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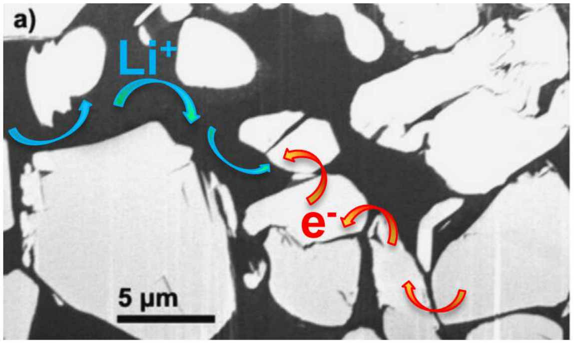

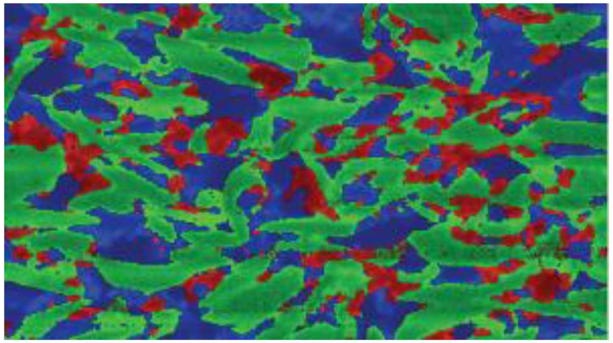

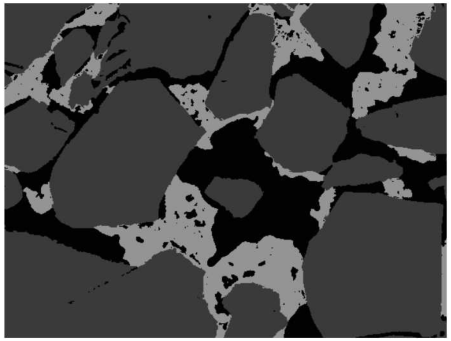

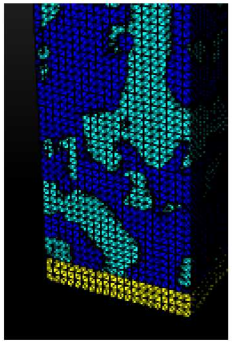

The role of polymer composite binder on mechanics and performance of lithium ion battery electrodes

T. Humplik, A.M. Grillet, D.A. Barringer, E.K. Stirrup, H. Mendoza, S.A. Roberts, C. Snyder, C.A. Apblett, and K. Fenton

2015 American Institute of Chemical Engineers Annual Meeting

November 10, 2015

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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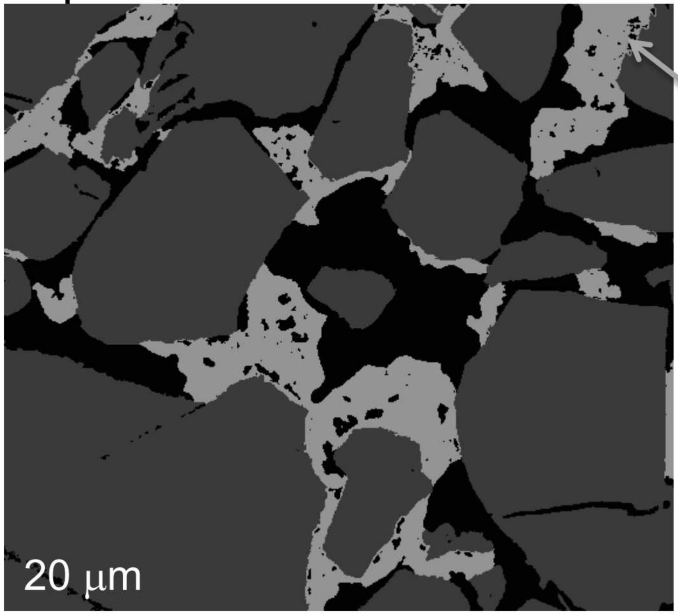
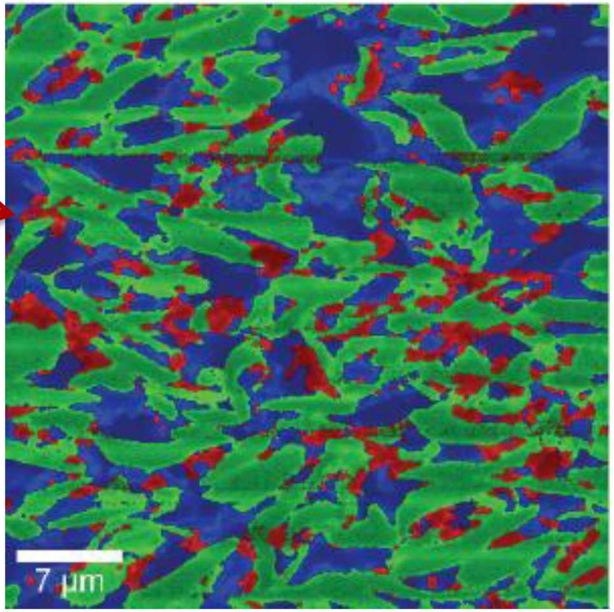
Batteries are actually complex composites

- Electrode active material particles are held together by binder
  - Binder is a mixture of polyvinylidene fluoride (PVDF) and carbon black
- Actual voltage depends on how efficiently lithium ions and electrons are transported



binder



Cathode
94wt% $LiCoO_2$
3wt% PVDF
3wt% CB
void

Anode
94wt% graphite
4wt% PVDF
2wt% CB
void

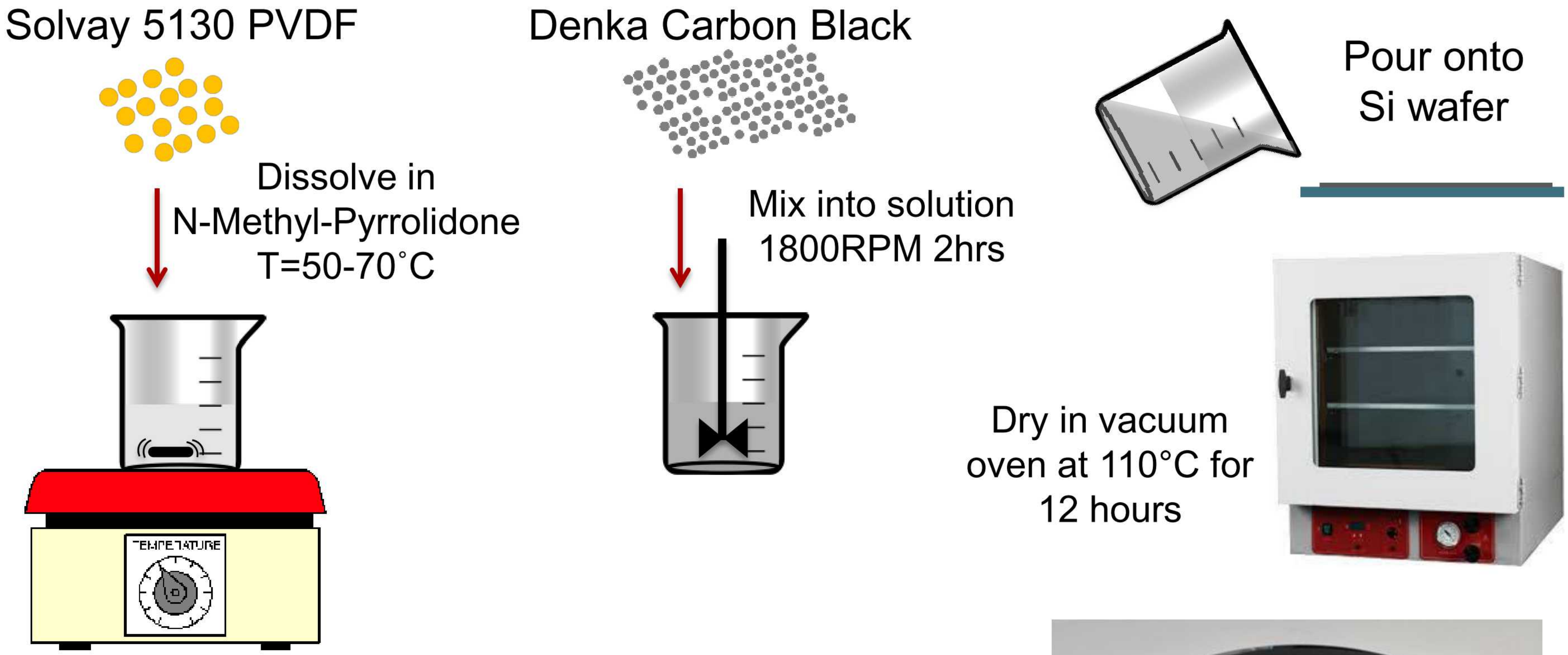
Hutzenlaub *et al.* (2012), Doyle et al (2003), Liu et al. (2012); Thomas Beechem (SNL)

