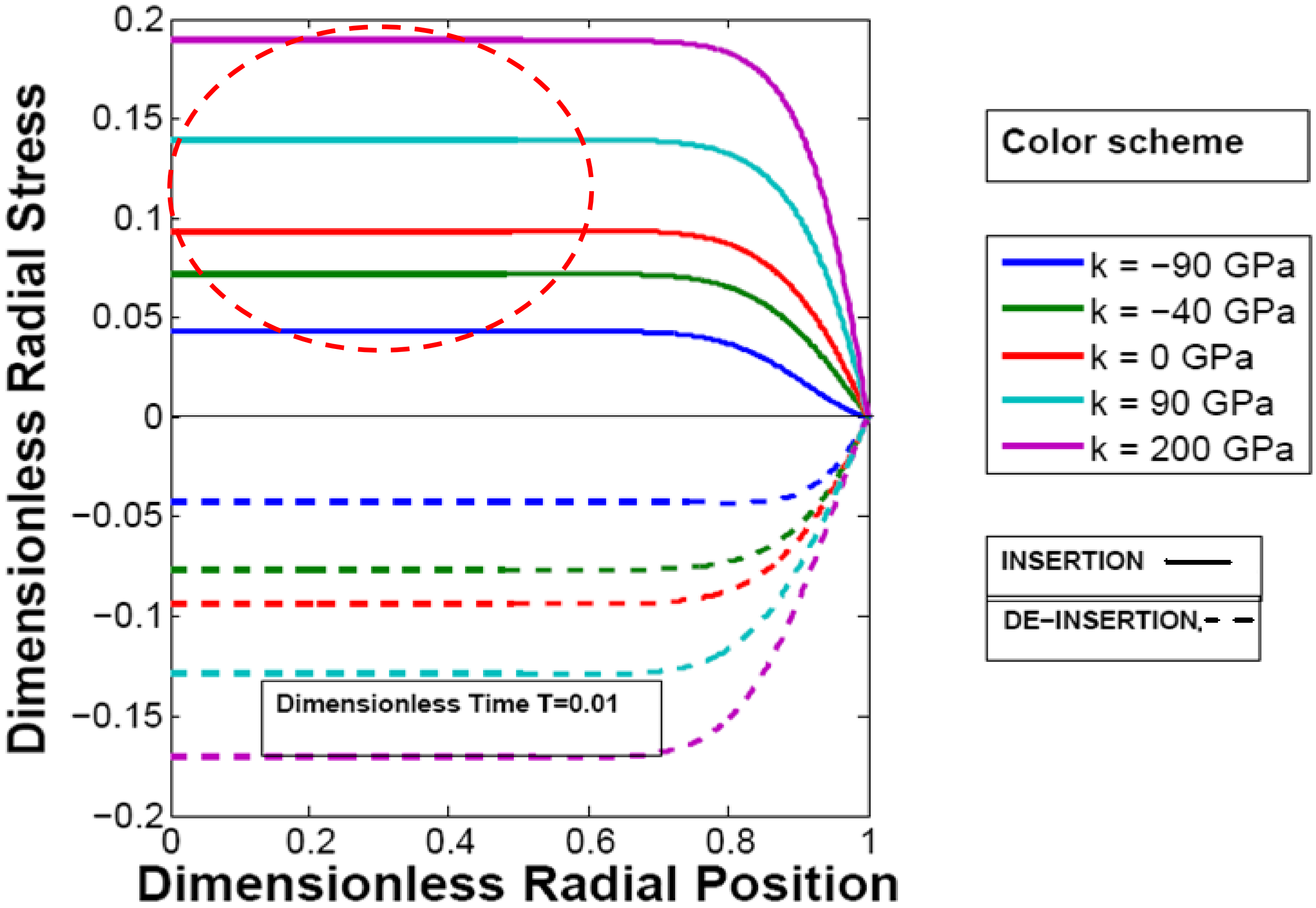
- Young's Modulus of electrode material as a linear function of Li concentration

  *E= E0 +k*C*

(*K= -90 Gpa, -40Gpa, 0Gpa , 90Gpa, 200 Gpa*)

