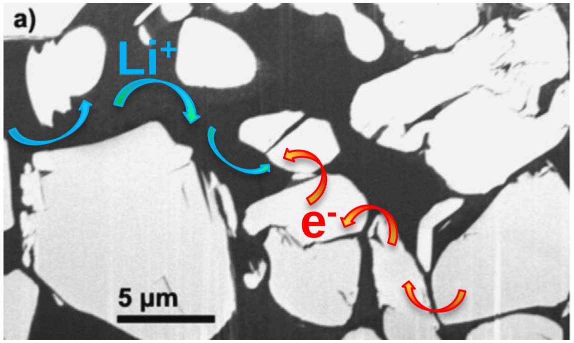

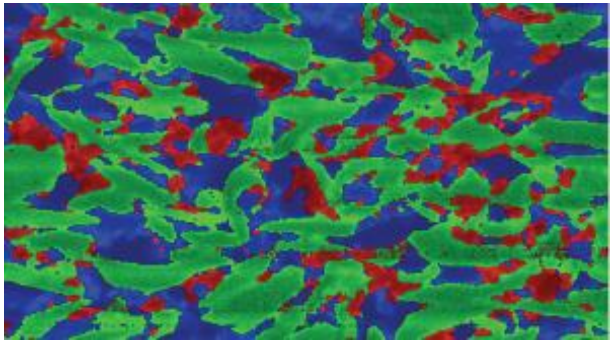

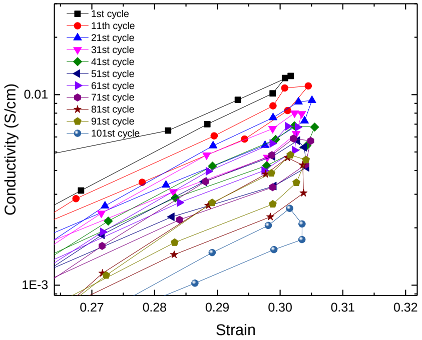

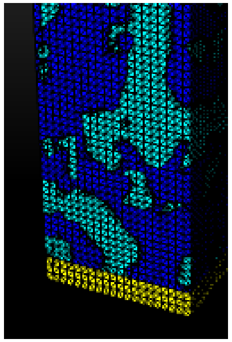

The role of polymer composite binder on mechanics and performance of lithium ion battery electrodes

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

June 2, 2016 #A02-0368

229th ECS Meeting

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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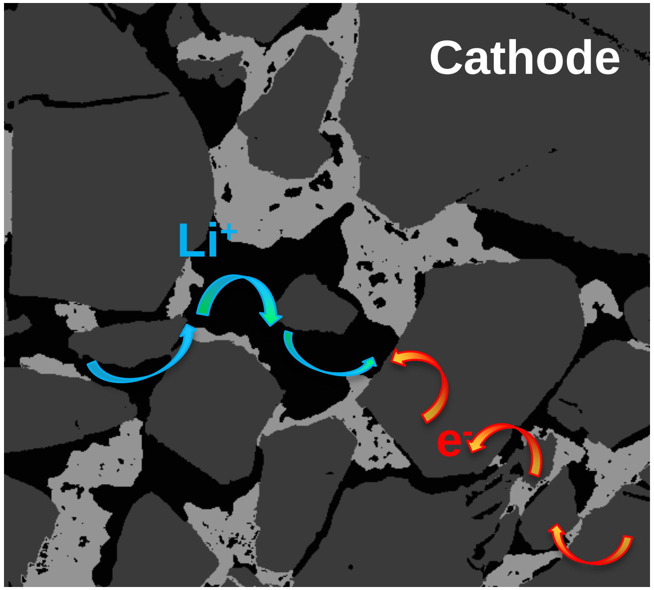
Battery Introduction

- 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

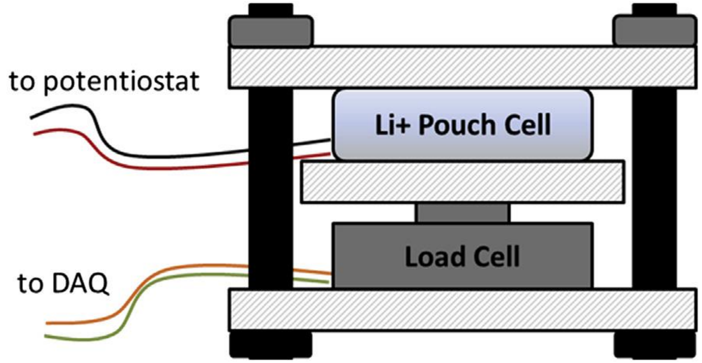
Outline

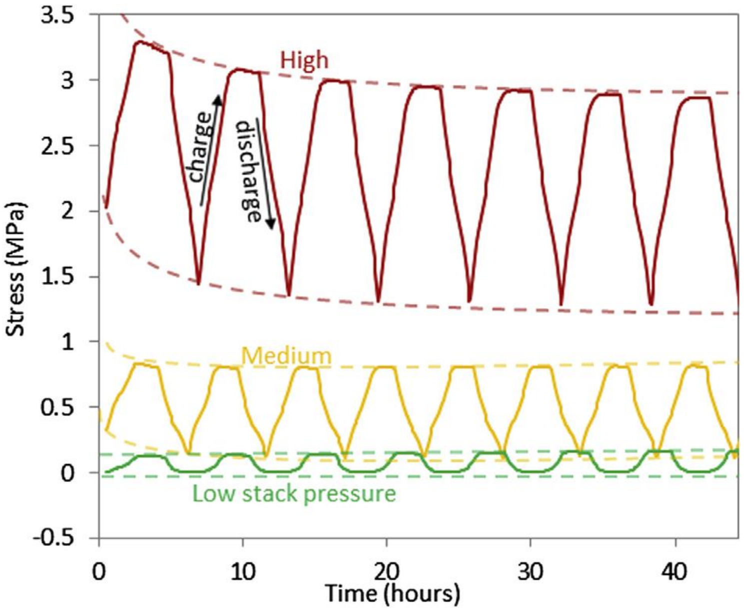
- Battery electrode binders play an important role both mechanically & electrochemically
- Coupled mechano-electrochemical characterization of binder
  - Mechanical stresses to mimic stresses during electrochemical cycling
  - Measure electrode strain and electrical conductivity
    - PVDF/CB binder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

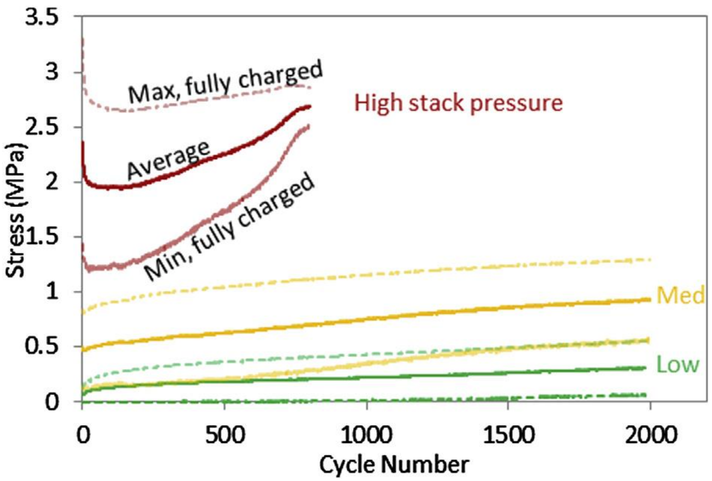
- Mechanical cycling of binder causes increased internal resistance which degrades battery performance

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

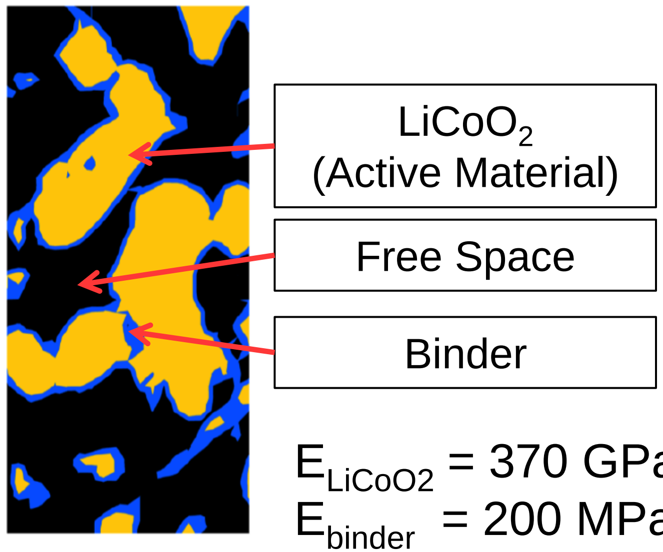




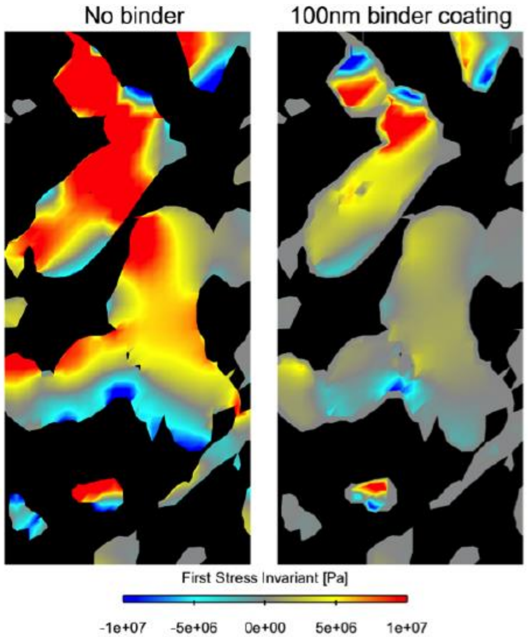


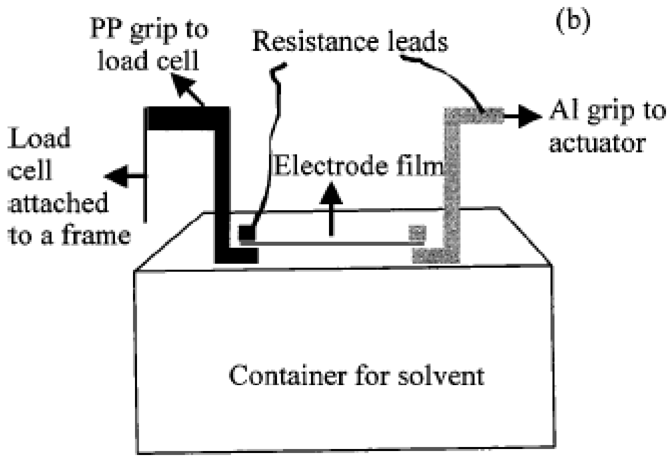
Role of Binder in Battery Cathodes

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



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

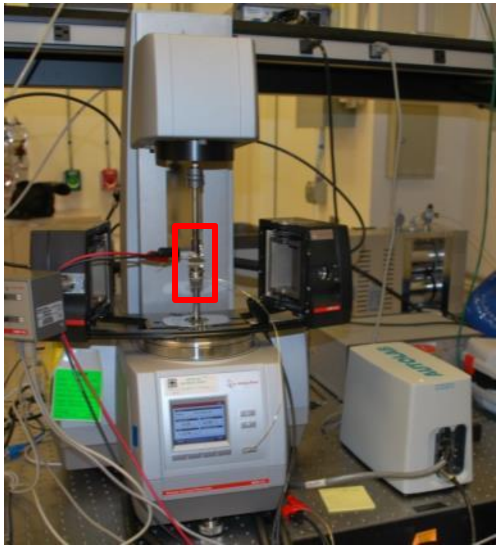




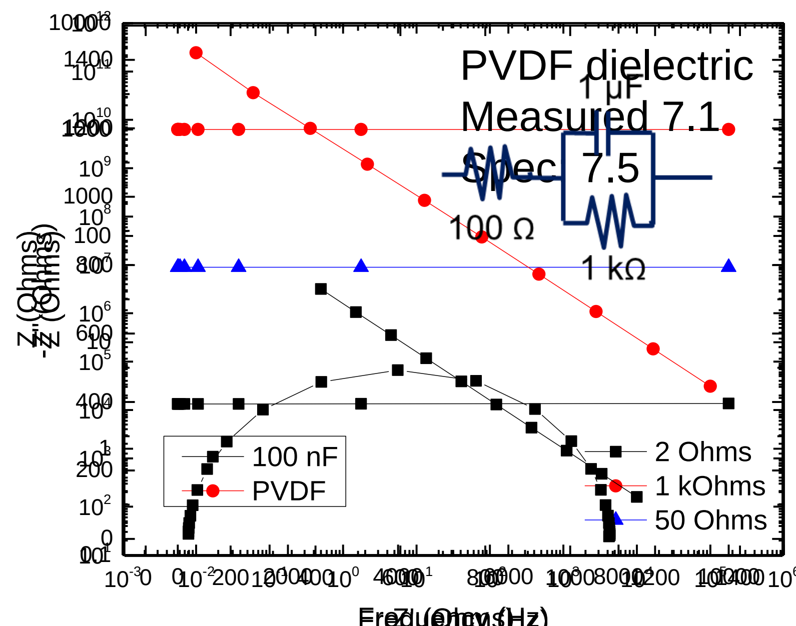
- Chen *et al.*[2] investigated the change in resistance of various PVDF/carbon composites (both wet and dry) and during initial cycling in tension
  - Small changes in resistivity with ~5 cycles number

