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High Energy Density Electrodes *via* Modifications to the Inactive Components and Processing Conditions

Vince Battaglia, Ph.D.

LBNL

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Project ID # **ES232**

Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/31/2018
- Percent complete: 16%

Budget

- Total project funding
  - DOE share: 100%
  - Contractor share: 0%
- Funding received in FY 2015
  - $0 M
- Funding for FY 2016:
  - $1 M (2.5 FTEs)

Barriers

- Barriers addressed (EV)
  - A. *Cost* - $133/kWh
  - C. *Performance* – 2/1, P/E for 30 seconds at 80% DOD
  - E. *Life* – 10 years

Partners

- Interactions / collaborations
  - Arkema
  - Umicore
  - Black Diamond Structures
  - Daikin America
  - Applied Spectra
  - BMR Program and LBNL
    - V. Srinivasan (LBNL)
    - D. Wheeler (BYU)
    - S. Harris (LBNL)
    - D. Parkinsen (LBNL)
    - G. Liu (LBNL)
    - K. Zaghib (HQ)

Relevance: Objectives and Impact

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- <u>Project Objective</u>:

To understand the materials and processing limitations to fabricating high loading Li-ion battery electrodes that still meet the P:E power target of 2:1 for 30 seconds at 80% DOD that contain a minimal fraction of inactive components.

  - Work to date (from Oct. '15 to Mar. '16):
    - Investigated different processing conditions on the cross sectional composition of electrodes:
      - Level of NMP in slurry
      - Rate of casting
      - Height of doctor blade
    - Investigated different inactive components on the ability to make thicker electrodes:
      - Two binder manufacturers
      - Two binders of different molecular weight
      - The effect of adding nanotubes
    - Perfected a method of cross sectioning electrodes and using EDX to quantify the average electrode composition from current collector to surface.
    - Sent samples to two institutions to investigate compositional changes on a sub-micron scale.

- <u>Relevance to VT Office</u>:

The VT Office is seeking to increase the penetration of electric vehicles by supporting research into the barriers preventing their adoption. Two of the main barriers are cost per kWh and energy density. This research addresses both.

- <u>Impact</u>:

If successful, this effort will result in an increase in the cathode's potential energy density by as much as 25 %, which will simultaneously impact battery cost per kWh, and may have a significant impact on the market acceptance of EVs.

Milestones

Date	Milestones and Go/No-go Decisions	Status
December 2015	Fabricate laminates of NCM cast to different thicknesses using standard materials and various processing conditions to determine their effect on overall electrode quality.	Met
March 2016	Fabricate laminates of NCM cast to different thicknesses using higher molecular weight binders and various processing conditions to determine their effect on overall electrode quality.	Met
June 2016	Fabricate laminates of NCM cast to different thicknesses using standard materials and various processing conditions on current collectors with a thin layer of binder and conductive additive pre-coated on the current collector to determine their effect on overall electrode quality.	On schedule
September 2016	Go/No-go. Determine if a high molecular-weight binder or pre-coated current collector is worth pursuing to achieve thicker electrodes based on ease of processing and level of performance.	On schedule

Technical Approach/Strategy

Investigating a number of materials and process modifications toward the fabrication of ultra-high loading electrodes as a result of access to several binder formulations, conductive carbon configurations, active material particle sizes, and consultation with electrode manufacturers. This work is supported by capabilities in macroscopic modeling and diagnostics that allows for the prediction of power performance and measurement of physical, chemical, and electrochemical properties of the laminates, respectively.

Materials | *Characterization and Modeling* | *Cell Manufacturers*

umicore

ARKEMA

Hydro Québec

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APPLIED SPECTRA

2015 → **2016** → **2017** → **2018**

BLACK DIAMOND STRUCTURES

DAIKIN

Effect of material properties and processing conditions on electrode uniformity

BYU

Combinations of materials and processes that provide engineering principles to electrode manufacturing.

ALS Synchrotron Infrared Beamlines

Combination of materials and processes that can be performed today

Hydro Québec

Technical Accomplishments

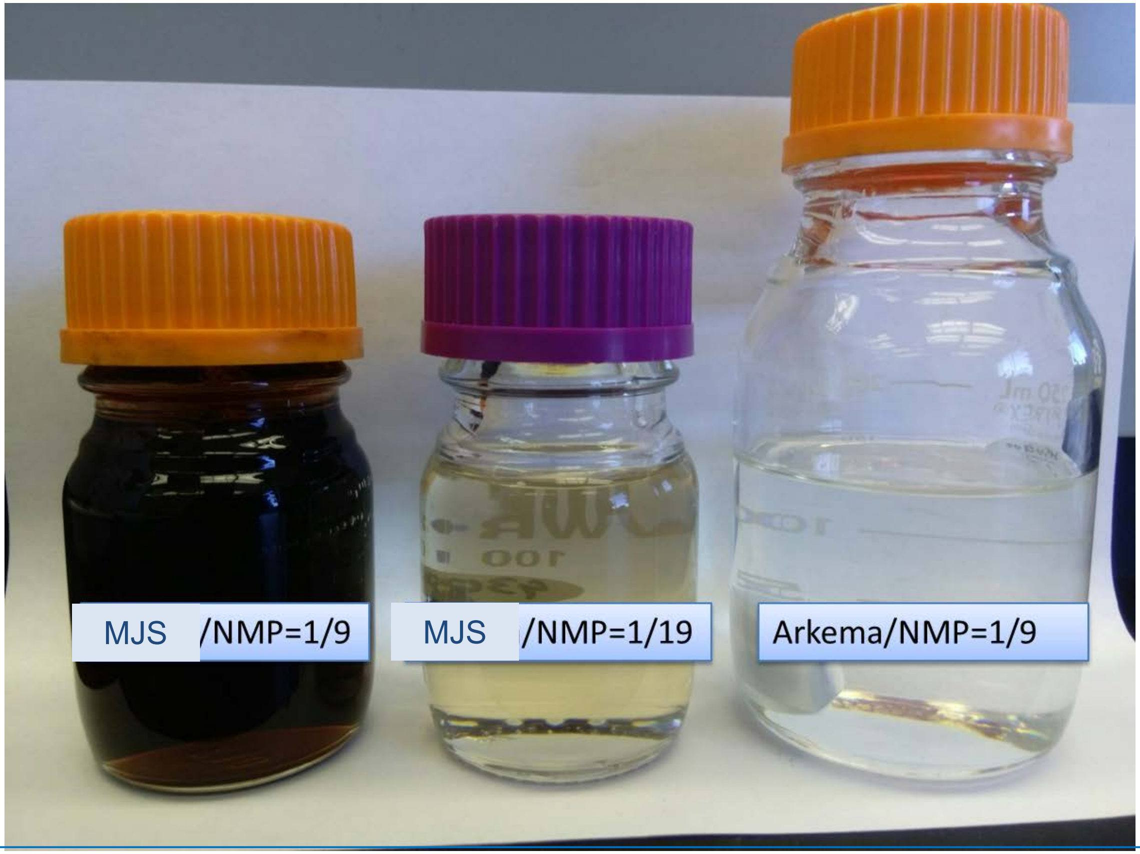
Since October: Scoping study

1. Assessed binders from two vendors on
    1. Solubility in NMP
    2. Ability to make comparable electrodes.
    3. Electrode uniformity
2. Assessed electrode processing conditions
    1. Slurry viscosity
    2. Casting speed
    3. Height of doctor blade
3. Assessed electrode performance (power and energy)
    - Electrode thickness
    - Electrode porosity

1.1 Solubility

With the plan to test the effect of slurry viscosity on laminate production quality, we needed to evaluate the solubility of our PVDF samples in NMP.