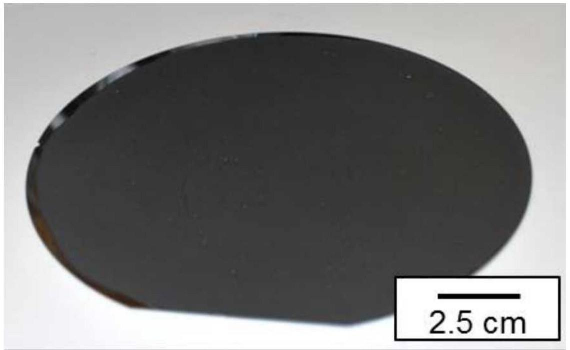
Outline

- Battery electrode binders play an important role both mechanically & electrochemically
- Mechanical characterization
  - Both dry and in the presence of electrolyte
- Microstructure modeling of battery cathode

- Binder plays a significant role in mitigating stress development in the cathode during charging

Synthesis of PVDF/CB Binder films

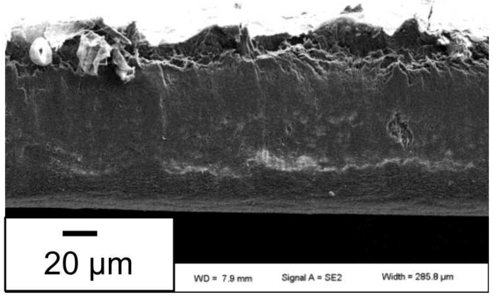


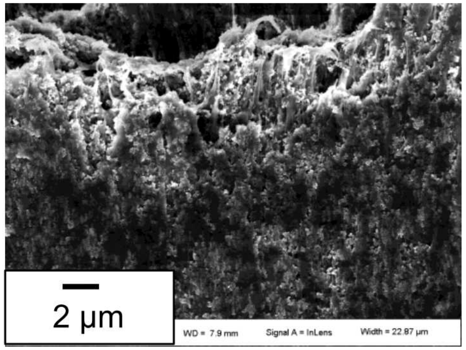


- Film thickness on the order of 100 - 200 µm

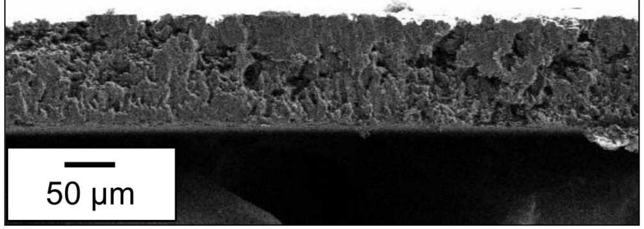
Morphology of PVDF/Carbon Black Composites

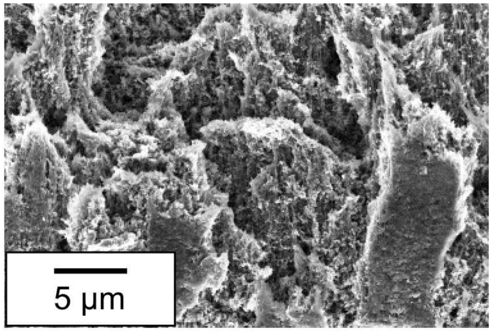
20wt% Carbon Black

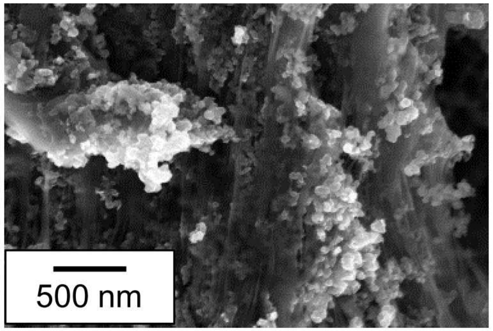




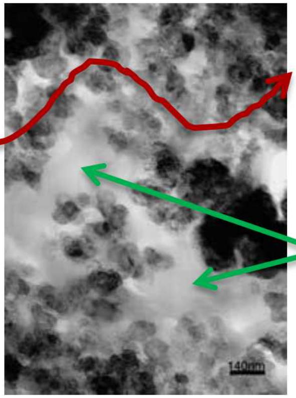
40wt% Carbon Black





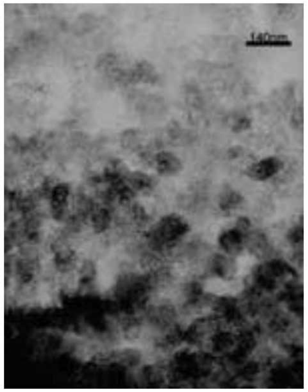


e⁻ paths



TEM of 33wt% CB in PVDF

Free PVDF

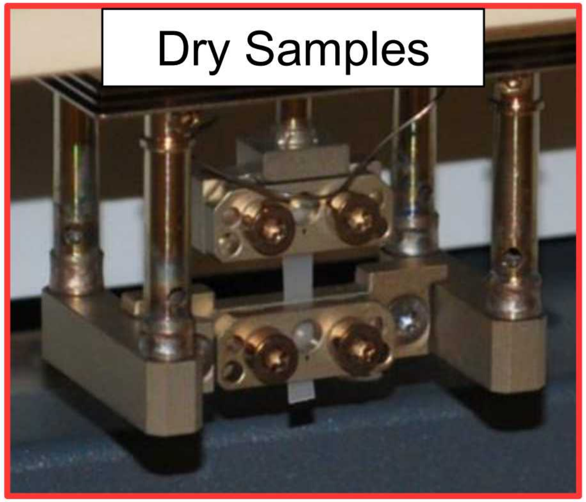


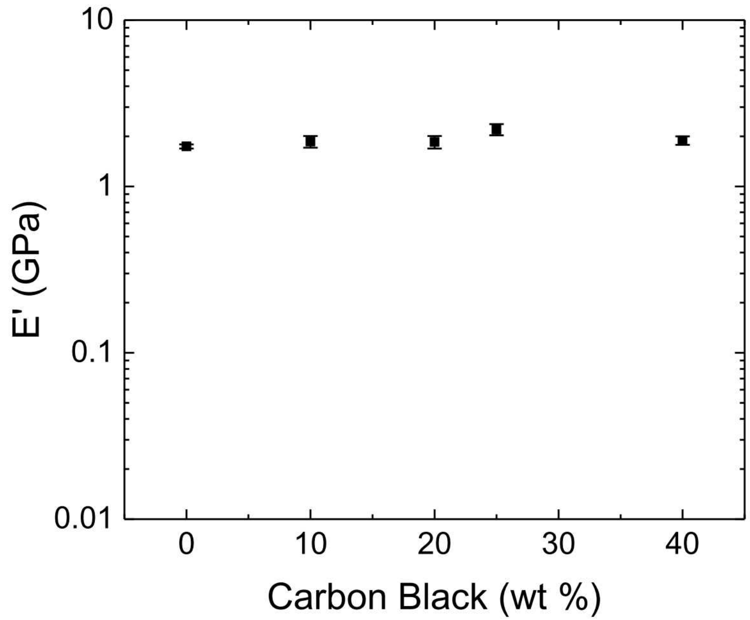
TEM of 45wt% CB in PVDF

No free PVDF

Mechanical Testing - DMA

- Netzsch Artemsis Dynamic Mechanical Analyzer





- Storage modulus >> Loss modulus for entire temperature range
- Despite large differences in morphology, no dependence on carbon black concentration
- Elastic modulus for dry binder ranges between 1.5 – 2.25 GPa

Electrolyte Swollen (Wet) Binder Properties

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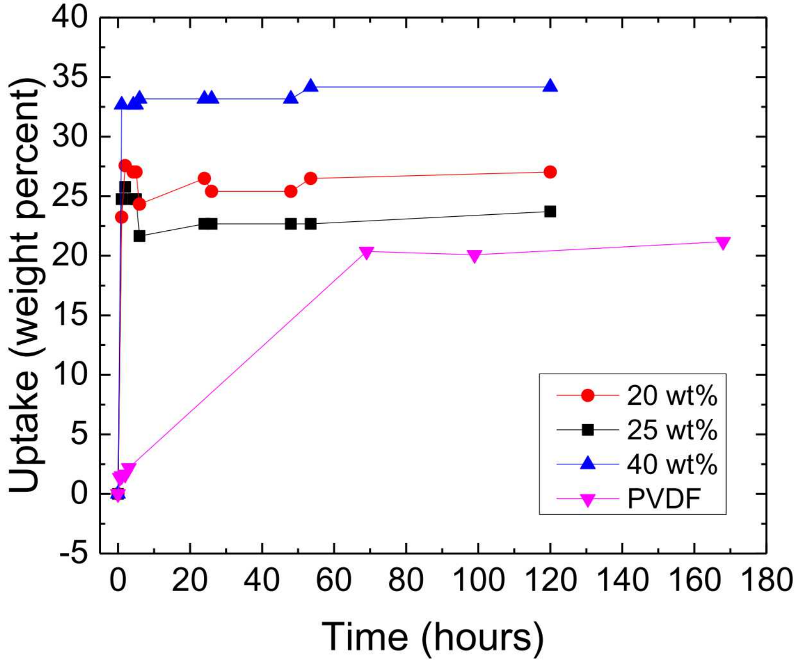

