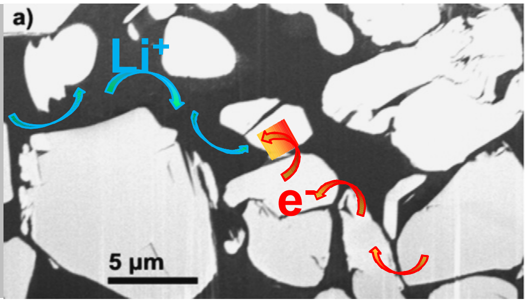
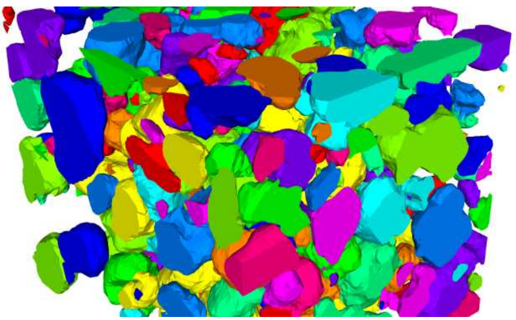
SAND2017-0143C

Conductivity Degradation of PVDF Binder During Cycling: Measurements and Simulations for Lithium Ion Batteries





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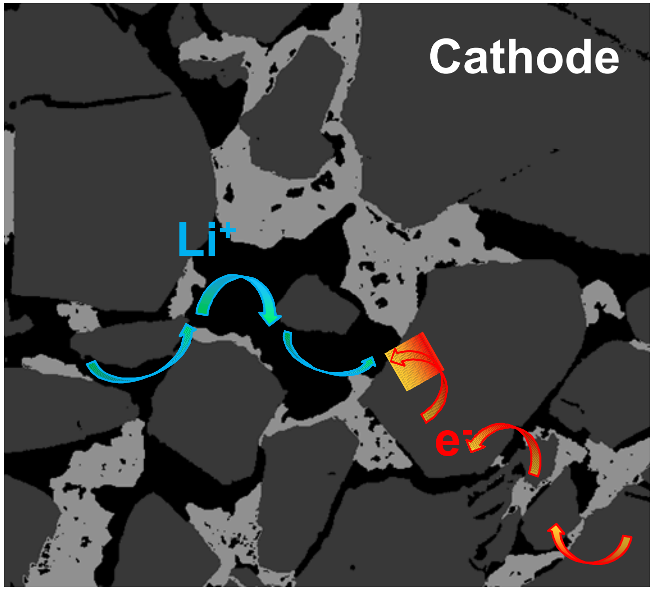
Battery Introduction

- Battery electrodes are multicomponent particle composites
  - Binder is a mixture of polyvinylidene fluoride (PVDF) and carbon black
  - Binder is important for mechanical stabilization and electrical conduction
  - Electronic Conductivity : Binder ~ graphite >> $LiCoO_2$

SEM image of $LiCoO_2$ cathode



94wt% $LiCoO_2$
3wt% PVDF
3wt% CB
} "Binder"
electrolyte

Battery voltage depends on how efficiently lithium ions and electrons are transported

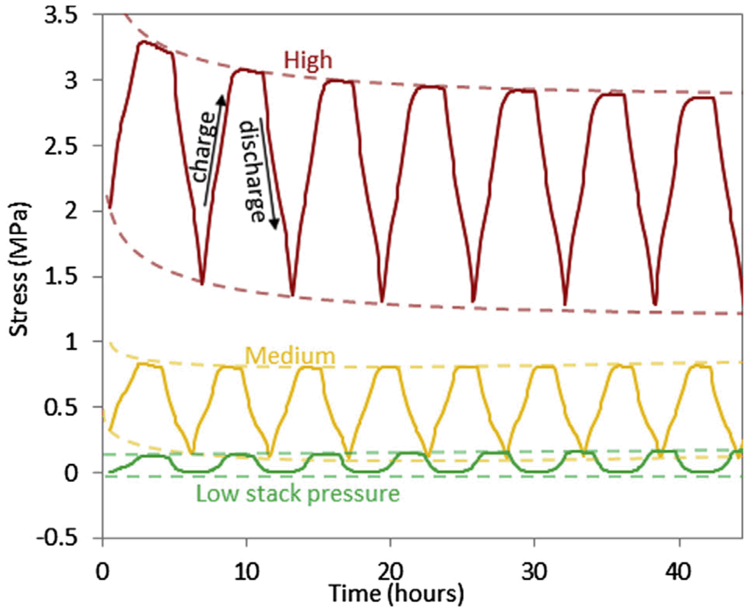
Outline

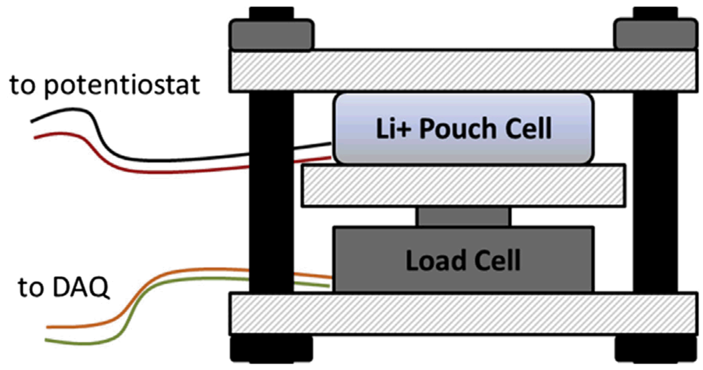
- Battery electrode binders play an important role both mechanically & electrochemically
- Coupled mechano-electrochemical characterization of binder
  - Mechanical stresses to mimic stresses during electrochemical cycling
  - Measure electrode strain and electrical conductivity
    - PVDF/CB binder films
    - $LiCoO_2$ cathodes
- Comparison to electrochemically cycled $LiCoO_2$:Graphite batteries
- Mesoscale simulations of composite cathodes with binder

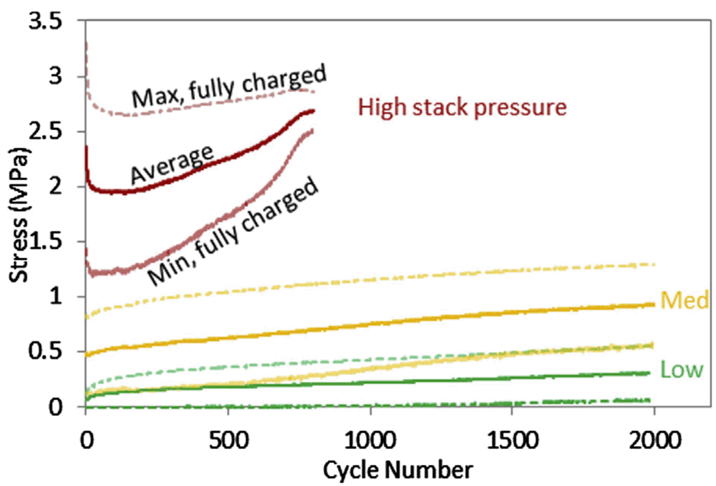
- Mechanical cycling of binder causes increased internal resistance which degrades battery performance

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

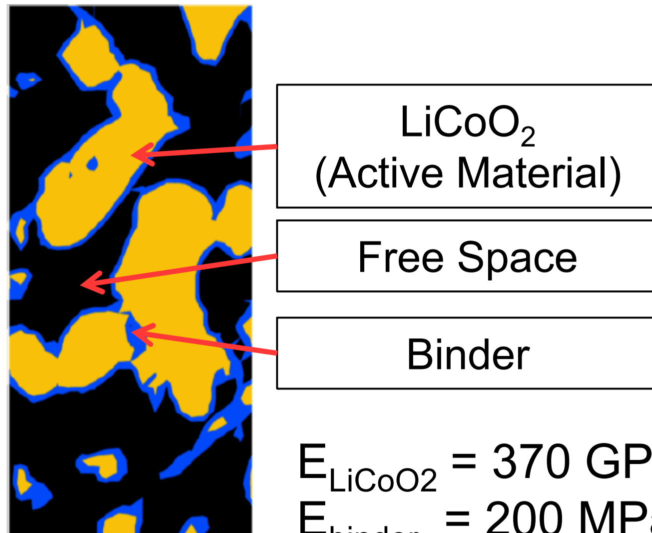




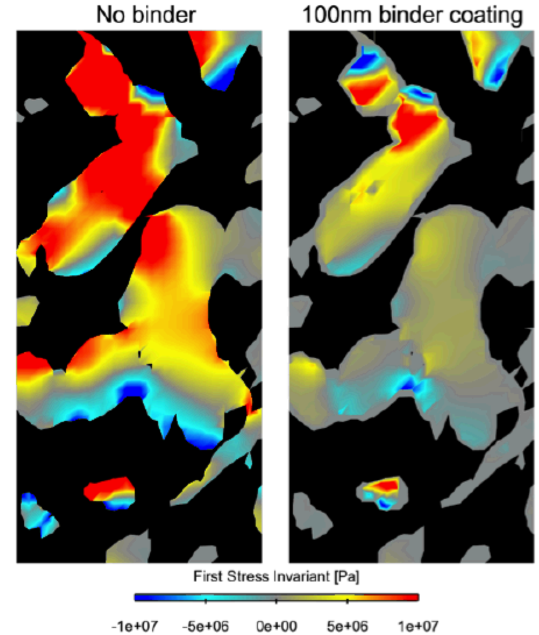


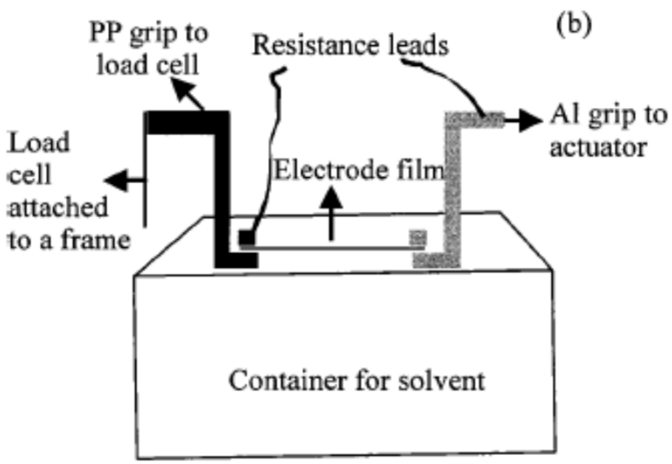
Role of Binder in Battery Cathodes

- Mendoza et al.[1] used experimental cathode microstructures to predict peak stresses during charging of 100's MPa
- Presence of 100nm binder could reduce stresses by 50%



E_{LiCoO2} = 370 GPa
E_{binder} = 200 MPa

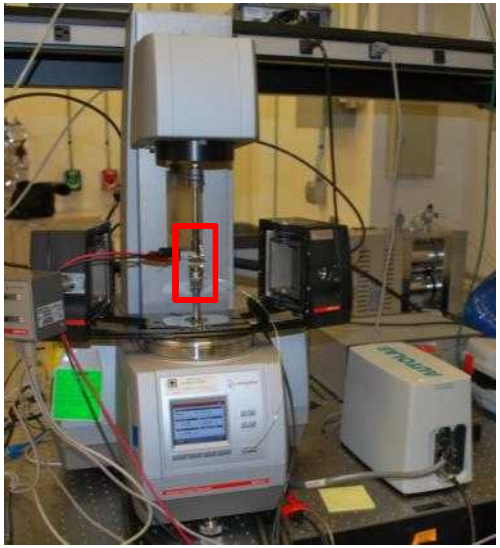




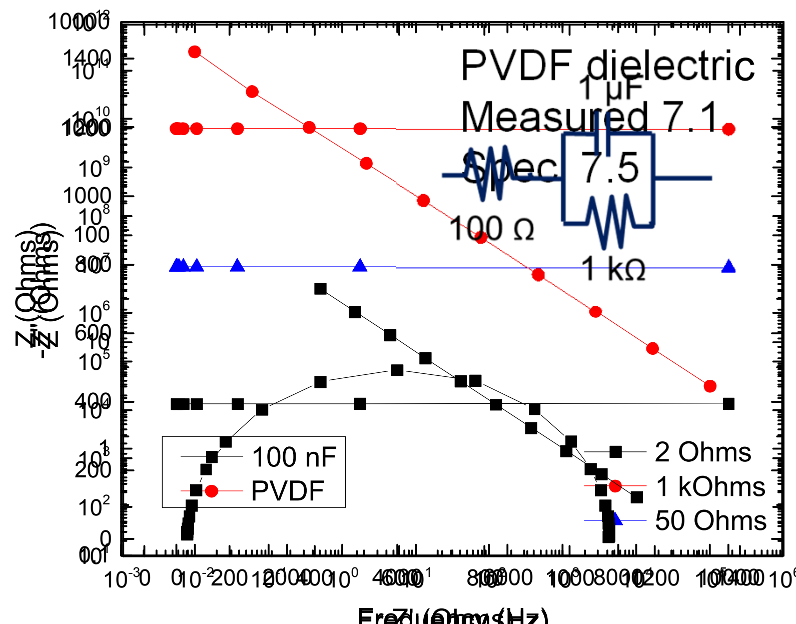
- Chen *et al.*[2] investigated the change in resistance of various PVDF/carbon composites (both wet and dry) and during initial cycling in tension
  - Small changes in resistivity with ~5 cycles number

1. Mendoza et al. *Electrochem Acta* (2016), Roberts et al. *JES* (2014) 2. Chen et al. (2003)

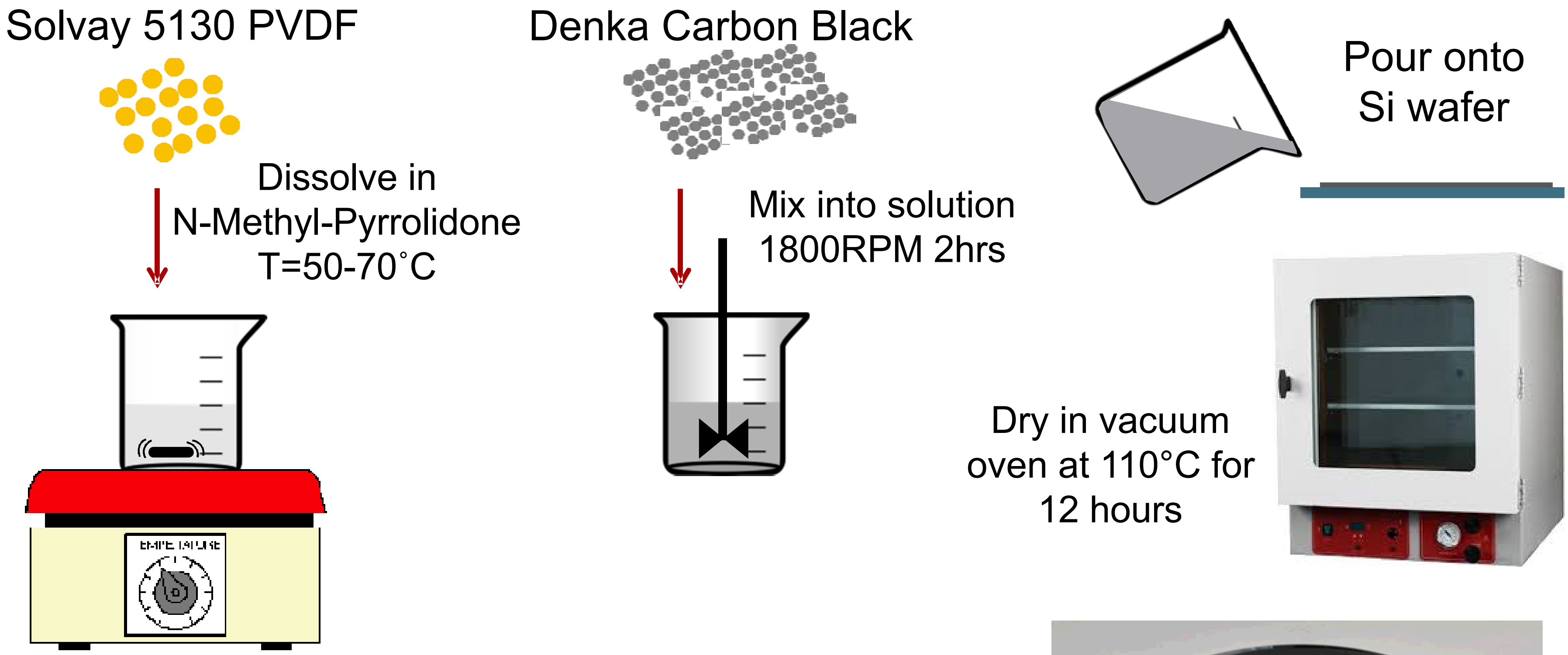
Mechanics/Impedance Measuring System

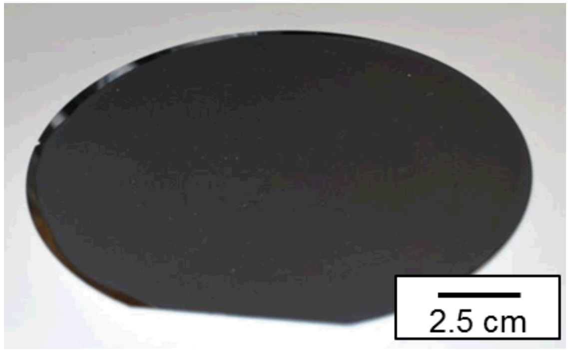


- Measure electrical properties of system during mechanical tests
  - Anton Paar MCR 502 rheometer
    - Compression of binder disks
  - Metrohm PGASTAT204/FRA 32
    - Potentiostat/galvanostat 10 µHz - 1 MHz
    - Welded wire leads to plates to reduce lead resistance
    - Performing Electrical Impendance Spectroscopy
- Qualified that combined tool can measure a variety of electrochemical systems