Visual results of the addition of low molecular-weight PVDF to NMP



At 10%, the polymer from the MJS did not completely dissolve and the solution turned a dark brown. It was fully soluble at 5%. The polymer from Arkema was clear and soluble at 10%. Higher fractions means higher viscosity and thicker electrodes that do not spread on deposition.

MJS – Major Japanese Supplier

1.2 Electrodes from New Binder Supplier

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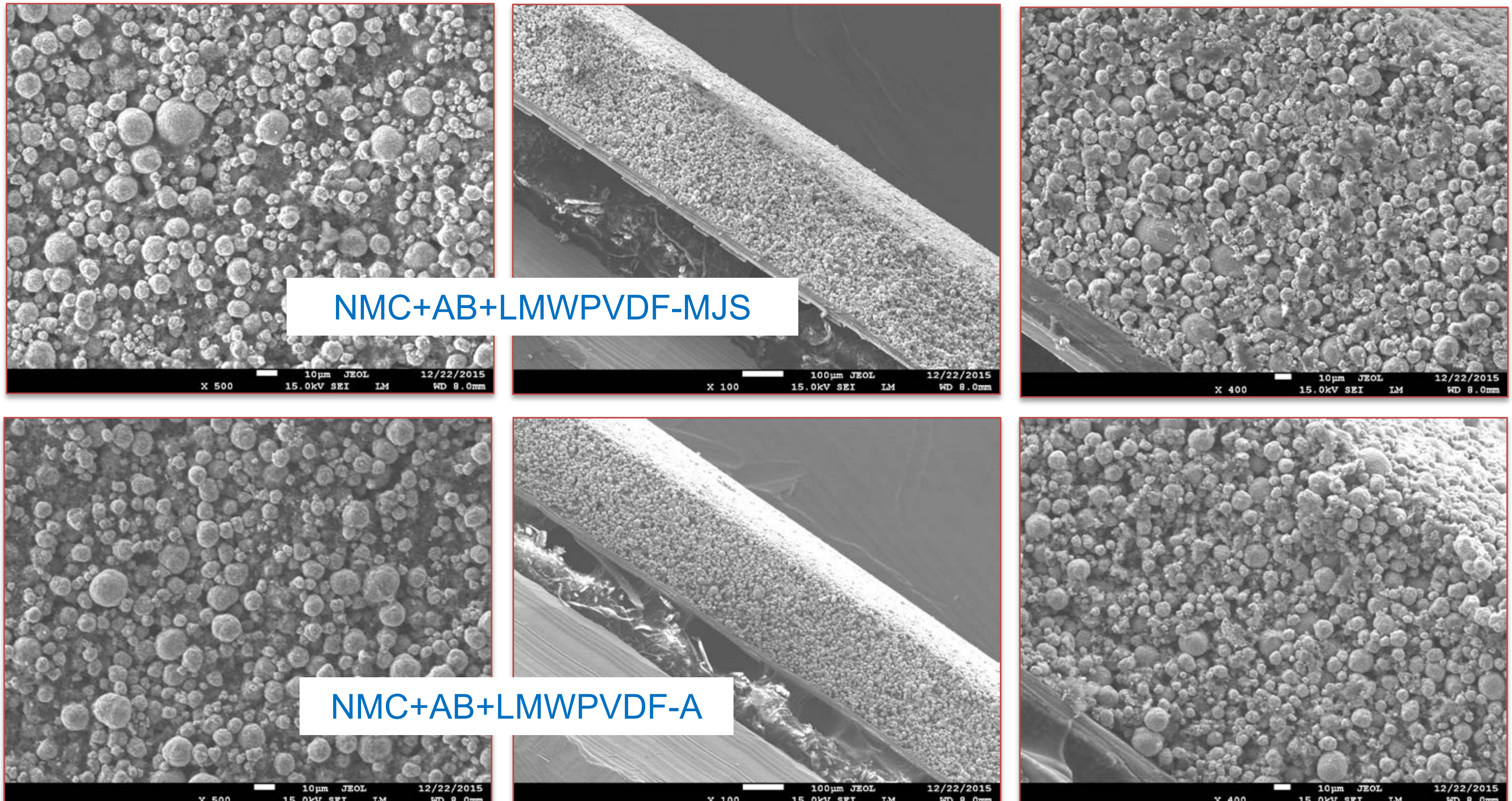
Surface | Cross section | Cross section



We have a long history of making quality electrodes from the binder from MJS.
Here we demonstrate that we can make comparable electrodes with Arkema's binders.

1.3 Electrode Uniformity

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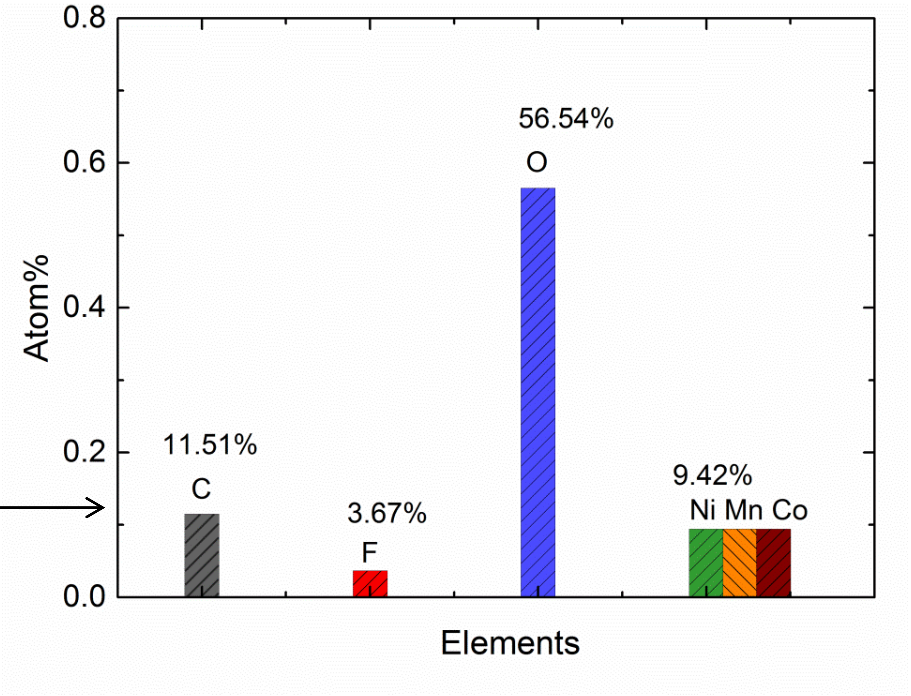
Electrode Composition

- NMC-based electrode
- NMC/PVDF/CB: *92.8/4/3.2 wt ratio*
- NMC: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
- PVDF: $(CH_2CF_2)_n$
- CB: *Carbon black*