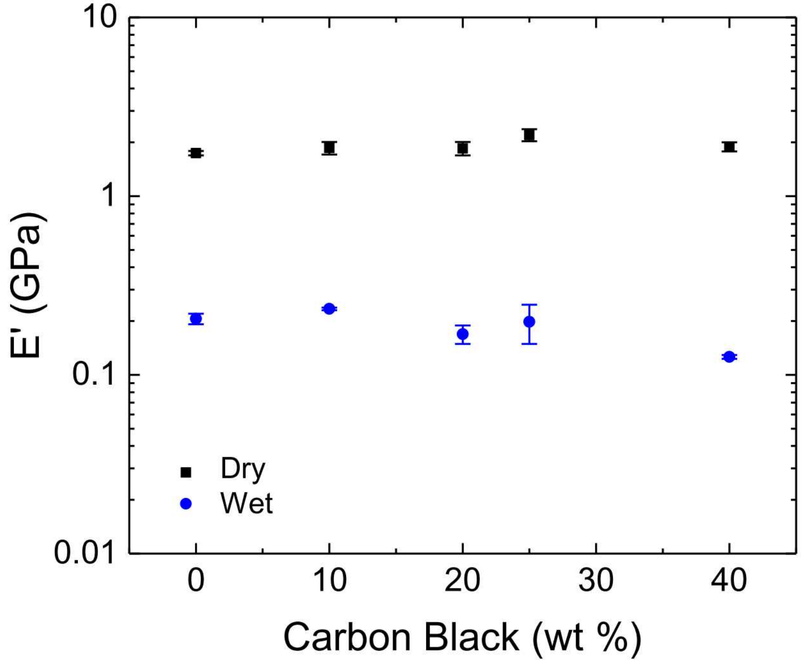

- Immersed binder samples within propylene carbonate (PC) for at least 24 hours
  - Samples absorb between 25 – 35 wt% in propylene carbonate within 6 hours of immersion
- Decreased modulus (≈ 200 MPa for wet binder compared to ≈ 2 GPa for dry)
- No clear trend as a function of carbon black weight percent
  - Perhaps a slight softening for wet binder

Reconstruction of Cathode Microstructures

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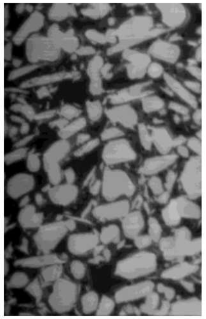
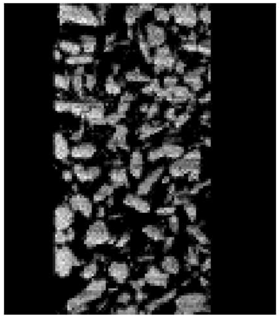
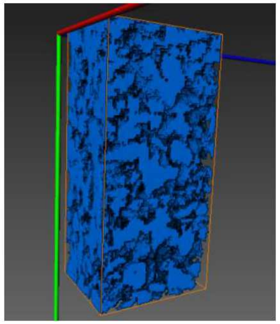
- Reconstruction using Avizo from EDS image slices at varying depths



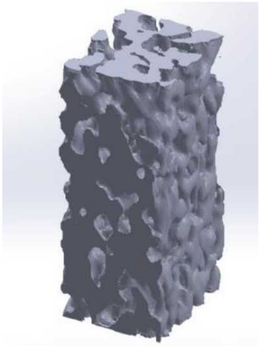
FIB/SEM/EDS images of $LiCoO_2$ cathode



Multivariate principal component analysis

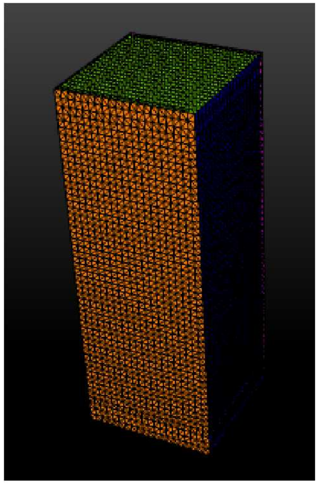


Binary mode recreated from images

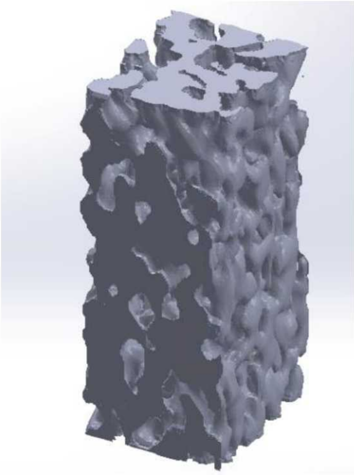


Surface mesh from binary model

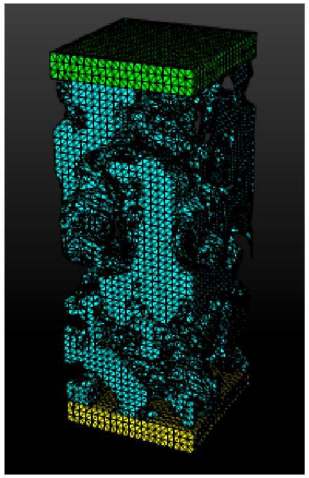
- Conformal Decomposition FEM (CDFEM), (Sandia method: Noble 2010)



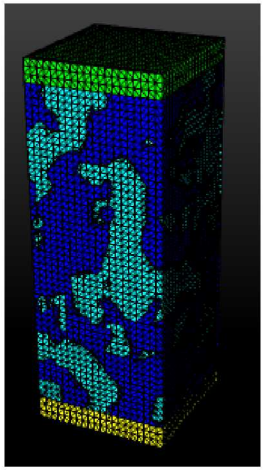
Background 3D mesh



Cathode surface mesh (STL)



3D Mesh superimposed on cathode particles



3D Mesh superimposed on cathode particles and electrolyte

Physics models: Electrochemistry

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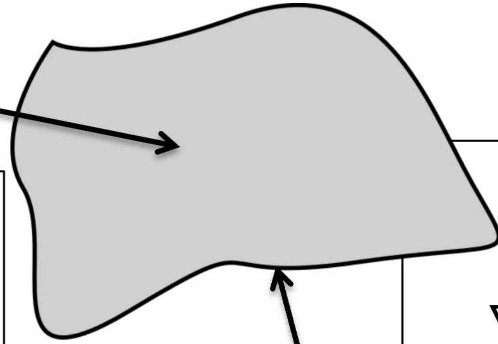
In the particle



In the electrolyte

- Ohm's Law

$$\underline{\nabla} \cdot \left(\sigma \underline{\nabla} \phi_{\mathrm{s}}\right) = 0$$

- Intercalated Li conservation

$$\frac{\partial C_{\mathrm{Li}}}{\partial t} + \underline{\nabla} \cdot \left[-M C_{\mathrm{Li}} \underline{\nabla} \left(\mu_{\mathrm{Li}}^{\mathrm{chem}} + \mu_{\mathrm{Li}}^{\mathrm{stress}}\right)\right] = 0$$

- Current conservation

$$\underline{\nabla} \cdot \left[F \left(\underline{J}_{\mathrm{Li}^+} - \underline{J}_{\mathrm{PF}_6^-}\right)\right] = 0$$

- Nernst-Planck fluxes

$$\underline{J}_i = -D_i \left(z_i C_i \frac{F}{RT} \underline{\nabla} \phi_{\mathrm{l}} + \underline{\nabla} C_i\right)$$

- Li^+ conservation

$$\frac{\partial C_{\mathrm{Li}^+}}{\partial t} + \underline{\nabla} \cdot \underline{J}_{\mathrm{Li}^+} = 0$$

- Electroneutrality

$$C_{\mathrm{PF}_6^-} = C_{\mathrm{Li}^+}$$

At the interface

- Butler-Volmer reaction rate

$$\underline{J} \cdot \underline{n} = j_0 \left[\exp\left(\frac{\alpha_a F \left(\phi_{\mathrm{s}} - \phi_{\mathrm{l}} - \phi_{\mathrm{eq}}\right)}{RT}\right) - \exp\left(\frac{-\alpha_c F \left(\phi_{\mathrm{s}} - \phi_{\mathrm{l}} - \phi_{\mathrm{eq}}\right)}{RT}\right)\right]$$

Physics models: Mechanics

- Intercalation-induced swelling causes a volumetric strain

$$\underline{\underline{E}} = \underline{\underline{E}}_{\text{elastic}} + \underline{\underline{E}}_{\text{swelling}}$$
$$= \underline{\underline{E}}_{\text{elastic}} + \underline{\underline{\alpha}} \Delta C_{\text{Li}}$$

- For a linear elastic constitutive behavior, swelling is converted to stress
  - Analogous to standard "coefficient of thermal expansion" approach

$$\underline{\underline{\sigma}} = \underline{\underline{\underline{\underline{C}}}} : \underline{\underline{E}}_{\text{elastic}}$$
$$= \underline{\underline{\underline{\underline{C}}}} : \underline{\underline{E}} - \underline{\underline{\underline{\underline{C}}}} : \underline{\underline{\alpha}} \Delta C_{\text{Li}}$$
$$= \underline{\underline{\underline{\underline{C}}}} : \underline{\underline{E}} - \underline{\underline{\beta}} \Delta C_{\text{Li}}$$