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

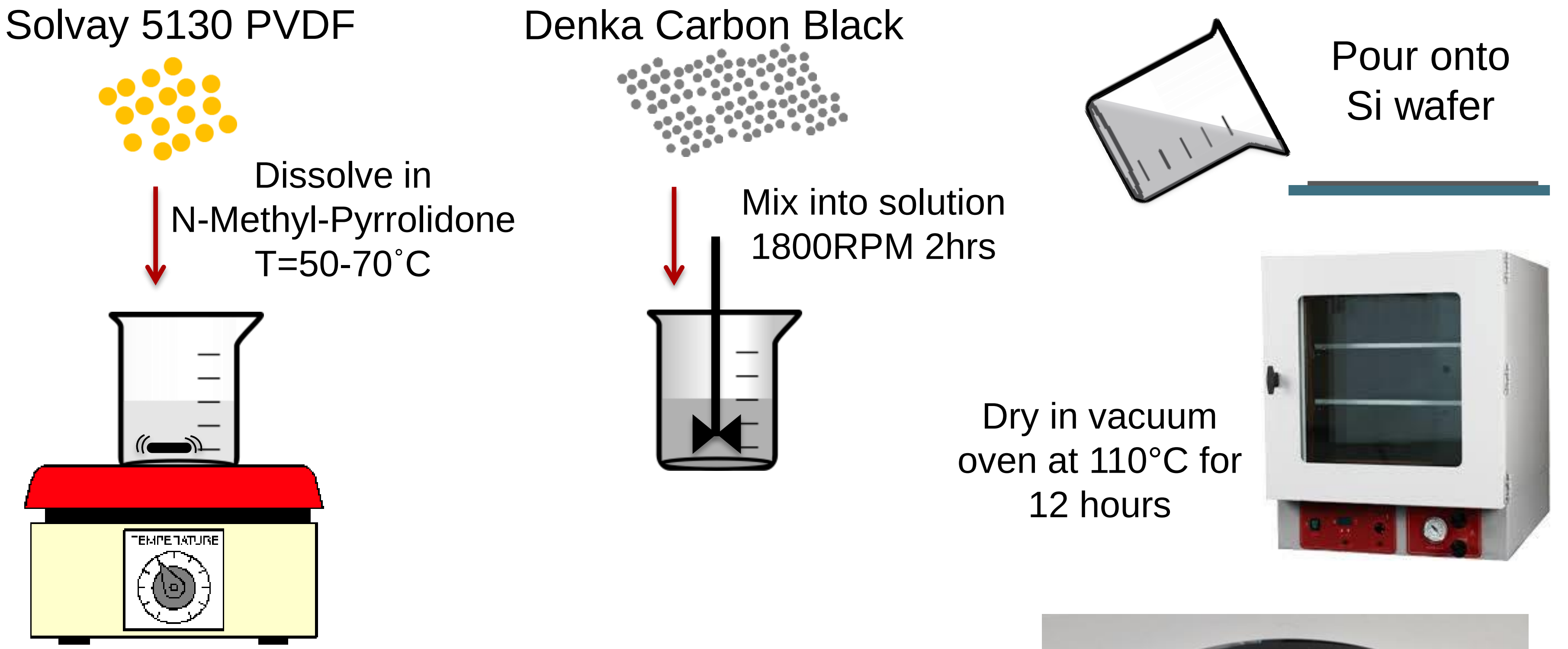
Rheometer/Impedance Measuring System

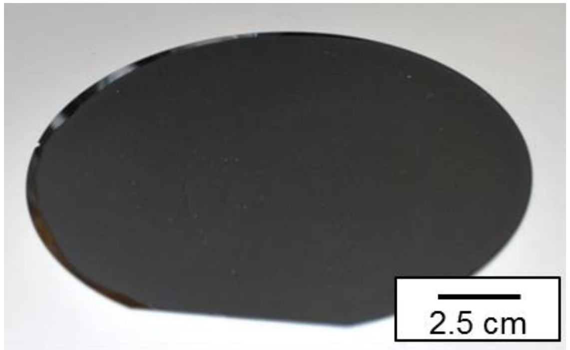


- Measure electrical properties of system during rheological tests
  - Anton Paar MCR 502 rheometer
    - Compression of binder disks
  - Metrohm PGASTAT204/FRA 32
    - Potentiostat/galvanostat 10 μHz - 1 MHz
    - Welded wire leads to plates to reduce lead resistance
    - Performing Electrical Impendence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



Synthesis of PVDF/CB Binder films



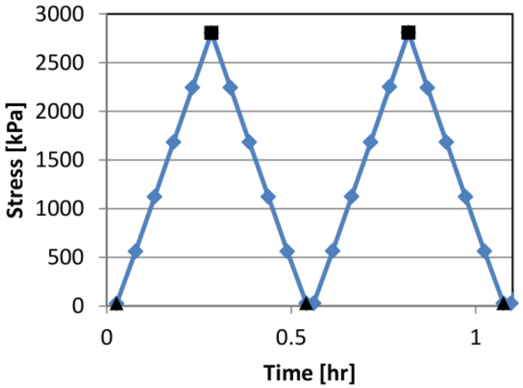


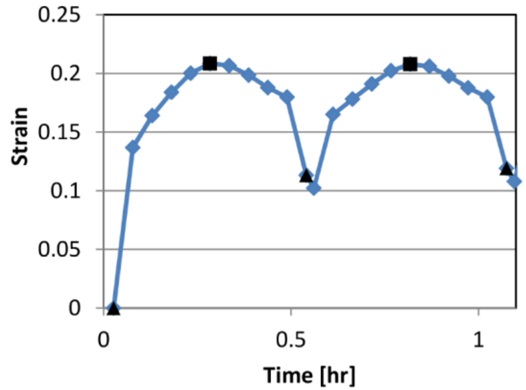
- Film thickness on the order of 70 - 200 µm

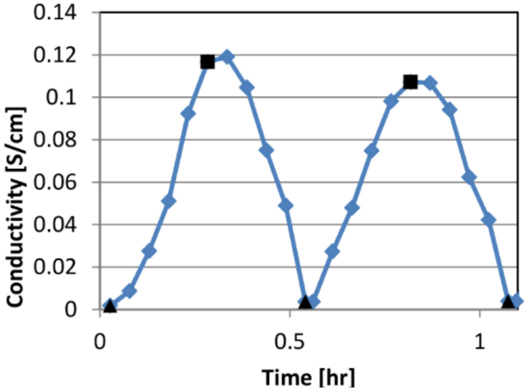
Mechanical Cycling of Dry Binder Film

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

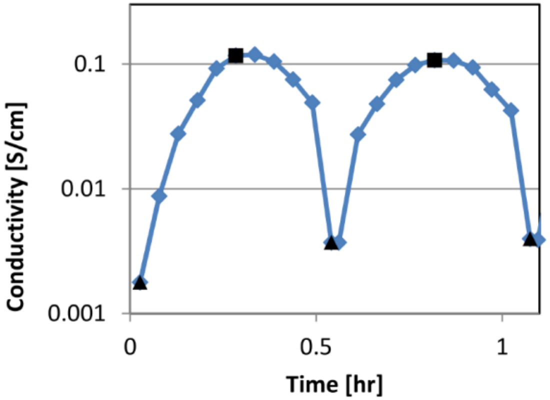
Procedure:
28 kPa – 2.8 MPa – 28 kPa at ~4C cycle rate





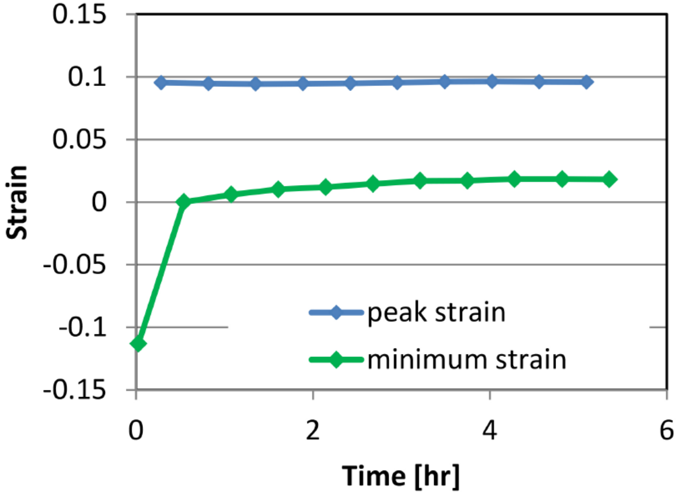


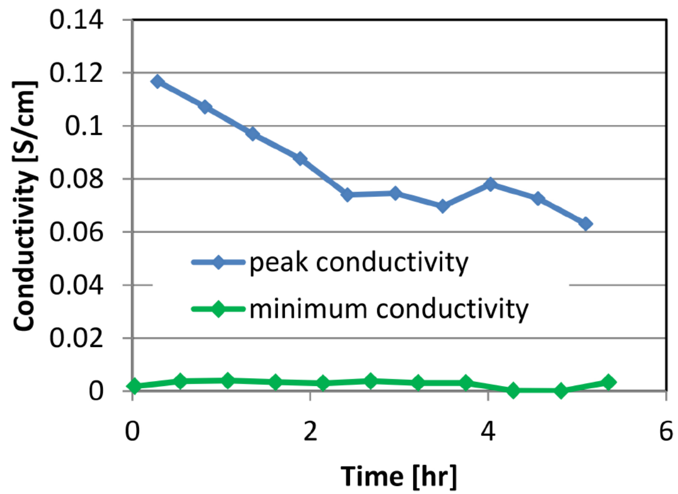
- Plastic deformation after first cycle (flattening of disks or surface non-uniformities)
- Exhibit strong dependence of applied load (and resulting strain) on conductivity of film
  - Changes by two orders of magnitude



Mechanical Cycling of Dry Binder Film

10 cycles at 4C

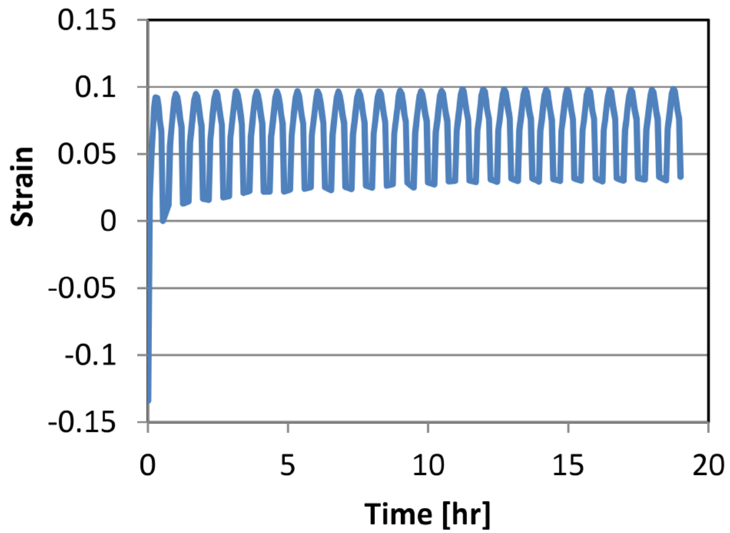


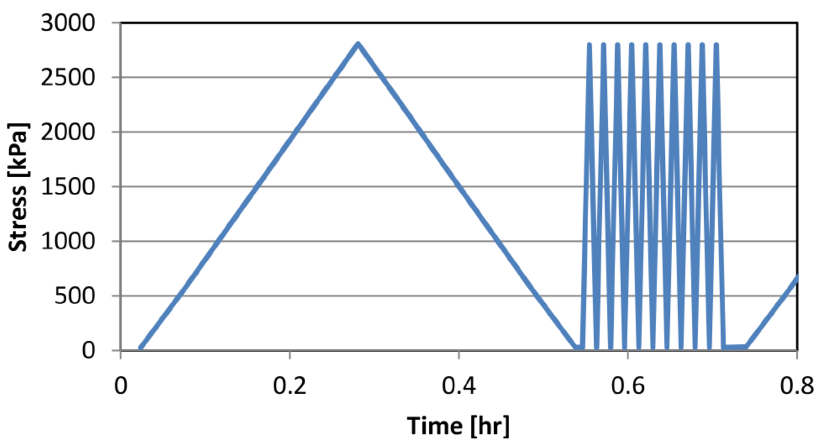


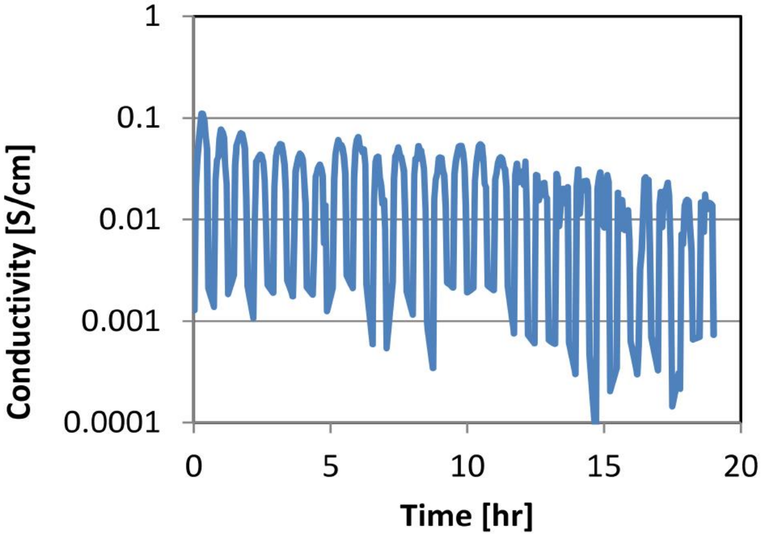
- Mechanical cycling
  - 27 kPa – 2.8 MPa – 27 kPa
  - 4C (cycle ≈ 32 min)
  - 10 cycles (5+ hours)
- Slow consolidation of binder film
- Significant 30% decrease in binder electrical conductivity after 10 cycles
- SEM imaging of binder films before and after cycling show no obvious morphology changes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

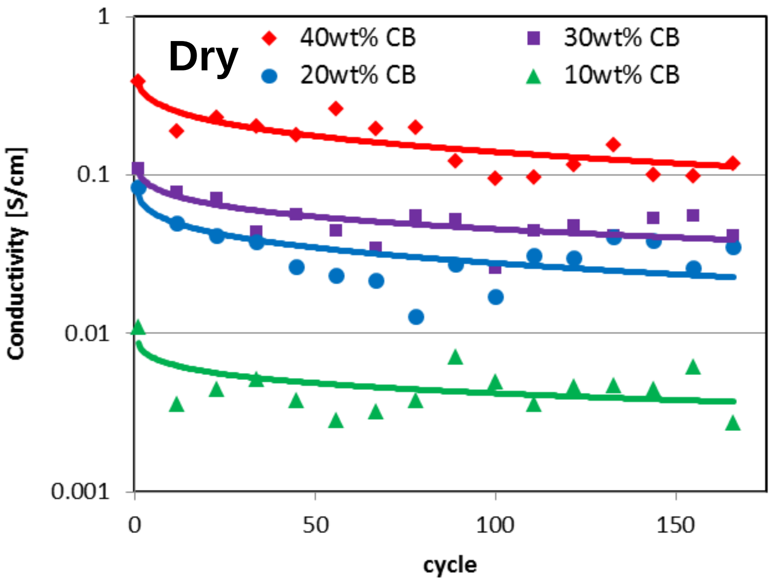


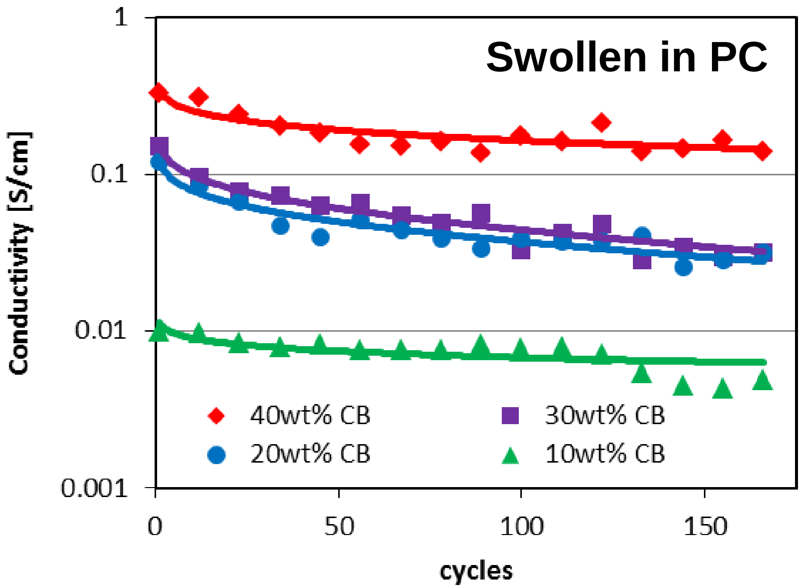




Mechanical Cycling of Swollen Binder Film

- 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)