- Theoretical atom%: *C, F, O, Ni, Mn, Co.*



1.3 Electrode Uniformity

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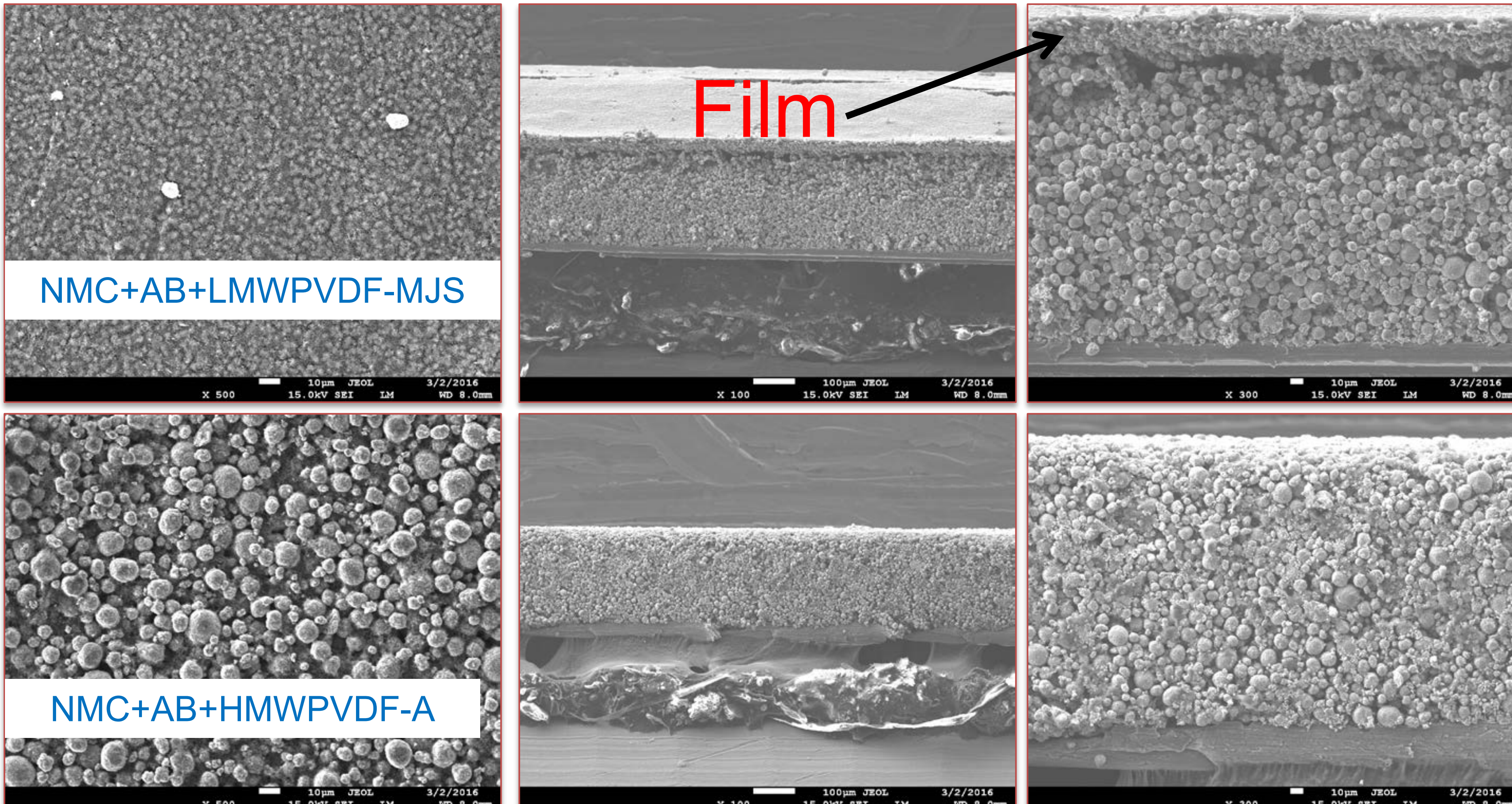
Effect of PVDF Molecular Weight on Laminate Compositional Uniformity for Thick Electrodes (cast to ~ 200 µm)

