High Energy Density Electrodes: An In Depth Investigation of Materials and Processes toward Thick Electrodes

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LBNL

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BERKELEY LAB
Bringing Science Solutions to the World

Project ID #
bat232

Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/31/2019
- Percent complete: 90%

Barriers

- Barriers addressed (EV)
  - A. *Cost* - $75/kWh
  - C. *Performance* - 2/1 P/E for 30 seconds at 80% DOD
  - E. *Life* - 10 years

Budget

- Total project funding
  - DOE share: 100%
  - Contractor share: 0%
- Funding for FY 2018:
  - $750 k (2.5 FTEs)

Partners

- Interactions / collaborations
  - Arkema
  - Umicore
  - Daikin America
  - BMR Program and LBNL
    - G. Liu (LBNL)
    - D. Parkinsen (LBNL)
    - D. Wheeler (BYU)
    - K. Zaghib (HQ)

Relevance: Objectives and Impact

Project Objective:

A fundamental understanding of the workings of high-loading electrode laminates.

- Work this year (from Apr. ’18 to Apr. ’19):
    - Investigated polymer morphology as it relates to
        - Drying temperature
        - Mixing conditions
        - Mechanical properties
        - Electrode resistance
        - Electrode cycleability

Relevance to VT Office:

The fabrication of thick electrodes addresses two main barriers for EV adoption: *cost per kWh* and *energy density*.

Every research group fabricating cells for *Battery 500* or *Extreme Fast Charging* or *general consumer consumption* should be aware of the effects of drying time and temperature on the morphology of the polymer and its ramifacations in the fabrication of thick electrodes.

Impact:

Fundamental understanding of the laminate structure as a function of its processing steps should accelerate the introduction of new technologies into cells and the rate at which battery engineers meet stringent performance targets.

Issues of Thick Electrodes

General Question

- Are today's batteries limited in thickness (50 to 70 μm) as a result of cell performance or manufacturing capability?
  - If one is using the standard electrode formulation and is not concerned with fast charging, today's batteries are limited by manufacturing issues

    Electrodes of 6 mAh/cm^2 are capable of C/3 discharge (but not presently seen in vehicles)

    However, these electrodes demonstrate:

    - Mud-cracking when dried too fast
    - Segregation of carbon / binder and active material when dried too slow
    - A mismatch between electrode performance and mechanical performance
      - Delamination
      - Poor rate performance
  - Our mission is to explore the physics that will lead to optimized mechanical and electrochemical properties of high loading electrodes (> 5 mAh/cm^2).

Fundamentally, we want to understand the relationship of the physical and chemical forces that lead to the final distribution of materials in a high loading electrode in order to modify the materials or process conditions to optimize electrode fabrication and performance.

Technical Approach/Strategy

To investigate modifications to materials and process conditions in the fabrication of ultra-high loading electrodes, utilizing a suite of national lab based diagnostic tools to explore the fundamental physics of electrode performance.

Materials *Process Conditions* *Diagnostics* *Engineering Principles*

Umicore

BYU - Wheeler

Arkema

Daikin-America

LBNL - Liu

Effect of material properties and processing conditions on electrode uniformity

ALS Synchrotron Infrared Beamlines

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

HydroQuebec

Combination of materials and processes that can be performed at today's speeds

Over the past four years we've been able to scope out the first two topics by conventional means (lab scale battery fabrication, viscometry, bend tests, adhesion tests). We have learned that: 1) suppliers matter (impurities), 2) mixing matters (order of mixing and type), 3) molecular weight matters (viscosity, adhesion, cohesion), 5) drying temperature matters (cracking, settling, electrochemical, mechanical properties), 6) calendering does not matter (although warmer temperatures allow for one pass through).

Milestones

Date	Milestones and Go/No-go Decisions	Status
December 2018	Develop a methodology for fabricating “thick” cathodes of NCM and establish the effect of drying temperature on electrode morphology.	Met
March 2019	Measure the mechanical and electrochemical properties of electrodes dried at different temperatures.	Met
June 2019	Perform cycle life testing and in depth analysis of capacity fade and impedance rise of cells produced by different mixing orders.	On schedule
September 2019	Perform comprehensive evaluation of electrodes produced by a hybrid mixing process.	On schedule

Technical Accomplishments

Previous Years

1. Assessed binder from US supplier
   - Purity and solubility in NMP (varied from vendor to vendor)
   - Ability to make electrodes with new binder supplier that are comparable to our present electrodes in performance.
   - Slurry processibility and electrode casting uniformity.