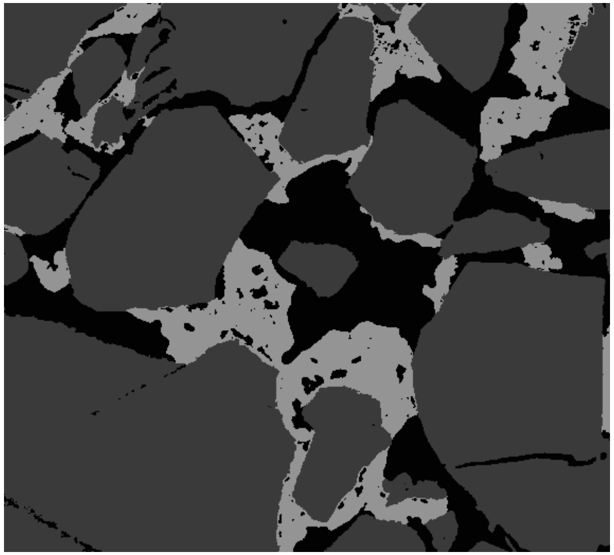


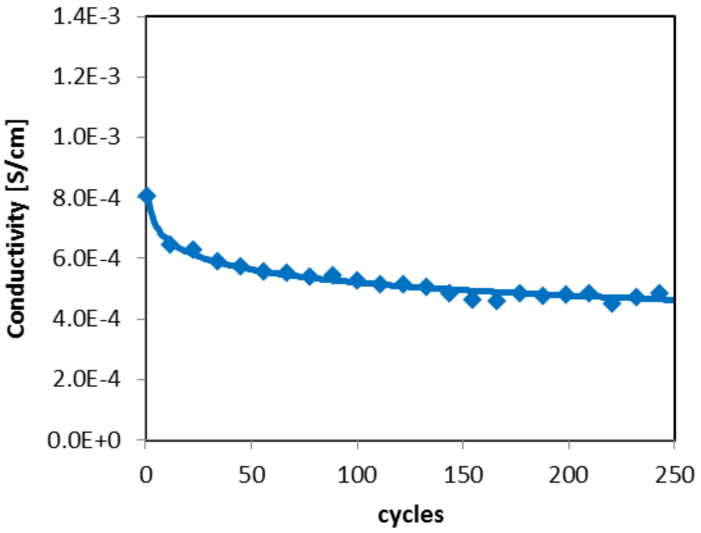
- Significant decrease in binder conductivity as a function of mechanical cycling between 45-75%
- Same for both Solvay 5130 and Kureha W #1300 battery grade PVDF polymers

Mechanical Cycling of $LiCoO_2$ Cathode

- Cathode depends on the binder for reducing internal resistance
  - Active material: $\sigma_{LiCoO2}=10^{-6}$ S/cm vs 0.5-0.05 S/cm for binder
  - Propylene carbonate solvent: $\sigma_{PC}=10^{-10}$ S/cm
- Similar trend in degradation of electronic conductivity of cathode
  - Binder conductivity changes could drive degraded battery performance

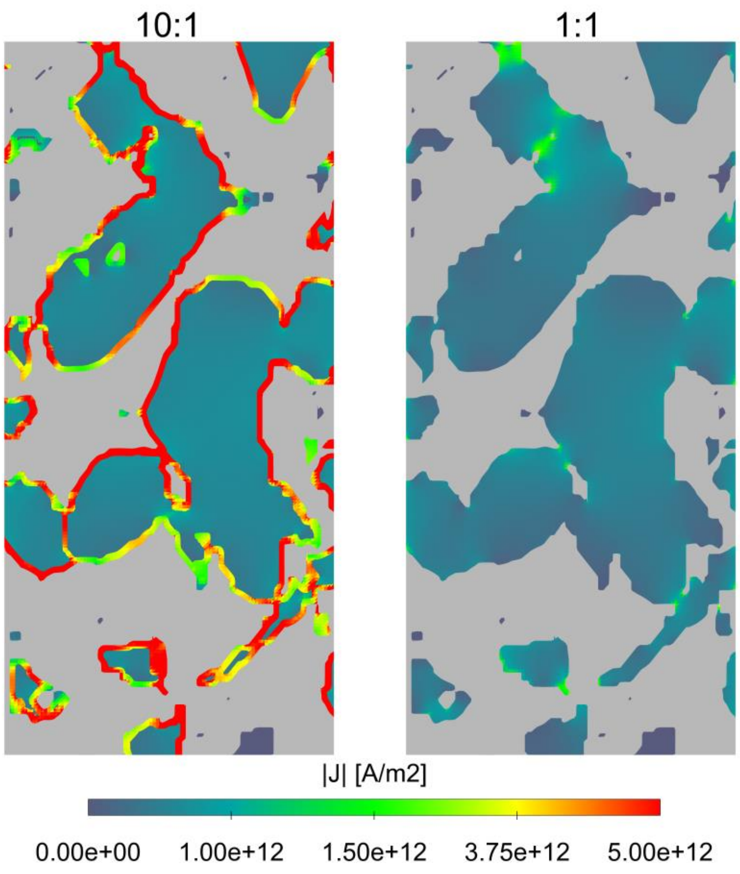
94wt% $LiCoO_2$
6wt% PVDF/CB
solvent

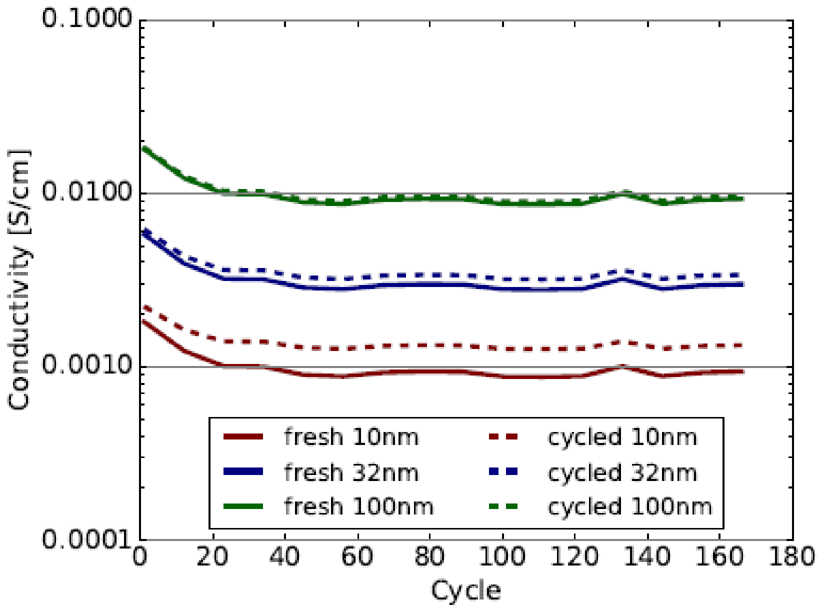




Impact of Binder Conductivity on Cathode

- Calculate the effective electrical conductivity of a representative cathode microstructure as the binder conductivity decreases.
- Based on cathode composition, 32nm coating of binder on active material

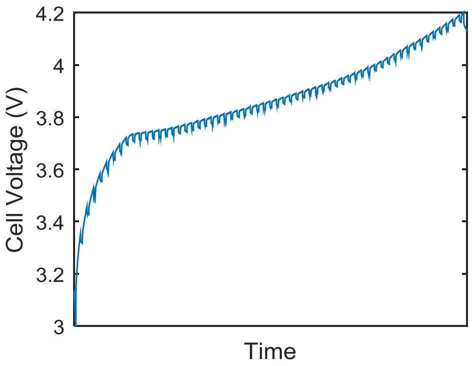


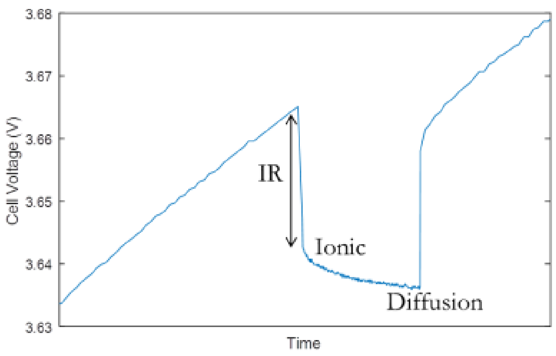


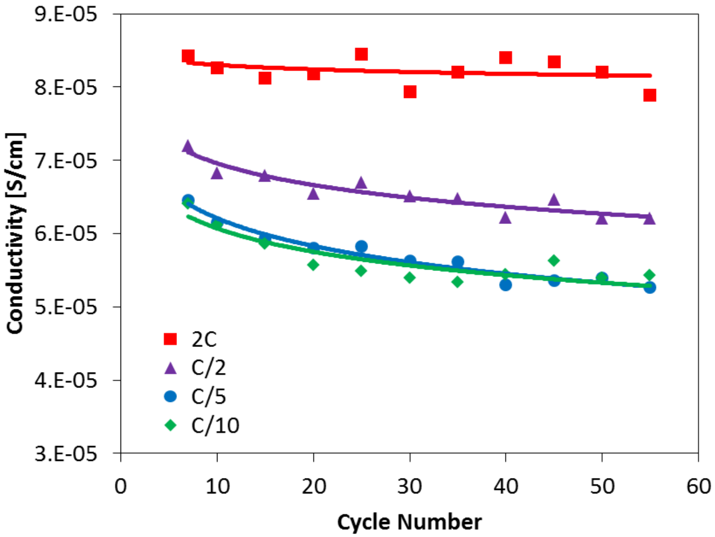
- Binder conductivity changes alone can account for decrease in cathode electrical conductivity

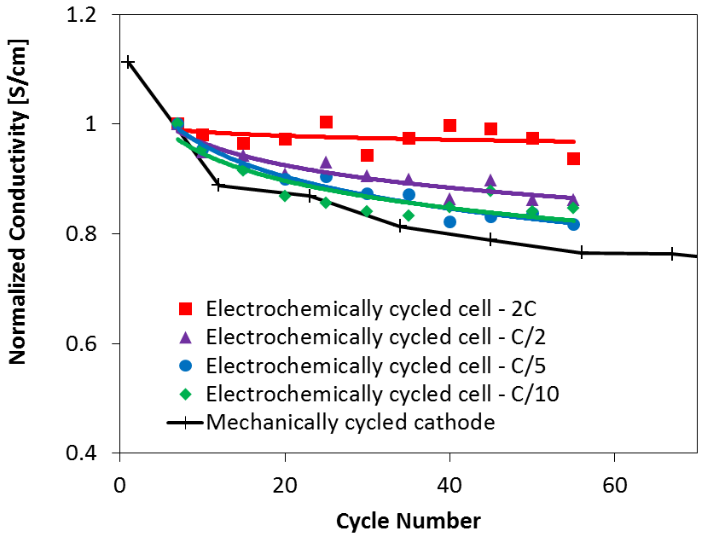
Electrochemical vs Mechanical Cycles

- Current interrupt testing to measure ohmic resistance of full cell between 3-4.2 V
- Ohmic resistance starts as 61% of total cell resistance as 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

Conclusions and Future Work

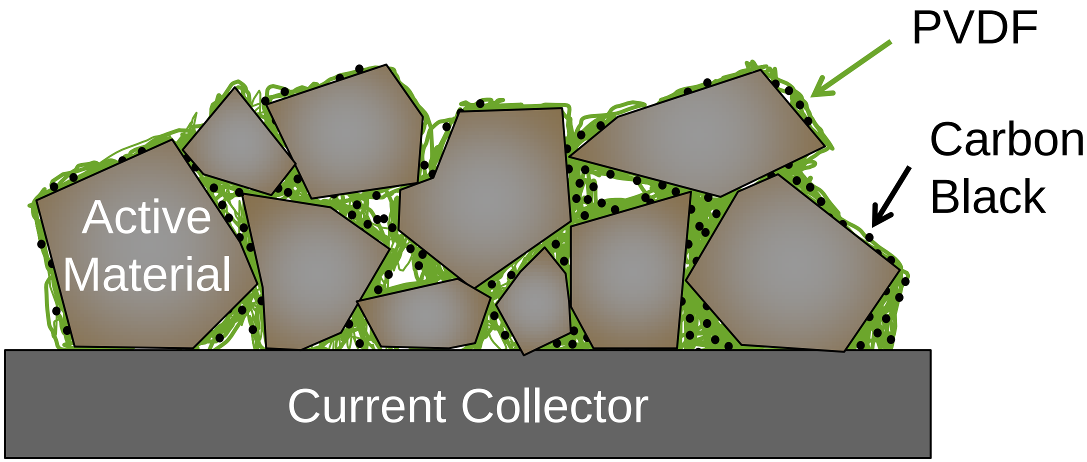
- Mechanical stress cycling causes PVDF/carbon black binder electrical conductivity to degrade 45-75% after 166 cycles
  - Carbon black fractions from 10-40wt%
  - Dry or swollen with electrolyte
  - Two PVDF manufacturers
- Mechanical stress cycling causes $LiCoO_2$ cathodes electrical conductivity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