Synthesis of PVDF/CB Binder films



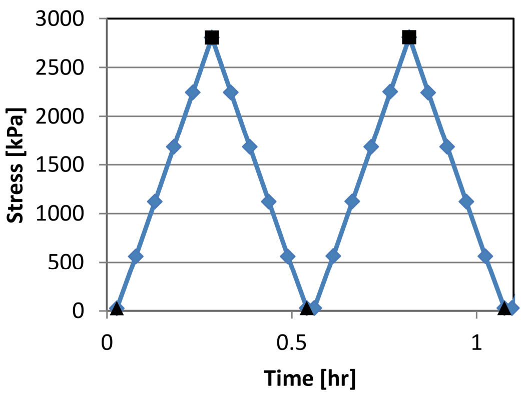


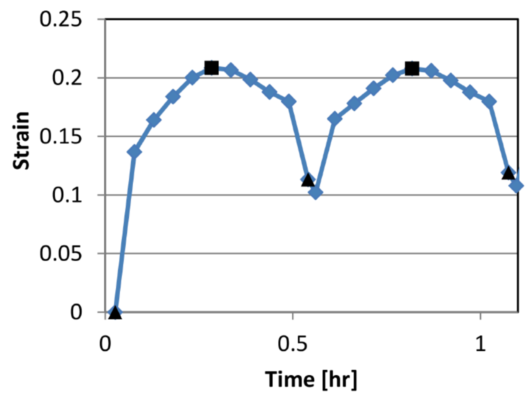
- Film thickness on the order of 70 - 200 µm

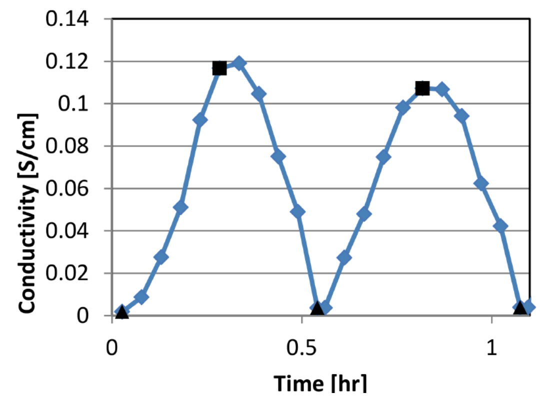
Mechanical Cycling of Dry Binder Film

PVDF/CB composite (30wt% CB)
(6x 5 mm diameter discs, ~500 µm thick)

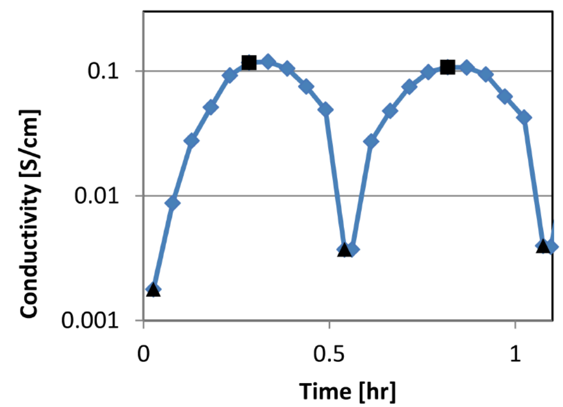
Procedure:
28 kPa – 2.8 MPa – 28 kPa at ~4C cycle rate



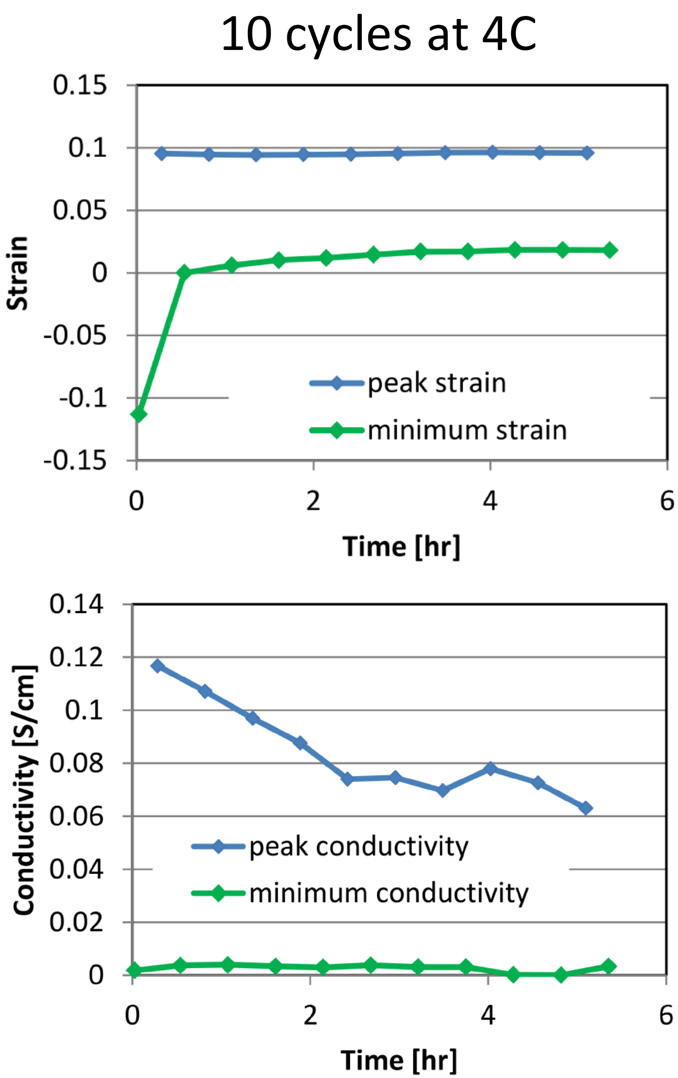




- Plastic deformation after first cycle (flattening of disks or surface non-uniformities)
- Electrical conductivity exhibits a strong dependence on applied load (and resulting strain)
  - Changes by two orders of magnitude



Mechanical Cycling of Dry Binder Film

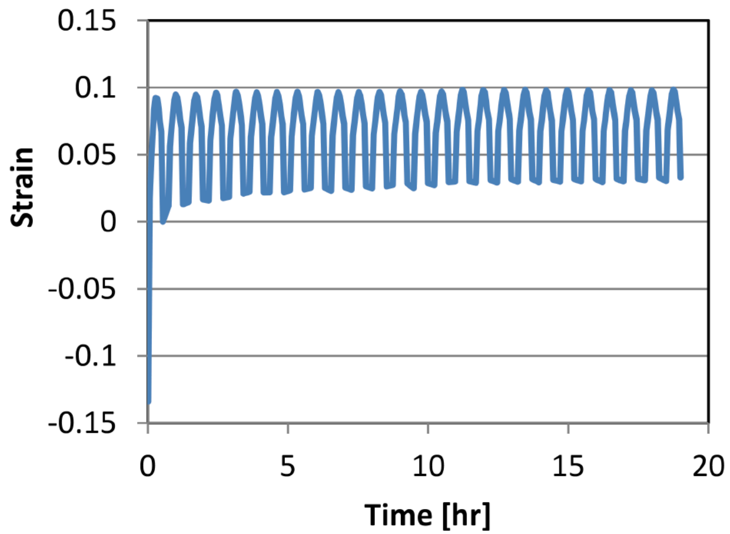


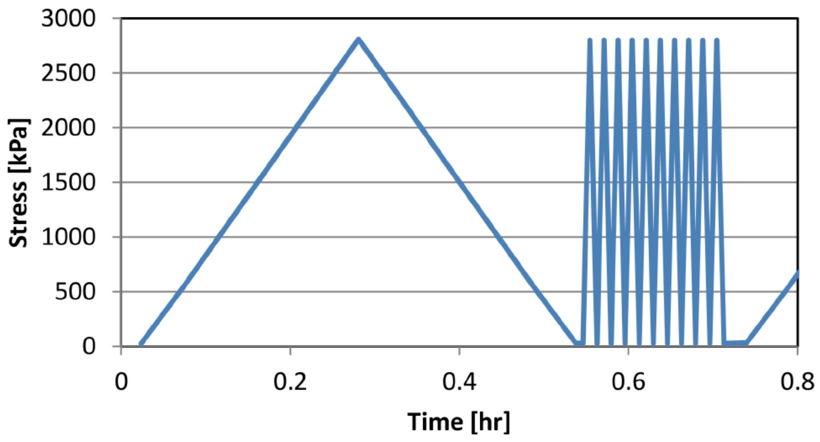
- Mechanical cycling
  - 27 kPa – 2.8 MPa – 27 kPa
  - 4C (cycle ≈ 32 min)
  - 10 cycles (5+ hours)
- Slow consolidation of binder film
- Significant 30% decrease in binder electrical conductivity after 10 cycles
- SEM imaging of binder films before and after cycling show no obvious morphology changes (cracks, delamination from the particles, etc.)

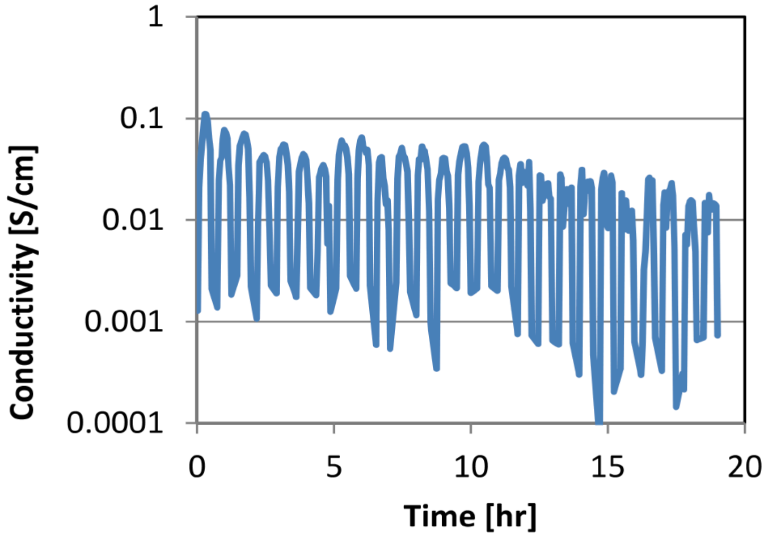
Mechanical Cycling of Dry Binder Film

Accelerated cycling

- 10 cycles at 120C between each measurement cycle at 4C
  - 28 kPa – 2.8 MPa – 28 kPa
  - 4C (cycle ≈ 32 min), 10x 120C (cycle ≈ 1min)
  - 266 total cycles (19 hours)
- 30wt% Carbon black dry binder film

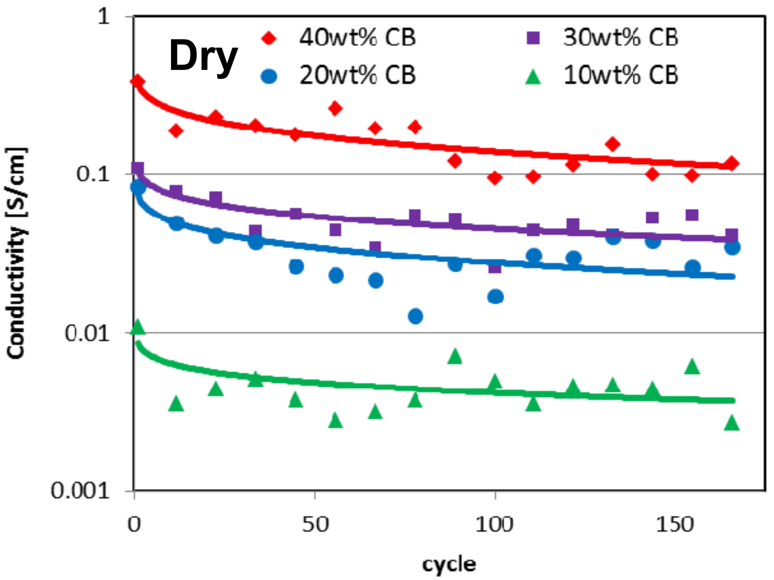


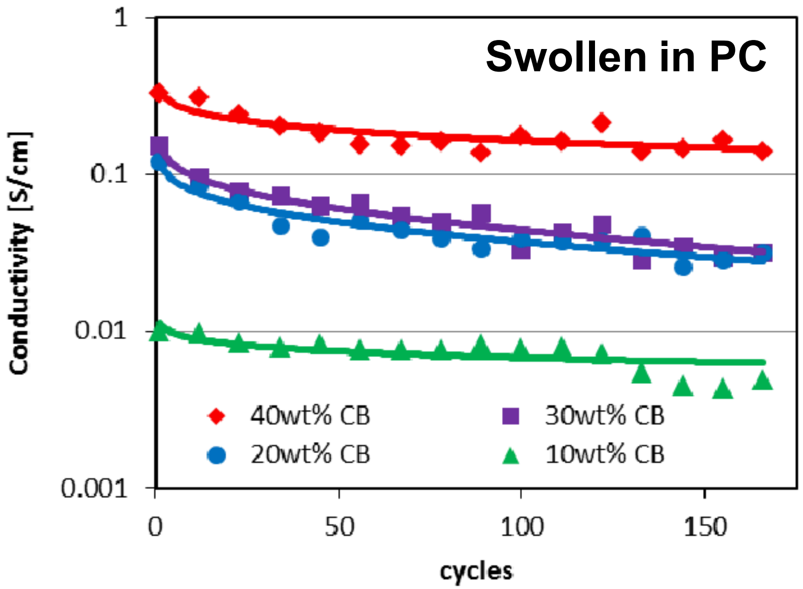




Mechanical Cycling of Swollen Binder Film

- Examined affect of carbon black concentration
- Binder absorbs 20-40wt% of propylene carbonate (PC) solvent
- Cycled using same accelerated cycling protocol
  - 4C (cycle ≈ 32 min), 10x 120C (cycle ≈ 1 min)



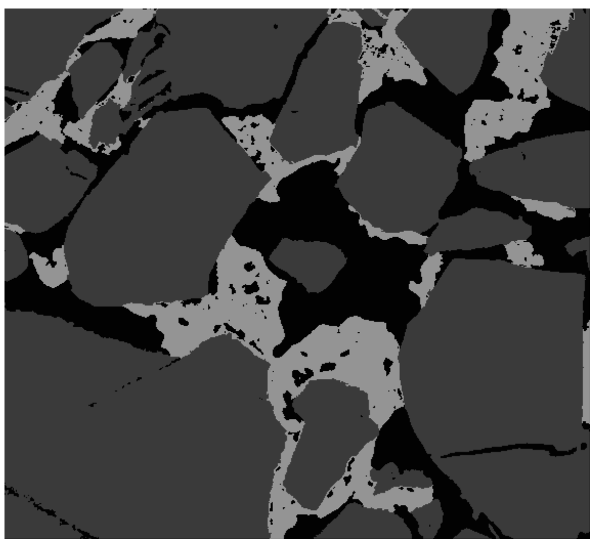


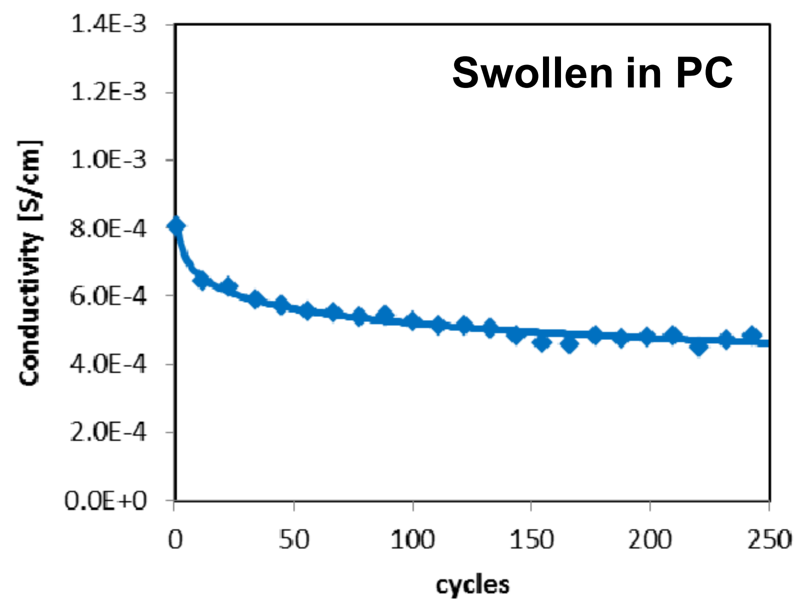
- Significant decrease in binder conductivity as a function of mechanical cycling between 45-75%
- Same for both Solvay 5130 and Kureha W #1300 battery grade PVDF polymers

Mechanical Cycling of $LiCoO_2$ Cathode

- Cathode depends on the binder for reducing internal resistance
  - Fresh $LiCoO_2$ active material: $\sigma_{LiCoO2}=10^{-6}$ S/cm vs 0.5-0.05 S/cm for binder
  - Cycled $LiCoO_2$ active material: $\sigma_{LiCoO2}=10^{-3}$ S/cm
  - Propylene carbonate solvent: $\sigma_{PC}=10^{-10}$ S/cm
- Similar trend in degradation of electronic conductivity of cathode:
  peak electronic conductivity declined by 42% after 166 mechanical cycles