- Generally, volumetric strain is isotropic

$$\underline{\underline{\beta}} = \beta \underline{\underline{\delta}}$$

- Stress governed by quasi-static momentum conservation

$$\underline{\nabla} \cdot \underline{\underline{\sigma}} + \underline{F} = \underline{0}$$

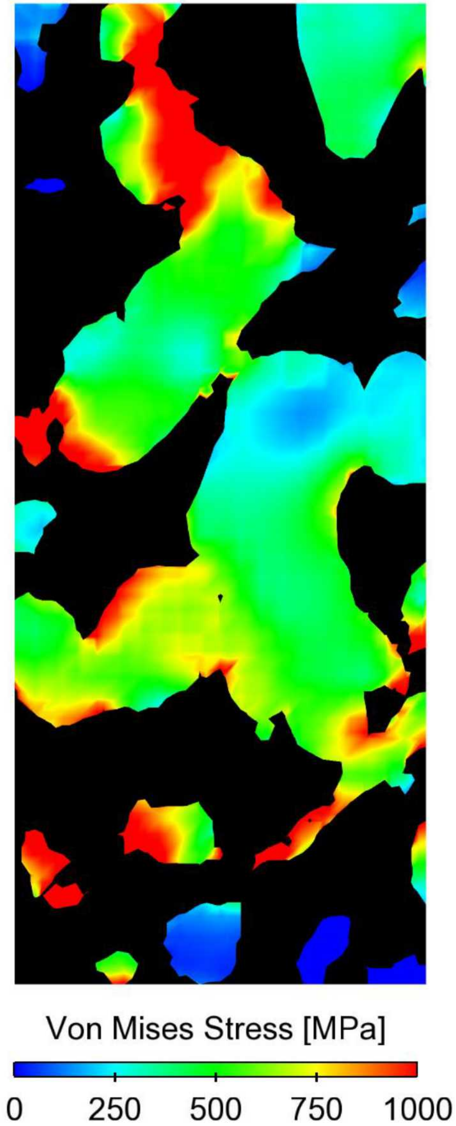
Problem definition

Modeling dynamics of $LiCoO_2$ cathode network under charging conditions with $LiPF_6$ as the electrolyte

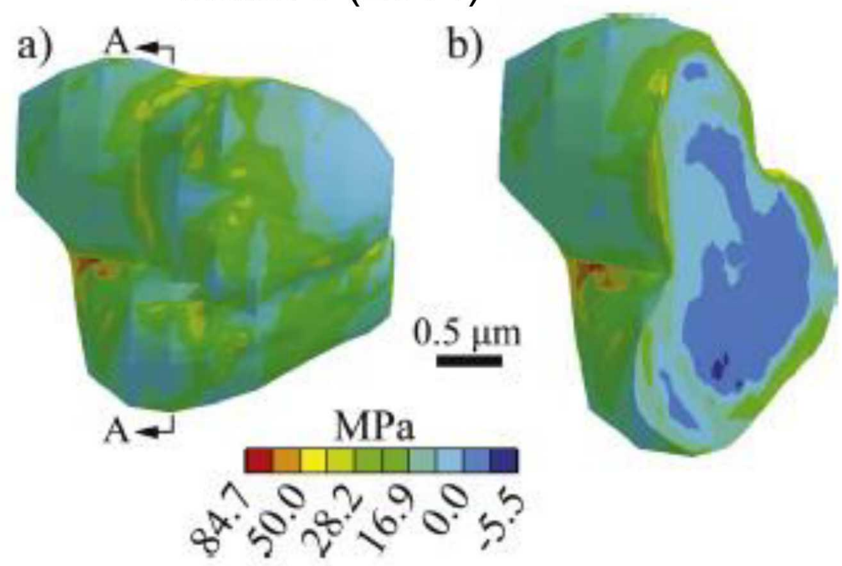
- Key Boundary Conditions
  - Domain
    - 6 [µm] x 6 [µm] x 14.3 [µm] cathode
  - Electrochemical
    - Constant Li+ at separator boundary
    - Constant current at collector
  - Mechanical
    - Sides of cathode are constrained (no macroscopic displacement of cathode)
    - Particles allowed to expand within the microstructure
    - Isotropic
    - No binder

- Key Model Parameters (Malave 2014)
  - E_{LiCoO2} = 370 [Gpa]
  - E_{binder} = 200 [MPa]
  - Beta = 48.8 [GPa/($\frac{mol}{m^3}$)]
  - Baseline simulation
    - 1C charging rate

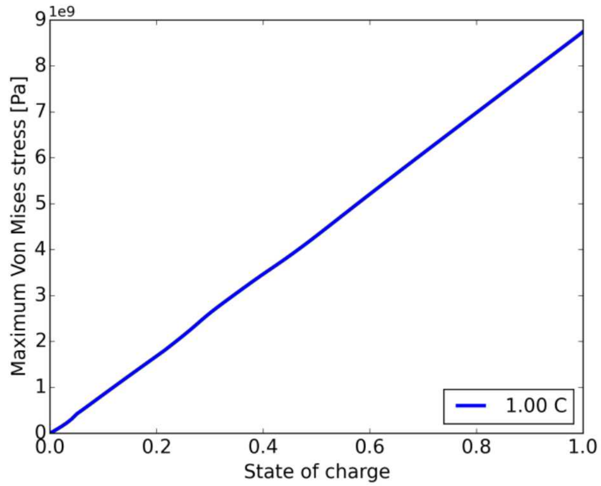
Malave *et al* (2014); Renganathan et al (2010); Rahani (2013)



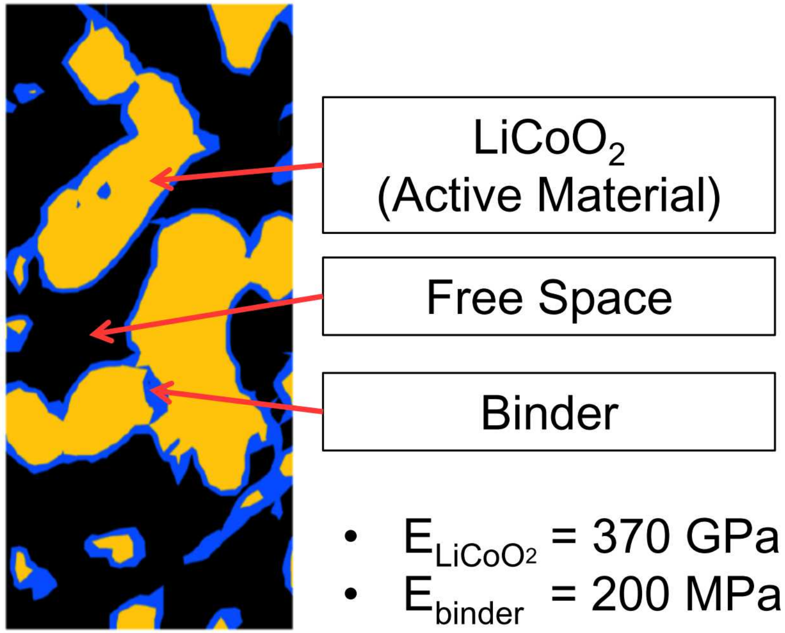
Malave (2014)



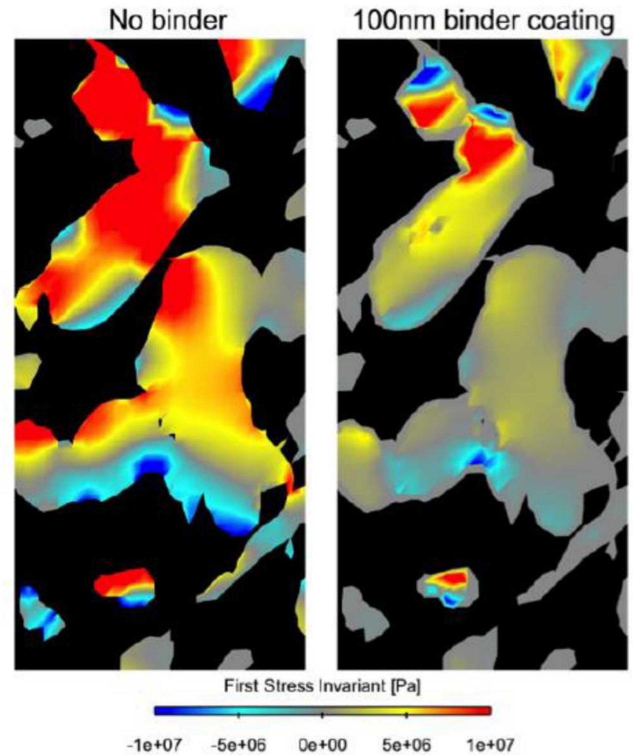
Particle confinement from microstructure leads to 100x higher stresses than isolated particles