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

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

EXTRA

Understanding the Role of the Binder



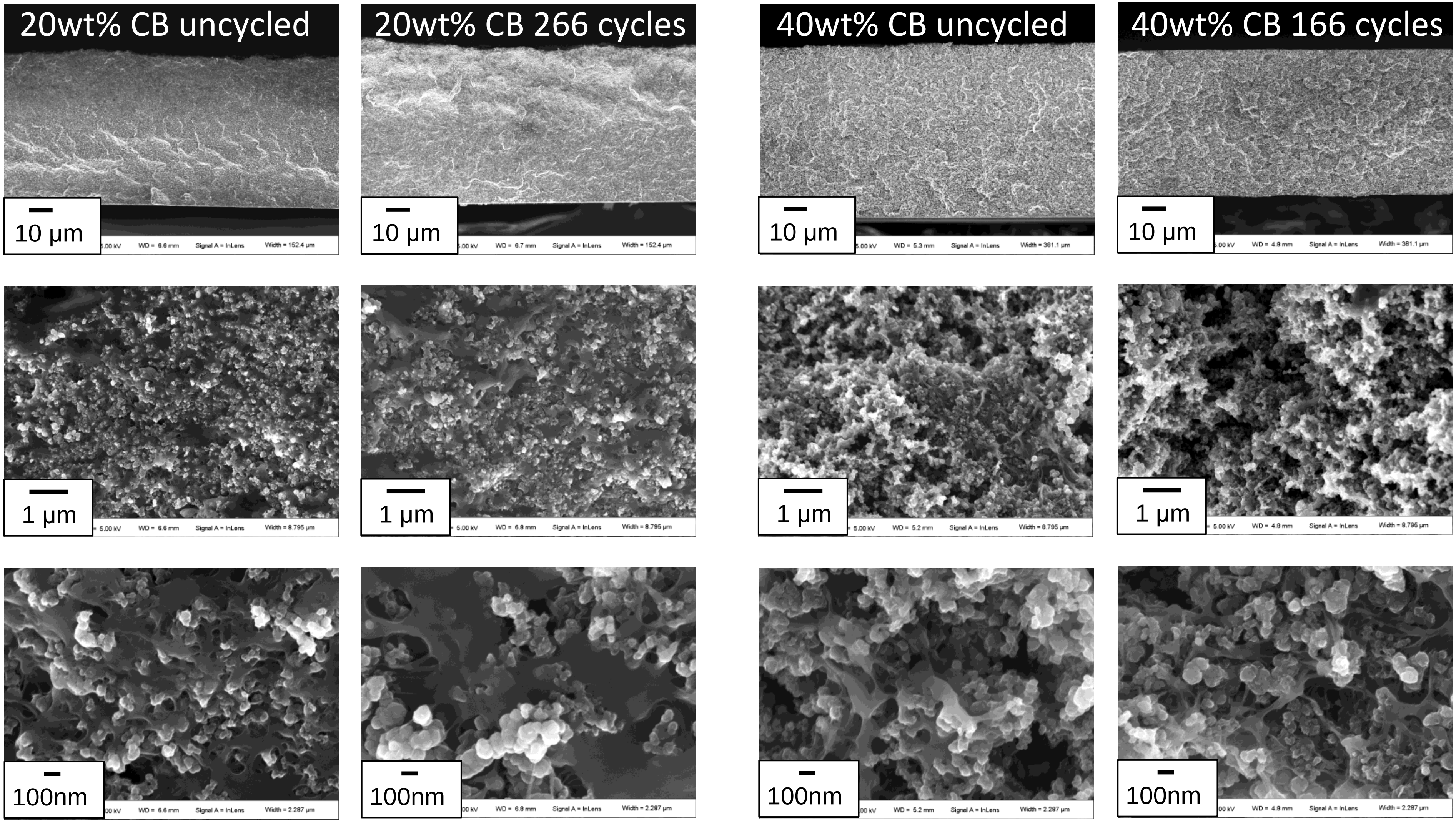
Mechanical

- 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

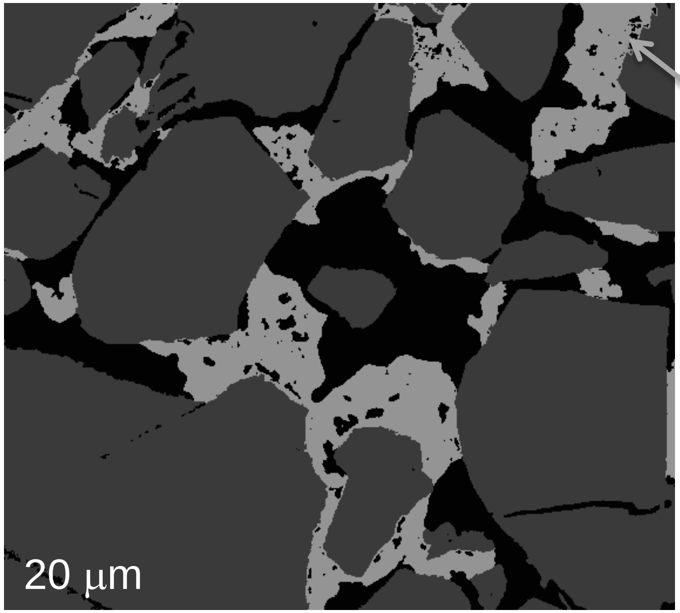
Morphology of PVDF/Carbon Black Composites

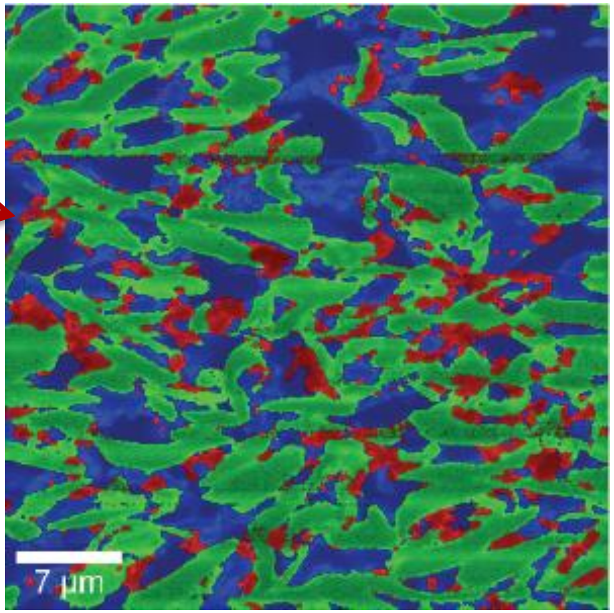


- No obvious cracks, delamination or other morphology changes

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 >> $LiCoO_2$

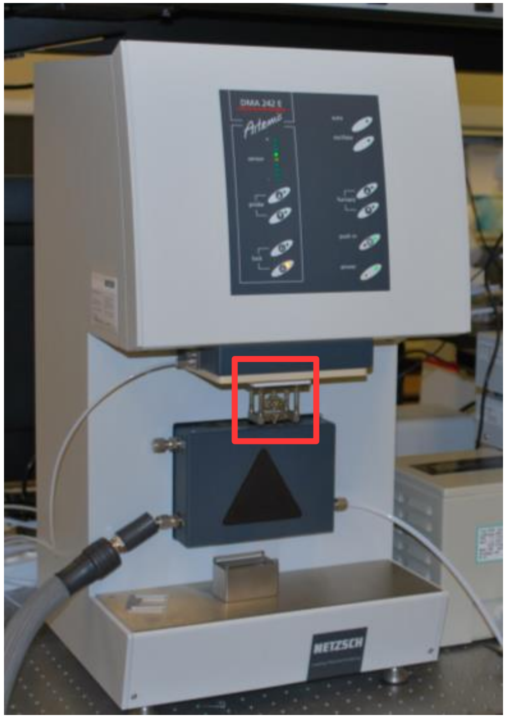


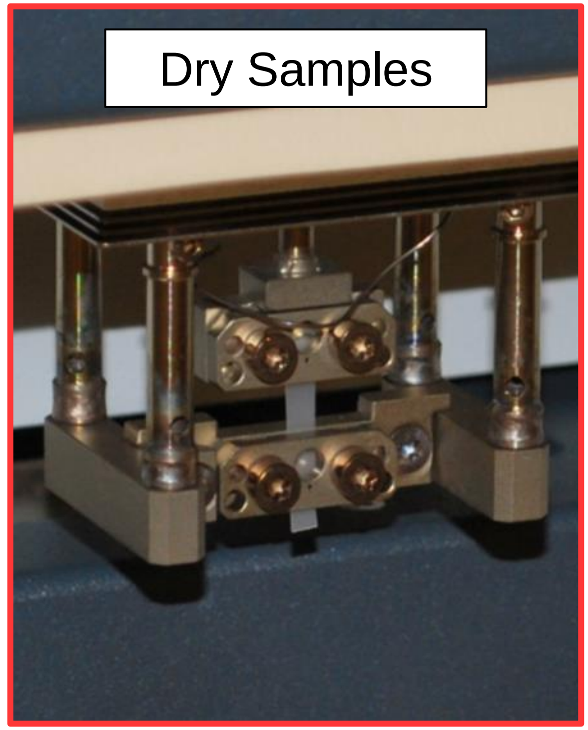


Cathode: 94wt% $LiCoO_2$, 3wt% PVDF, 3wt% CB, **void**

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

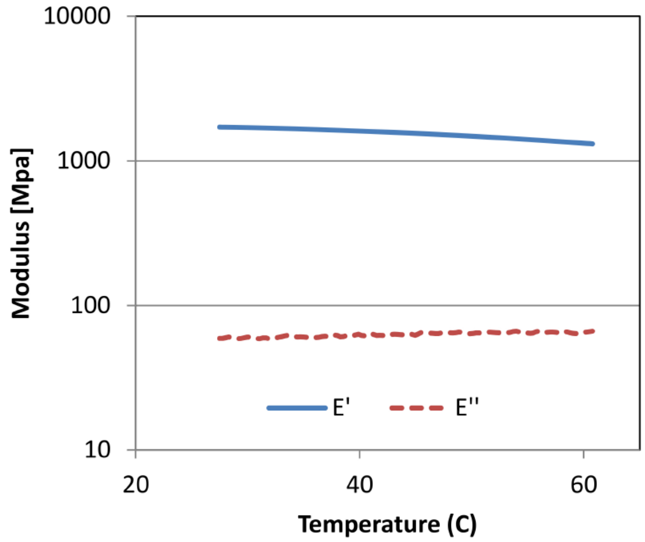
Mechanical Testing - DMA

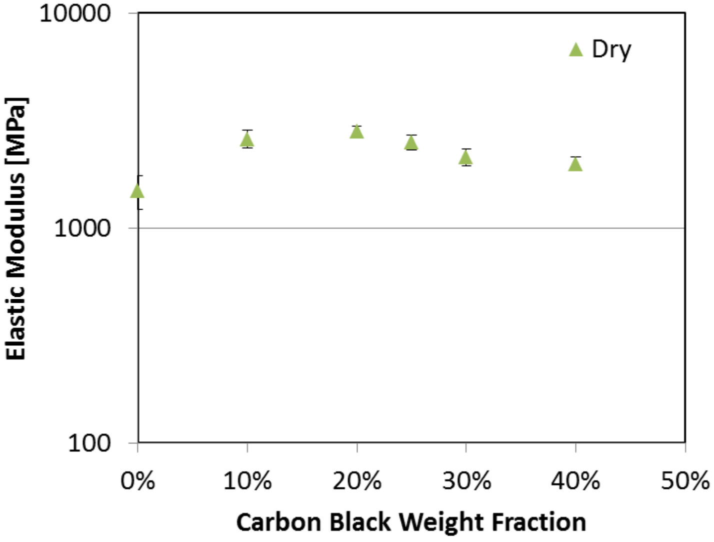




- Netzsch Artemsis Dynamic Mechanical Analyzer
  - Probe E’, E” from 1 – 10 Hz from 25 – 65 ^{o}C for dry samples
  - Probe E’, E” from 1 – 50 Hz at room temperature for electrolyte (propylene carbonate) immersed samples

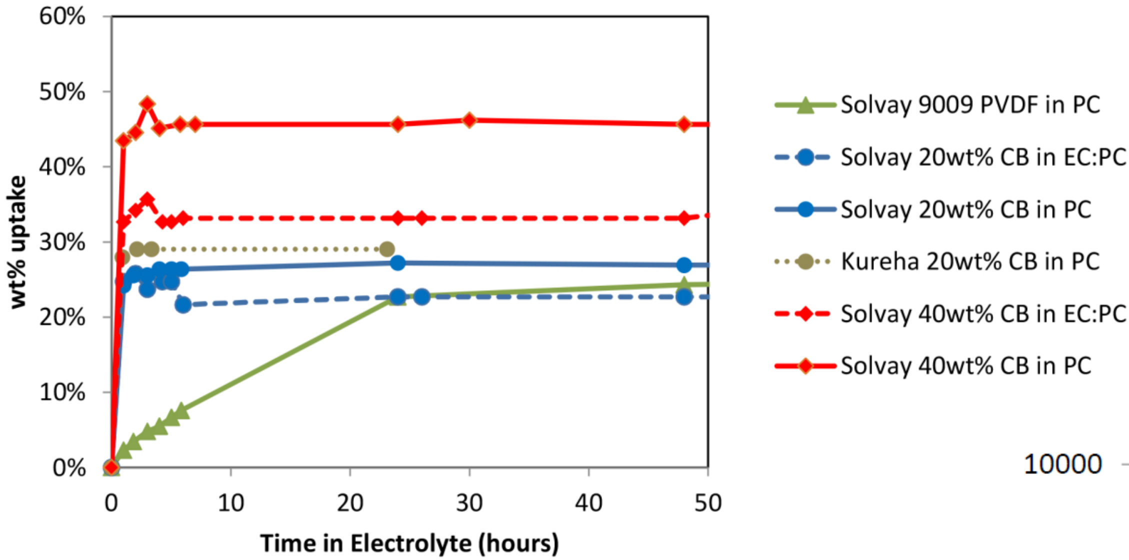
Mechanical Properties – Dry Binder



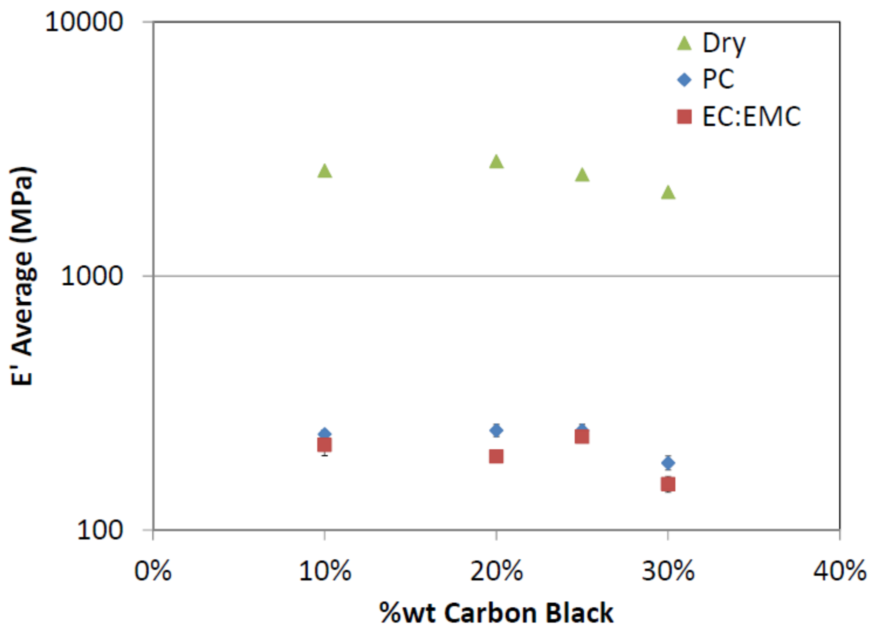


- Storage modulus >> Loss modulus for entire temperature range
- Binder softens at higher temperature
- Despite large differences in morphology, no dependence on carbon black concentration
- Elastic modulus for dry binder ranges between 1.5 – 2.8 GPa