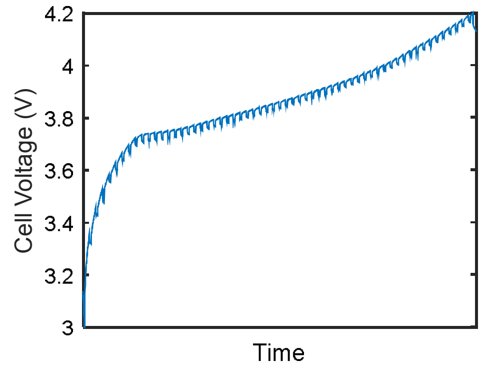
94wt% $LiCoO_2$
6wt% PVDF/CB
solvent

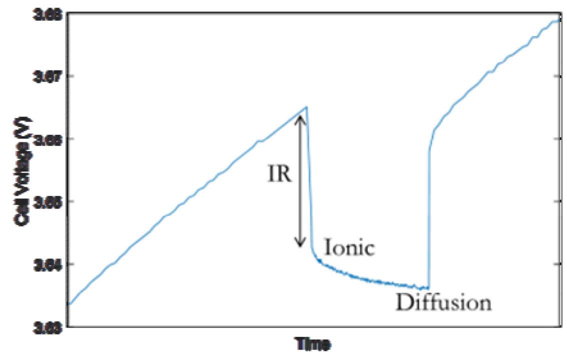


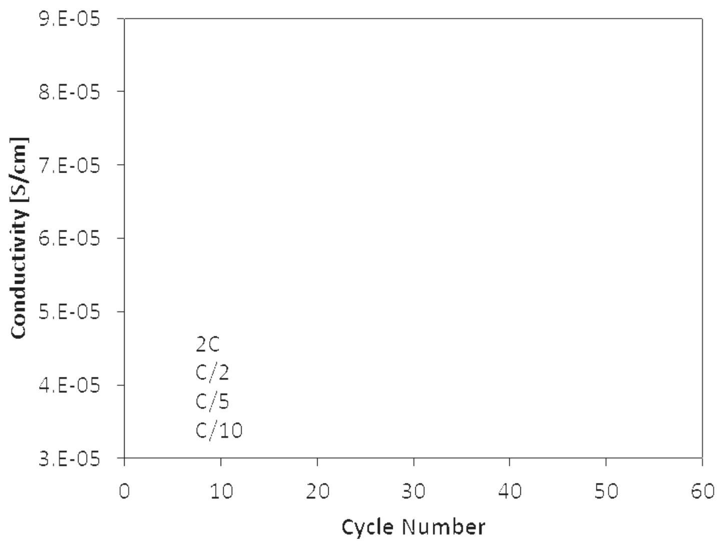


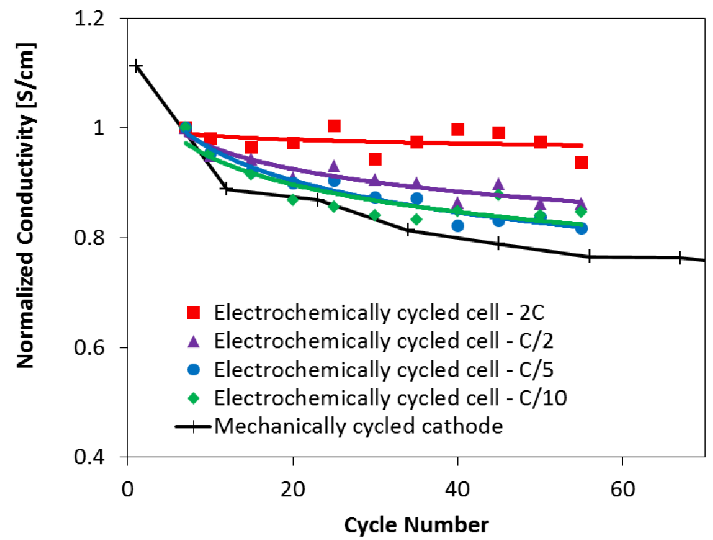
Electrochemical vs Mechanical Cycles

- Current interrupt testing to measure ohmic resistance of full cell between 3-4.2 V
- Ohmic resistance starts as 61% of total cell resistance at C/10 charging rate





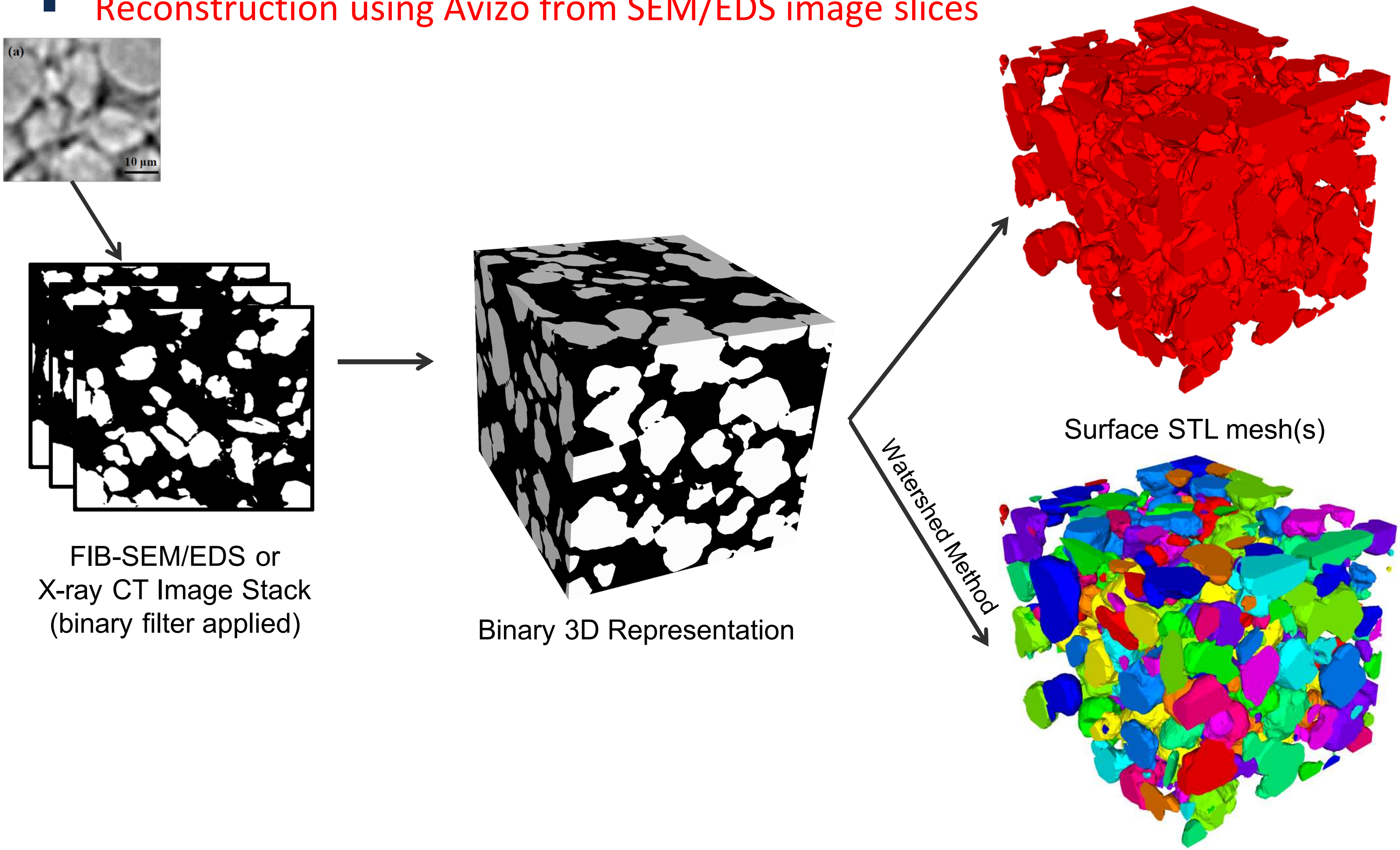




- Between cycle 7-57 cycles, electrochemical cycling reduced cell conductivity by 12-26% compared to a 31% decrease for mechanical cycling of the cathode

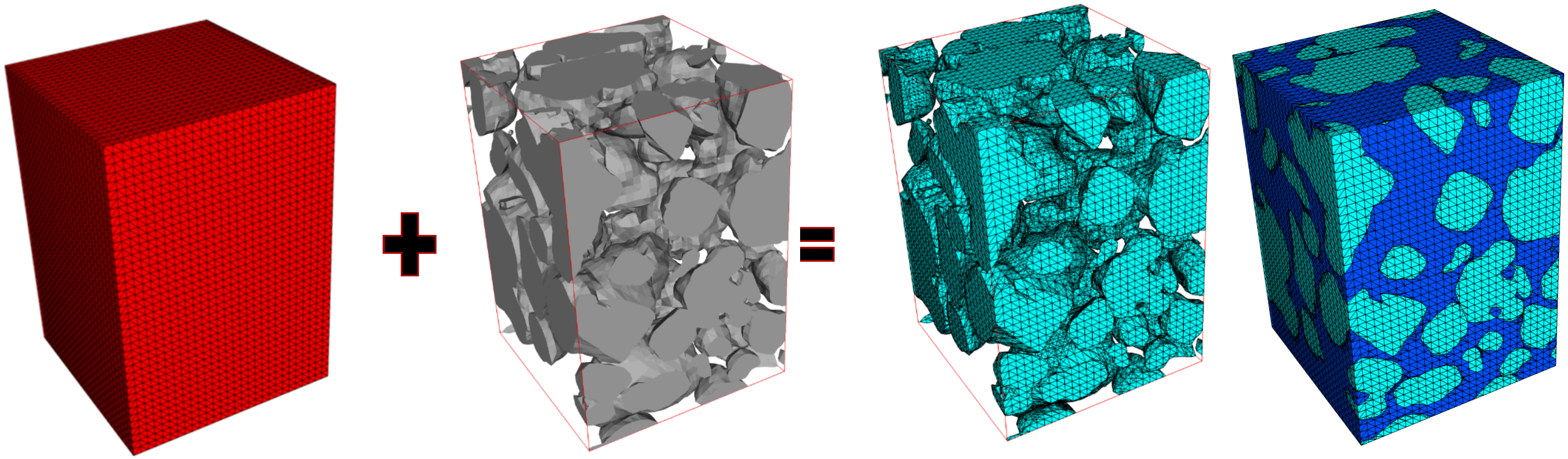
Reconstruction Approach

- Reconstruction using Avizo from SEM/EDS image slices

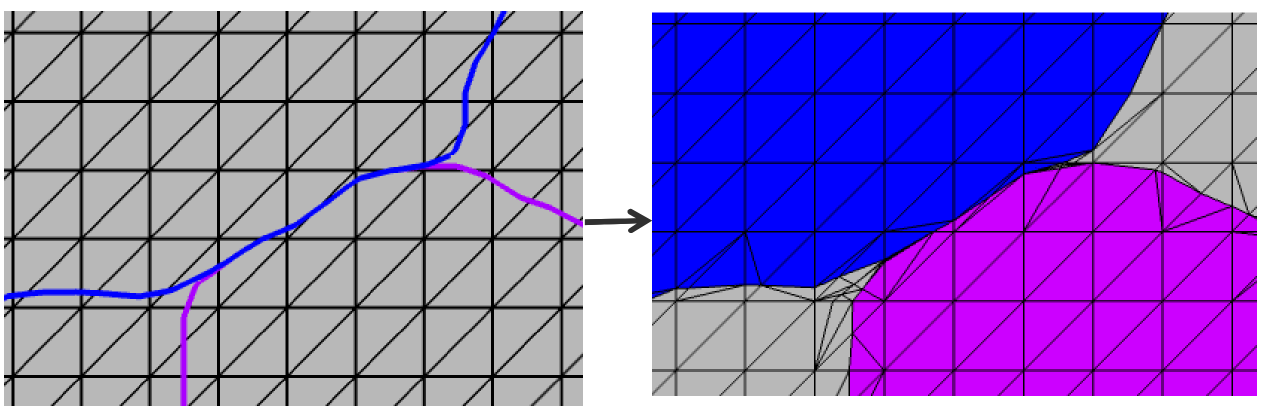


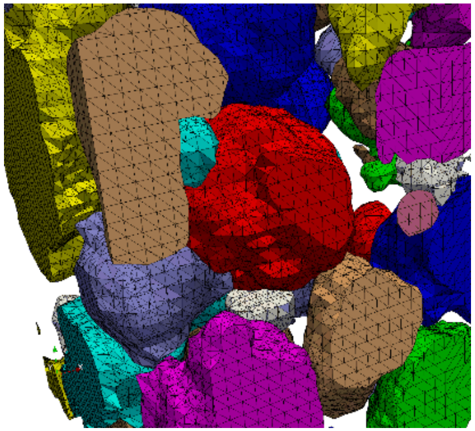
Reconstruction Approach

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



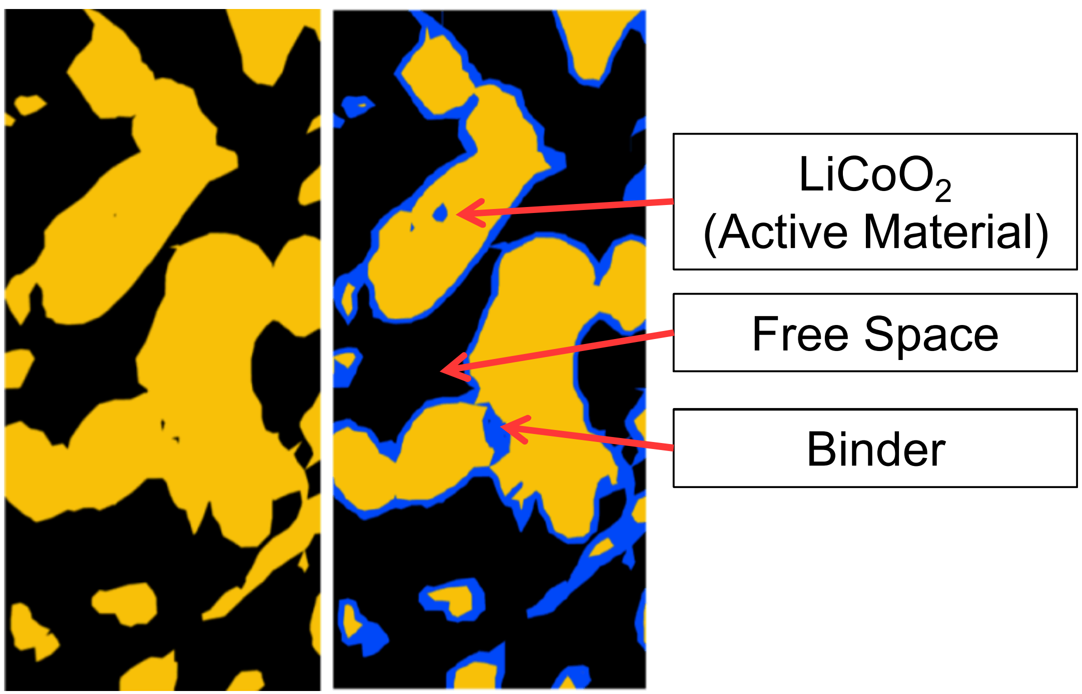
Background 3D mesh | Cathode Surface(s) (STL) | Cathode Particles Mesh | Particles+Electrolyte Mesh

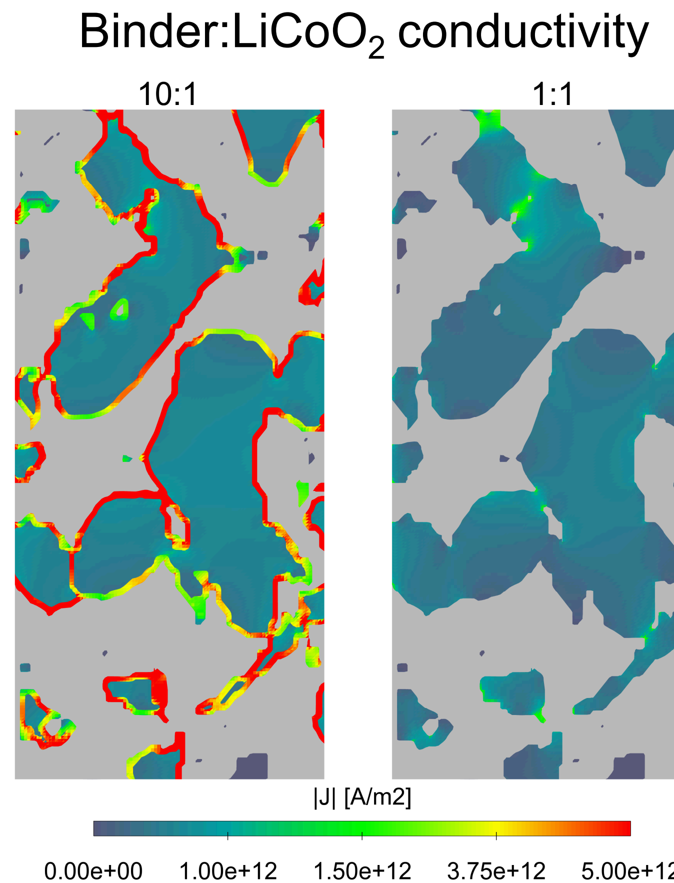




Electrical Conductivity in a Cathode

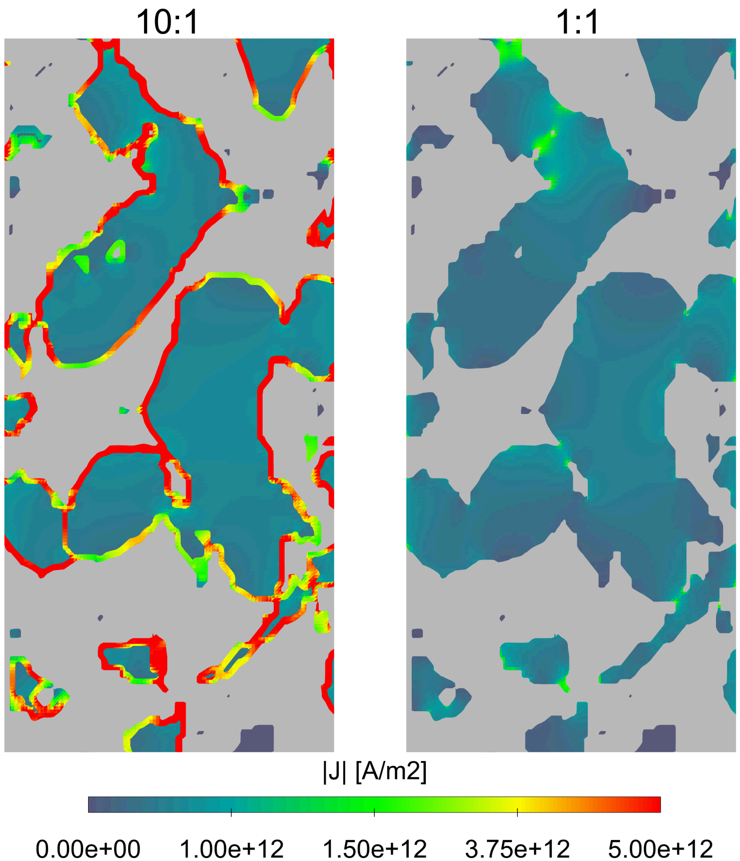
- Calculate the effective electrical conductivity of a representative cathode microstructure as a function of the binder conductivity.
- Highest current densities are always located in the binder phase.