Importance of Binder in Cathode Mechanics



- E_{LiCoO_2} = 370 GPa
- E_{binder} = 200 MPa



- Calculate the stress and effective modulus in the cathode due to an imposed tensile strain
- Polymeric binder covering decreased maximum observed stress
  - Dry binder – decrease of 30%
  - Wet binder – decrease of 51%

Conclusions and Future Work

- Mechanical properties
  - Binders are generally elastic solids
    - Dry: E= 2GPa, Wet: E=200 MPa
    - Properties of composites do not depend on carbon concentration
- Binder has a large impact on mechanical stress generated during charging

- Future work:
  - Impact of cycling on the properties of the binder
  - Active work on modeling stress development in electrodes

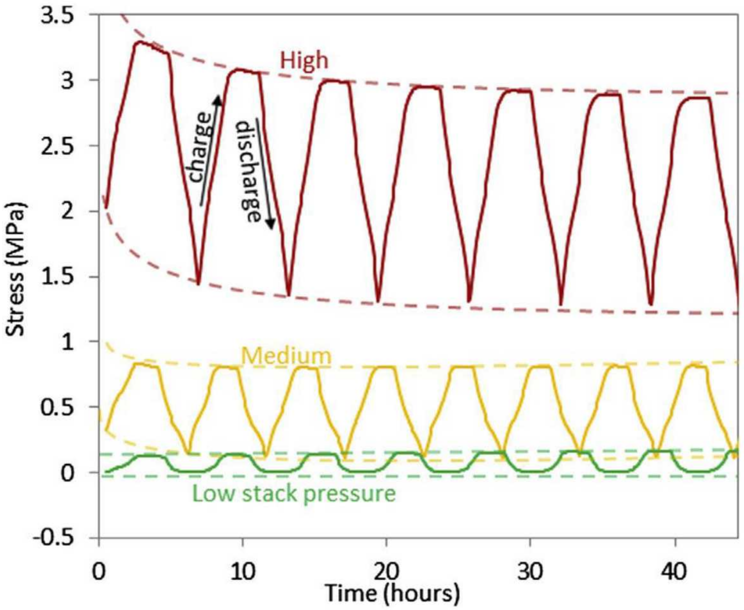
- We are currently looking for two postdoctoral fellows for a related battery research project – http://www.sandia.gov/careers/
  - Job ID # 651454 – modeling
  - Job ID # 651319 – experimental

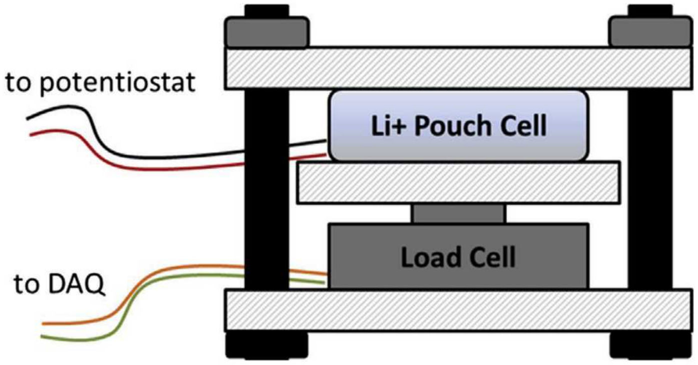
- This work was funded as part of Sandia's Laboratory Directed Research and Development Program.

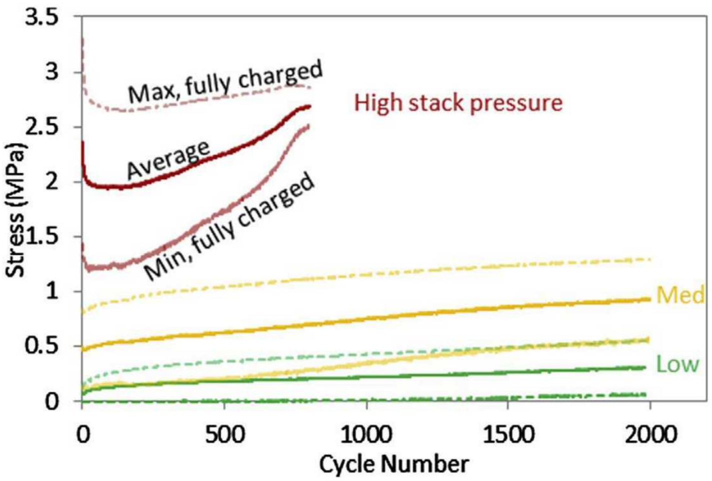
EXTRA

Both electrodes swell during charging!

- Constrained battery pouch cell experiments by Cannarella & Arnold
  - See large changes in stress during cycling as cathode and anode swell during charge and shrink during discharge
  - Electrodes want to swell after repeated cycling resulting in increased stresses with time







Understanding the Role of the Binder

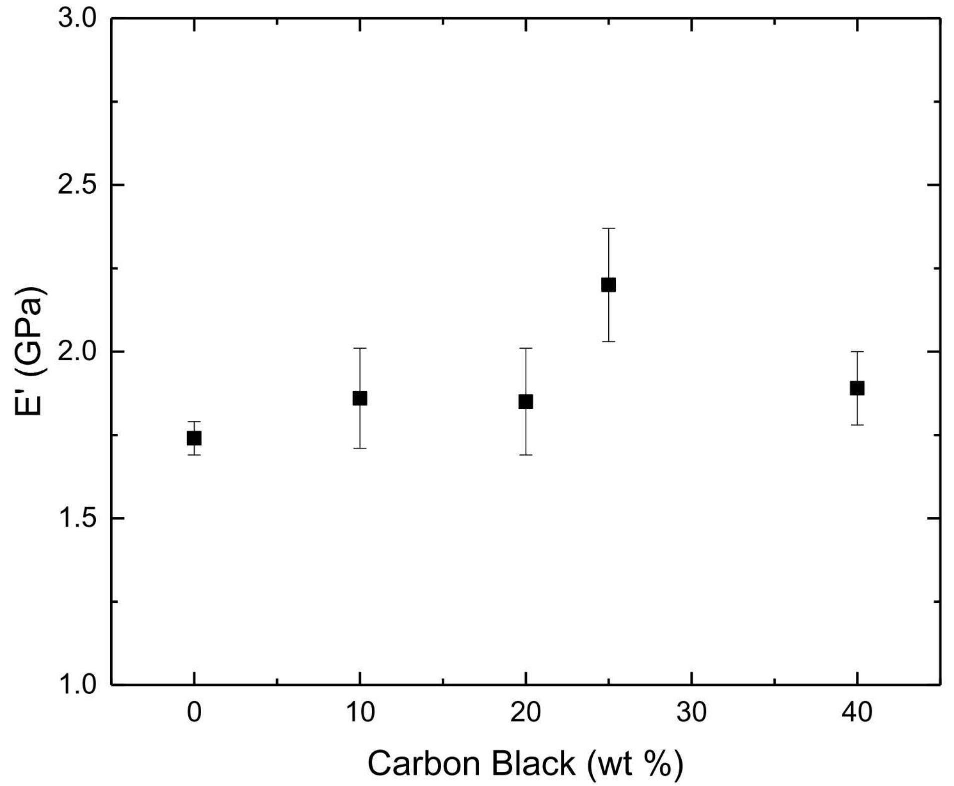
Mechanical

- Mitigating stresses of swelling/ contracting active materials
- Maintaining adhesion of active materials to conductive network

Electrical

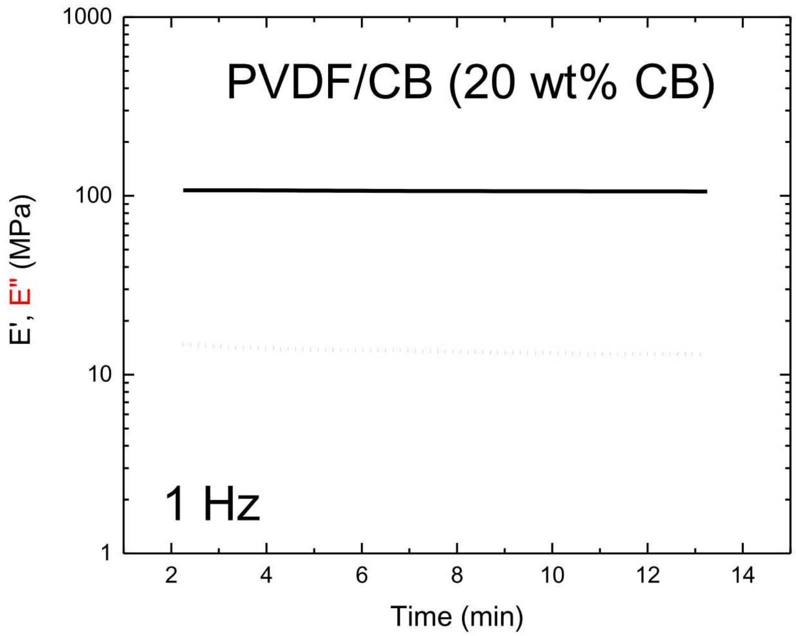
- Provide pathway for electron transfer through electrodes
- Decrease resistance (*i.e.,* loss) for cathode