Electrolyte Swollen (Wet) Binder Properties

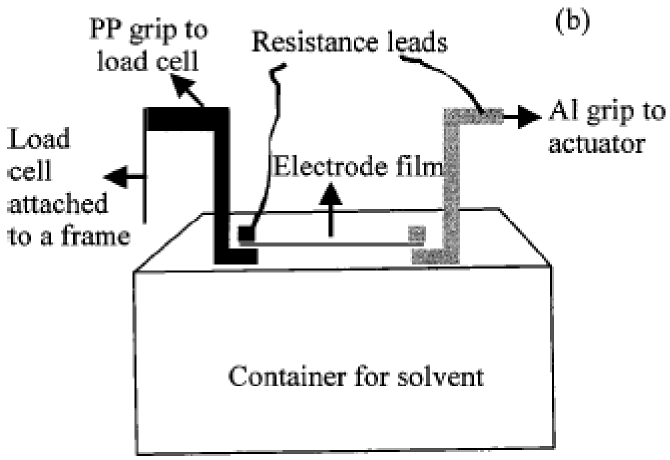


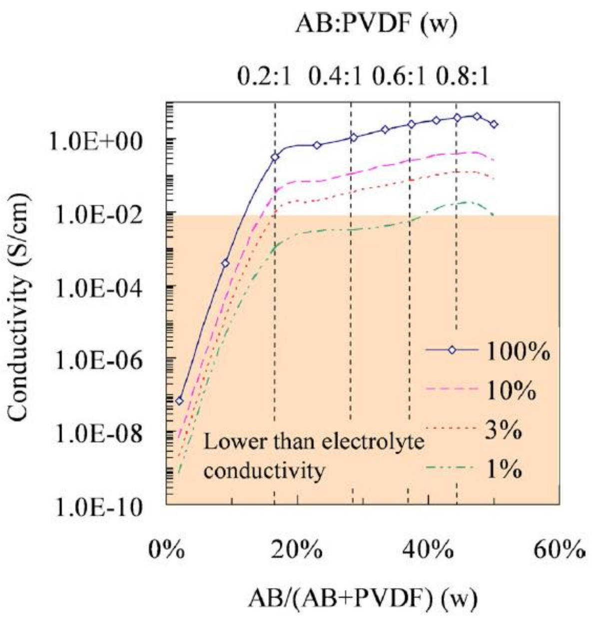
- Immersed binder samples within propylene carbonate (PC) for at least 24 hours
  - Samples absorb between 25 – 45 wt% in propylene carbonate within 2 hours of immersion



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

Binder Conductivity in Literature





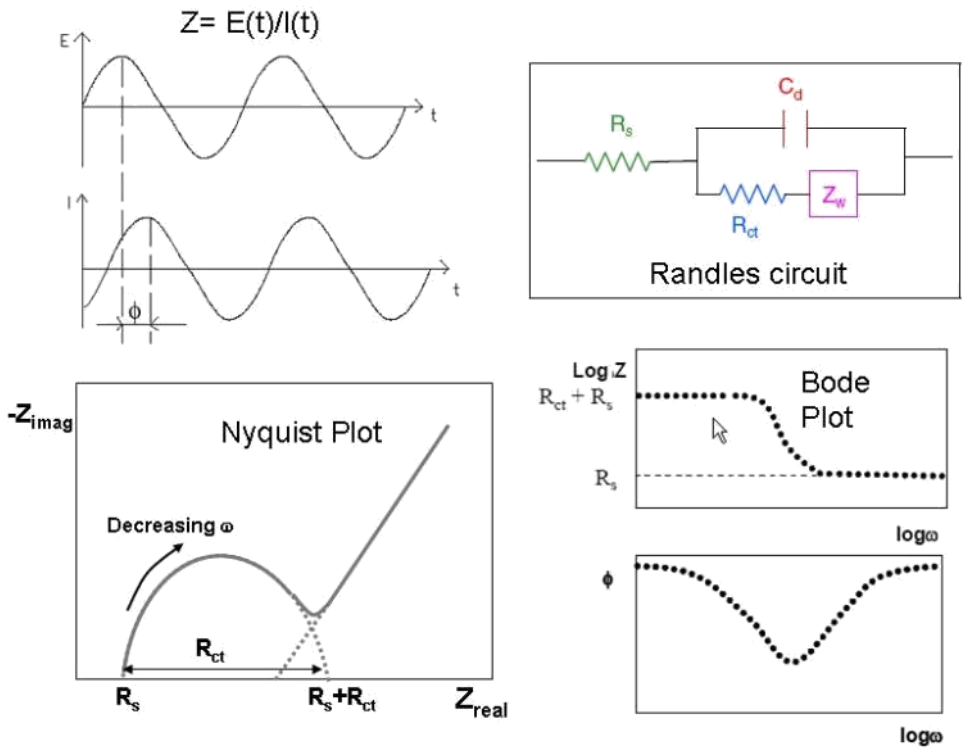
- Chen *et al.*[1] investigated the change in resistance of various PVDF/carbon composites (both wet and dry) and during initial cycling in tension
  - Small changes in resistivity with ~5 cycles number
- Liu *et al.*[2,3] investigated the effect of varying carbon concentration on film conductivity
  - 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

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

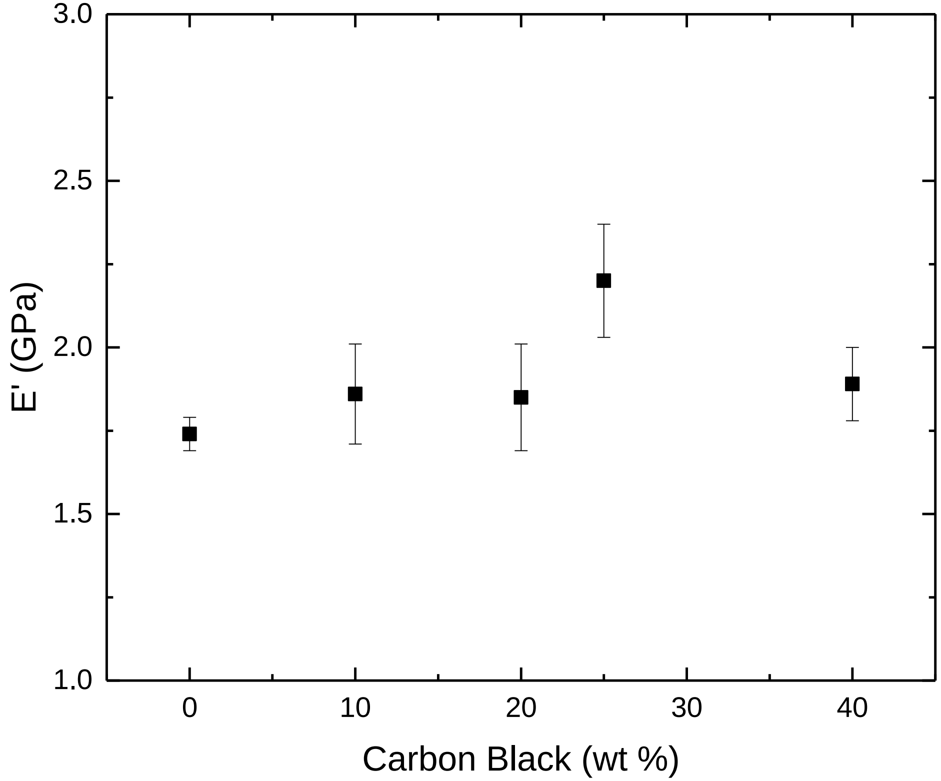
$$Z = \frac{E sin(\omega t)}{I sin(\omega t + \phi)}$$



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

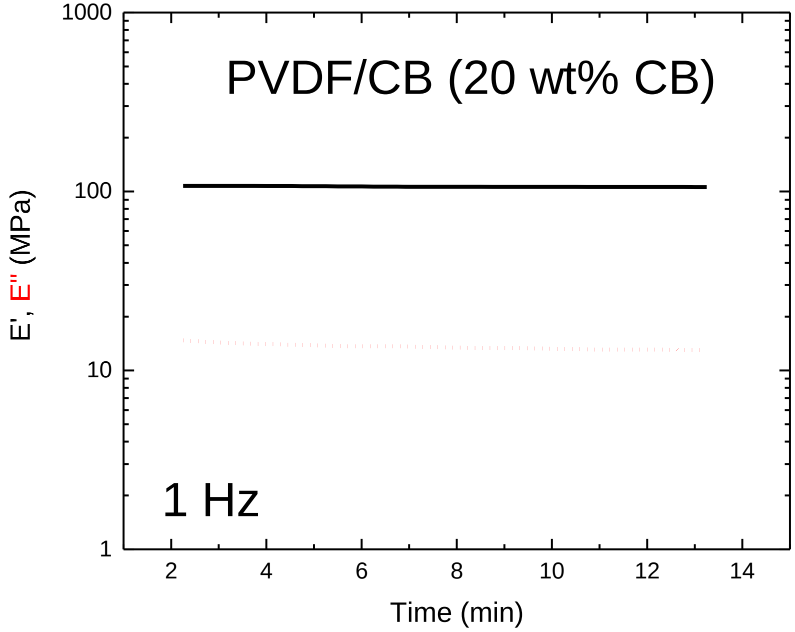
M. Pacios *et al.* (2011). DOI: 10.5772/10594.

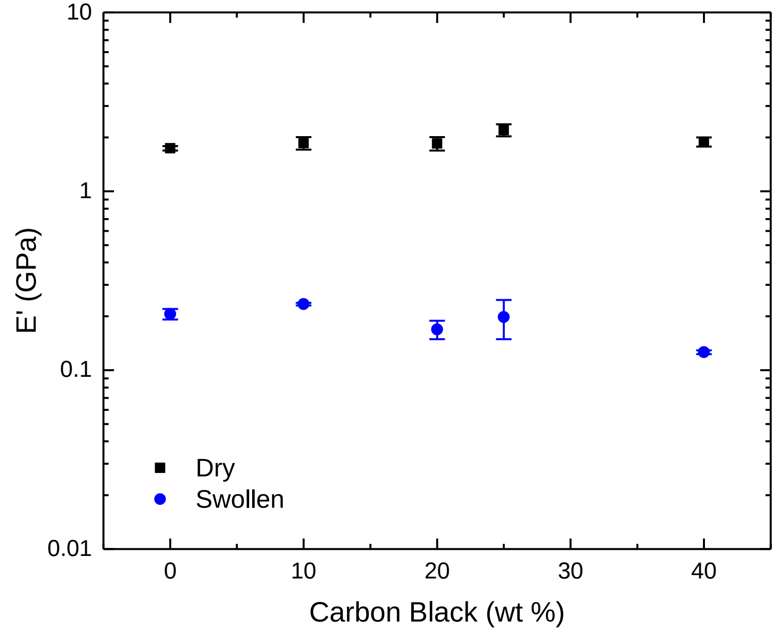
Mechanical Properties – Dry Binder



- 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

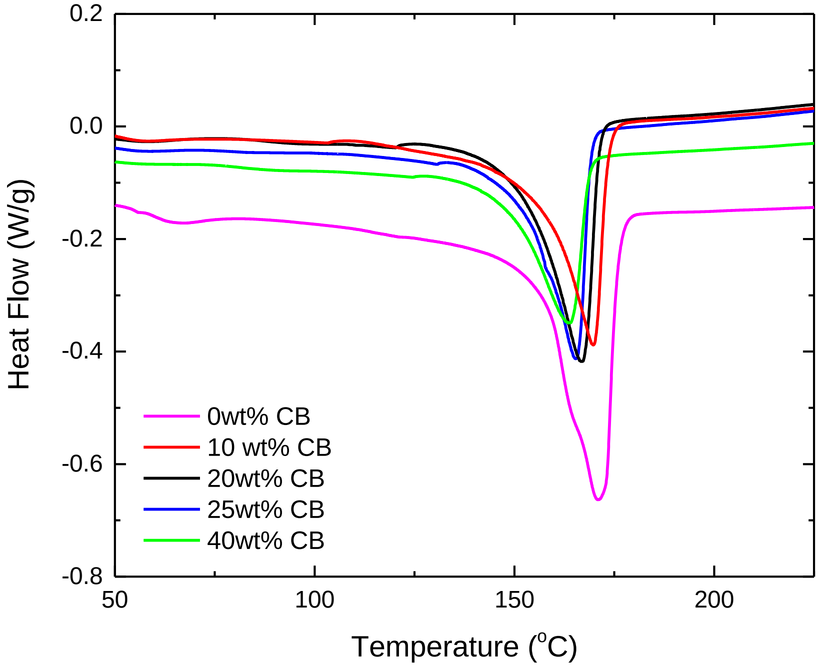
Mechanical Properties - Swollen





- 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



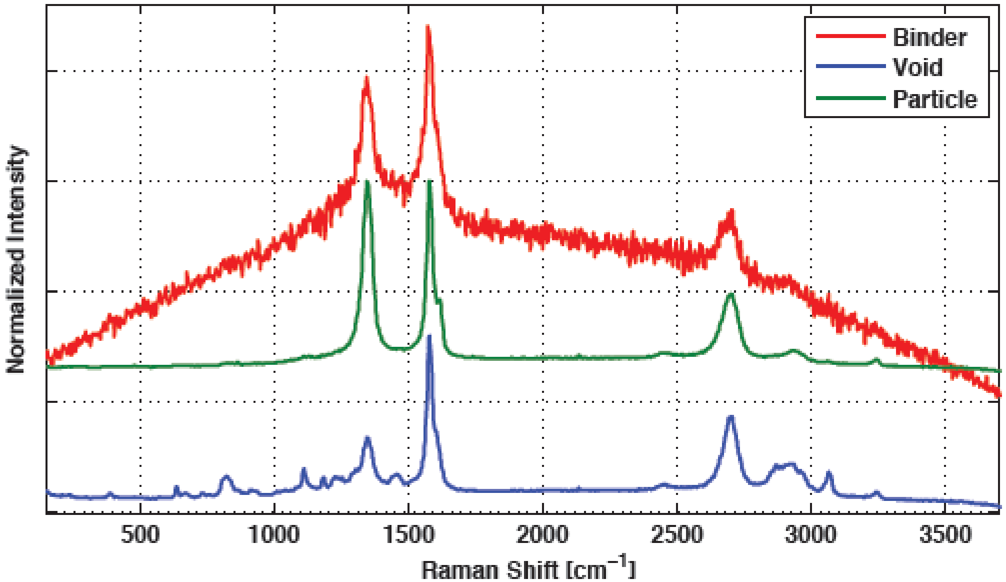
% CB	Normalized H_{sl} (J/g)	% Crystallinity
0.0	47.0	0.45
10.0	43.2	0.41
20.0	38.3	0.37
25.0	41.7	0.40
40.0	44.5	0.43