2. Assessed electrode casting conditions
   - Casting speed
   - Height of doctor blade

3. Assessed electrode performance (power and energy)
   - Electrode thickness
     - Electrodes as high as 6 mAh/g in loading can be discharged in three hours and provide 30 sec of power equivalent to twice the energy.
   - Electrode porosity (must keep above 37%)
     - Calendering to below 40% porosity weakens, flattens, and fractures the secondary particles of NCM used for these tests.

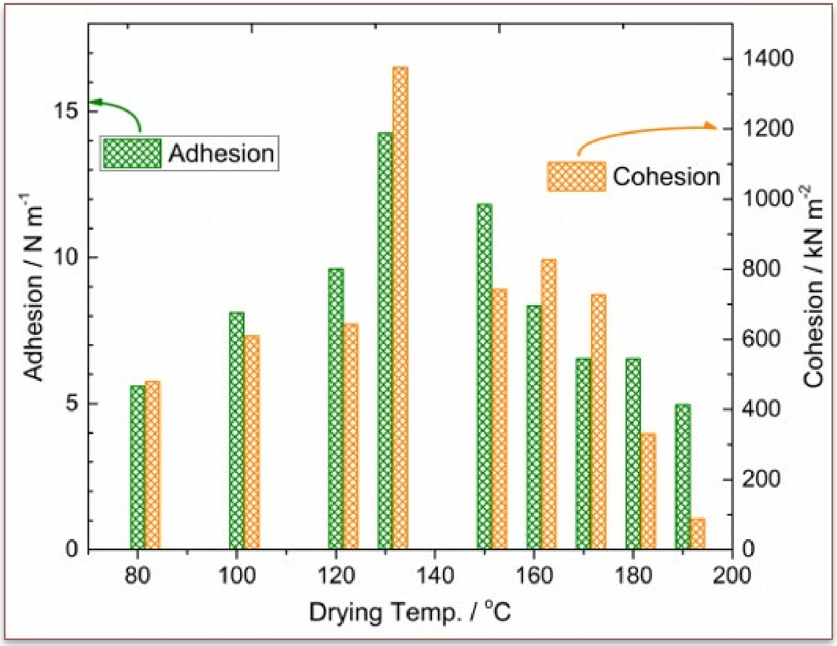
4. Assessed effects of calendering at different temperatures
   - Calendaring at higher temperatures reduces the electrode bounce back but has little effect on the ability to compress to lower porosity or any other electrode properties.

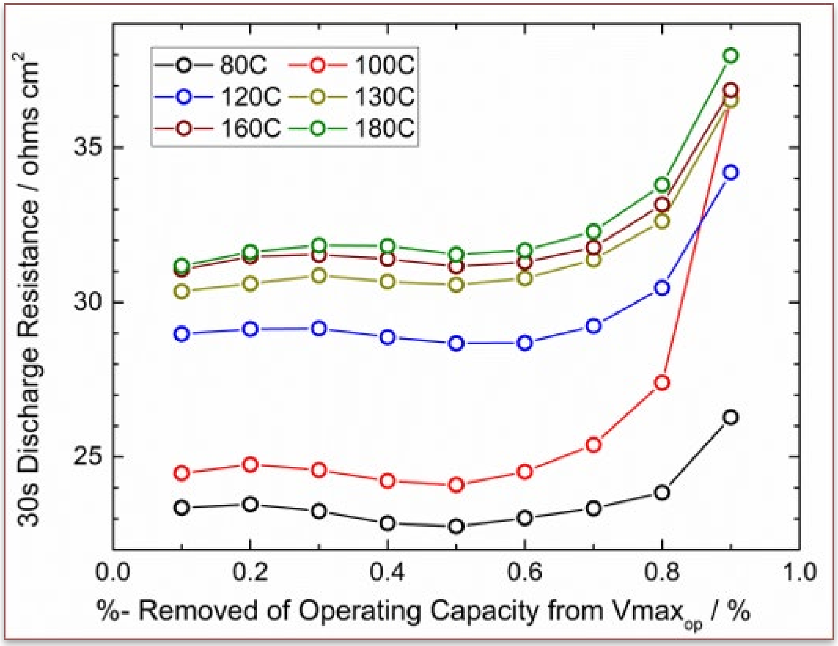
5. Determined optimum binder fraction
   - The optimum amount of polymer binder (1:0.8 polymer to carbon ratio) is *ca*. 3 to 4 % for electrodes of 250 μm.
     - Too much, and the electrode is too stiff and breaks under the strain of bending
     - Too little and the electrode has little adhesive or cohesive strength.