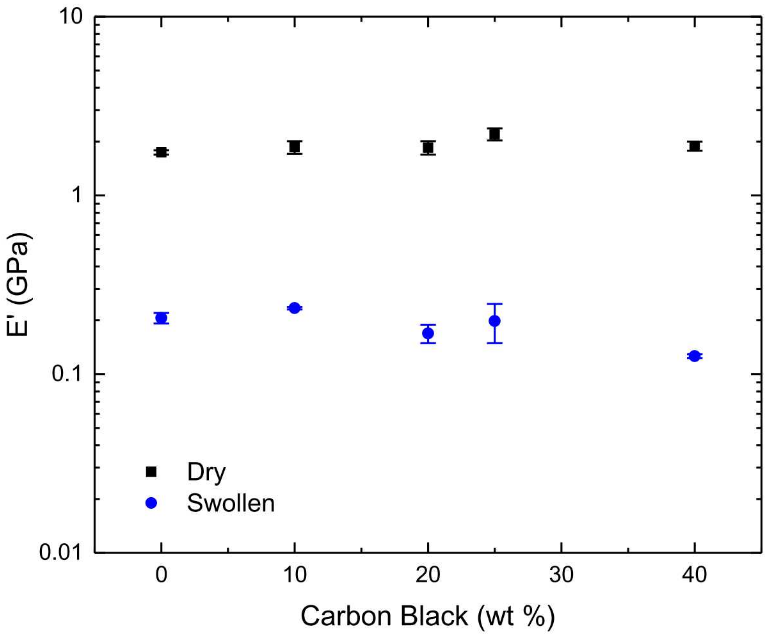
Mechanical Properties – Dry Binder



- No clear trend in modulus for varying CB weight percent
- Elastic modulus for dry binder ranges between 1.5 – 2.25 GPa
- Probe crystallinity with DSC to investigate microstructure of composites

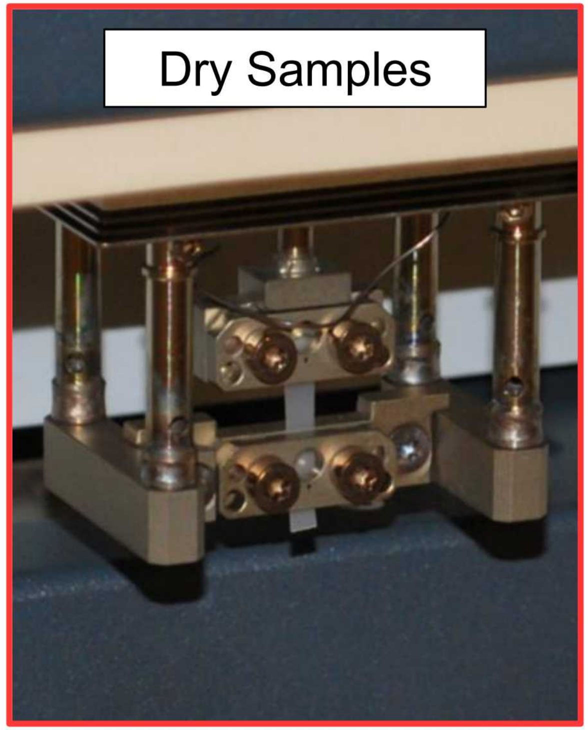
Mechanical Properties - Swollen





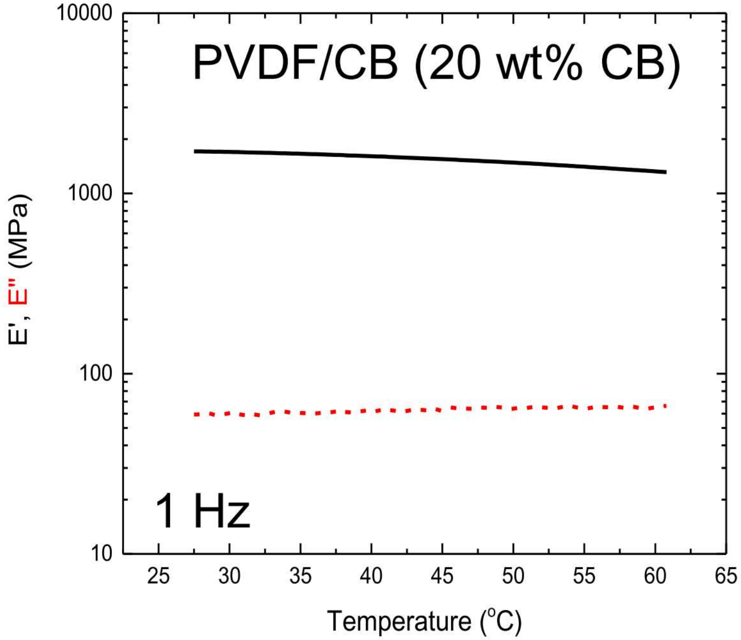
- Immersed samples within propylene carbonate (PC) for at least 24 hours
  - Samples absorb between 25 – 35 wt% in propylene carbonate within 6 hours of immersion
- Decreased modulus (≈ 200 MPa for swollen compared to ≈ 2 GPa for dry)
- No clear trend as a function of carbon black weight percent

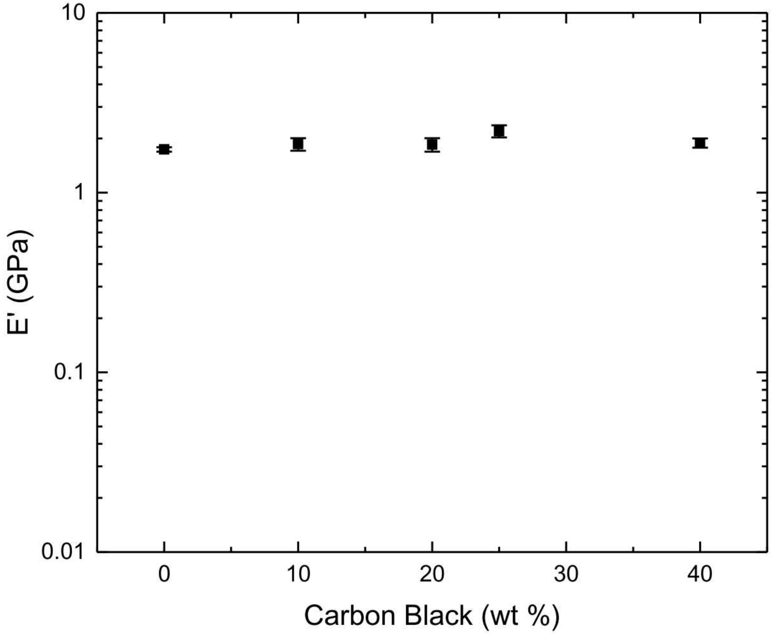
Mechanical Testing - DMA

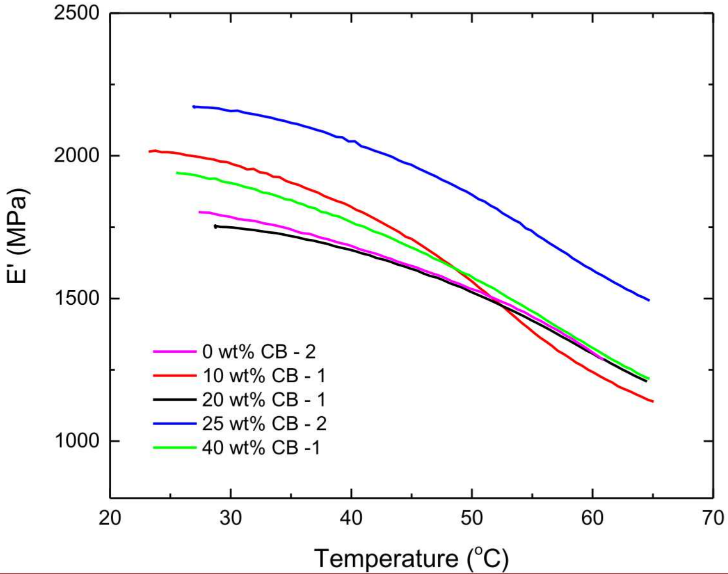


- Netzsch Artemsis Dynamic Mechanical Analyzer
  - Probe E’, E” from 1 – 10 Hz from 25 – 65 ^{0}C for dry samples
  - Probe E’, E” from 1 – 50 Hz at room temperature for electrolyte (propylene carbonate) immersed samples