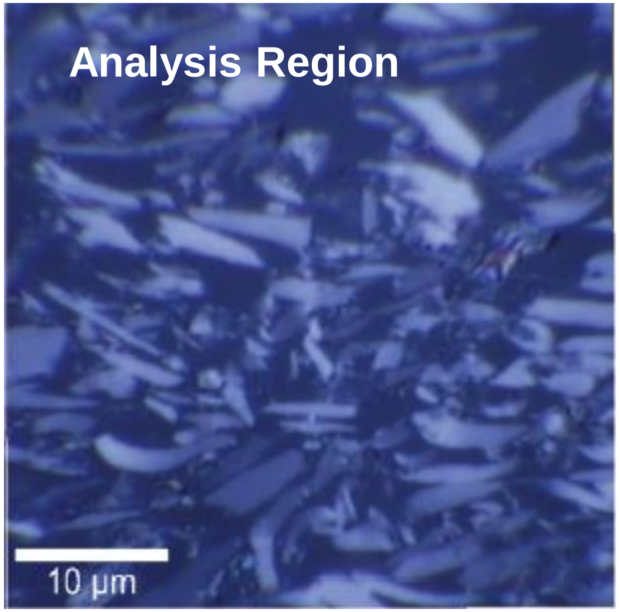
- Investigated % crystallinity using differential scanning calorimetry by quantifying latent heat of fusion and compared against fully crystalline PVDF (H_{sl} = 104.7 J/g)[1]
  - Adding carbon black does not change PVDF crystallinity
  - Hypothesize that crystalline PVDF structure controlling mechanical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

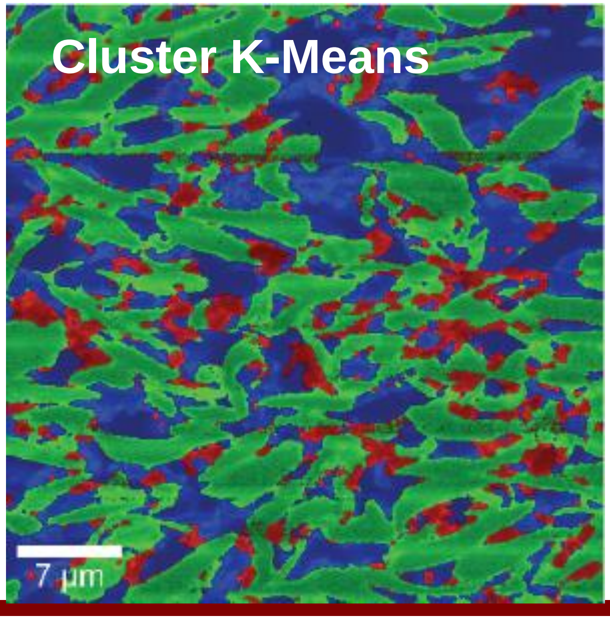
1. Lui *et al., J.Electrochem. Soc. 159 (2012)*

Raman Microscopy w/ Thomas Beechem

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





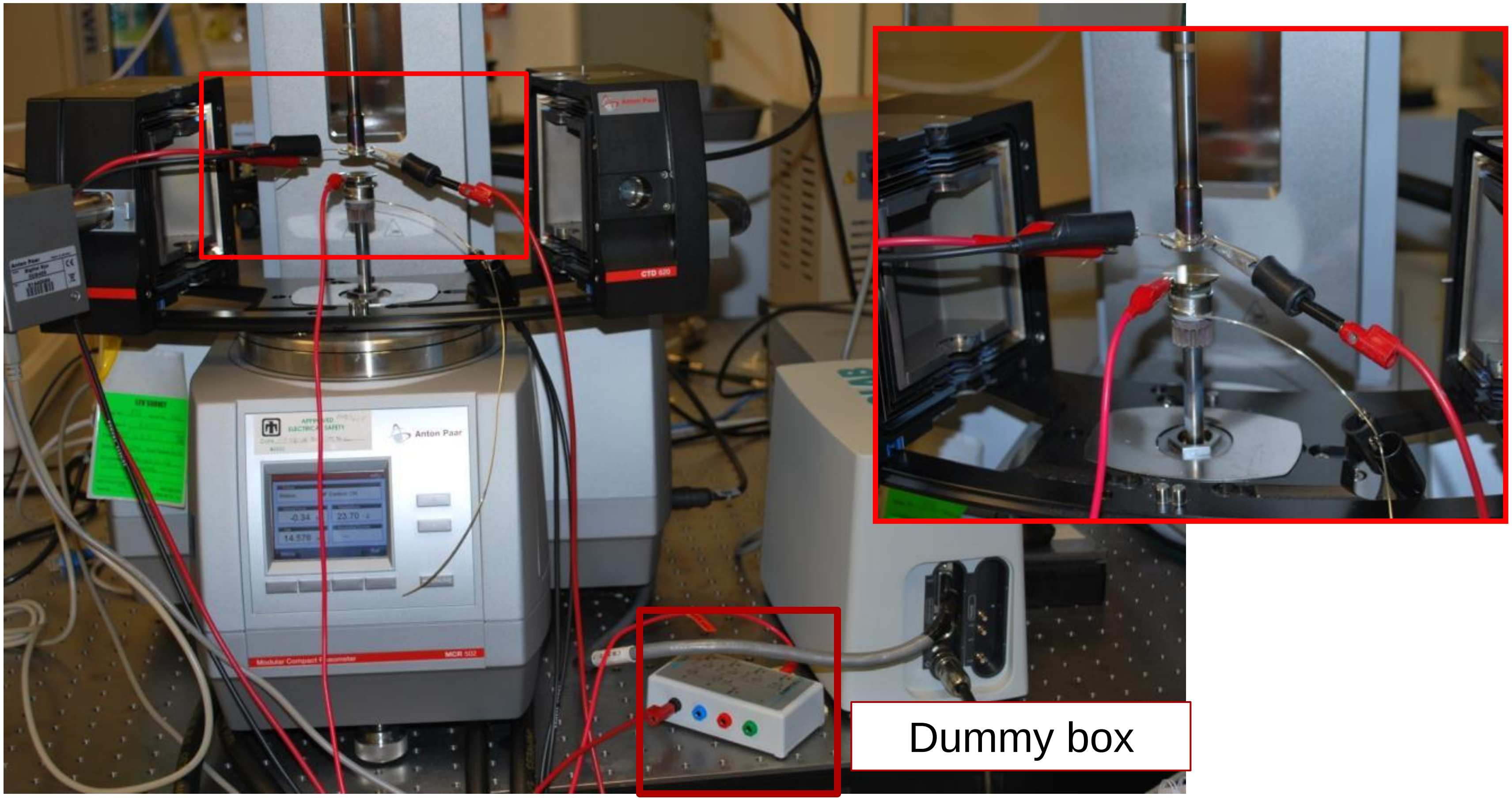


First mesoscale binder structures for an anode!

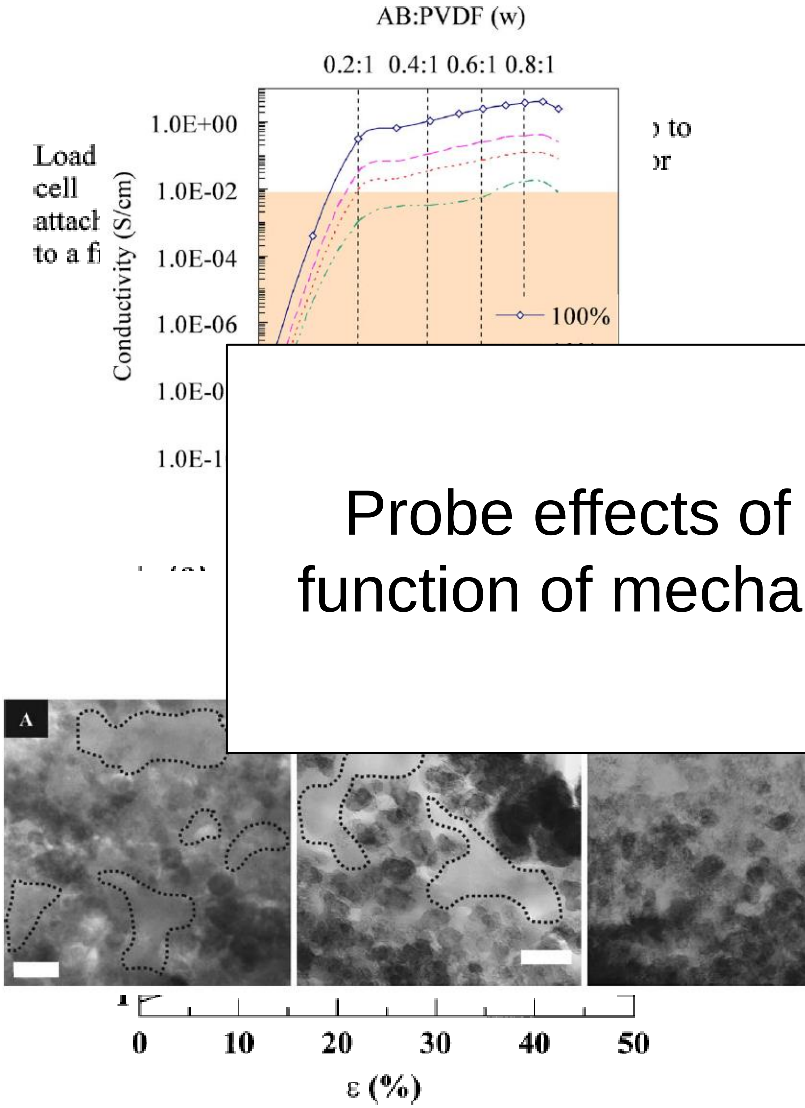
Raman may also be able to distinguish local states of charge in graphite particles

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



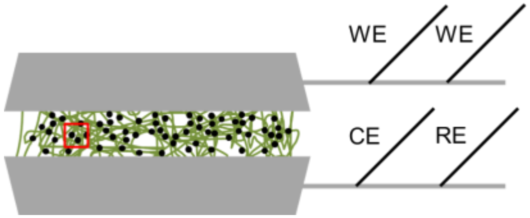
Binder Conductivity in Literature

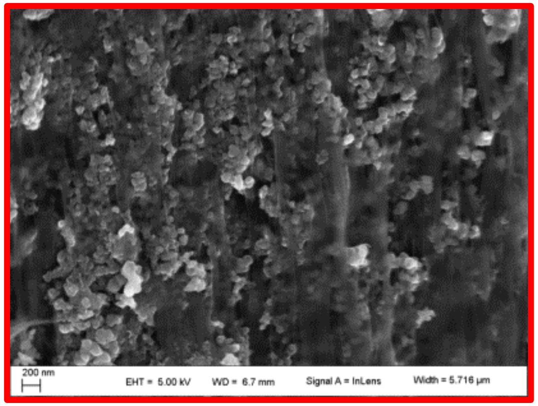


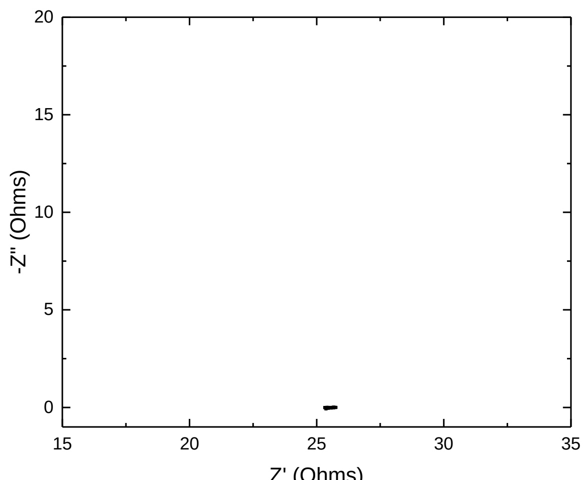
- Chen *et al.*[1] investigated the change in resistance of various PVDF/carbon composites (both swollen and dry) and during initial cycling in tension
  - with
  - of
  - on
  - Developed models to predict binder conductivity
  - Substantial characterization of binder morphology, organization with varying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