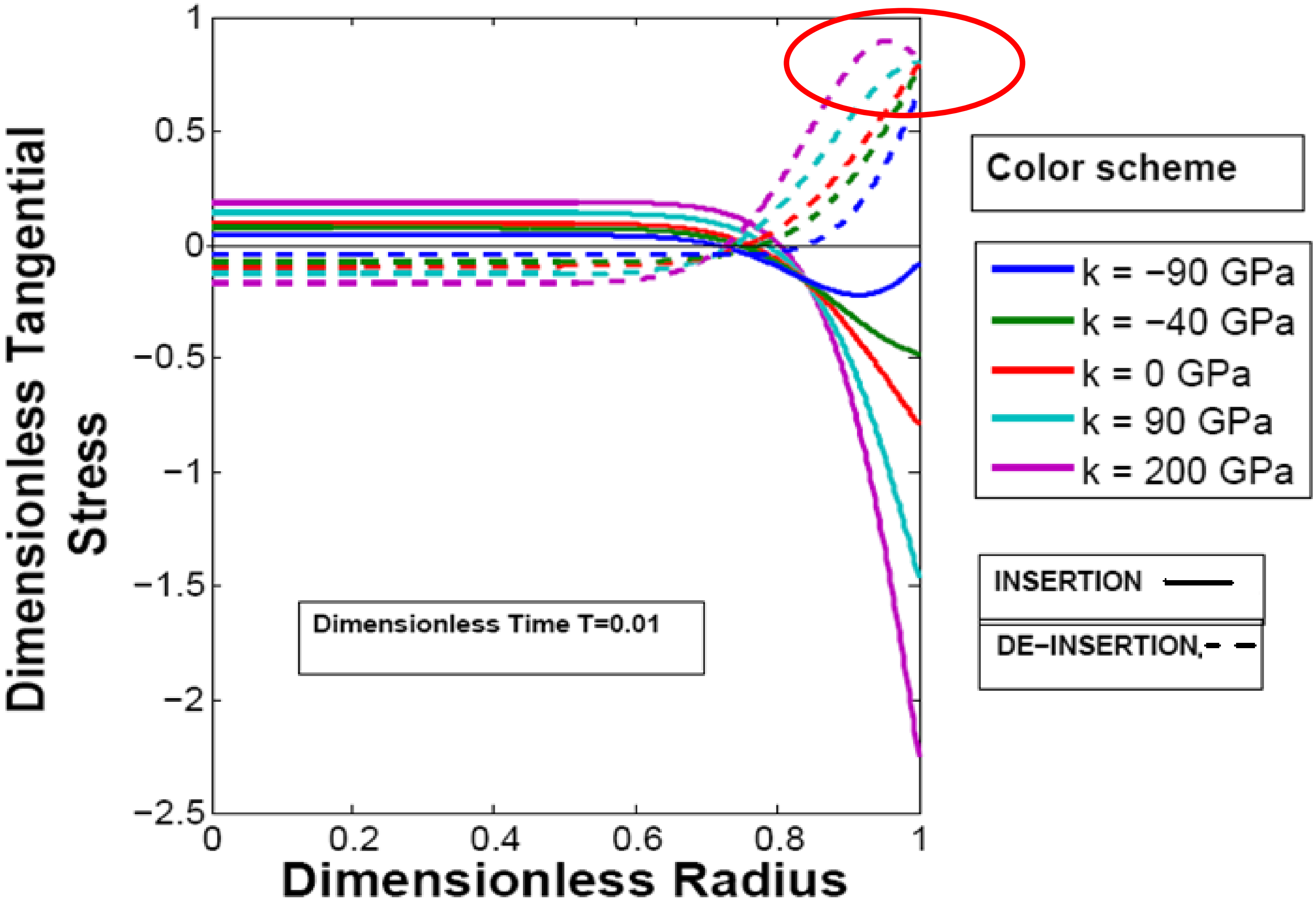
Concentration profiles are symmetric during insertion and de-insertion

Softening electrode is less likely to crack in the center during Li insertion



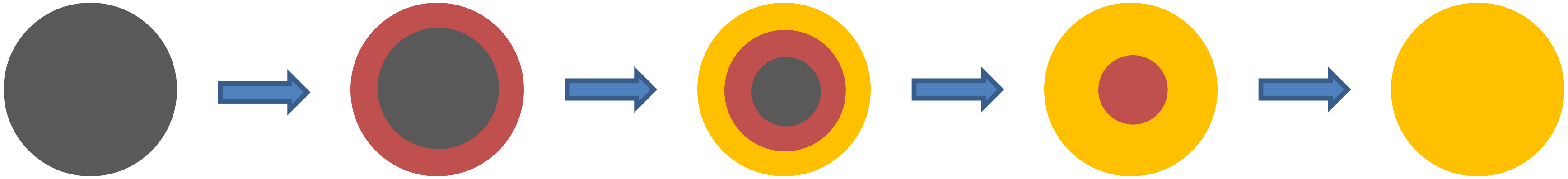
[R.D. Deshpande, Y. Qi, Y.T. Cheng, **J. Electrochemical Society**, 157, A967 (2010)]

Hardening electrode is less likely to crack at the surface during Li removal



Influence from micro-structures

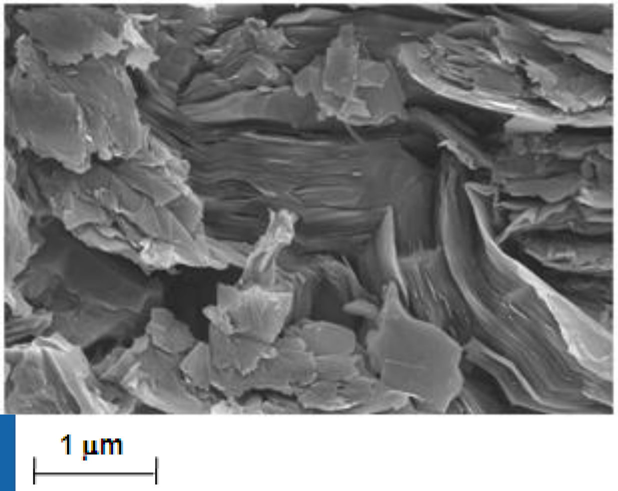
Shrinking Core Model: Li transport within particles is macro-homogeneous.