Mechanical Properties – Dry Binder

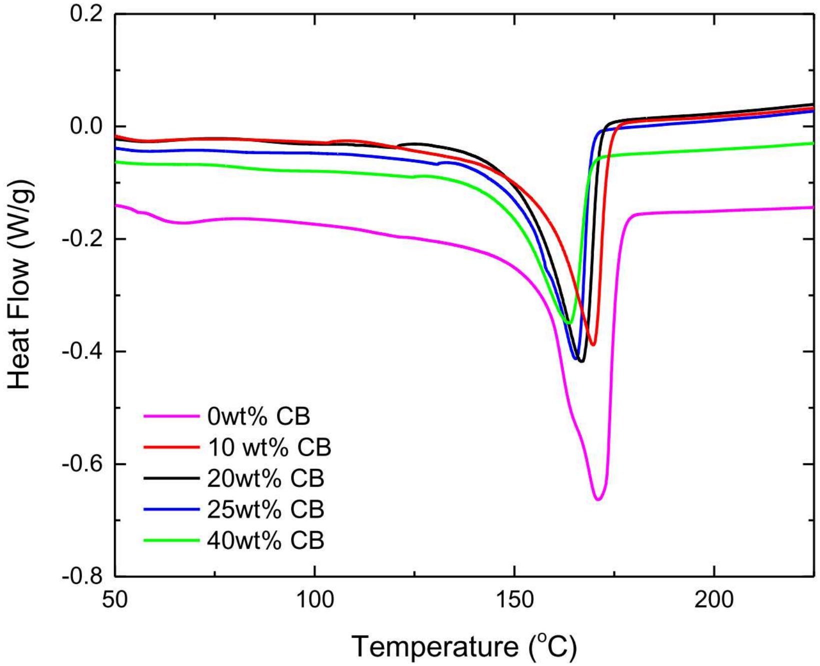






- Storage modulus >> Loss modulus for entire temperature range
- Binder softens at higher temperature
- Despite large differences in morphology, no dependence on carbon black concentration
- Elastic modulus for dry binder ranges between 1.5 – 2.25 GPa

Differential Scanning Calorimetry



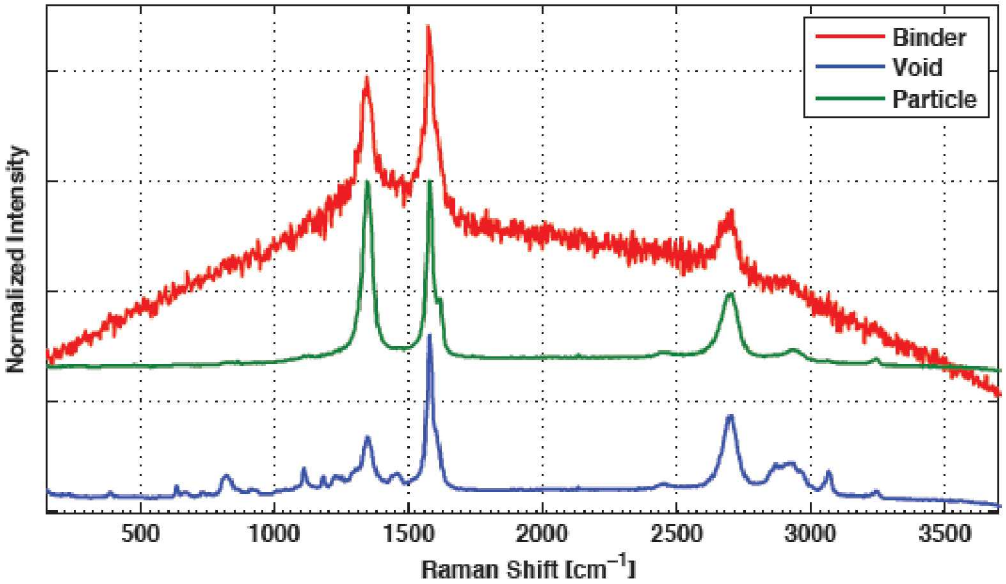
% CB	Normalized H_{sl} (J/g)	% Crystallinity
0.0	47.0	0.45
10.0	43.2	0.41
20.0	38.3	0.37
25.0	41.7	0.40
40.0	44.5	0.43

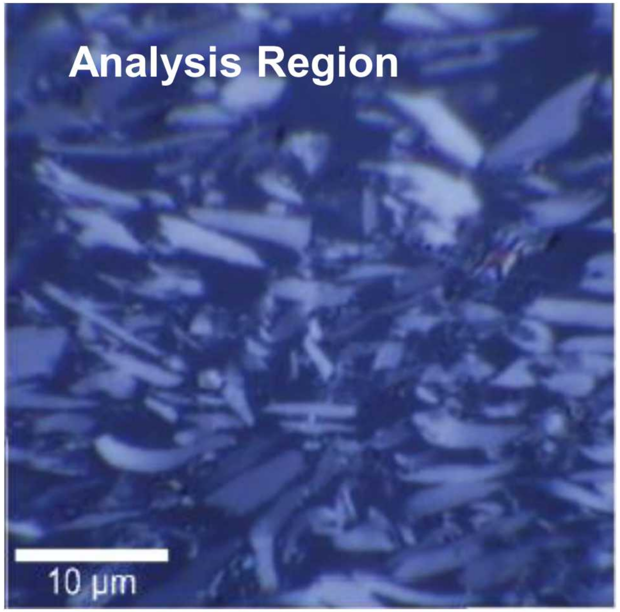
- Investigated % crystallinity using differential scanning calorimetry by quantifying latent heat of fusion and compared against fully crystalline PVDF (H_{sl} = 104.7 J/g)[1]
  - Adding carbon black does not change PVDF crystallinity
  - Hypothesize that crystalline PVDF structure controlling mechanical properties

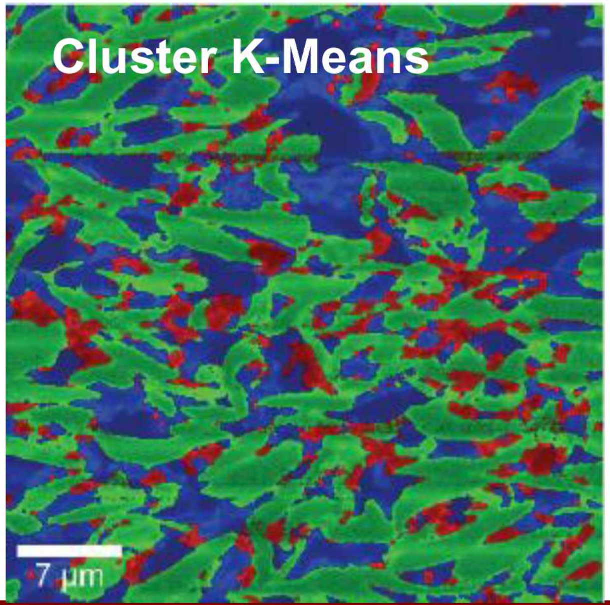
1. Lui *et al., J.Electrochem. Soc. 159 (2012)*

Raman Microscopy w/ Thomas Beechem

- How to get the microstructure of the anode?
  - Graphite : PVDF/carbon black : epoxy (void)
  - Chemical similarity foils traditional



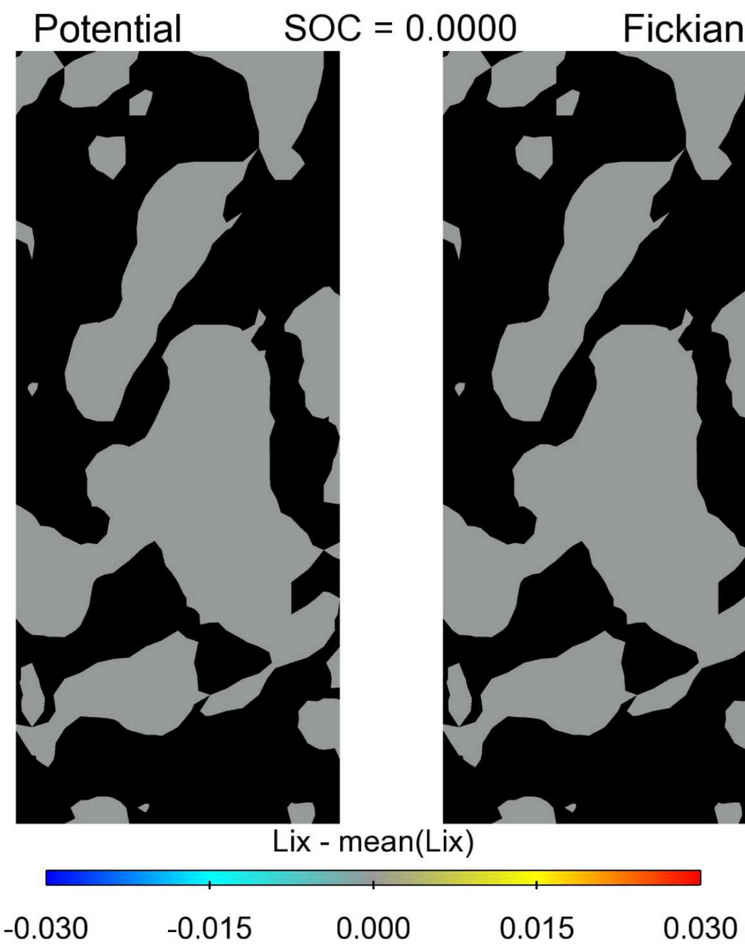




First mesoscale binder structures for an anode!