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

Measurements on Dry Binder

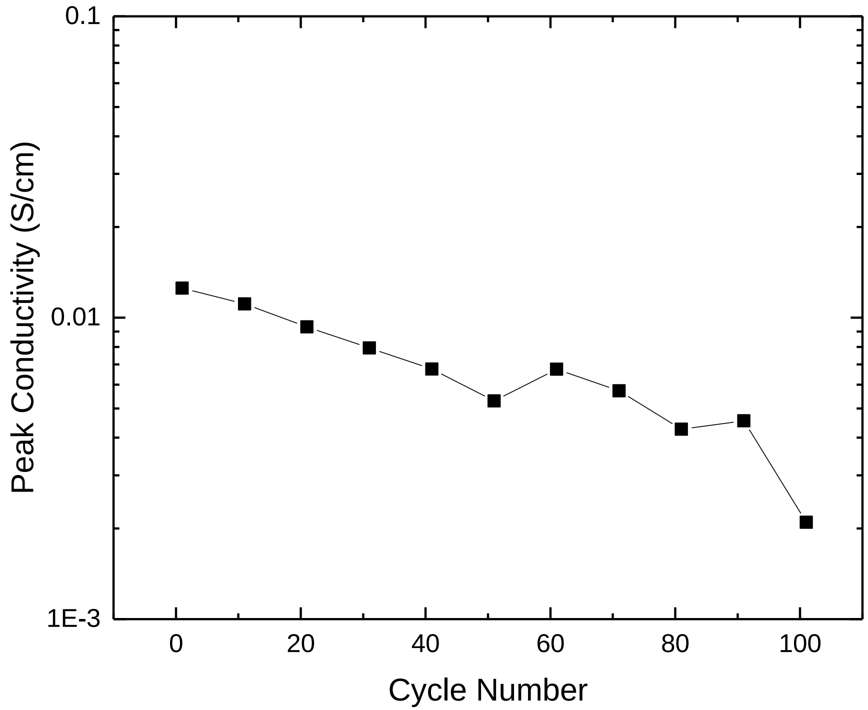






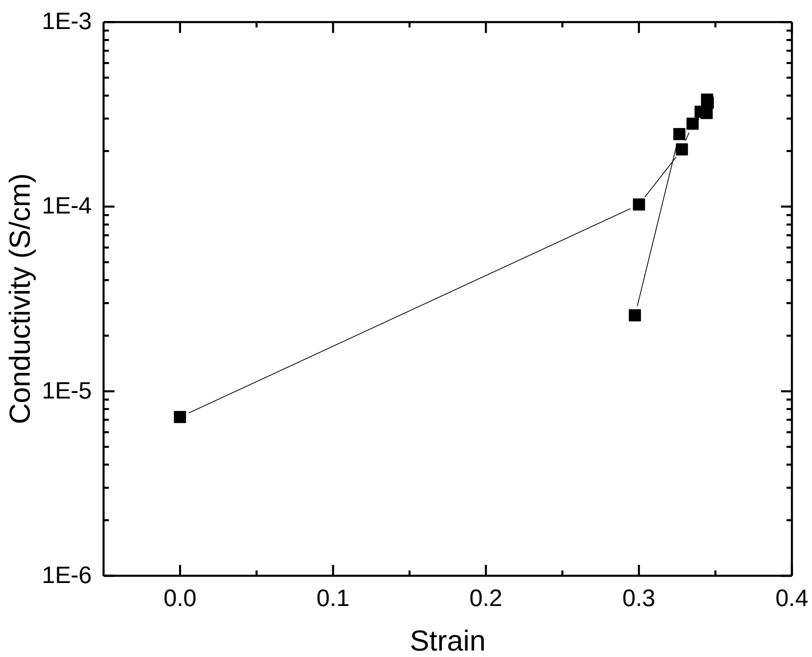
- Frequency response shows purely resistive behavior
  - No imaginary impedance (current measurement is completely in phase with applied voltage)
  - **(easy system to characterize)**
- Using film dimensions, values can be converted to a conductivity
- Investigate conductivity as a function of the applied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

Cycling Behavior of Dry Composite Binder



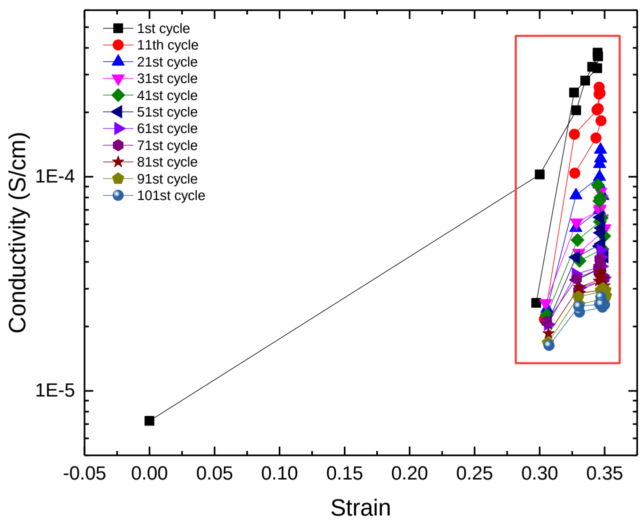
- Conductivity at 2.5 MPa (peak load/stress) as a function of cycle number
- PVDFCB – 40 wt%

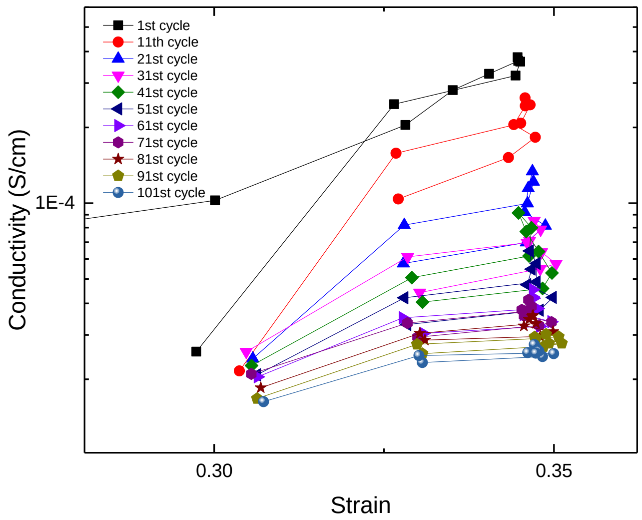
Cycling Behavior of LCO Cathode



- 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

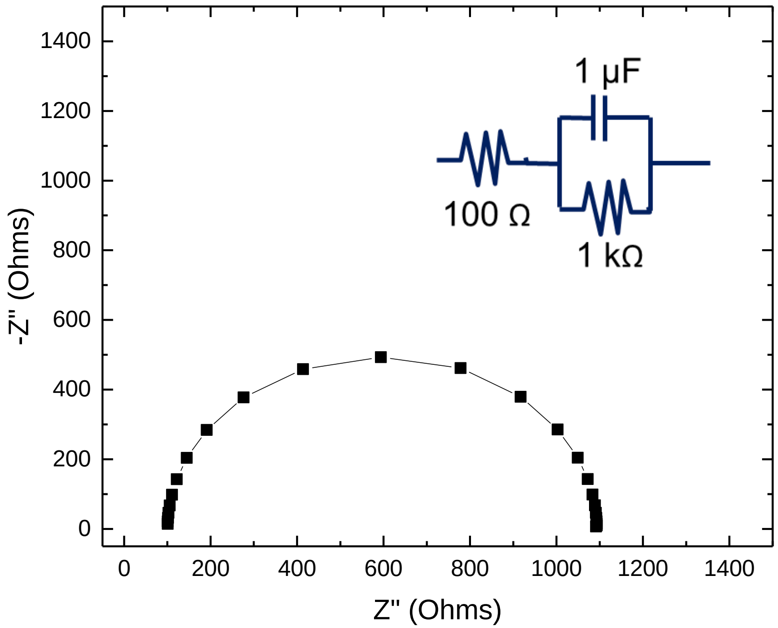


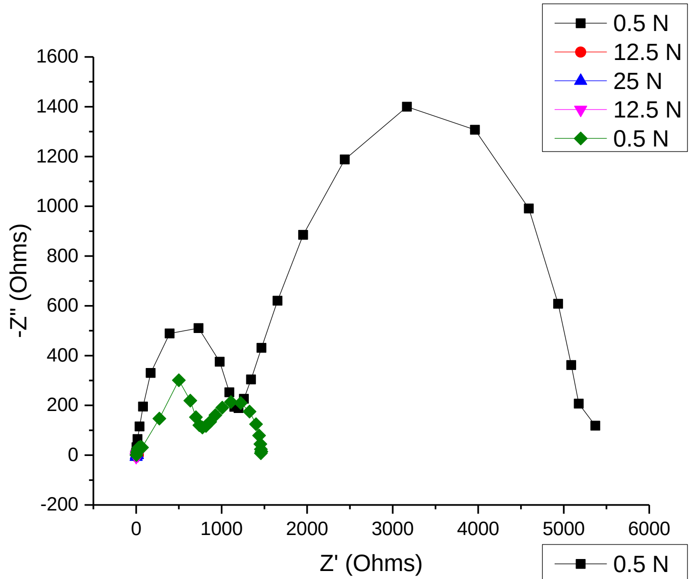


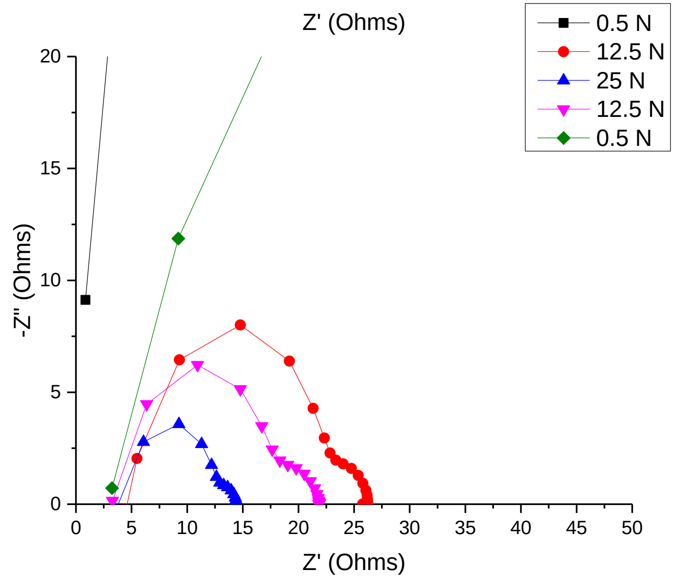
- Procedure:
  - 250 kPa – 2.5 MPa – 250 kPa
    - 5C (cycle ≈ 24 min), 9x 120C (cycle ≈ 1 min)
    - 101 total cycles
- Just as with the binder, the conductivity as a function of cycling drops substantially (greater than an order of magnitude)
- (just a note)
  - Interesting that the conductivity doesn't 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?

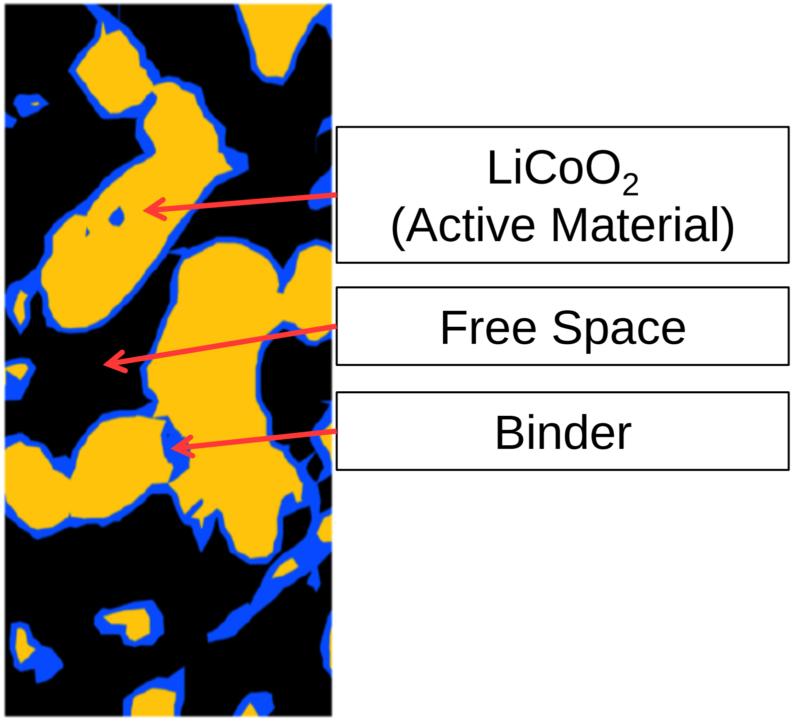


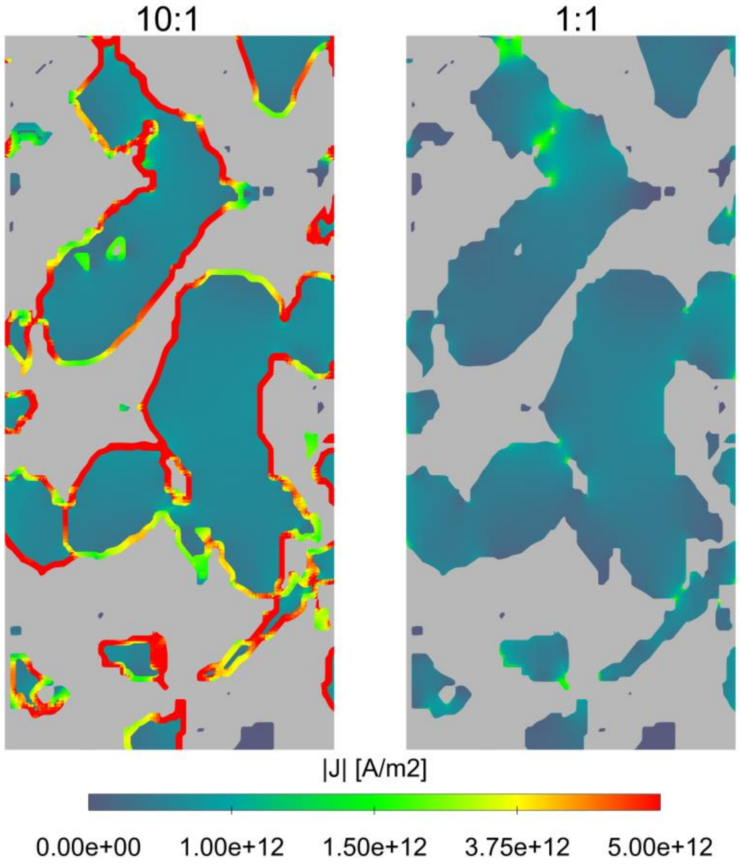




Impact of Binder Conductivity on Cathode

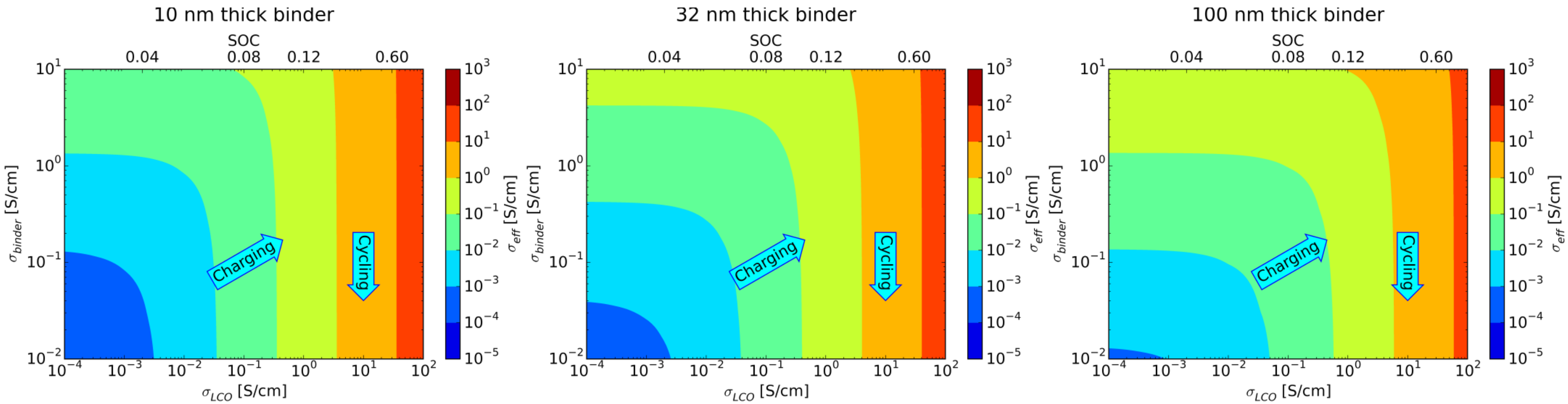
- Calculate the effective electrical conductivity of a representative cathode microstructure as the binder conductivity decreases.