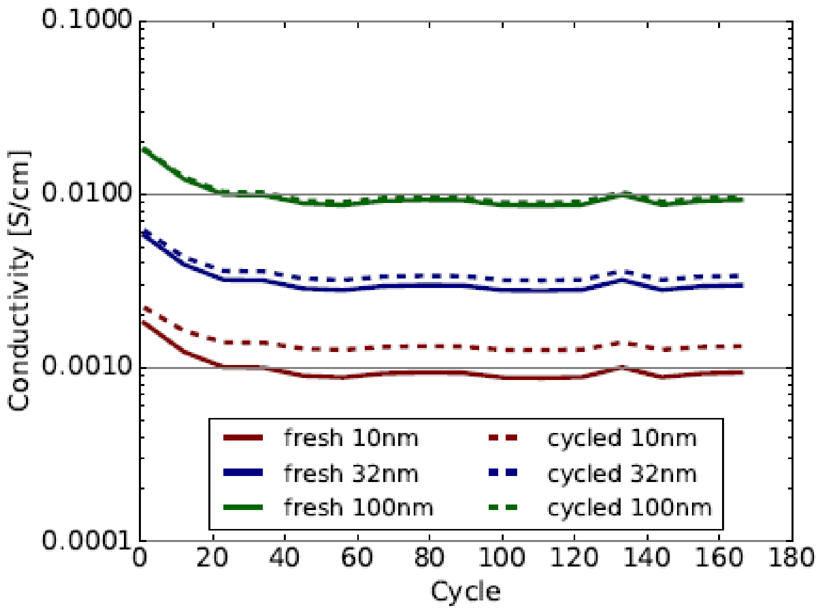




Impact of Binder Conductivity Decline

- Calculate the effective electrical conductivity as the binder conductivity decreases.
- Based on cathode composition, 32nm coating of binder on active material
  - For 40wt% CB, predict 56% decline in cathode peak electrical conductivity compared to 42% decrease in the experiment





- Binder conductivity changes alone can account for decrease in cathode electrical conductivity

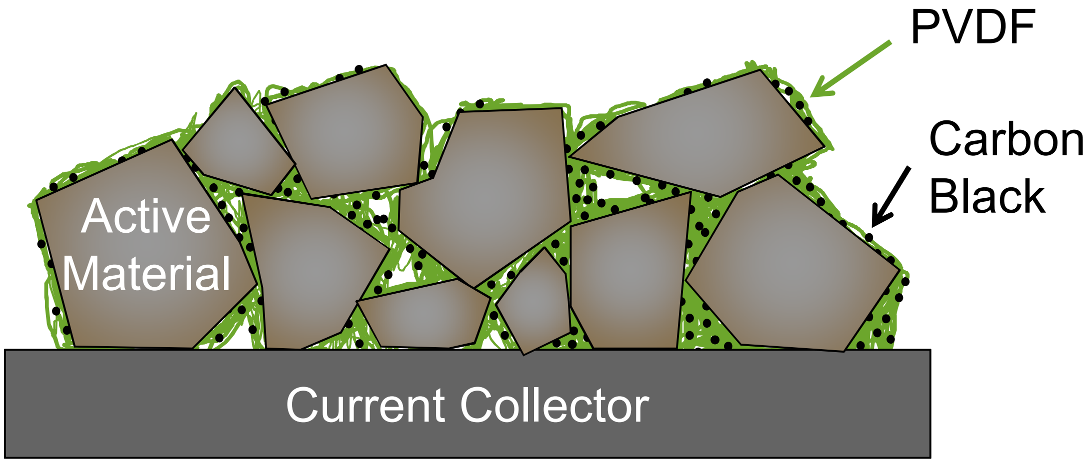
Conclusions

- Mechanical stress cycling causes PVDF/carbon black binder electrical conductivity to degrade 45-75% after 166 cycles
  - Carbon black fractions from 10-40wt%, Dry or swollen with propylene carbonate, Two PVDF manufacturers
- Mechanical stress cycling causes $LiCoO_2$ cathodes electrical conductivity to decrease by 29-42% after 166 cycles
- Electrochemical cycling causes full cell electrical conductivity to decrease by 12-26% after 50 cycles
  - Cathode conductivity decreased by 31% with mechanical stress cycles
- Mesoscale mechanical modeling shows binder degradation can account for the decline in cathode conductivity
- Mechanical stresses generated during electrochemical cycling degrade the binder electrical conductivity and increase the battery's internal resistance

- Grillet et al. J. Electrochem. Soc. v163(9) (2016) doi: 10.1149/2.0341609jes.
- Roberts et al. Journal of Electrochemical Energy Conversion and Storage v13 (2016) doi: 10.1115/1.4034410.
- Mendoza et al. Electrochem Acta v190 (2016) doi:10.1016/\-j.electacta.2015.12.224.

EXTRA

Understanding the Role of the Binder



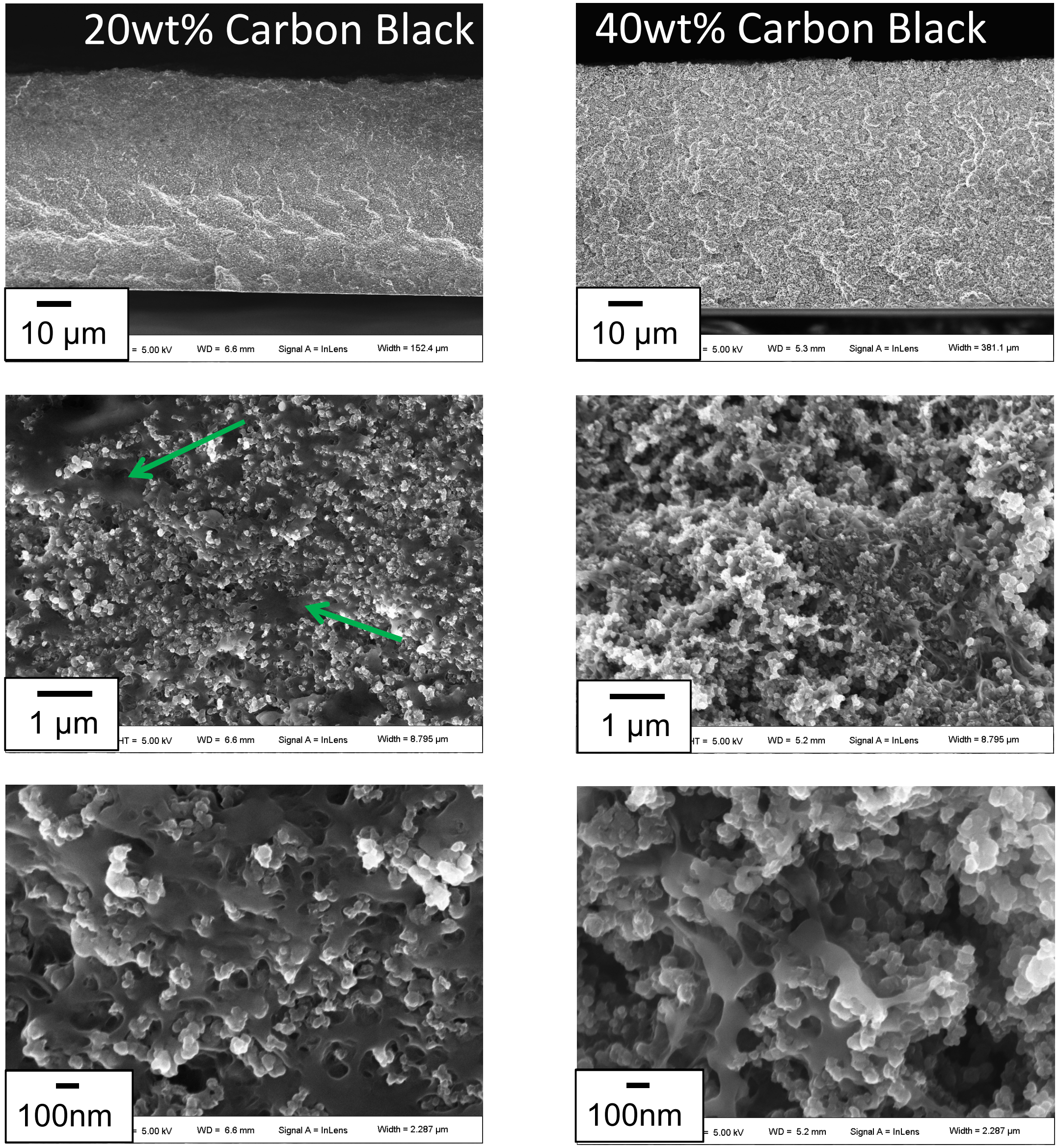
Mechanical

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

Electrical

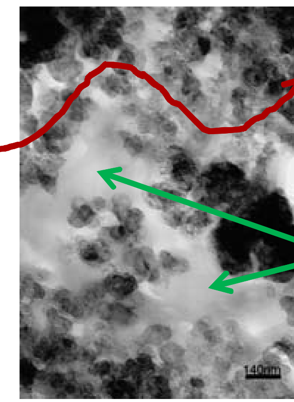
- Provide pathway for electron transfer through electrodes
- Decrease resistance (*i.e.,* loss) for cathode

Morphology of PVDF/Carbon Black Composites



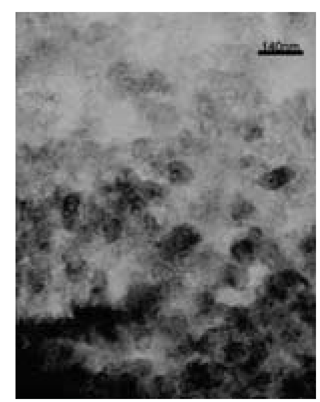
- Electron Microscopy of PVDF/Carbon Black Composites – 40% porous
- Lower carbon black fractions have regions of free PVDF

e⁻ paths



TEM 33wt% CB in PVDF

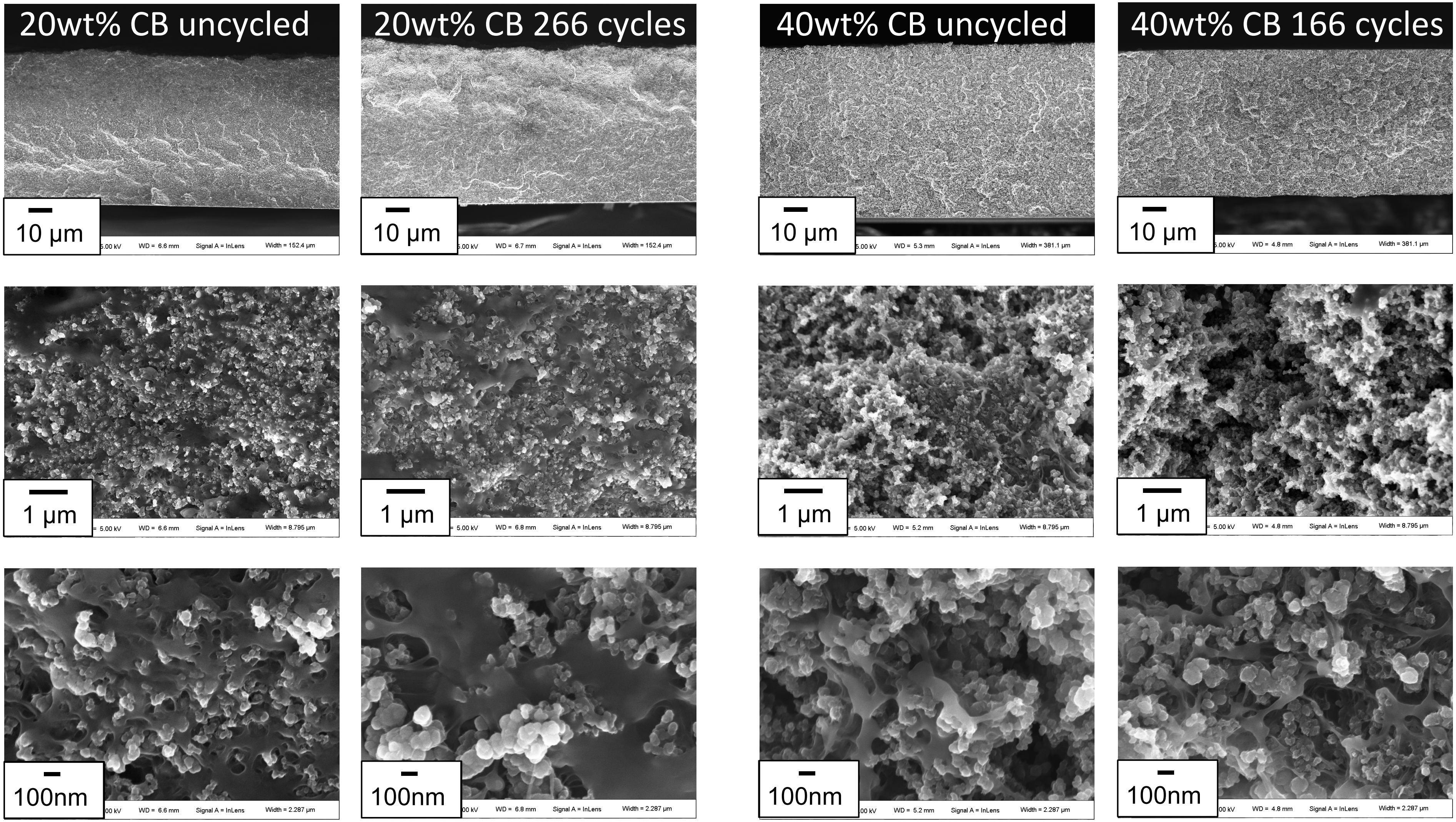
Free PVDF



TEM 45wt% CB in PVDF

No free PVDF

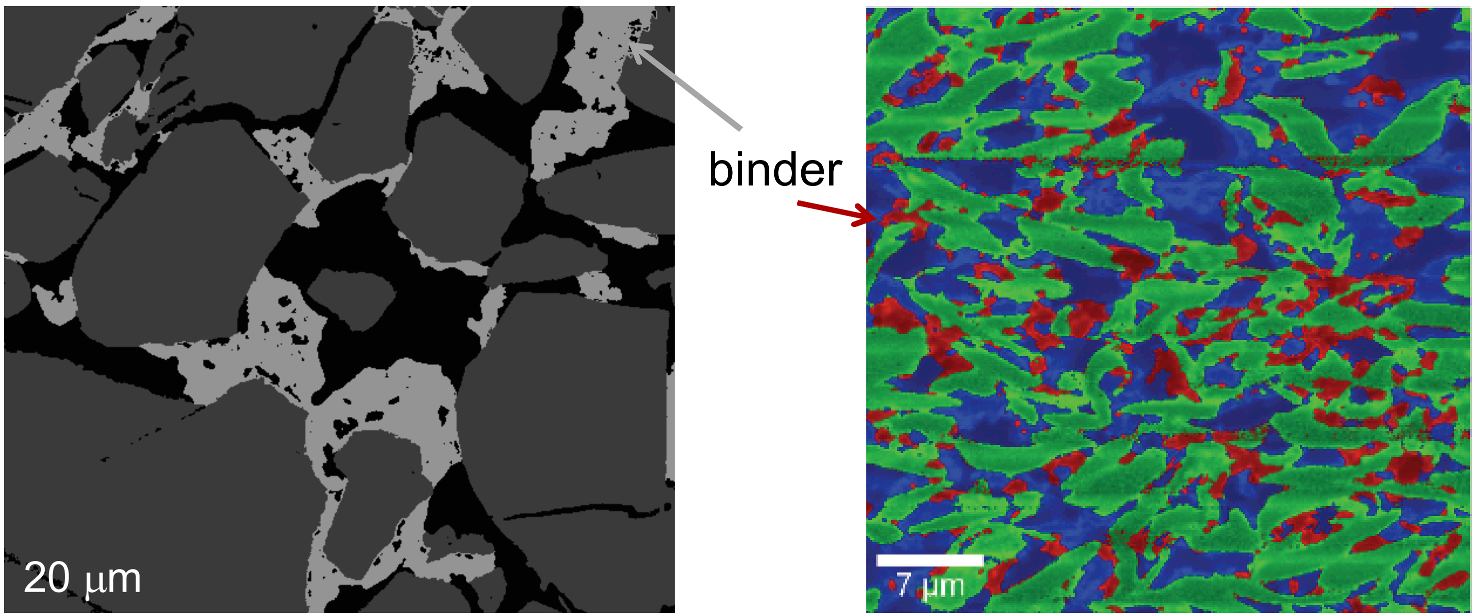
Morphology of PVDF/Carbon Black Composites



- No obvious cracks, delamination or other morphology changes

Batteries are actually complex composites

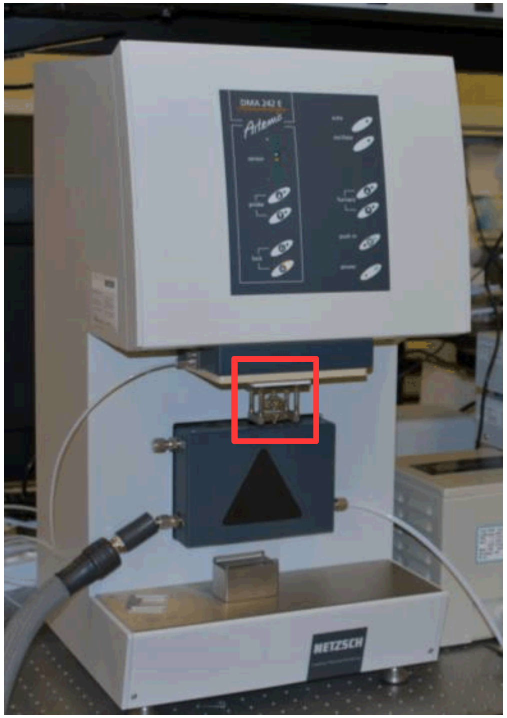
- Electrode active material particles are held together by binder
  - Binder is a mixture of polyvinylidene fluoride (PVDF) and carbon black
  - Electronic Conductivity : Binder ~ graphite >> $LiCoO_2$