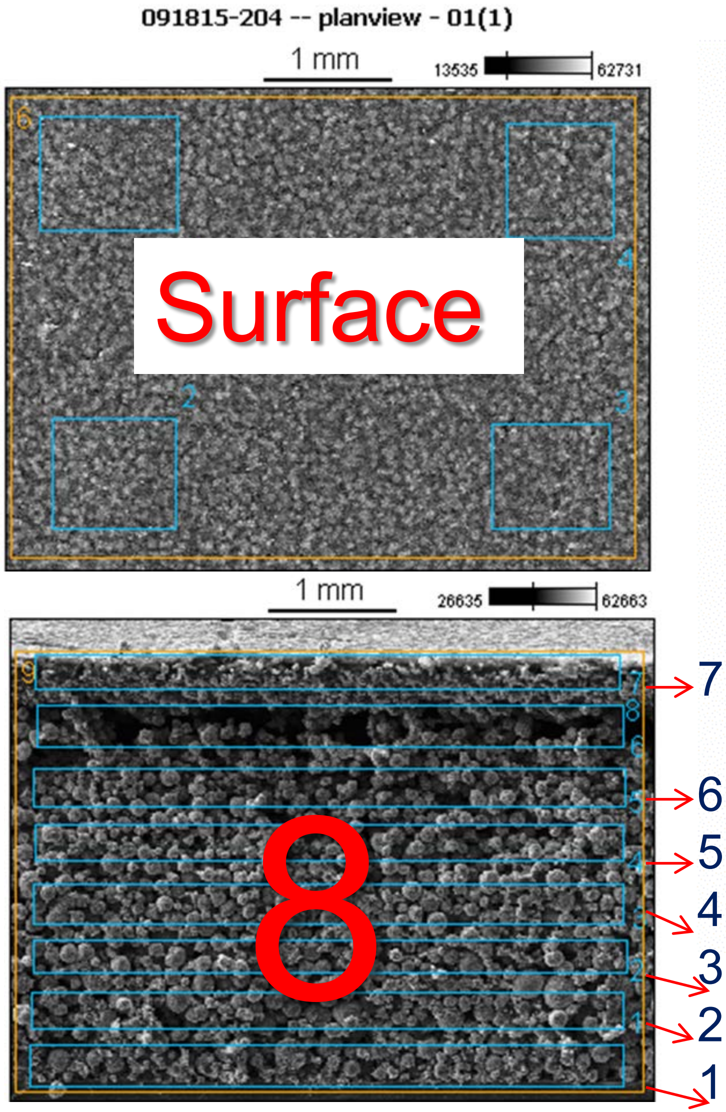
Surface | Cross section | Cross section

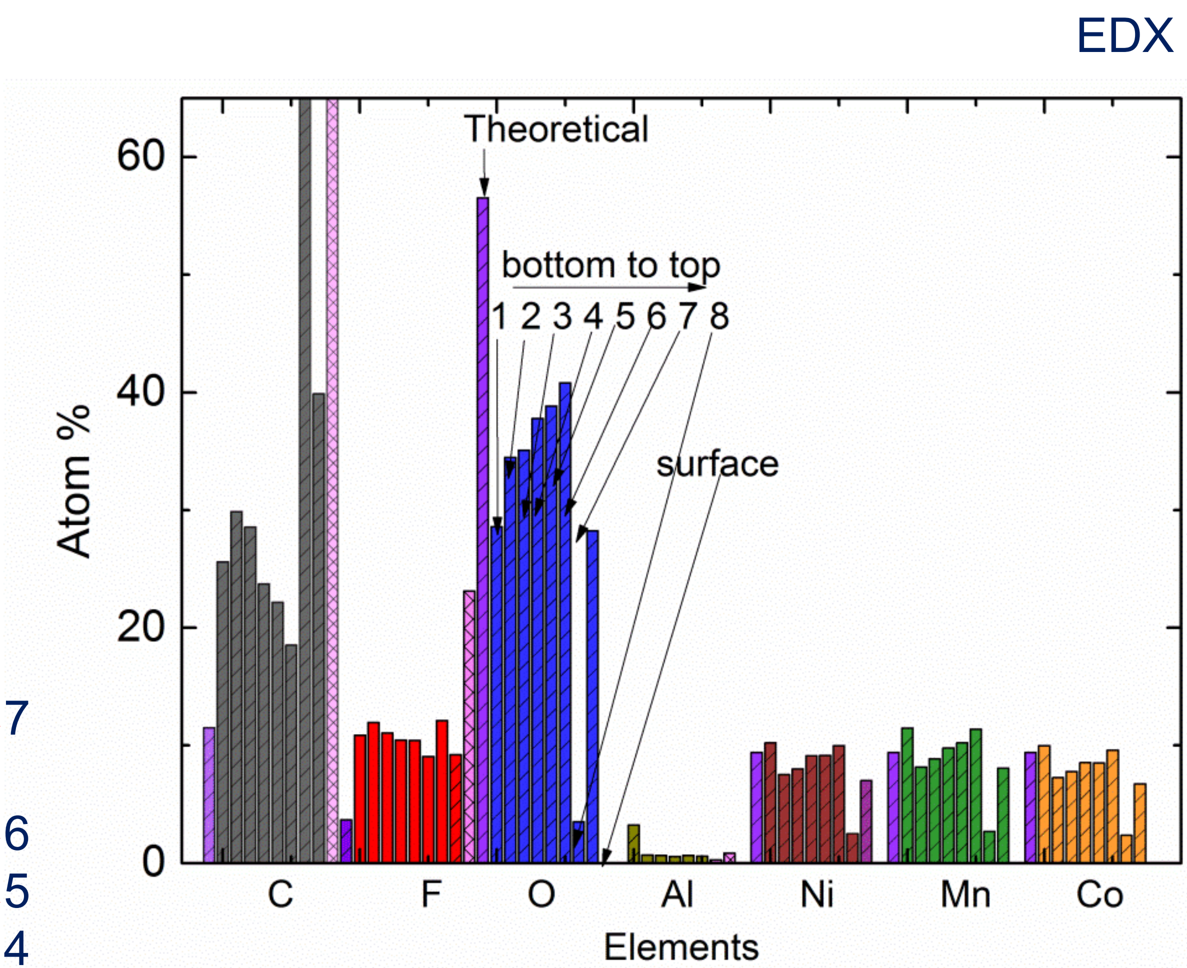


Separate film seen on the low molecular-weight electrode covering the active material.

1.3 Electrode Uniformity

NMC+AB+**LMWPVDF**-MJS





Composition non-uniform.
One measures excess carbon and fluorine at the surface

1.3 Electrode Uniformity

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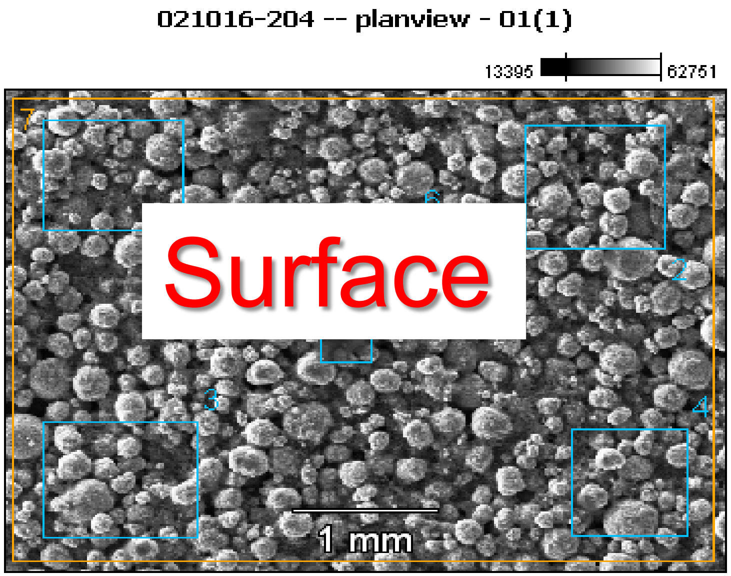
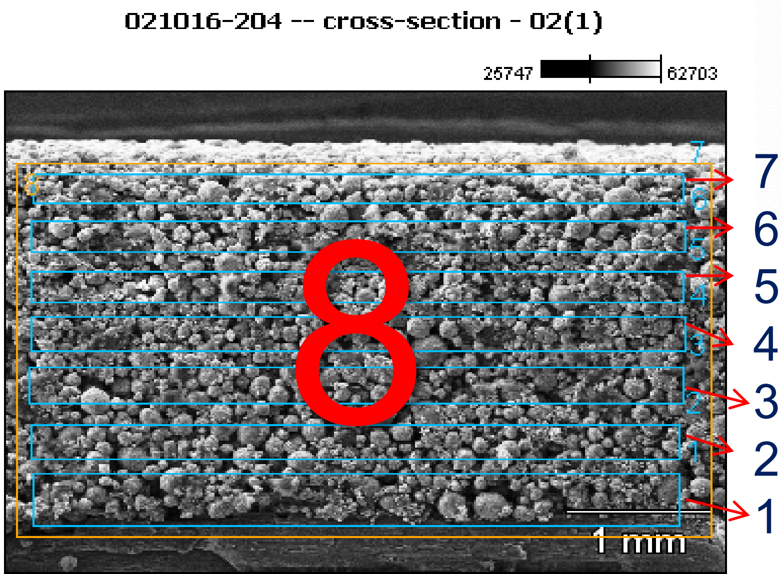
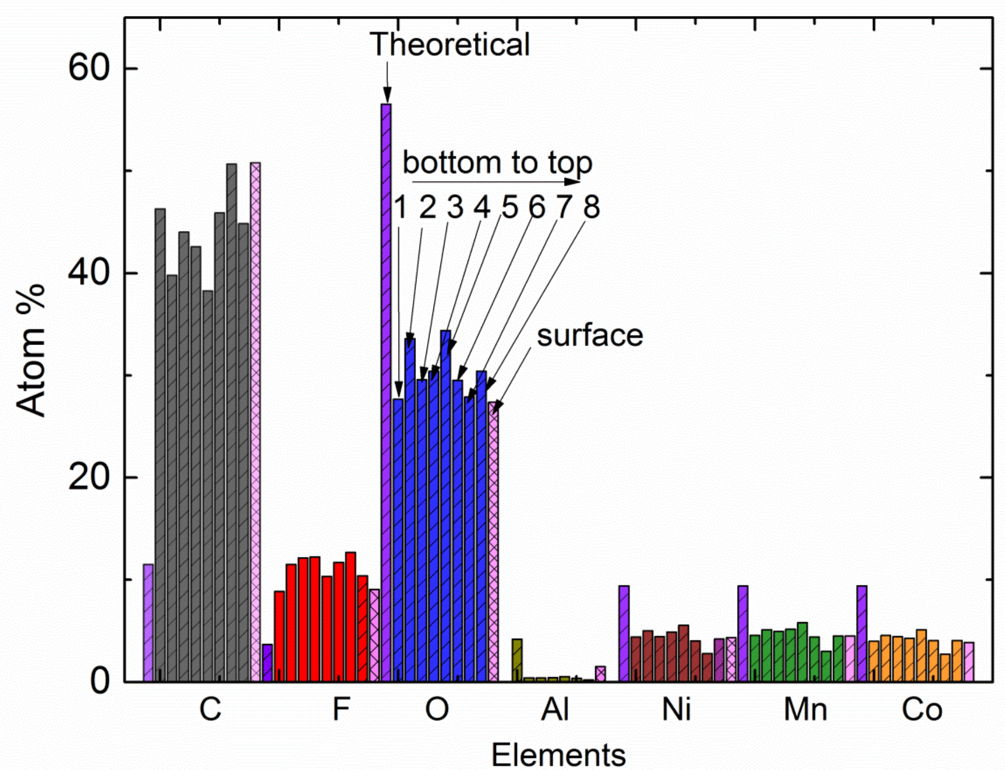
NMC+AB+**HMWPVDF**-A