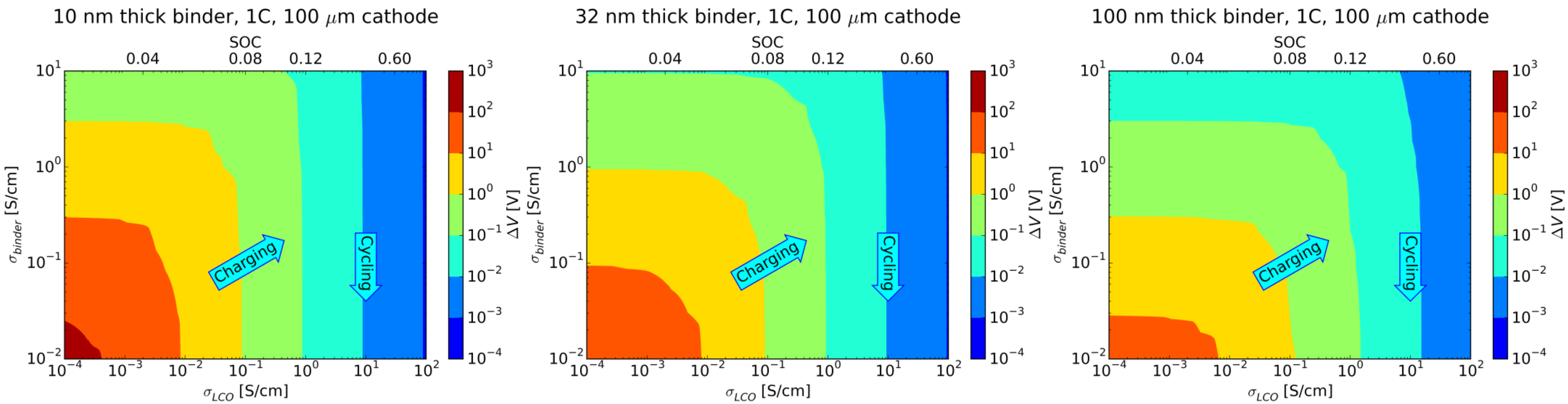
Effective conductivity

- 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?



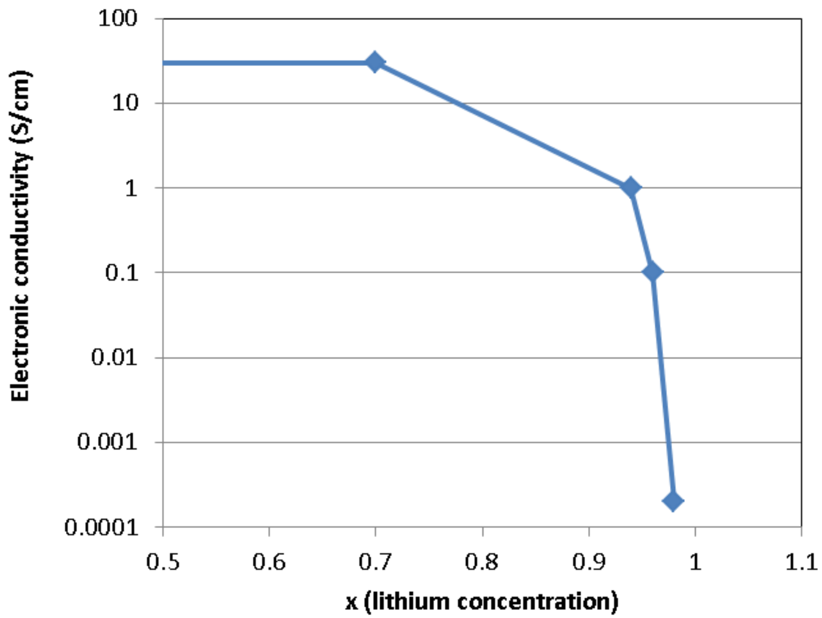
Voltage drop

- 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



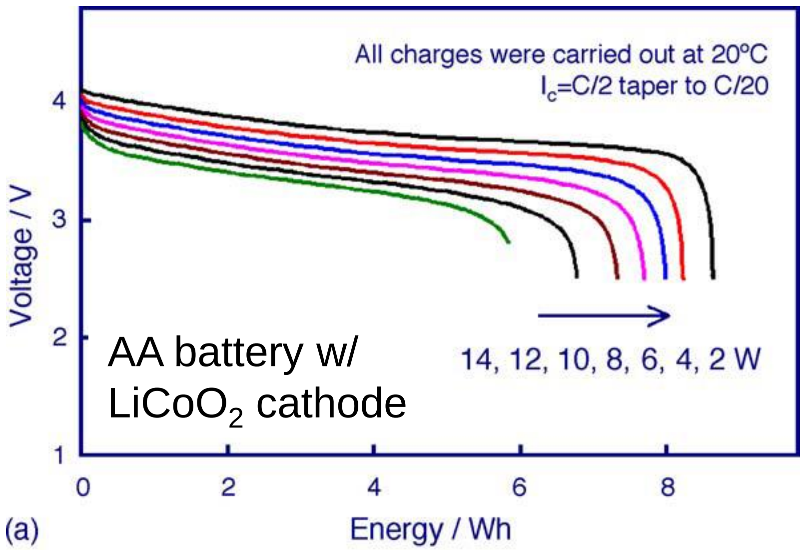
Electronic Conductivity of LiCoO2

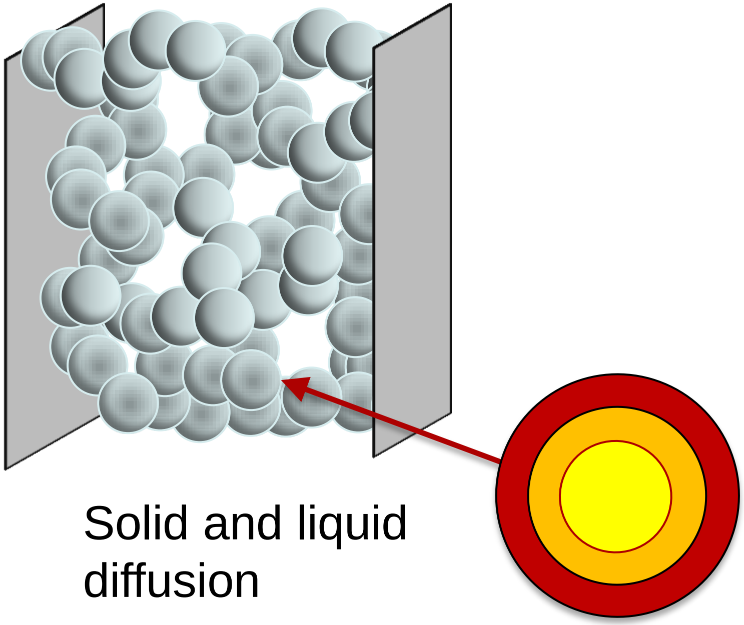
- Electronic conductivity as a function of degree of lithiation shows an insulator to metal transition during deintercalation of lithium.
  - Li_xCoO_2



High Power Draw Limitations

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

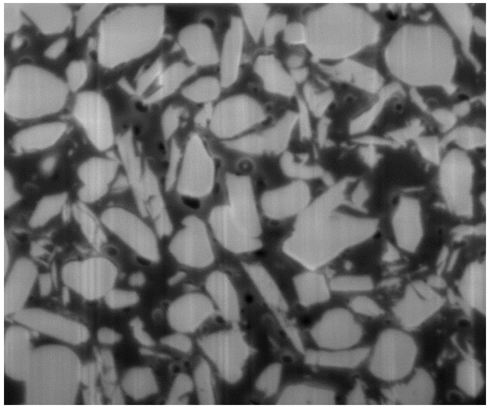




- Part of a larger effort at Sandia to develop predictive models for battery performance
  - Electrochemical, mechanical, and thermal dependence

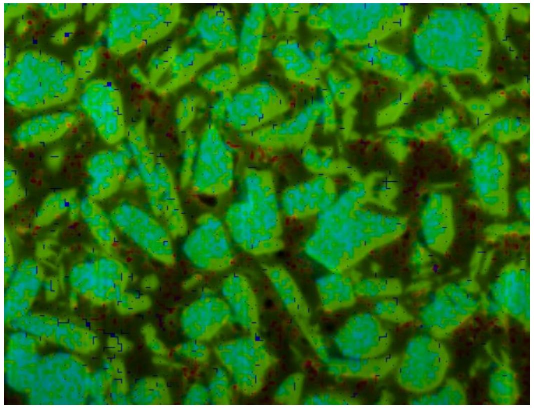
Location of Binder

Focused Ion Beam
Cross-section

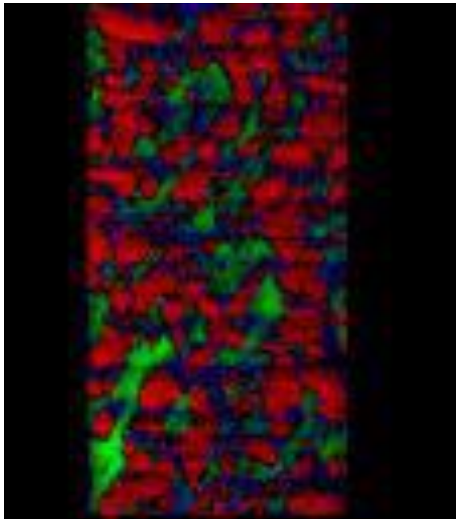


LiCoO2 particles
55 vol% active material
mean particles size 2.3microns
Aspect ratio of 1.7

Energy Dispersive Spectroscopy
chemical composition



Multivariate principal
component analysis



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

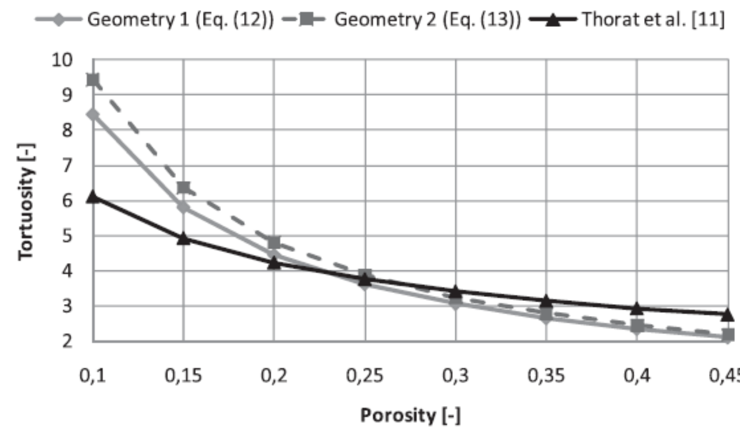
Binder found in the small spaces between particles

Tortuosity, Porosity and Network Conductivity

(a) (b) (c)

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)

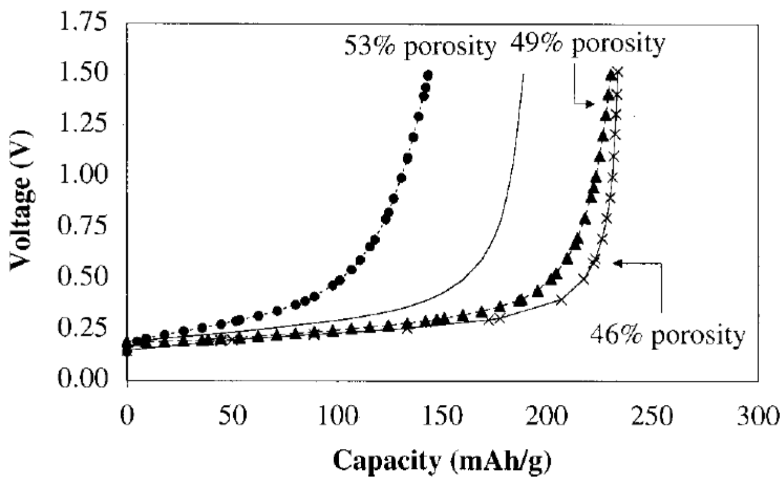
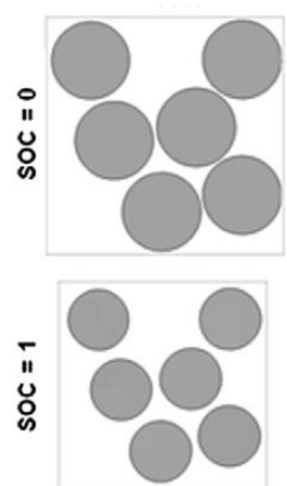


Figure 4. Half-cell voltage curves for anode pieces recovered from cycled cells. Half-cells were discharged to 0.010 V at C/2 followed by a constant potential step with a C/20 current cutoff. Voltage curves shown are for a 1C charge to 1.50 V. Circles: prismatic cell (300 cycles), line: prismatic cell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