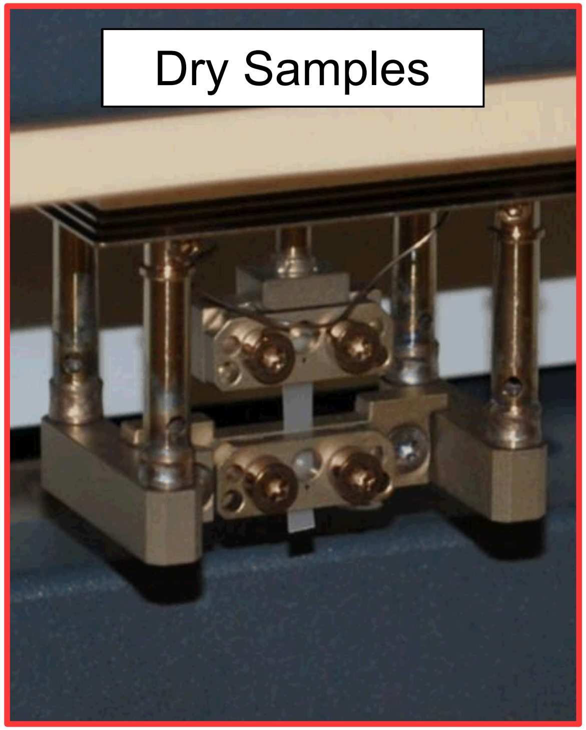


Cathode: 94wt% $LiCoO_2$, 3wt% PVDF, 3wt% CB, **void**

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

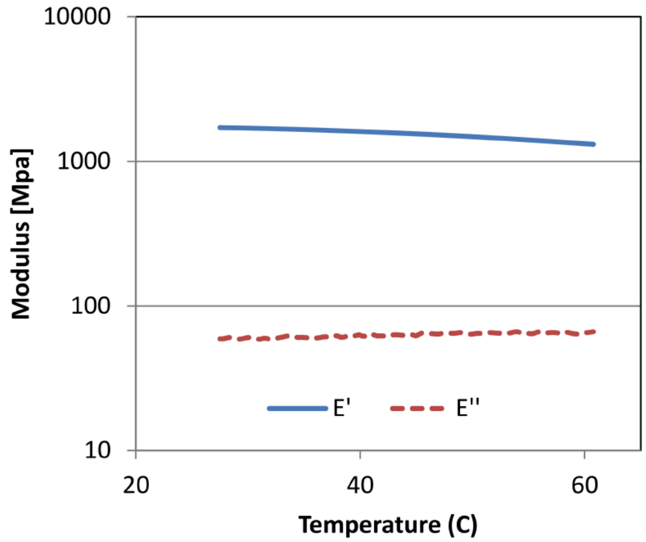
Mechanical Testing - DMA

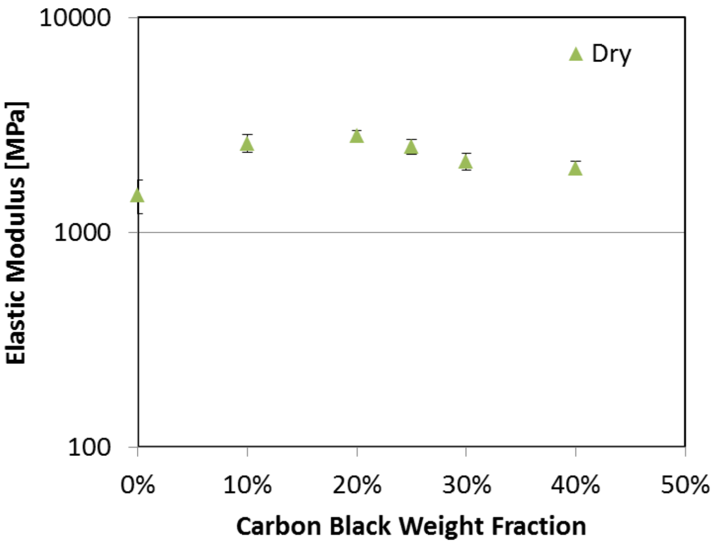




- Netzsch Artemsis Dynamic Mechanical Analyzer
  - Probe E’, E” from 1 – 10 Hz from 25 – 65 ^{o}C for dry samples
  - Probe E’, E” from 1 – 50 Hz at room temperature for electrolyte (propylene carbonate) immersed samples

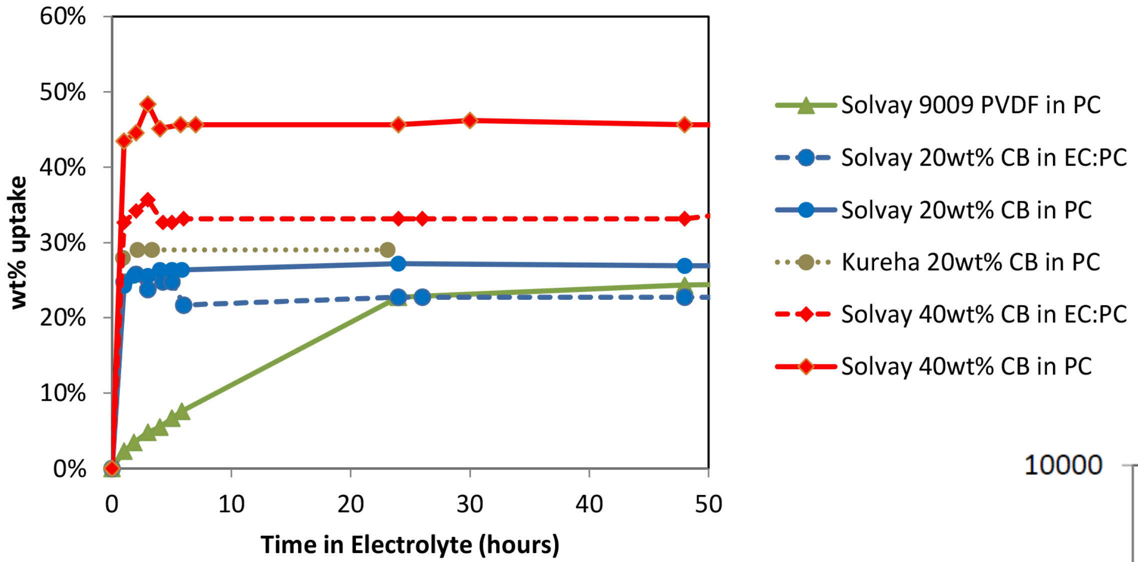
Mechanical Properties – Dry Binder



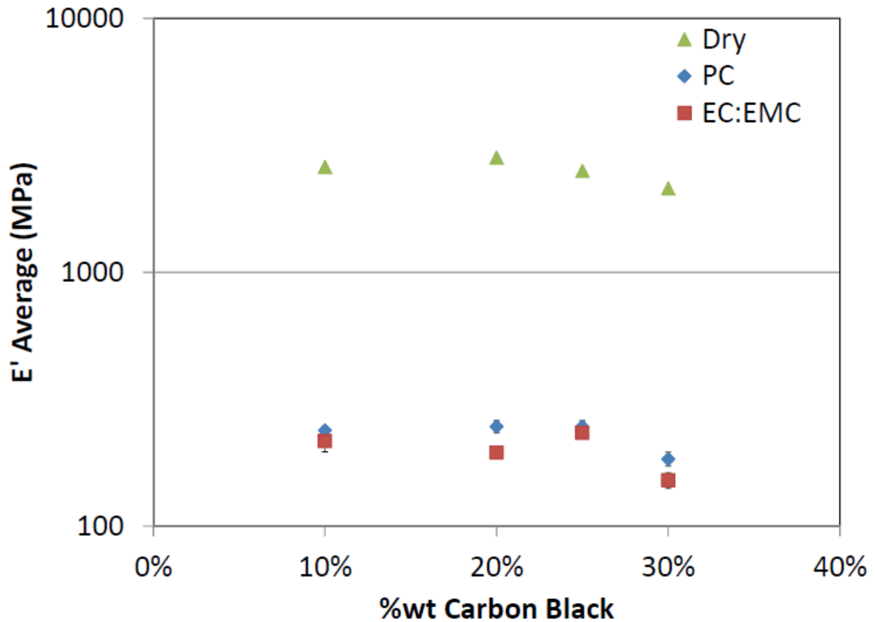


- Storage modulus >> Loss modulus for entire temperature range
- Binder softens at higher temperature
- Despite large differences in morphology, no dependence on carbon black concentration
- Elastic modulus for dry binder ranges between 1.5 – 2.8 GPa

Solvent Swollen (Wet) Binder Properties

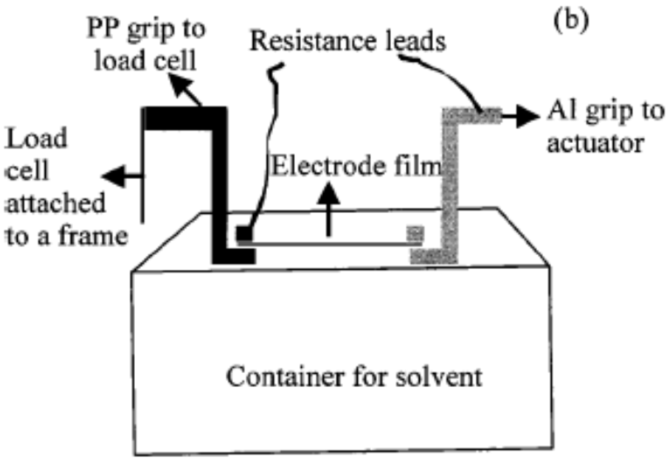


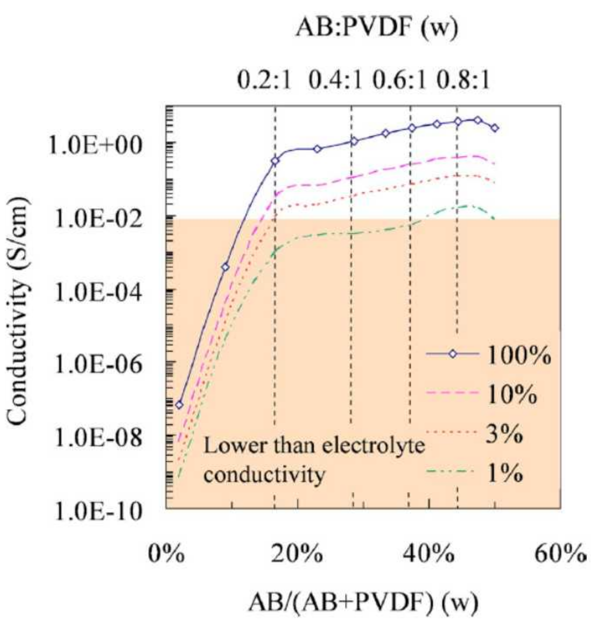
- Immersed binder samples within propylene carbonate (PC) for at least 24 hours
  - Samples absorb between 25 – 45 wt% in propylene carbonate within 2 hours of immersion



- Decreased modulus (≈ 200 MPa for wet compared to ≈ 2.4 GPa for dry)
- Peak modulus around 20wt% carbon black

Binder Conductivity in Literature





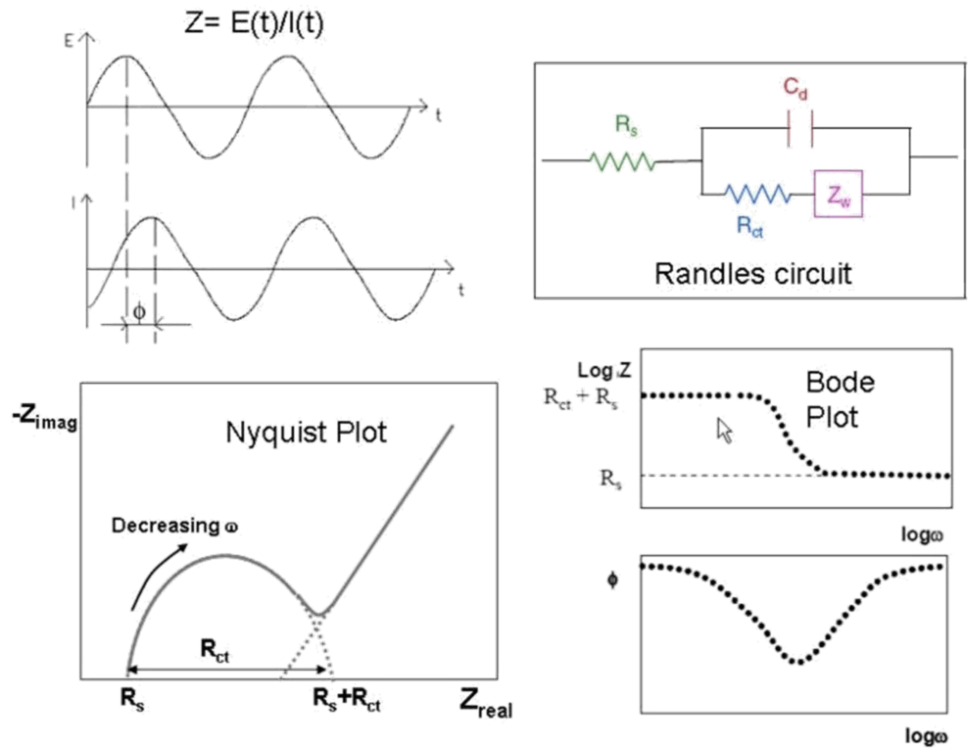
- Chen *et al.*[1] investigated the change in resistance of various PVDF/carbon composites (both wet and dry) and during initial cycling in tension
  - Small changes in resistivity with ~5 cycles number
- Liu *et al.*[2,3] investigated the effect of varying carbon concentration on film conductivity
  - Substantial characterization of binder morphology, organization with varying CB concentration
- They both used 4 point probe technique to calculate conductivity
  - We are using oscillatory method
  - Measure different conductivities

1. Chen et al. (2003) 2. Liu et al. (2012) 3. Liu et al. (2008)

Electrical Impedance Spectroscopy

$$Z = \frac{E_t}{I_t}$$

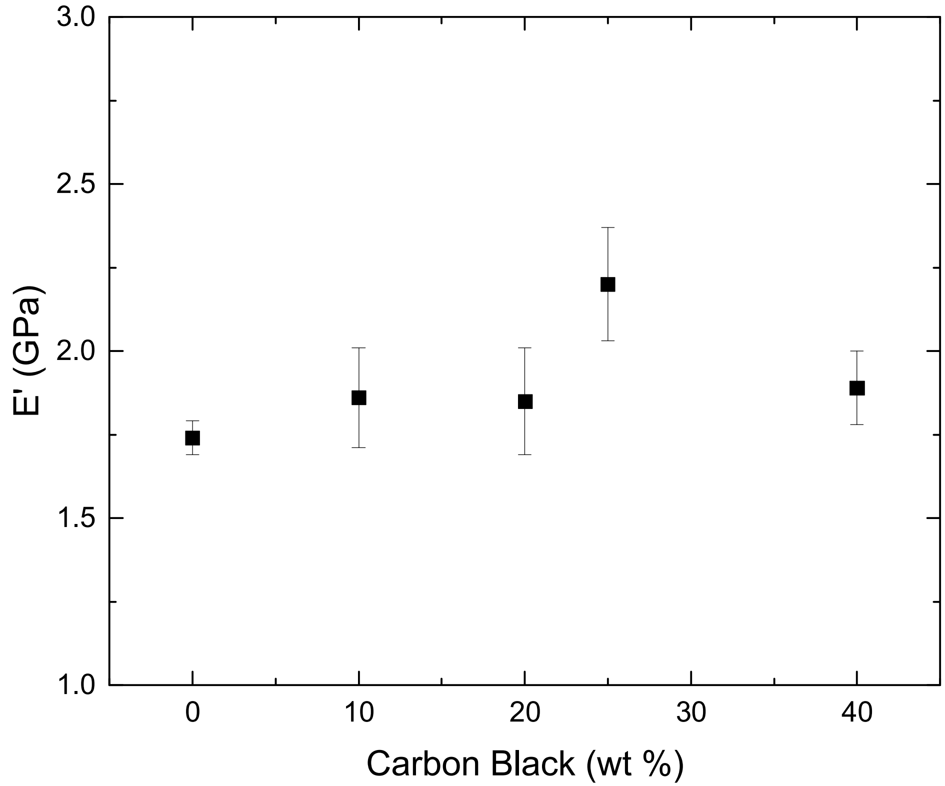
$$Z = \frac{E\sin(\omega t)}{I\sin(\omega t + \phi)}$$



- AC equivalent to Ohm's Law
- Useful for characterizing electrochemical systems with various complex equivalent circuits (multiple resistances, capacitors, *etc.*)

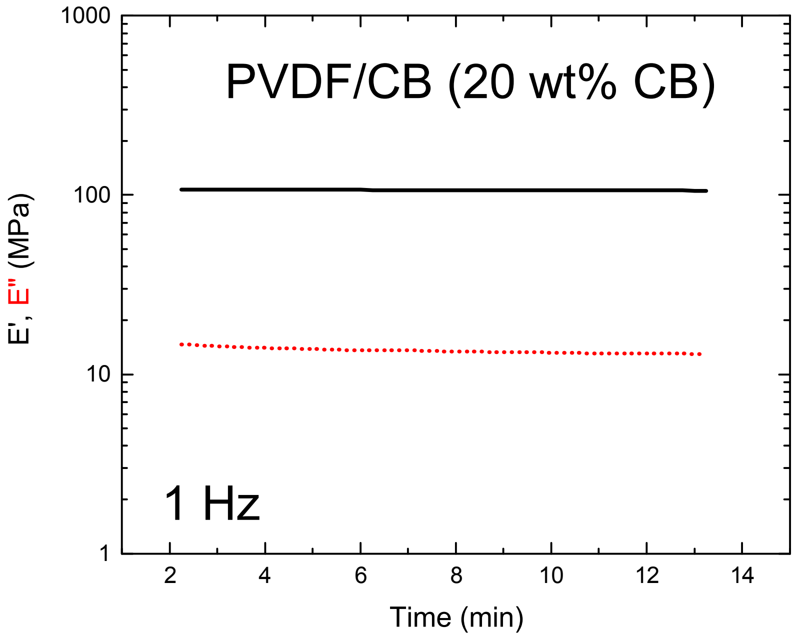
M. Pacios *et al.* (2011). DOI: 10.5772/10594.