EDX



Composition much more uniform from top to bottom.

Carbon and fluorine greater than theoretical; O, Ni, Co, and Mn less than theoretical, indicating a coating of the latter by the former.

2.1 Process Conditions: Slurry Viscosity

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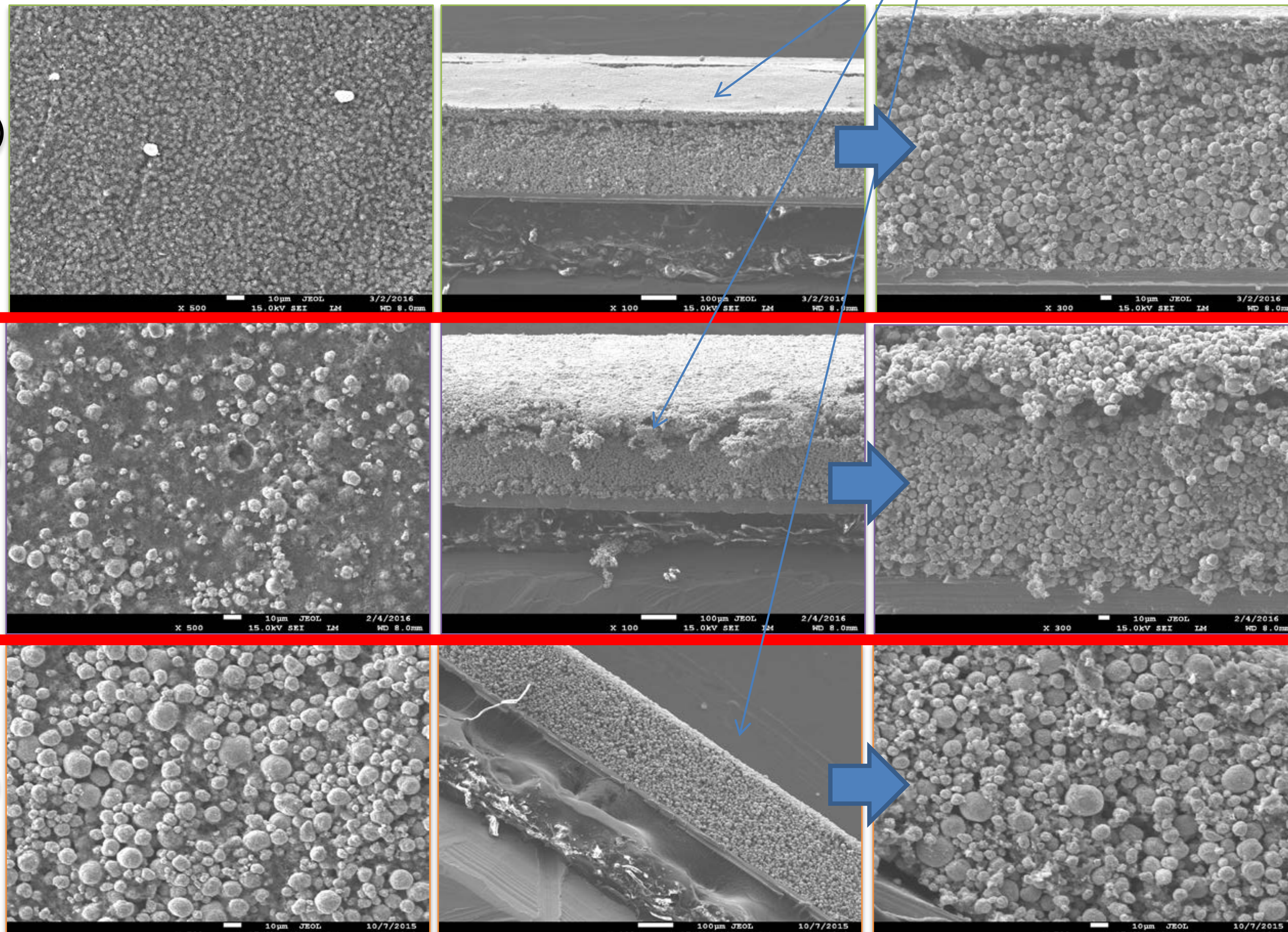
Surface | LMWP-MJS | Surfaces

Viscosity
~100 p
(@ 1.0 rpm)

Viscosity
~200 p
(@ 1.0 rpm)

Viscosity
~300 p
(@ 1.0 rpm)



Excess conductive agent found on surfaces for viscosities below 300 p measured at 1 rpm.