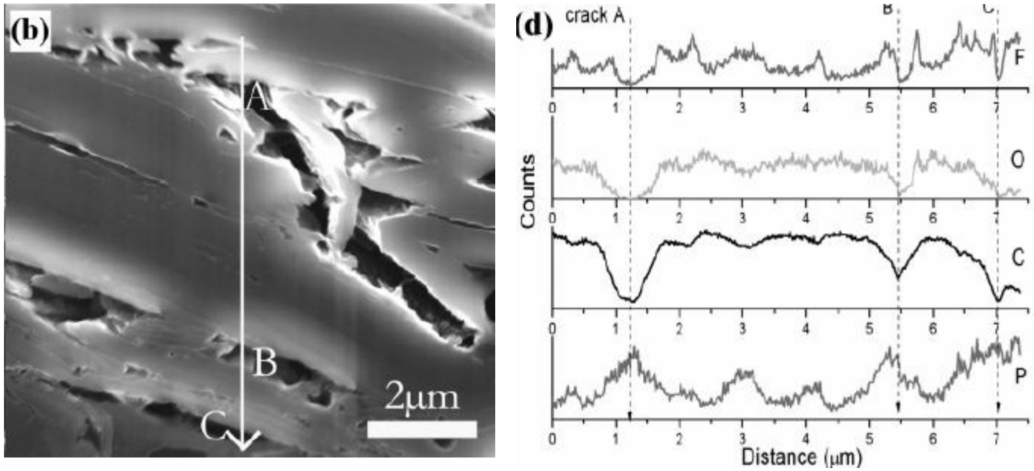


Can solid spheres or fibers represent real electrodes?

Inside of an electrode particles.

graphite particle





New Insight into the Solid Electrolyte Interphase with Use of a Focused Ion Beam

Hong-Li Zhang, Feng Li, Chang Liu, Jun Tan, and Hui-Ming Cheng*

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

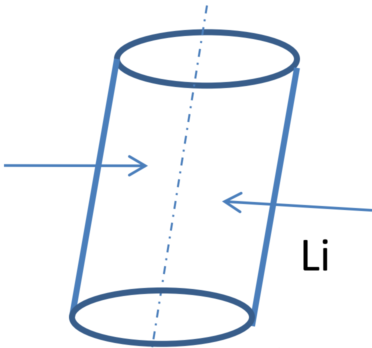
Received: June 20, 2005; In Final Form: September 6, 2005

J. Phys. Chem. B **2005,** *109,* 22205−22211

Diffusion in a cylindrical particle (1 μm) with a small pore (10 nm)

- Diffusion of Li^+

$$\frac{\partial c}{\partial t} = \mathcal{D}\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r}\right)$$



- Under a potentiostatic charging-discharging condition or constant concentration of Li ions surrounds the electrode particle.
- Compare Three Cases: *a=1% R*
  - **Solid electrode**, no pore

$$\begin{cases} C(r,0) = C_0, & for\ 0 \le r \le R \\ C(R,t) = C_R, & for\ t \ge 0 \\ C(0,t) = finite, & for\ t \ge 0 \end{cases}$$

  - **Filled mesopore:**

Pre-existing coaxial pore of radius *a*, filled with electrolyte

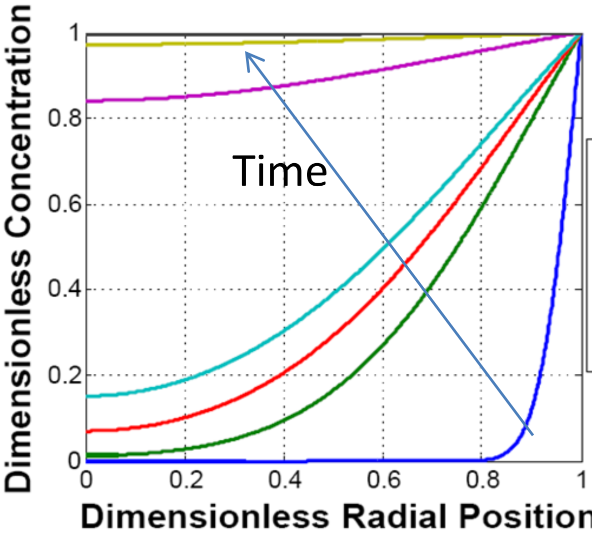
$$\begin{cases} C(r,0) = C_0, & for\ 0 \le r \le R \\ C(R,t) = C_R, & for\ t \ge 0 \\ C(a,t) = C_R, & for\ t \ge 0 \end{cases}$$

  - **Empty mesopore:** Pre-existing coaxial pore of radius *a*, empty (not accessible to the electrolyte)

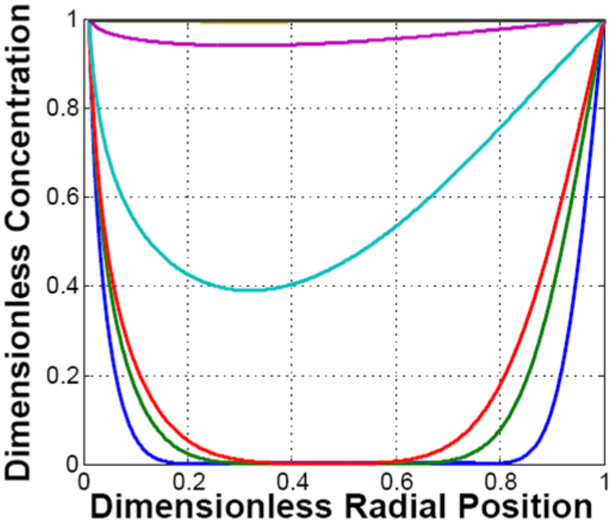
$$\begin{cases} C(r,0) = C_0, & for\ 0 \le r \le R \\ C(R,t) = C_R, & for\ t \ge 0 \\ \frac{dC(a,t)}{dx} = 0, & for\ t \ge 0 \end{cases}$$