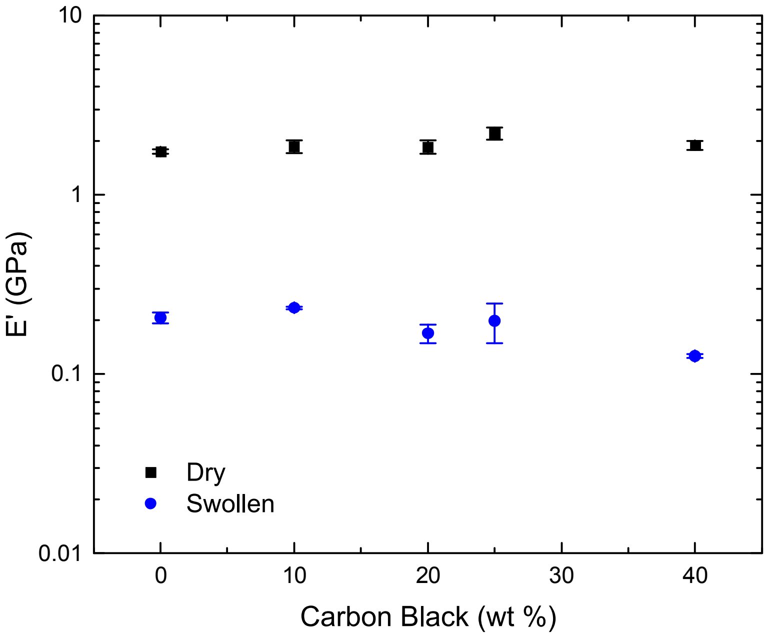
Mechanical Properties – Dry Binder



- 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

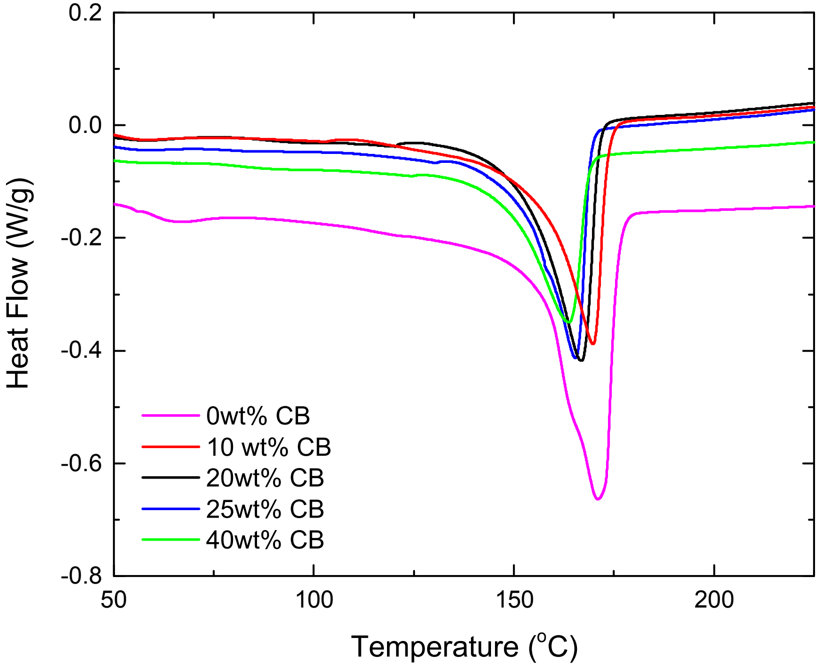
Mechanical Properties - Swollen





- 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

Differential Scanning Calorimetry



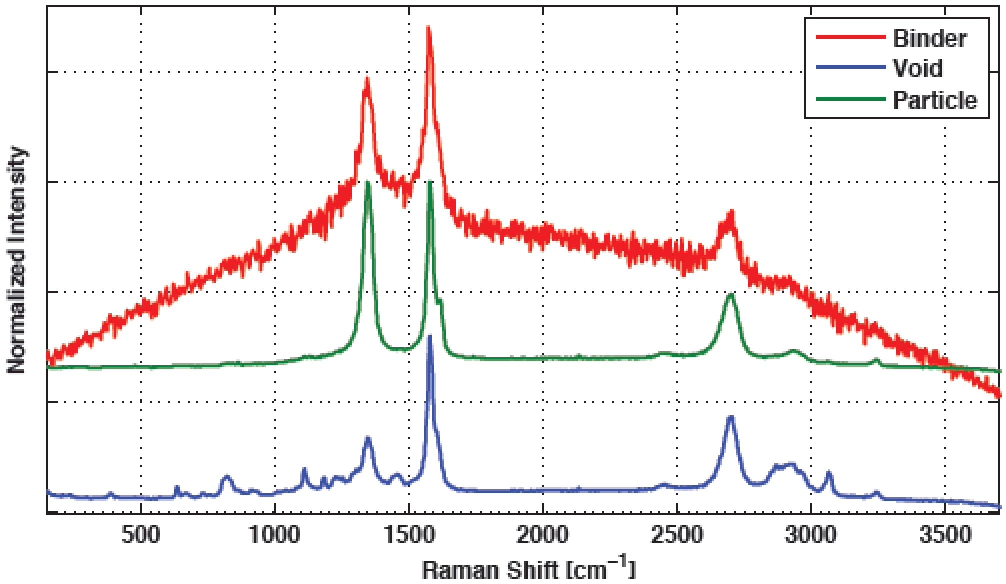
% CB	Normalized H_{sl} (J/g)	% Crystallinity
0.0	47.0	0.45
10.0	43.2	0.41
20.0	38.3	0.37
25.0	41.7	0.40
40.0	44.5	0.43

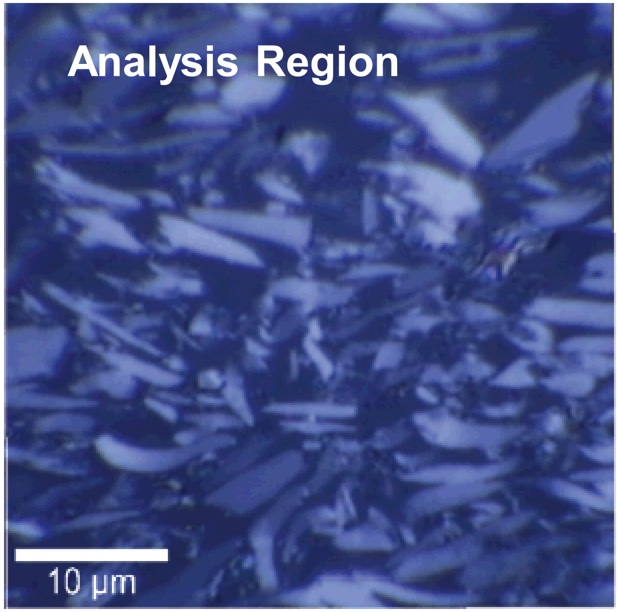
- Investigated % crystallinity using differential scanning calorimetry by quantifying latent heat of fusion and compared against fully crystalline PVDF (H_{sl} = 104.7 J/g)[1]
  - Adding carbon black does not change PVDF crystallinity
  - Hypothesize that crystalline PVDF structure controlling mechanical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

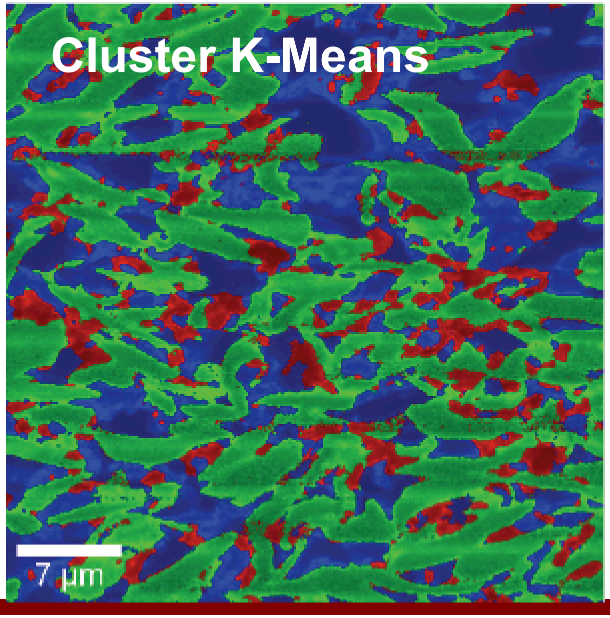
1. Lui *et al., J.Electrochem. Soc. 159 (2012)*

Raman Microscopy w/ Thomas Beechem

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





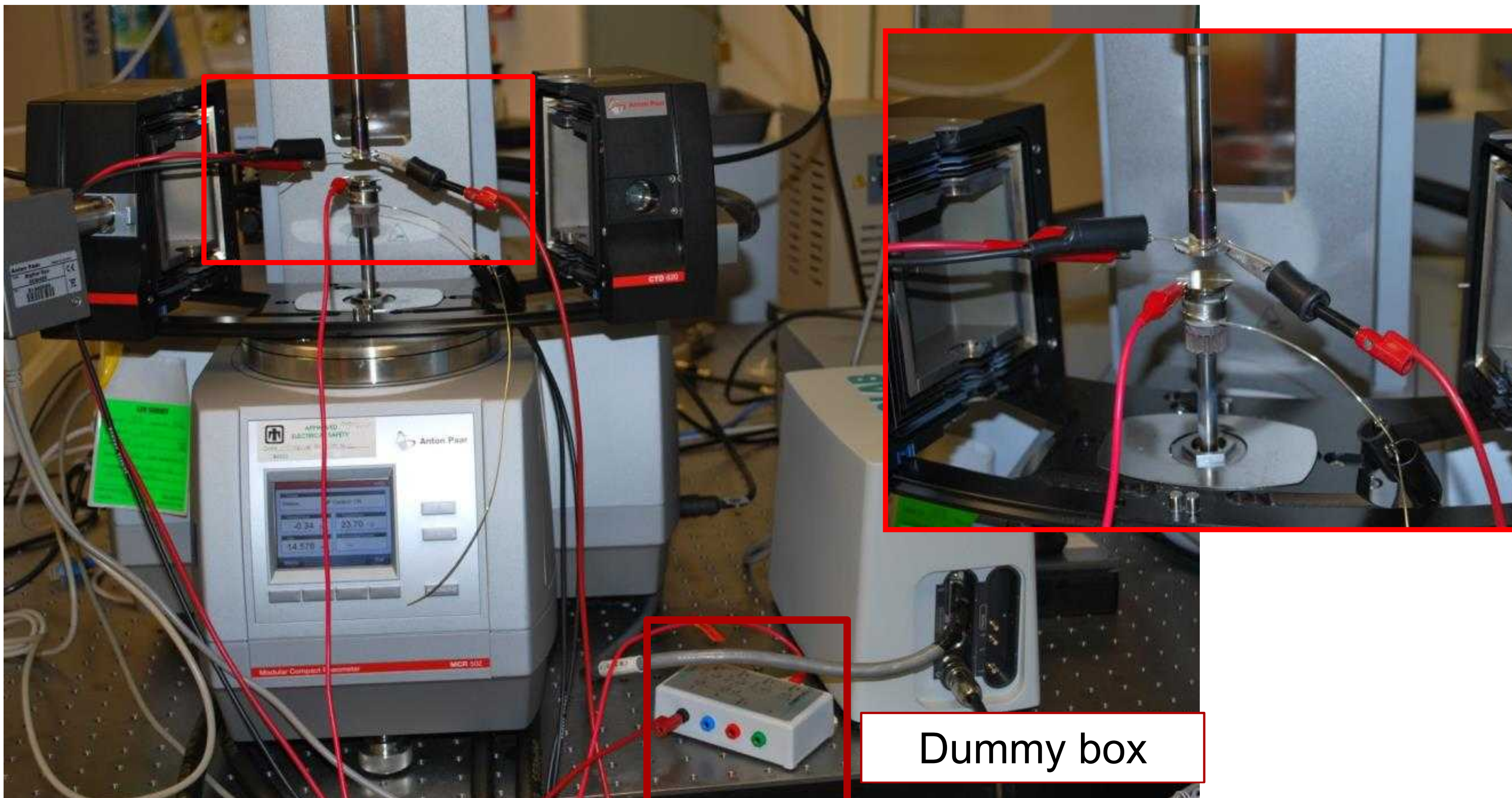


First mesoscale binder structures for an anode!

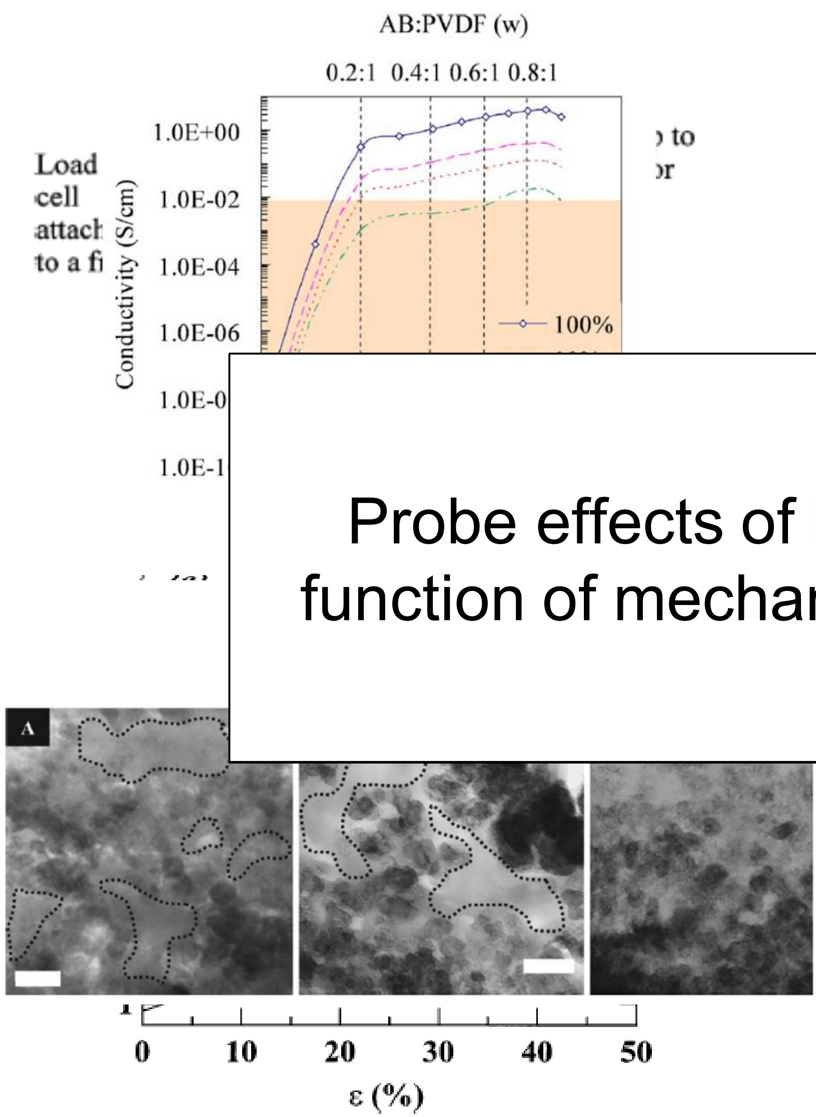
Raman may also be able to distinguish local states of charge in graphite particles

Testing contact/system/lead resistance

1. Ran potentiostat into dummy box (100 ohm resistor + (1000 ohm resistor in parallel with 1 uF capacitor)
2. Connected alligator clips into system, hooked into same dummy box connections



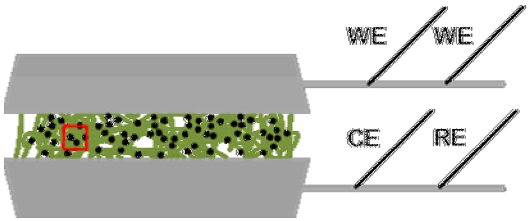
Binder Conductivity in Literature

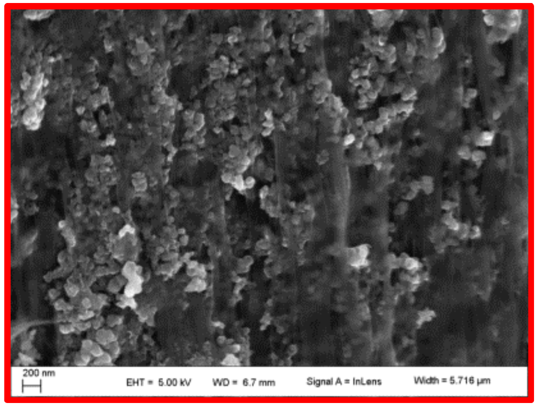


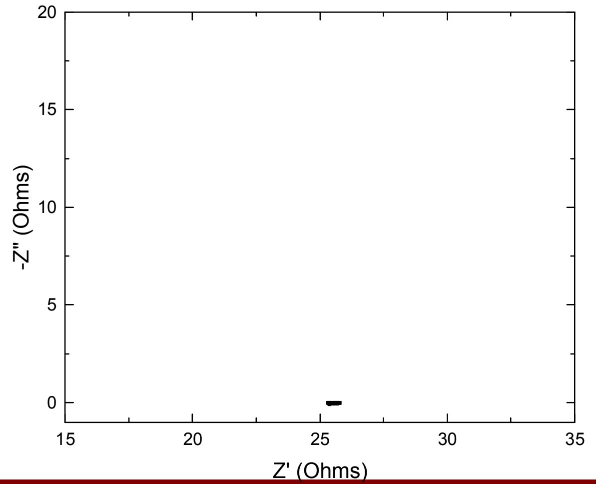
- Chen *et al.*[1] investigated the change in resistance of various PVDF/carbon composites (both swollen and dry) and during initial cycling in tension
  - with
  - of
  - on
  - Developed models to predict binder conductivity
  - Substantial characterization of binder morphology, organization with varying CB concentration