2.2 Process Conditions: Casting Speed

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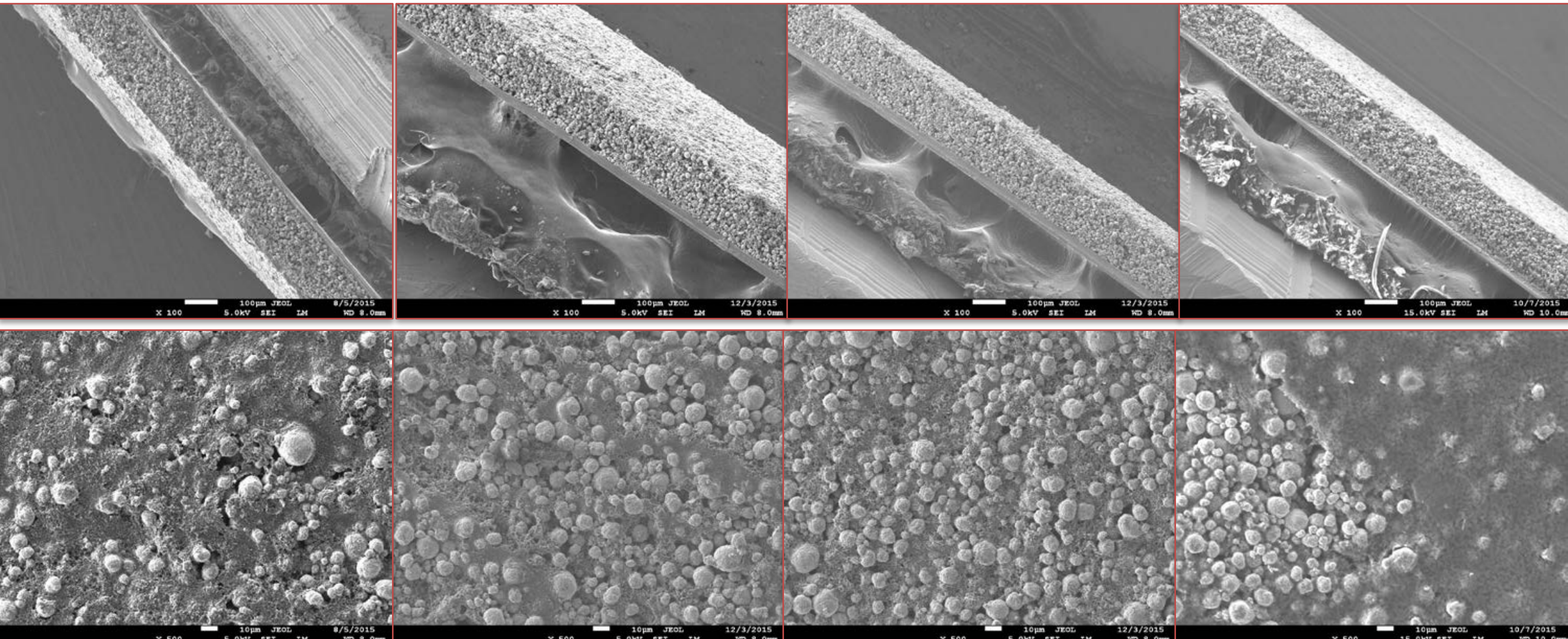
Viscosity 200 p (@ 2 RPM); LMWP-MJS; Doctor blade height ~ 500 μm

Speed ~1.0 cm/s, Thickness ~ 180μm	Speed ~3.0 cm/s, Thickness ~ 162μm	Speed ~6.0 cm/s, Thickness ~ 160μm	Speed ~10.0 cm/s, Thickness ~ 160μm



Patchy

Above a casting speed of 6 cm/s results in a non-uniform surface.

2.3 Process Conditions: Height of Doctor Blade

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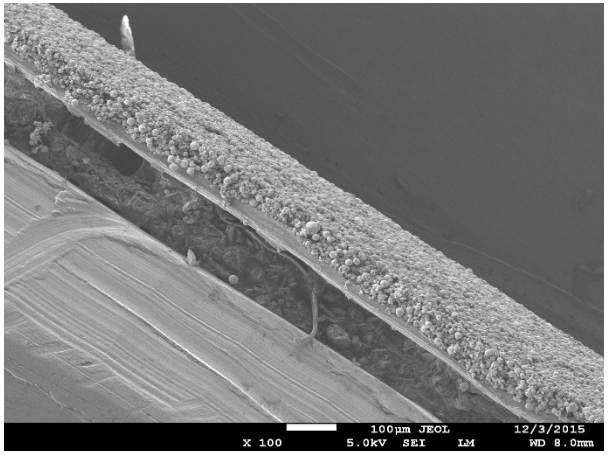
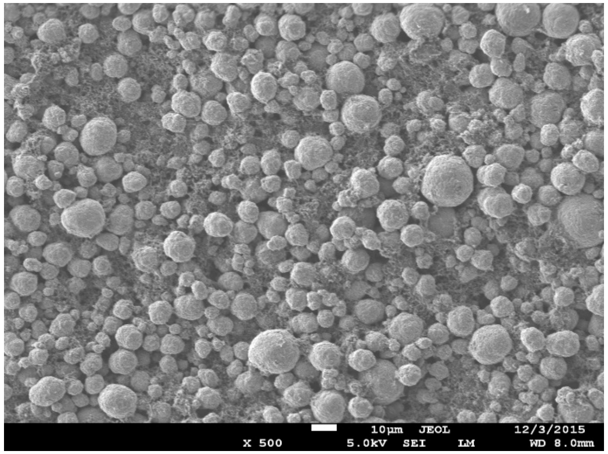
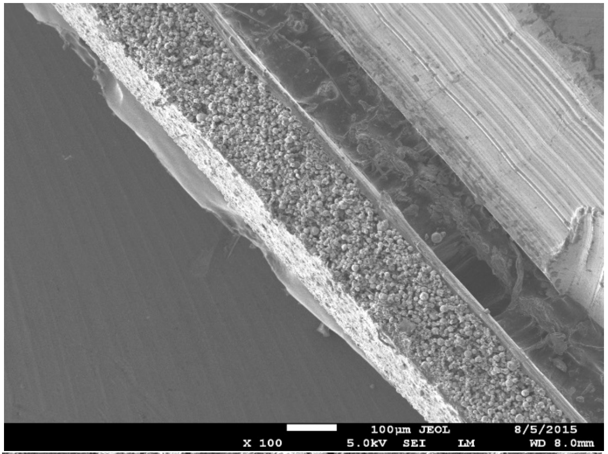
Viscosity ~100 p (@ 2 rpm); Casting speed ~ 1.0 cm/s; LMWP-MJS

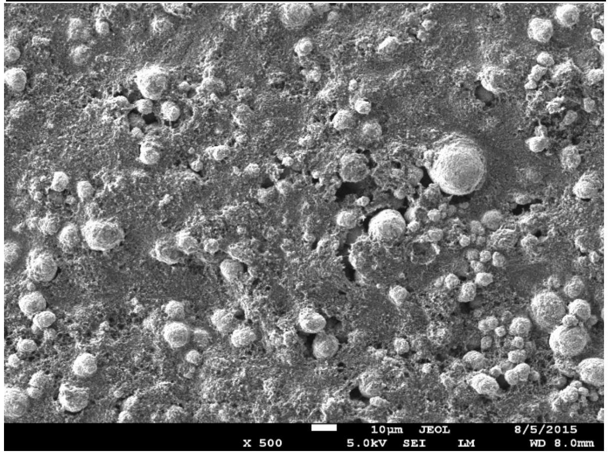
Height ~ 240 µm



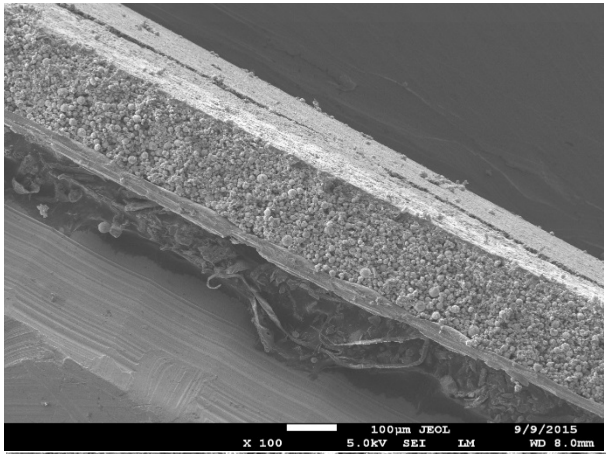


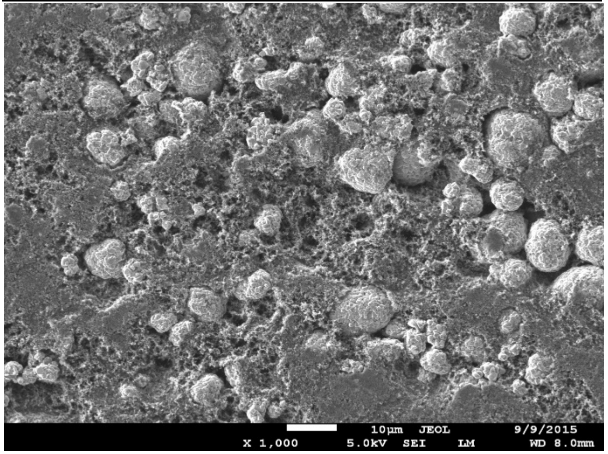
Height ~ 500 µm





Height ~ 600 µm





Increases in the height of the doctor blade result in an accumulation of conductive carbon on the surface.