Filled Mesopores Enhance Diffusion

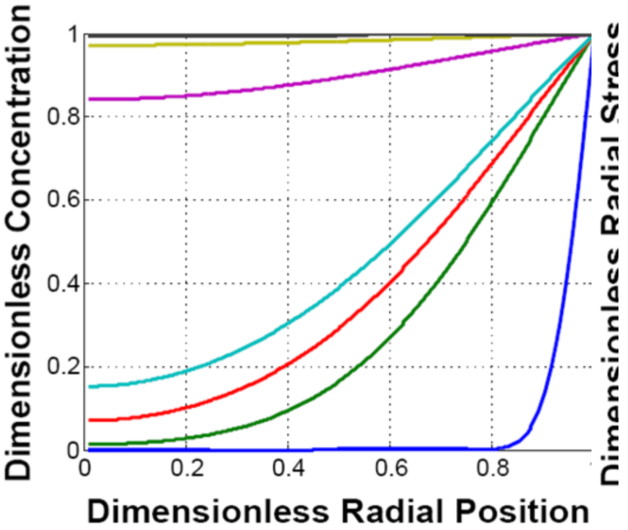
Solid electrode



Filled mesopore

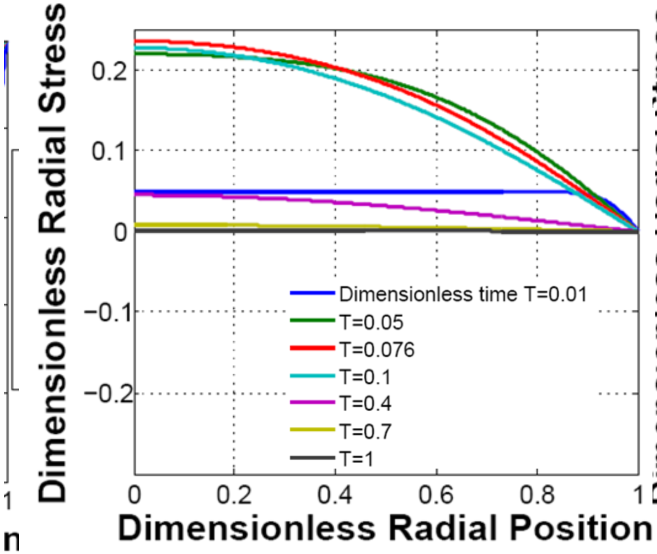


Empty mesopore

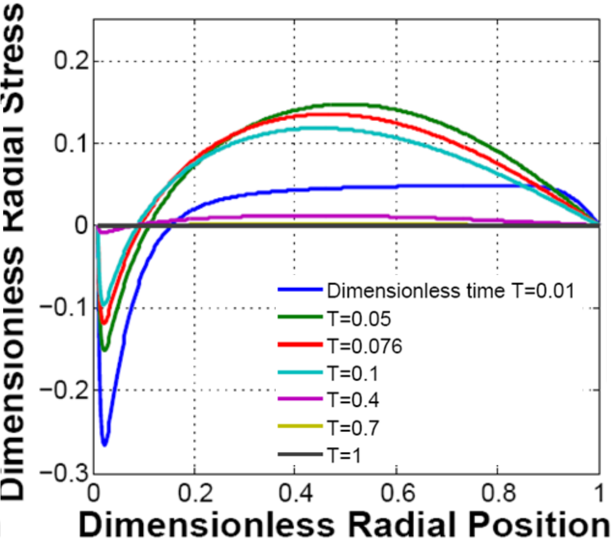


Radial Stress During Lithiation

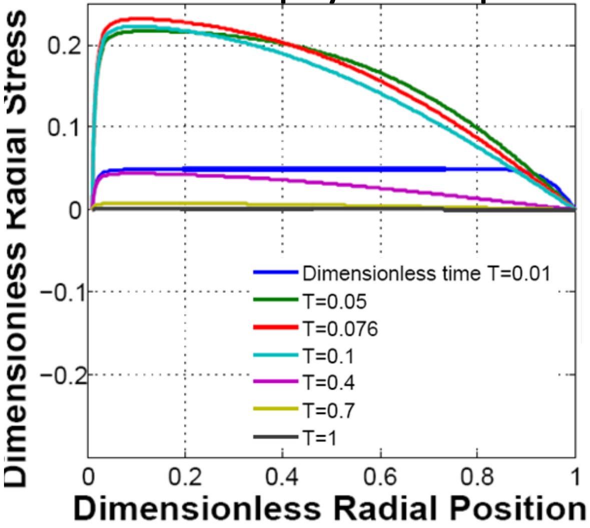
Solid electrode



Filled mesopore



Empty mesopore

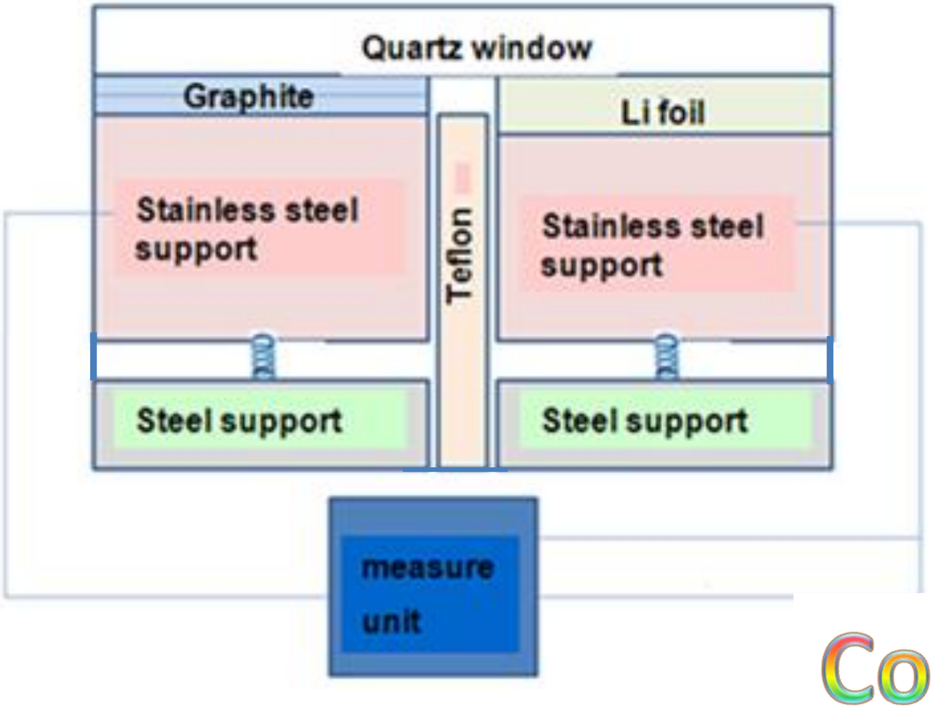


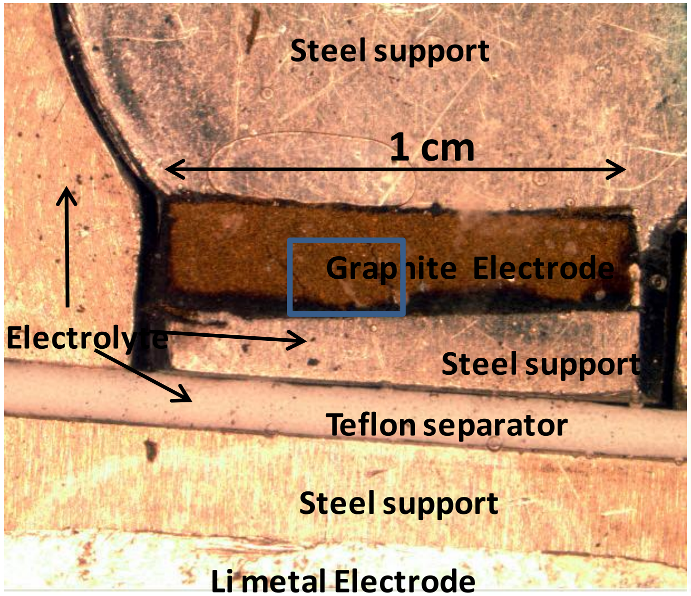