Probe effects of binder conductivity as a function of mechanical compressive cycling

Measurements on Dry Binder

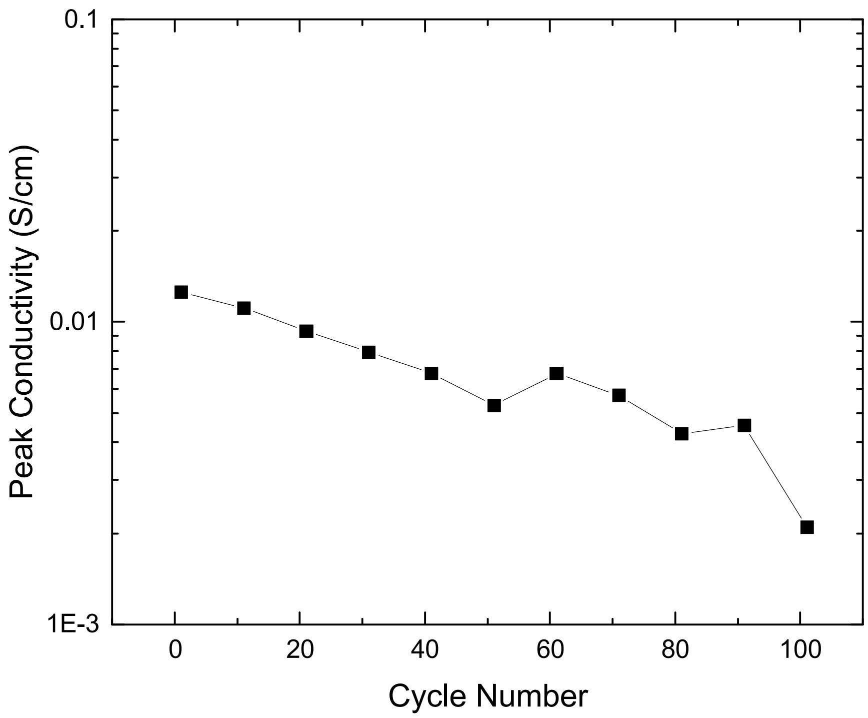






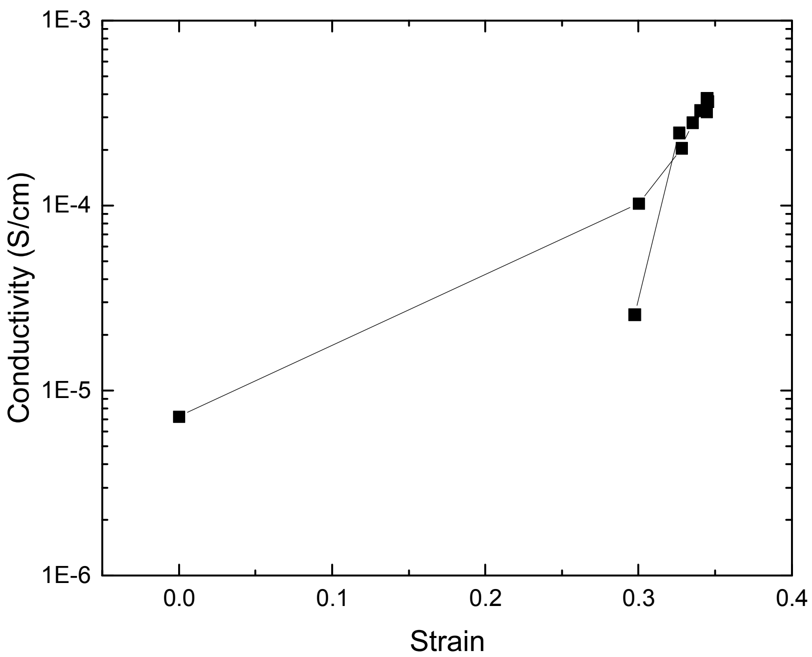
- Frequency response shows purely resistive behavior
  - No imaginary impedance (current measurement is completely in phase with applied voltage)
  - **(easy system to characterize)**
- Using film dimensions, values can be converted to a conductivity
- Investigate conductivity as a function of the applied load and mechanical cycle

Cycling Behavior of Dry Composite Binder



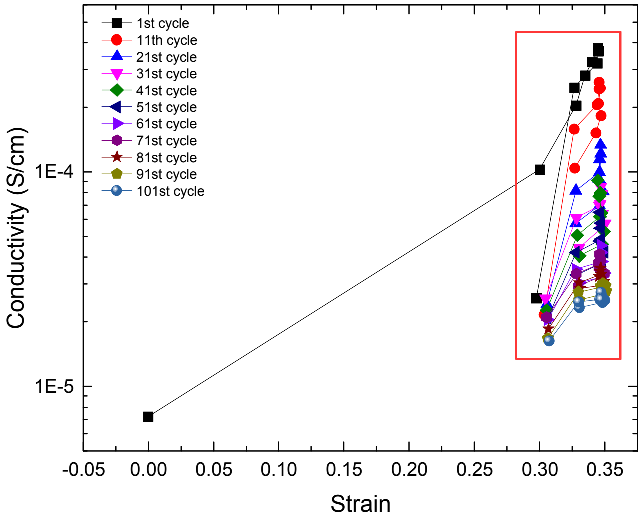
- Conductivity at 2.5 MPa (peak load/stress) as a function of cycle number
- PVDFCB – 40 wt%

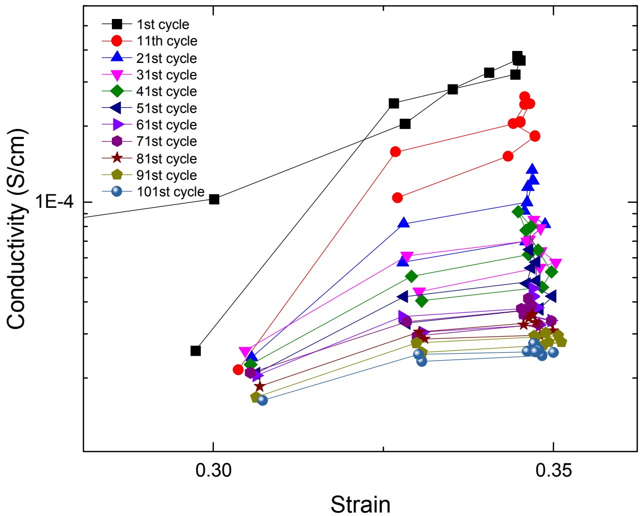
Cycling Behavior of LCO Cathode



- I do not know the specifics of the cathode that we used other than:
  - 94 wt% $LiCoO_2$
  - 3 wt% PVDF
  - 3 wt% Denka CB
- Cathode exhibits a similar trend in increasing conductivity as a function of applied compressive stress
- Peak conductivity of cathode is almost two orders of magnitude lower than comparable binder
  - (40wt% vs. 50wt%)

Cycling Behavior of LCO Cathode

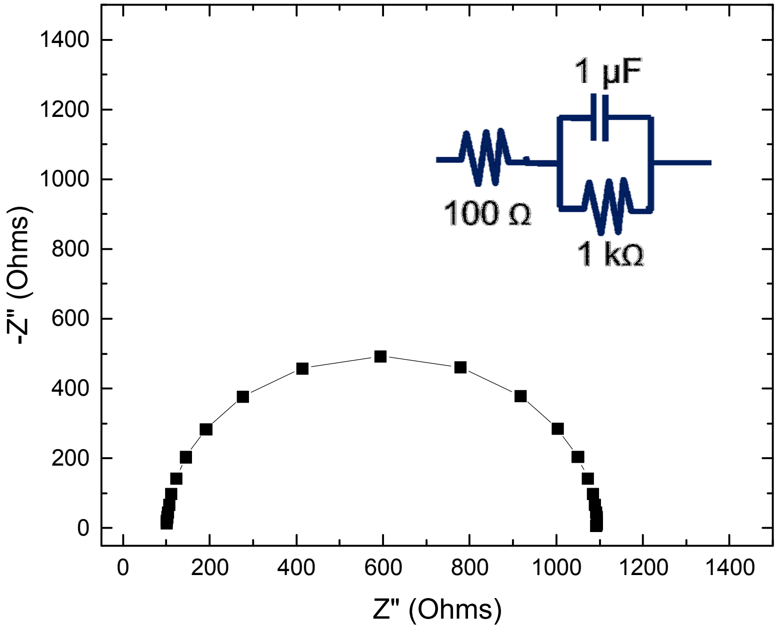


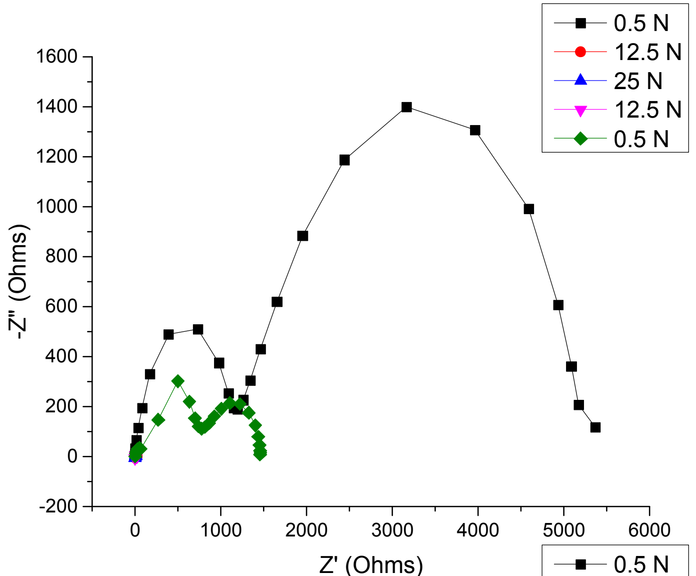


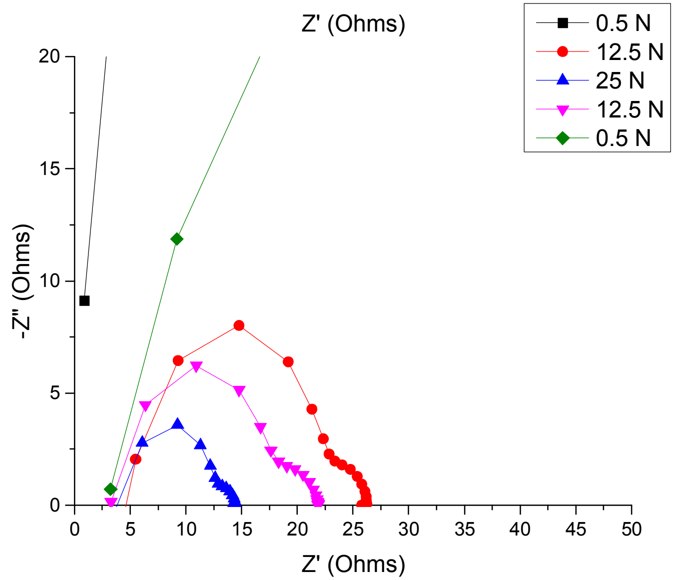
- Procedure:
  - 250 kPa – 2.5 MPa – 250 kPa
    - 5C (cycle ≈ 24 min), 9x 120C (cycle ≈ 1 min)
    - 101 total cycles
- Just as with the binder, the conductivity as a function of cycling drops substantially (greater than an order of magnitude)
- (just a note)
  - Interesting that the conductivity doesn't drop dramatically from the first cycle to the 11th (after the apparently huge plastic deformation)

Wet cathode Electrical Impedance Spectroscopy

- 1MHz – 50 mHz, 10 mV
- Possibly crushed swollen cathode?

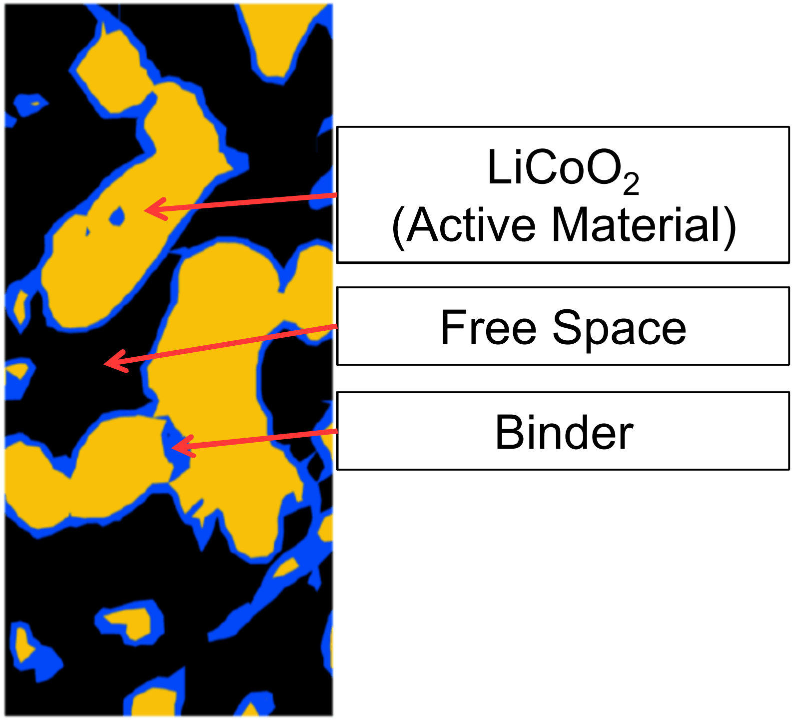


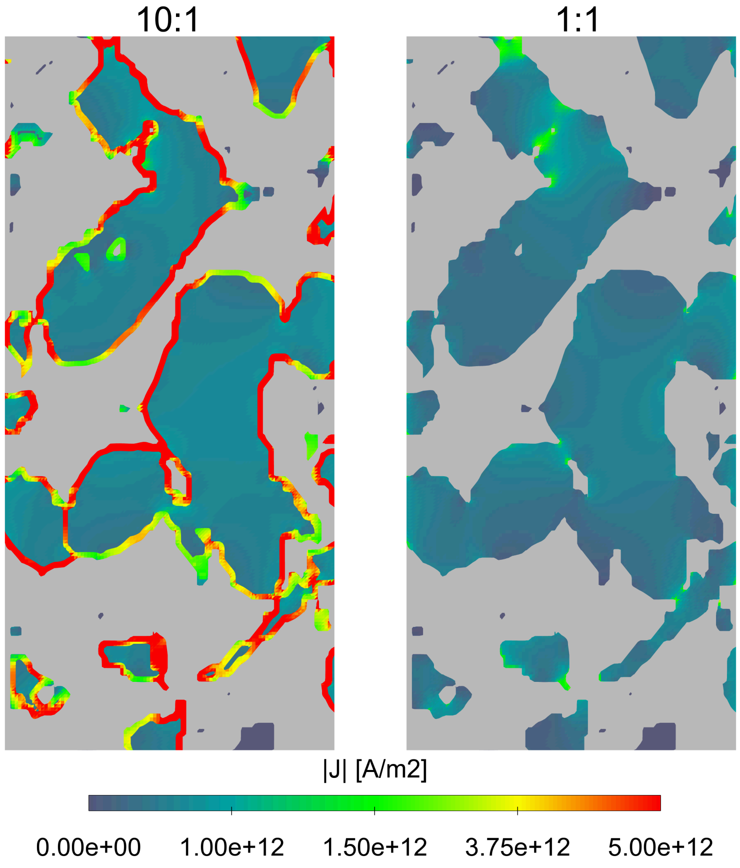




Impact of Binder Conductivity on Cathode

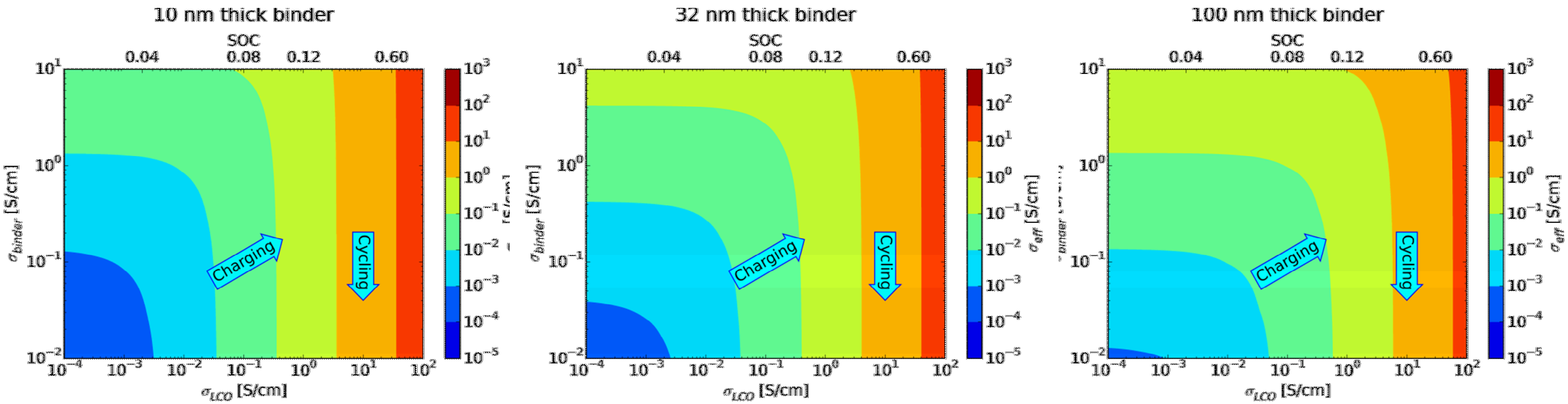
- Calculate the effective electrical conductivity of a representative cathode microstructure as the binder conductivity decreases.