Raman may also be able to distinguish local states of charge in graphite particles

Fickian model comparison

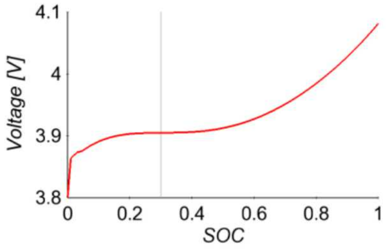


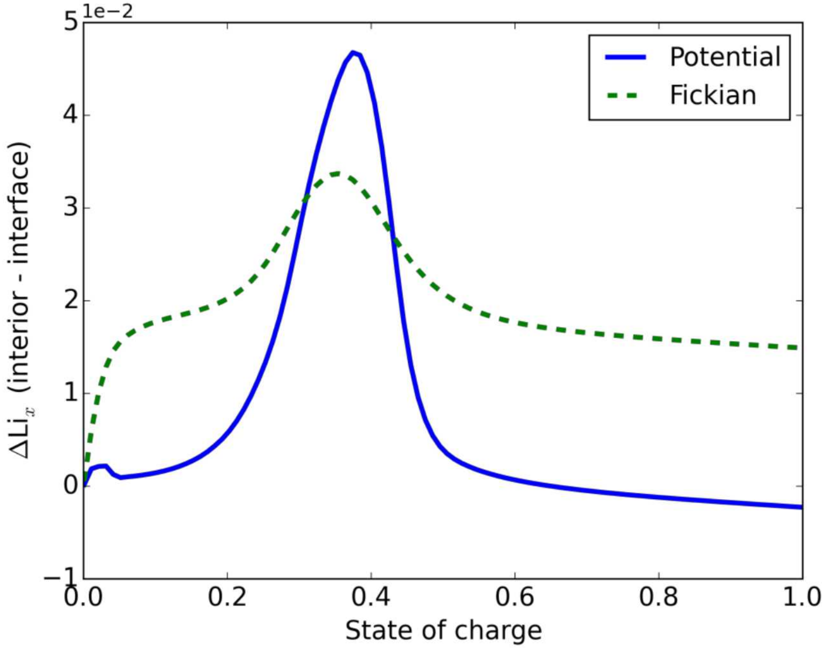
- Fickian model:

$$\underline{J}_{\mathrm{Li}} = -D\underline{\nabla}C_{\mathrm{Li}}$$

- Chemical potential model:

$$\underline{J}_{\mathrm{Li}} = -MC_{\mathrm{Li}}\underline{\nabla}\mu_{\mathrm{Li}}^{\mathrm{chem}}$$

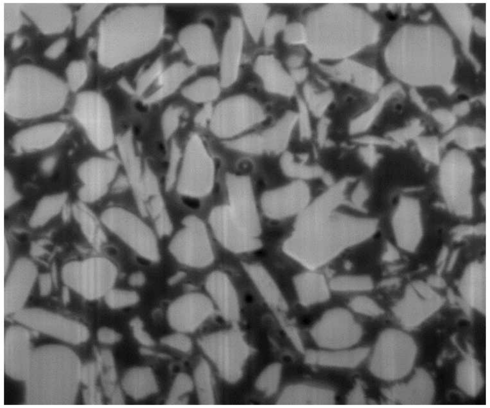




Fickian model shows unrealistically high concentration gradients throughout charge

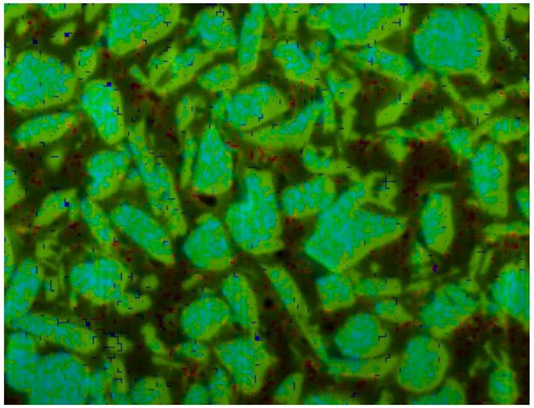
Location of Binder

Focused Ion Beam Cross-section

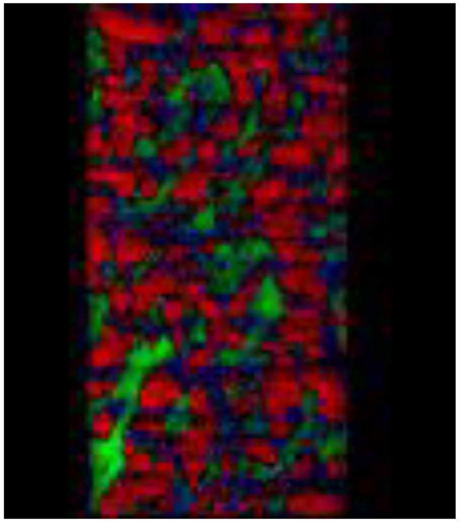


LiCoO2 particles
55 vol% active material
mean particles size 2.3microns
Aspect ratio of 1.7

Energy Dispersive Spectroscopy chemical composition



Multivariate principal component analysis



Red – $LiCoO_2$
Blue – PVDF/CB binder
Green - void

Binder found in the small spaces between particles

Tortuosity, Porosity and Network Conductivity

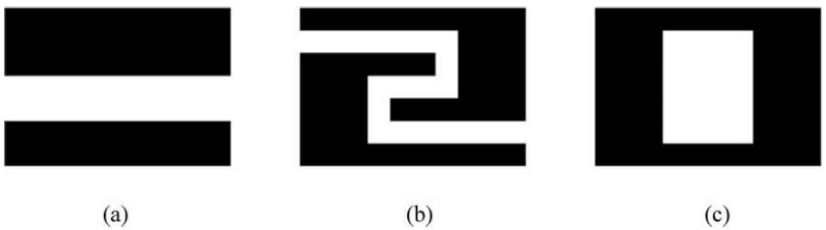
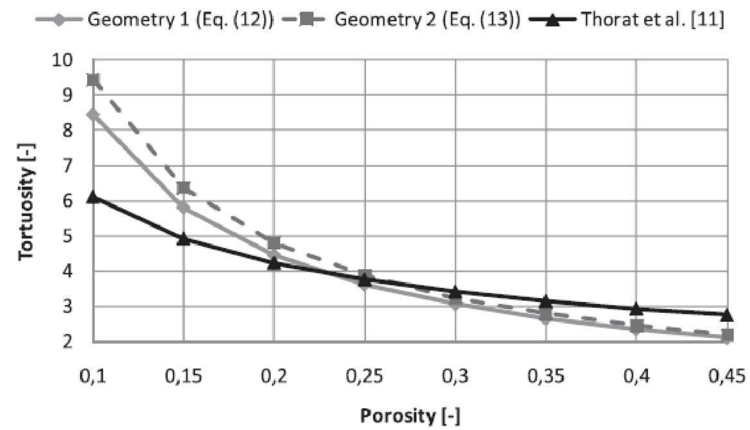


Figure 2. Three 2D porous media with a porosity of 2/7 and tortuosities of 1 (a), 2 (b), and infinity (c). While (a) and (b) show open pores, (c) displays a clc pore that does not contribute at all to material transport.

Kehrwald et al. (2011)



Rubino et al. (2001)

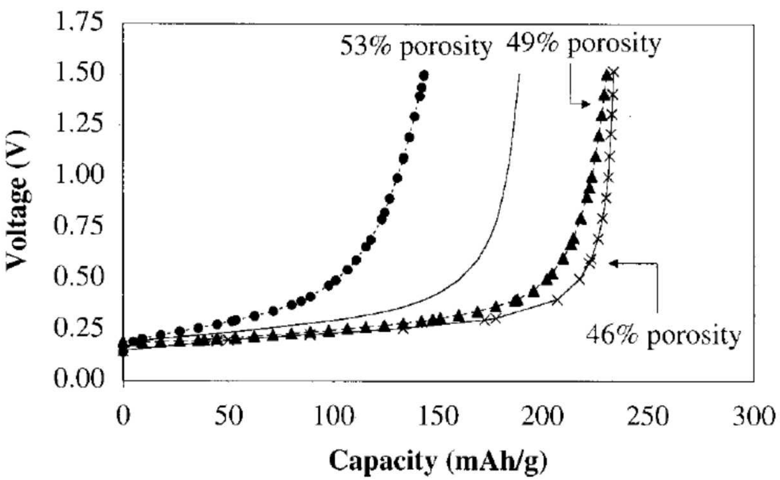
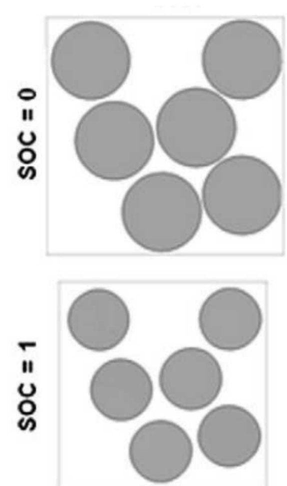


Figure 4. Half-cell voltage curves for anode pieces recovered from cycled cells. Half-cells were discharged to 0.010 V at C/2 followed by a constant potential step with a C/20 current cutoff. Voltage curves shown are for a 1C charge to 1.50 V. Circles: prismatic cell (300 cycles), line: prismatic cell (300 cycles, recompacted), triangles: cylindrical cell (300 cycles), crosses: prismatic cell (formation only). Curves represent the best cell of two.



Awarke et al. (2011)
Network conductivity