3.1 Resistance *vs.* Thickness

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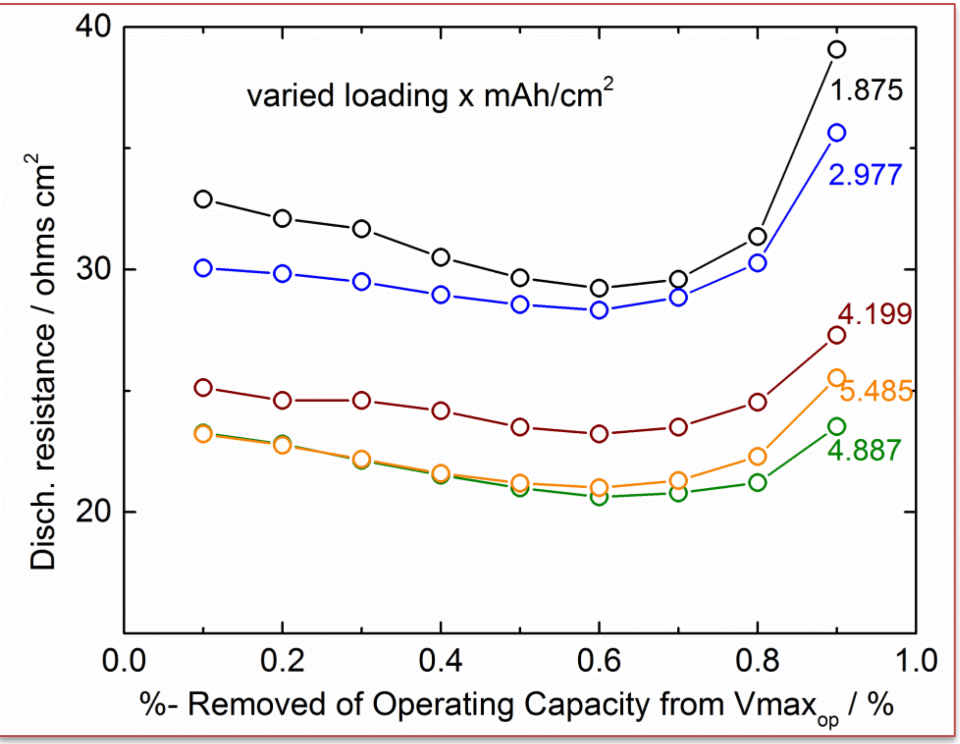
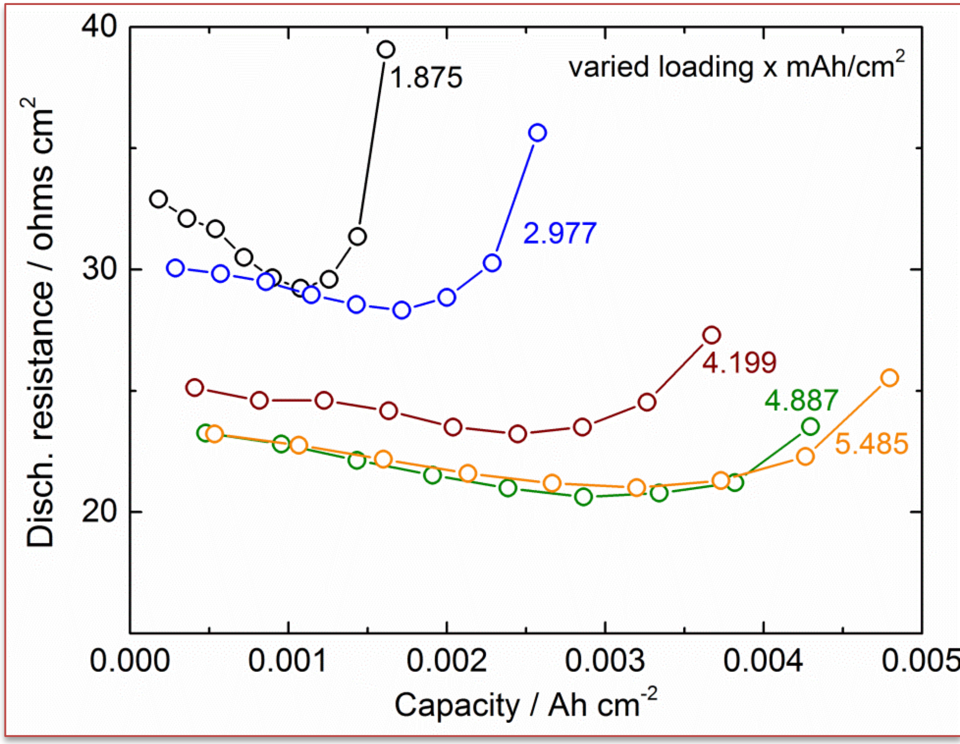
Five electrodes of differing loadings fabricated from the same slurry of low-molecular weight PVdF.