Solid electrode particle fails at the center. Presence of the pore prevents failure at the center and reduces failure inside the particle.

[S. J. Harris, R.D. Deshpande, Y. Qi, I. Dutta, Y.T. Cheng, **J. Mat. Res.,** 25, 1433 (2010)]

Visualization of Diffusion Induced Deformation

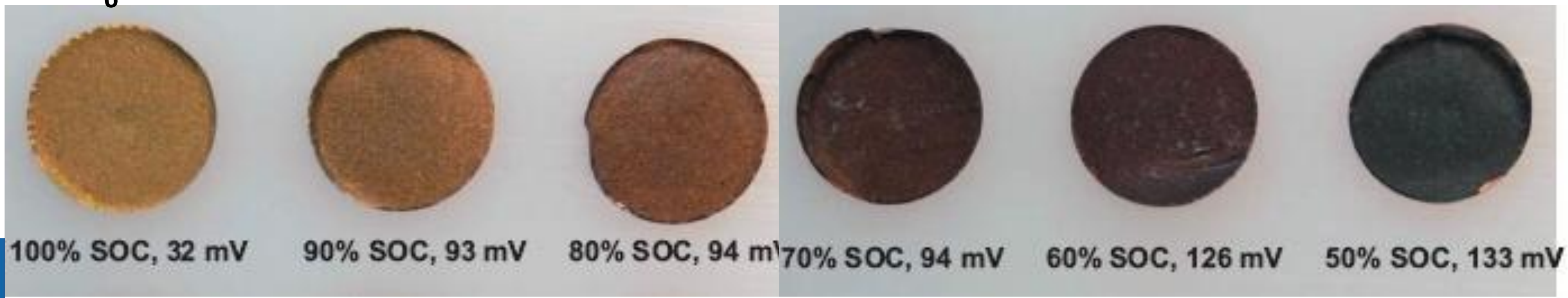
Step 1: Optical Half-Cell to visualize Li diffusion





Color maps (Li concentration)