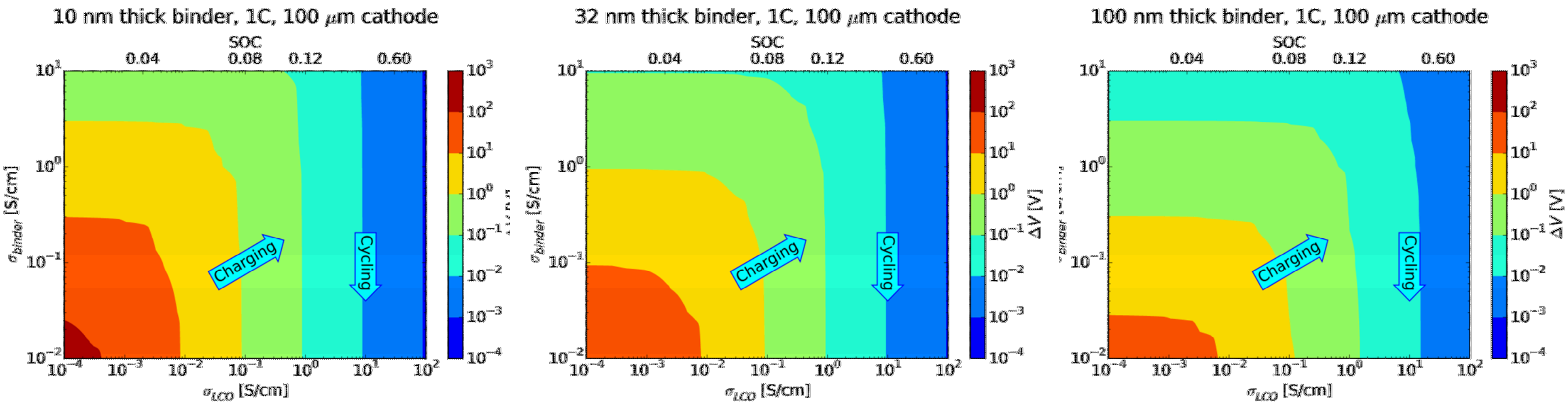
Effective conductivity

- Effective conductivity of the network with 3 binder thicknesses
- Conductivity increases during charging
  - LCO conductivity increases
  - Binder becomes stress and increases conductivity
- With cycling, network conductivity decreases (but only at low SOC)
  - Binder conductivity decreases with cycling
  - Most apparent for low SOC and thick binder coatings
- Is this a potential mechanism of capacity fade; losing the last 5-10% of capacity due to low effective conductivity?



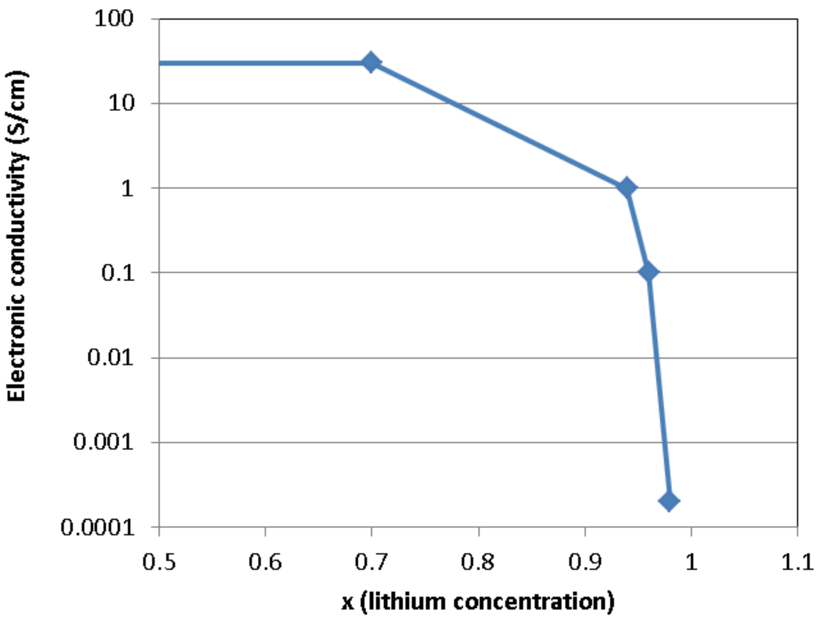
Voltage drop

- Another way to look at this is in terms of the voltage drop across the cathode
  - 100 um cathode, 1C (dis)charge rate
- At high SOC, there is very little voltage drop (< 0.1V for SOC > 0.1)
- For the last 5% SOC (discharging), the binder conductivity becomes important
  - Binder conductivity degradation from cycling could significantly increase voltage drop, into the 1-10 V range (rendering battery useless)
- Voltage drop scales linearly with current, so this is exacerbated for higher discharge rates



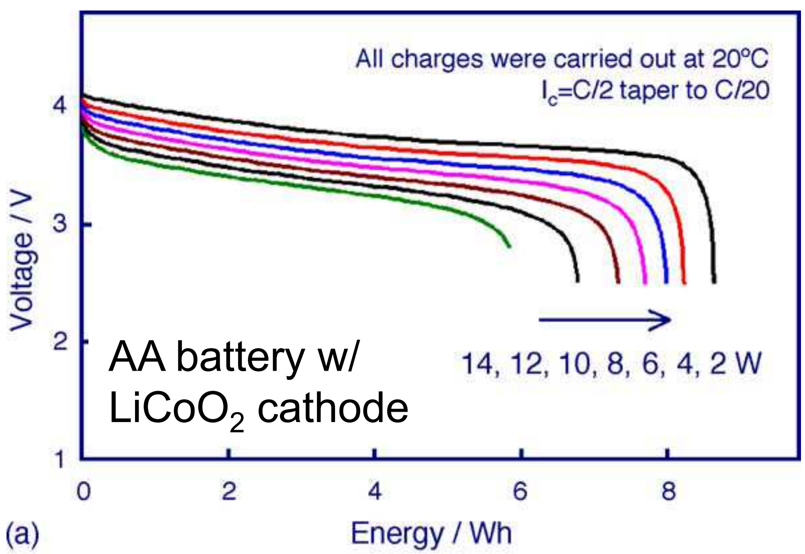
Electronic Conductivity of LiCoO2

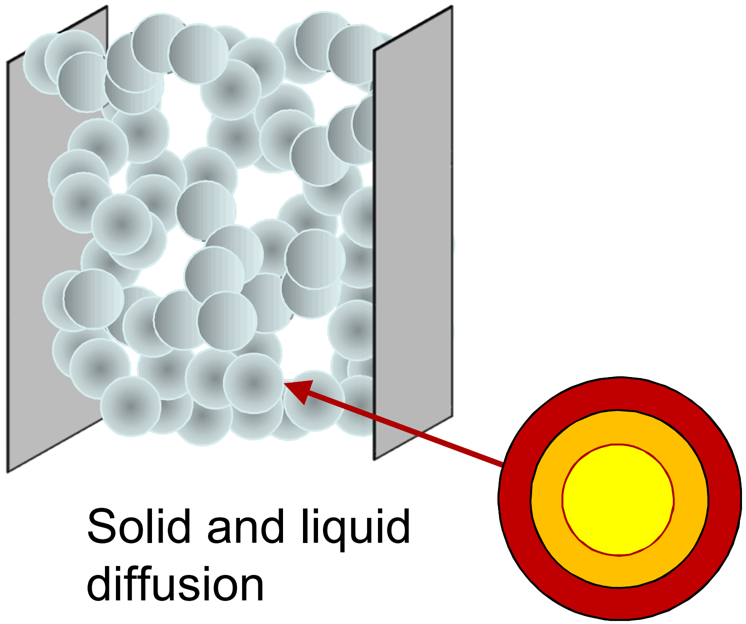
- Electronic conductivity as a function of degree of lithiation shows an insulator to metal transition during deintercalation of lithium.
  - Li_xCoO_2



High Power Draw Limitations

- Voltage drops caused by battery internal resistance
  - Transport limitations – ohmic losses, lithium ion depletion
  - Reaction rate limitations



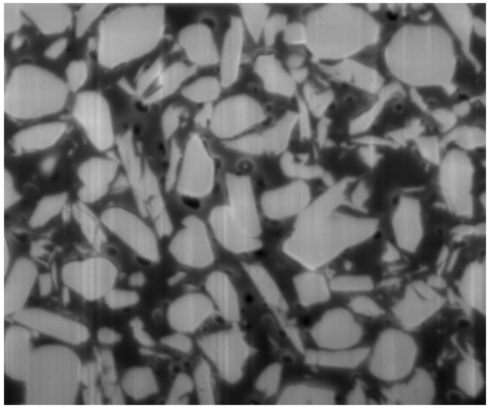


- Part of a larger effort at Sandia to develop predictive models for battery performance
  - Electrochemical, mechanical, and thermal dependence

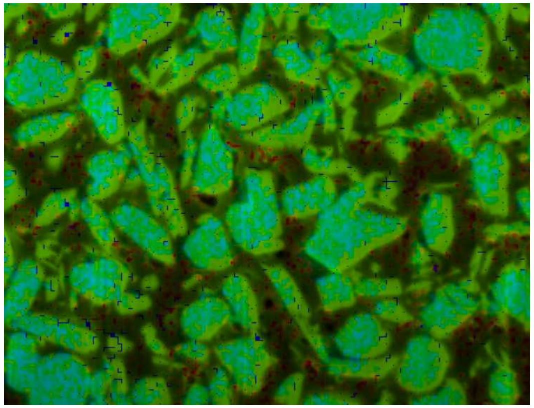
S.S. Zhang et al. / Journal of Power Sources 160 (2006) 1403–1409

Location of Binder

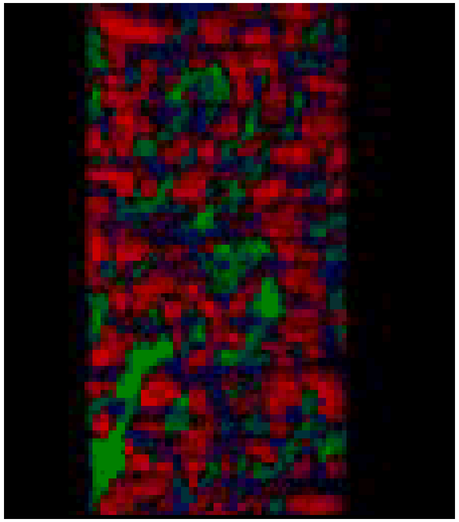
Focused Ion Beam Cross-section



Energy Dispersive Spectroscopy chemical composition



Multivariate principal component analysis



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

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

Binder found in the small spaces between particles

Mendoza et al (submitted)

Tortuosity, Porosity and Network Conductivity

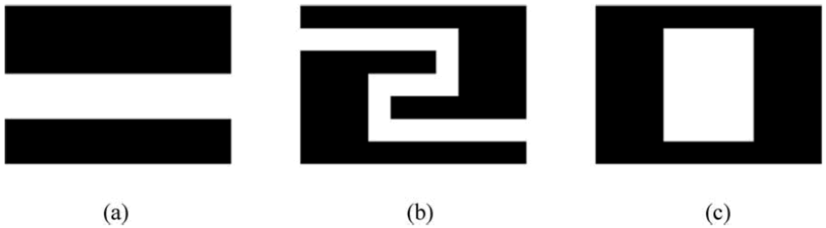
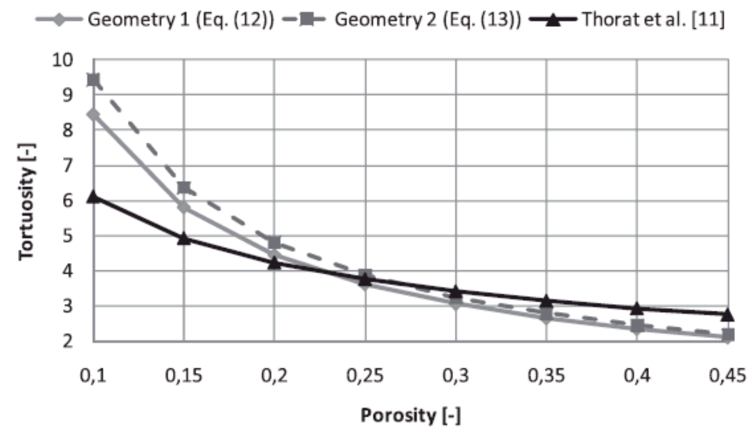


Figure 2. Three 2D porous media with a porosity of 2/7 and tortuosities of 1 (a), 2 (b), and infinity (c). While (a) and (b) show open pores, (c) displays a clc pore that does not contribute at all to material transport.

Kehrwald et al. (2011)



Rubino et al. (2001)

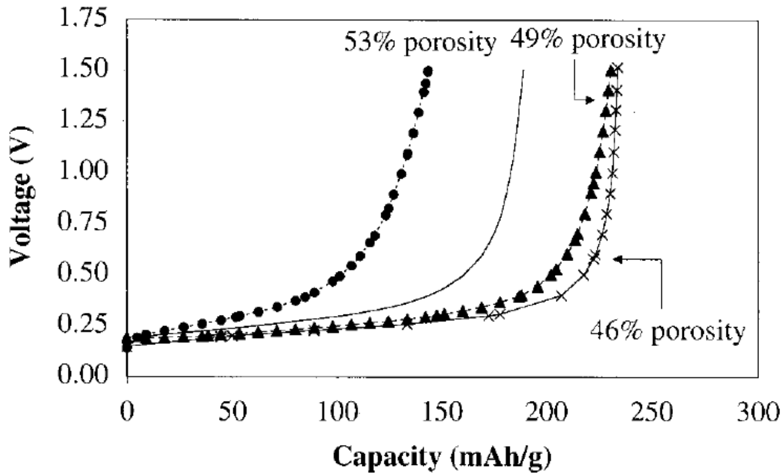
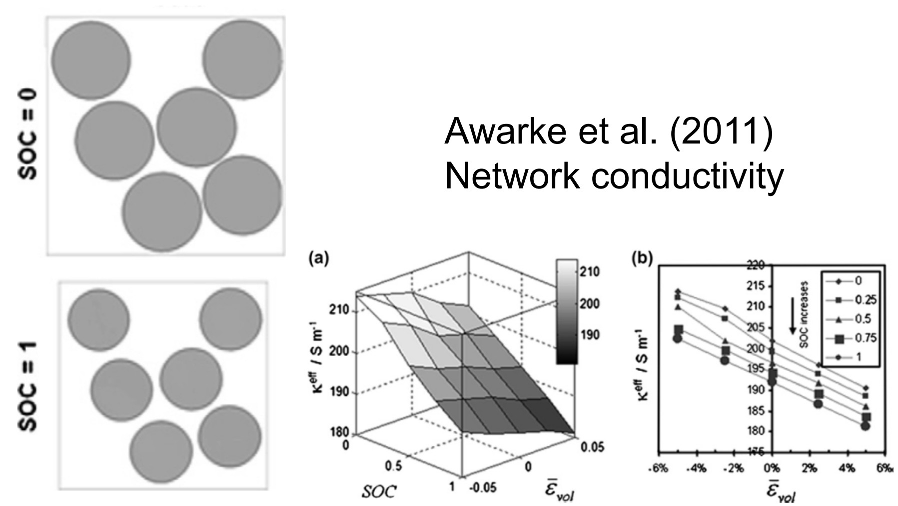
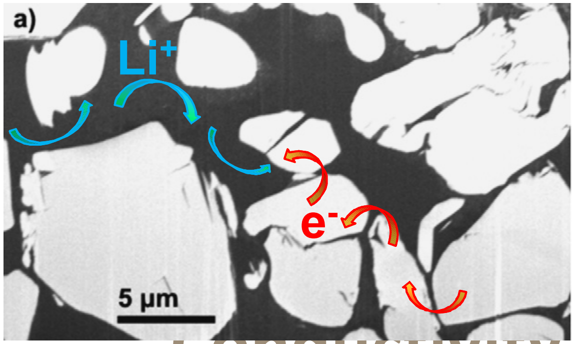
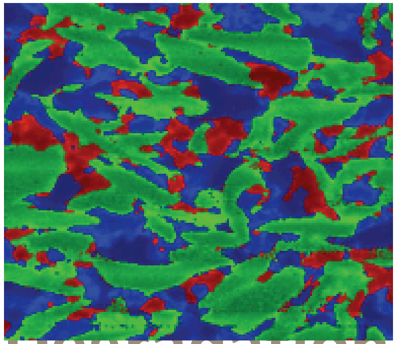
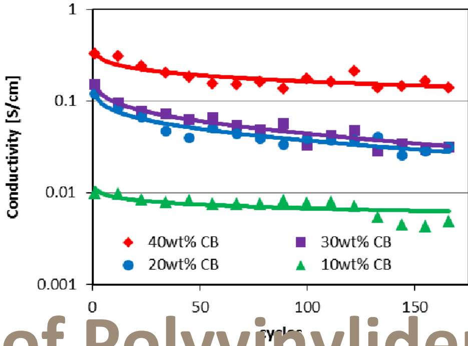


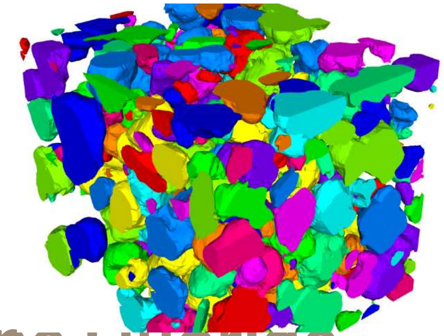
Figure 4. Half-cell voltage curves for anode pieces recovered from cycled cells. Half-cells were discharged to 0.010 V at C/2 followed by a constant potential step with a C/20 current cutoff. Voltage curves shown are for a 1C charge to 1.50 V. Circles: prismatic cell (300 cycles), line: prismatic cell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







Conductivity Degradation of Polyvinylidene Fluoride Binder During Cycling: Measurements and Simulations for Lithium Ion Batteries

Anne M. Grillet, Thomas Humplik, Emily K. Stirrup, David A. Barringer, Scott A. Roberts, Chelsea M. Snyder, Madison R. Janvrin & Chris A. Apblett

June 2, 2016 #A02-0368

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