<u>Superficial Area Resistance as a function of DOD.</u>

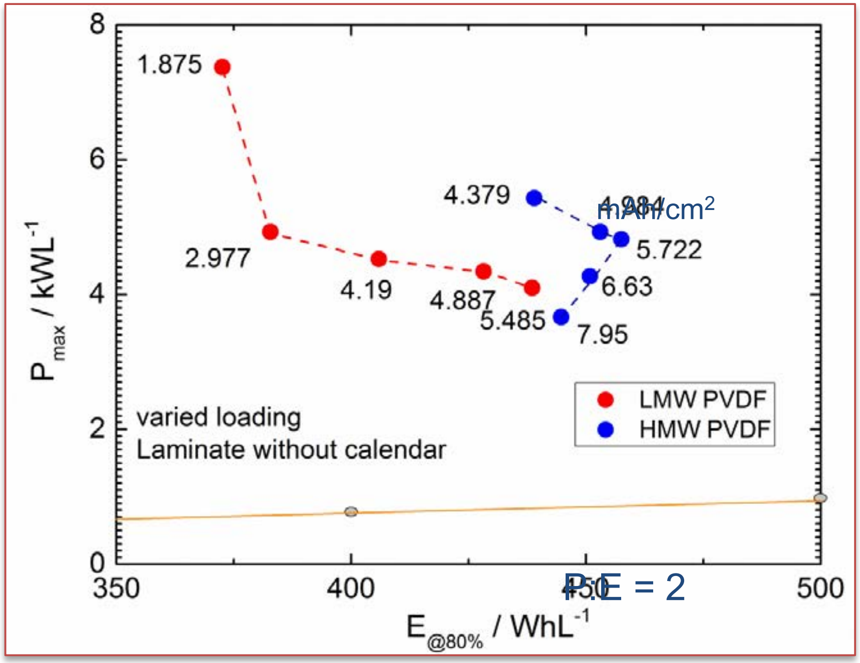




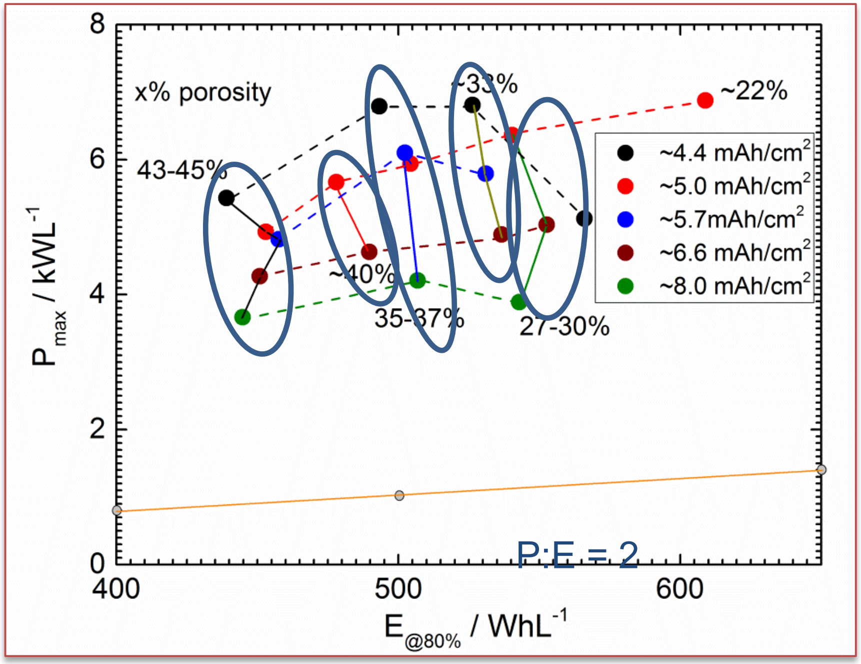
Superficial Area Resistance decreases with thickness until the loading reaches ~ 5.5 mAh/cm^2, *i.e.,* the resistance is dominated by active material intercalation until electrolyte ohmic resistance becomes a factor.

3.2 Peak power *vs*. Energy @80% DOD

Two Molecular Weight Binders;
No Calendering



High Molecular-Weight Binder;
Various Porosities



- Without calendering, able to construct thicker, higher-power electrodes w/high MW binder.
- The energy density peaks at 5.722 mAh/cm² for high MW binder electrodes, not calendered.

- Energy density at C/3 is slightly impacted by thickness and strongly improved by less porosity.
- Pulse power density reduced by thickness.

Data points to higher molecular-weight binders and electrodes of low porosity.

Responses to Previous Year Reviewers' Comments

- New Project

Collaboration and Coordination

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Partnerships / Collaborations	
ARKEMA INNOVATIVE CHEMISTRY	Provides binders of PVdF of different molecular weights, some blends, and some experimental binders.
umicore	Provides active materials with different particle size distributions.
BLACK DIAMOND STRUCTURES	Provides a conductive carbon additive that enhances the cohesive strength of the laminate.
DAIKIN	Provides battery-grade electrolyte.
BYU (Brigham Young University, Provo, Utah)	Provides separators and performs calculations of the drying configurations of particles in electrodes.
Hydro Québec	Provides current collectors, other cell parts, equipment for making cells, and expertise on cell manufacturing.
APPLIED SPECTRA	Provides measurement of electrode composition as a function of depth from the surface.
BERKELEY LAB	Colleagues provide capabilities in macroscopic modeling and characterization of laminates using the techniques at the ALS and NCEM.

Remaining Challenges and Barriers

- There are several materials and properties
  - ✓ Binders of varying molecular weights, nanotubes and acetylene black, secondary particle size of active material, amount of NMP in slurry…
- There are several processing steps and conditions
  - ✓ Mixing time, coating speed, temperature of slurry, coating speed, drying rate…
- There are several electrode qualities
  - ✓ Uniformity of component distribution, adherence to current collector, cohesion of film, power capability…

Finding correlations between them that will provide guiding principles for making thick laminates of excellent quality is a key challenge.

Proposed Future Work

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Summary of Results

- High viscosity is needed to make thick standing electrodes with uniform composition.
  - Requires a binder that dissolves in small amounts of NMP.
  - Arkema's is better at this than the MJS.
- High molecular weight binder better for maintaining a uniform composition in thick electrodes.
- Too high a casting speed has a negative impact on the laminate component uniformity.
- 30-second peak power pulse still well above the goal for our thickest electrodes.
- Laminates greater than 5 mAh/cm^2, energy limited by C/3 discharge rate (not its ability to perform 30 s power pulse). Thicker electrodes show less pulse power capability and slightly better energy density.
- Porosity has a significant impact on energy density
  - Is this a result of geometric expectations or changes in transport properties.

Key Challenges

- Find correlations between coating uniformity and dimensionless process parameters such as Reynolds number and Drag Coefficient (ratio of gravitational force to inertial force during settling).

Proposed Work

- **FY 16**
  - Complete scoping study (materials based)
    - Evaluate even higher molecular weight binders and some average MW binders.
    - Evaluate mixtures of molecular weights.
    - Evaluate electrodes of higher active material fraction.
    - Measure viscosity at high shear rates as expected through the doctor blade at 10 cm/s (5000 s^{-1}).
    - Determine the state of electrodes compressed to lowest porositities.
    - Evaluate different conductive additives
    - Evaluate the effect of a combination of particle sizes.
    - Determine best route for improved energy density: increasing the fraction of active material, increasing the electrode thickness , or decreasing the porosity
- **FY 17**
  - Scoping study (process based)
  - Assess impact of calendering at different temperatures.
  - Assess impact of mixing for different lengths of time..
  - Assess impact of coating of slurry at different temperatures.
  - Evaluate the impact of material and process changes on electrode cycleability.
- **FY18**
  - Establish general correlations between material attributes and electrode processibiity.
  - Establish a set of materials and processing conditions for fabricating high energy density electrodes.
  - Meet with competent electrode manufacturers and understand the limitations of proposed changes to processing conditions.
  - Consider compromises in materials and processing conditions that could be implemented on today's fabrications lines to increase electrode loadings.

Summary

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Relevance

- The work is focused on increasing the energy density of electrodes, a top VTO priority; this will also help reduce system cost, another top priority.

Approach

- Assess effect of material properties on processing conditions, and electrode uniformity and quality, by testing different active material sizes, binders, and conductive agents.
- Assess change of processing conditions on electrode quality and performance (power, energy, and life.)
- Use advanced diagnostics to provide understanding between materials, processing, and electrode quality.

- **Technical Accomplishments**
  - Established a number of competent suppliers for all materials of significance.
  - Begun scoping of material effects on electrode uniformity; assessed effects of:
    - Binder source
    - Binder molecular weight
    - Addition of NMP (viscosity)
    - Height of doctor blade
    - Casting speed
  - Used EDX to measure electrode atomic composition from current collector to surface.
- **Future Work**
  - Understand and establish correlations of materials properties to electrode performance.
  - Assess additional processing conditions, e.g.
    - Mixing time
    - Temperature of calendering
    - Drying rate