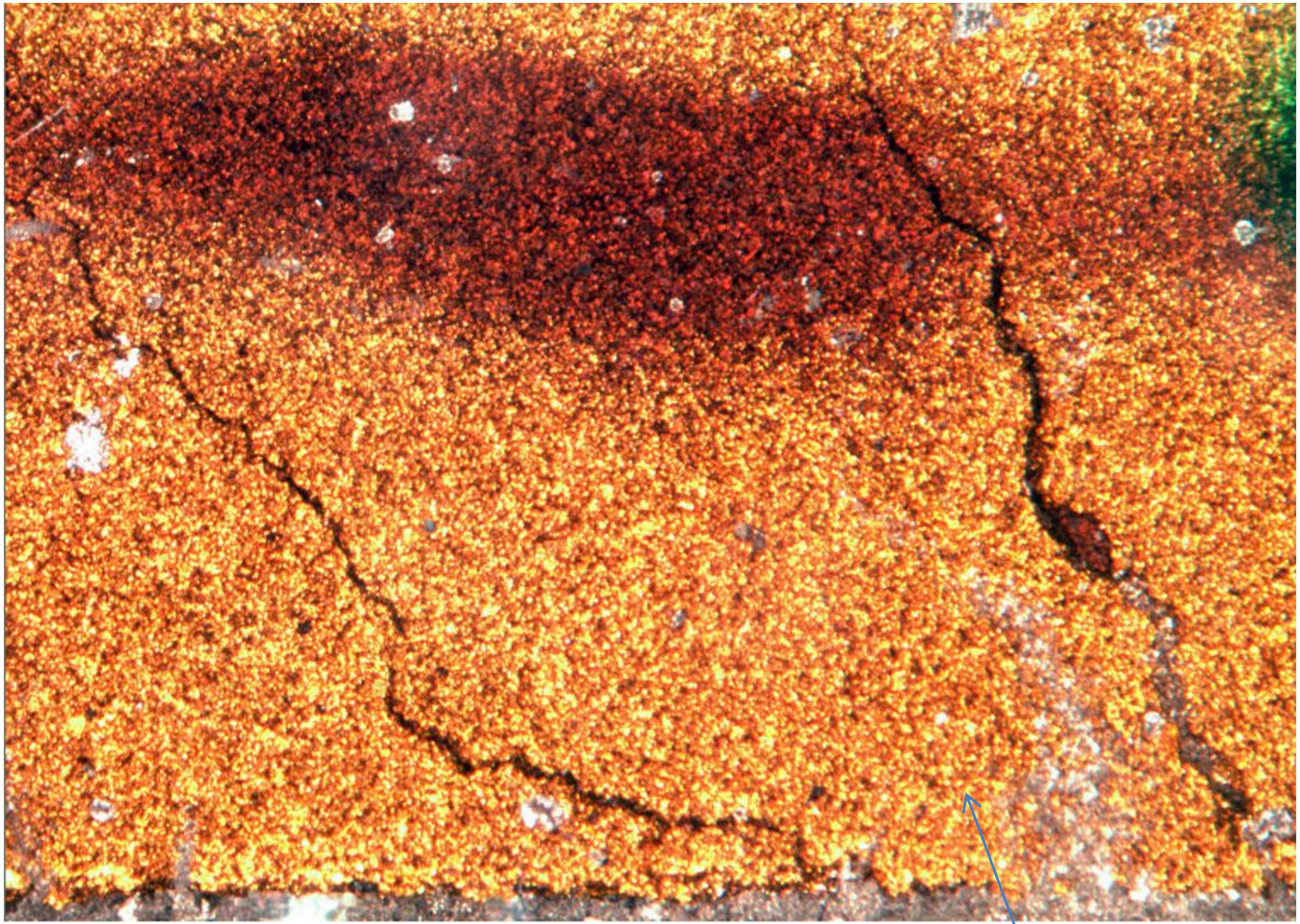
LiC$_6$ **LiC$_{12}$**



P. Maire, A. Evans, H.Kaiser, W. Scheifele, and P.Novák, *J. Electrochem. Soc.* , ***155*** **,** 862 (2008)

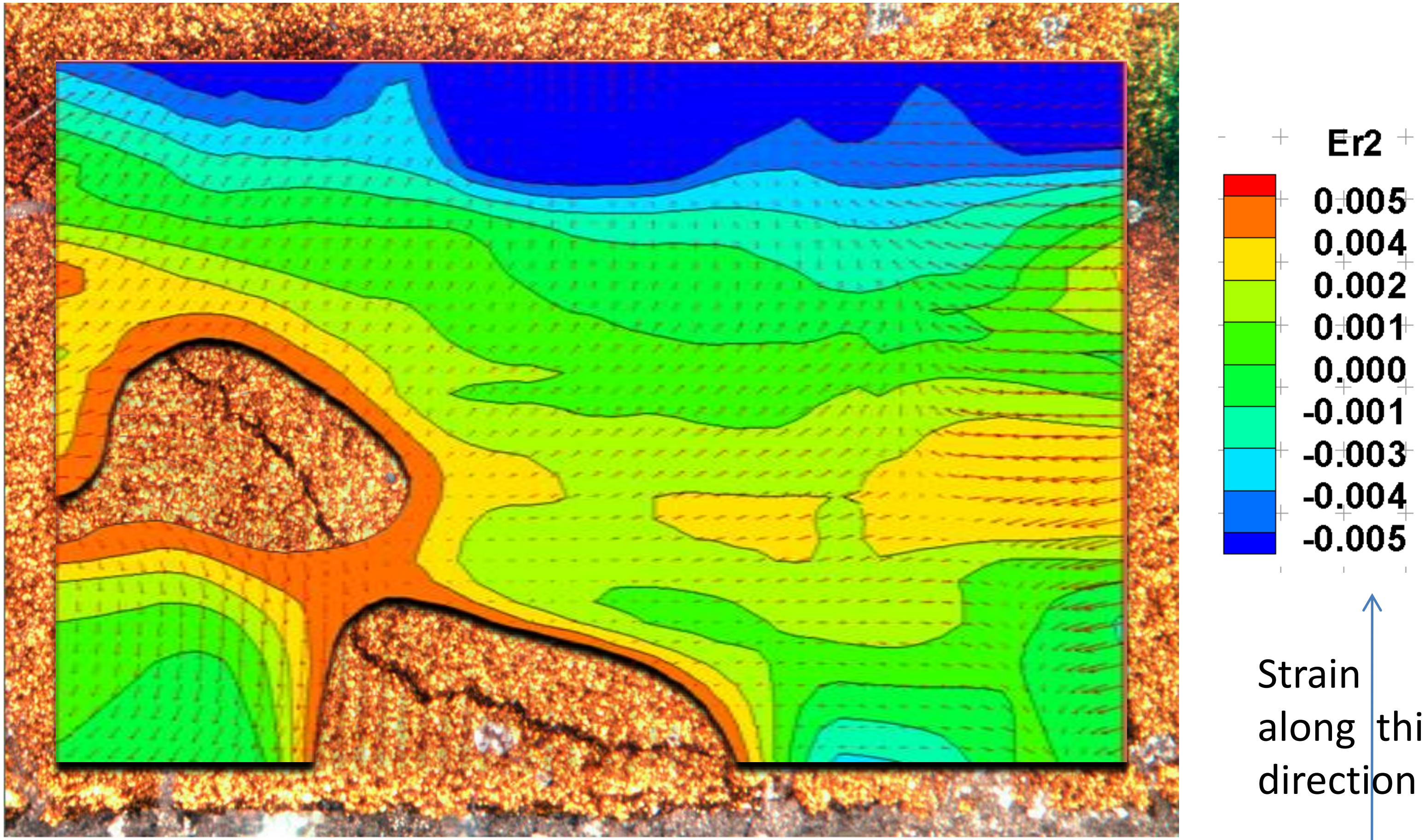
Color maps Li concentrations and diffusion

T2



Li diffusion

DIC Strain Map along major Diffusion Direction

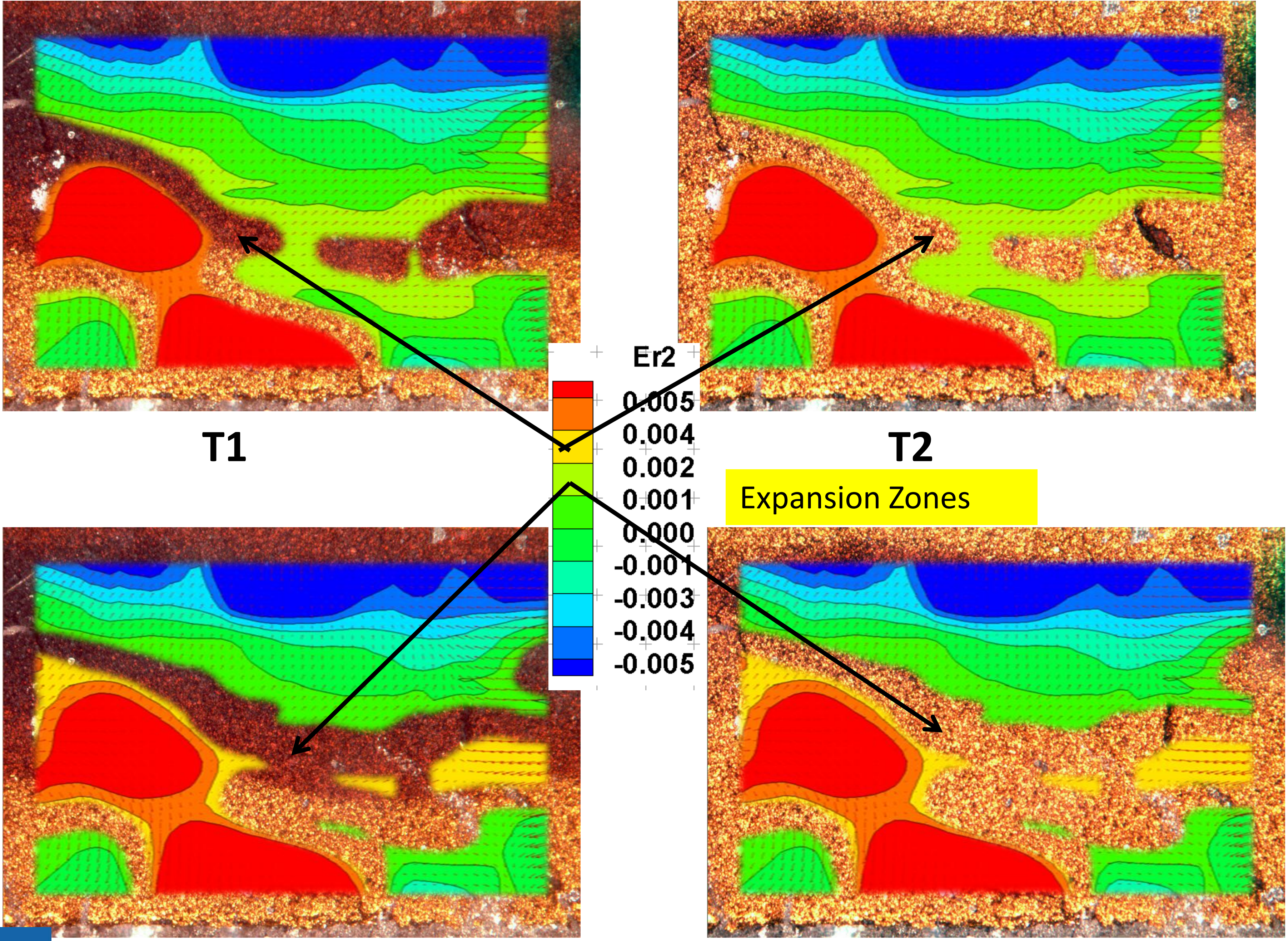


Strain along this direction

From T1 to T2

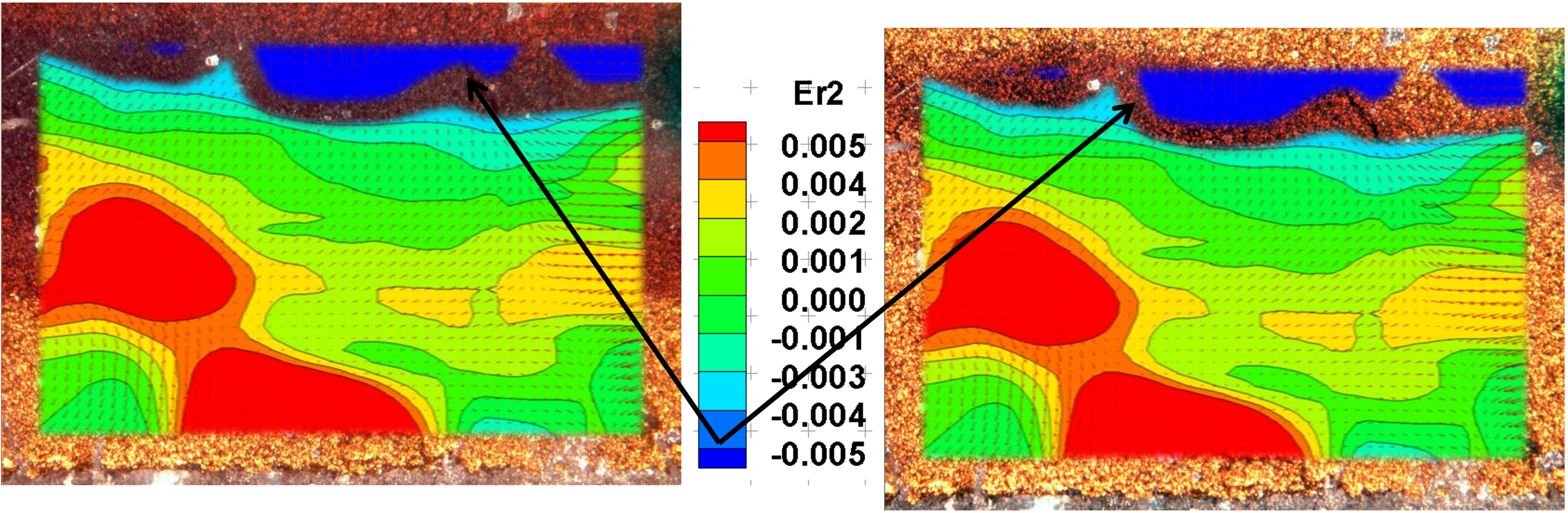
Li main diffusion direction

[Y. Qi and S.J. Harris, **J. Electrochemical Society**, 157, A741-A747, (2010)]


Er2
0.005
0.004
0.002
0.001
0.000
-0.001
-0.003
-0.004
-0.005
T1
T2
Expansion Zones

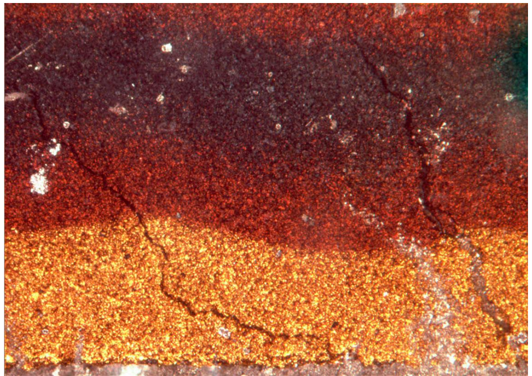
Li stiffening is responsible for the compression during Lithiation

T1 **T2**



Compression Zones

Li main diffusion direction, strain direction



Conclusions and future work

- Li stiffens graphite during intercalation (proved by DIC)
- Li softens Si during lithiation
- The fracture energy of Li-graphite decreases with voltage
- Most material properties are functions of SOC
- Internal defects can change diffusion and diffusion induced stress

- Future Work: To connect material chemistry and structure with degradation mechanisms
    - Chemistry, Surface treatment, Particle structure, Defects
    - Microstructure (packing, porosity …)
- Goal: To <u>model</u> failure modes and <u>predict</u> batteries life