6. Established facilities to conduct drying experiments of electrodes
   - Temperatures above 140 °C lead to cracking
   - Low temperatures lead to poor adhesion but low impedance

Technical Accomplishments

Where we left off a year ago…





The mechanical properties of electrodes increased with drying temperature to 130°C, then decreased

- Above 130°C, the electrodes were susceptible to cracking

The resistance of the electrodes increased with drying temperature to 130°C, then leveled off.

These competing effects demanded we take a closer look at the electrodes, more specifically, the binder.

Technical Accomplishments

This Year

The focus of the work this year was binder morphology

1. Drying temperature impacts the type of binder crystallinity.
2. The type of crystallinity affects the ionic mobility.
3. The order of mixing of the components affects the degree of agglomeration of carbon and binder.
4. The degree of agglomeration impacts the distribution of the binder in the electrode.
5. The degree of agglomeration also impacts the drying time and the propensity to “mud” crack.

- Electrodes are presently under cycling tests to determine long term impacts of binder morphology.

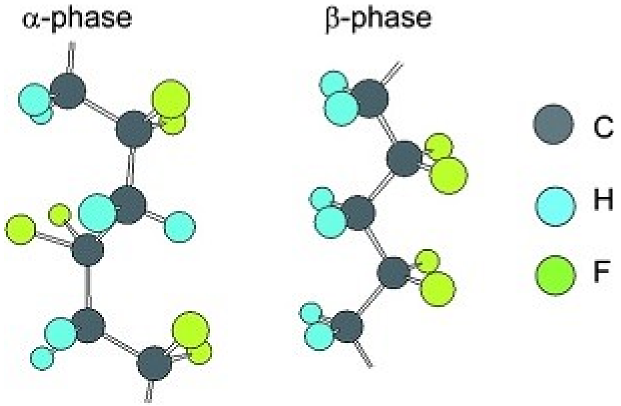
- Improved processing conditions for high loading electrodes are underway.

We have a much better fundamental understanding of electrode functionality than ever before.

Technical Accomplishments

We hypothesized that the change in electrode performance with drying temperature is linked to the binder morphology.

- PVdF is partially crystalline at room temperature.
  - When dried from solutions at temperatures below 70°C, it takes on the more polar β-phase configuration, with its C-F bonds aligned.
  - When dried from solutions above 110°C, it takes on the α-phase, with its C-F bonds mixed.
  - Dried from solutions at temperatures in between 70 and 100°C leads to a mixture of α + β.

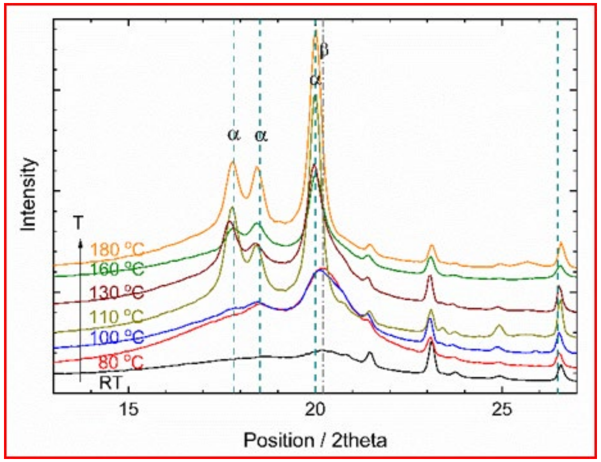


(Source: Royal Society of Chemistry)

Technical Accomplishments

To test this, we cast films of PVdF and dried them at different temperatures, ranging from room temperature to 180^{o}C. X-ray data were taken of the films to assess crystallinity.

- Peaks at or near 18, 18.5 and 20^{o} 2θ are associated with the α phase
- The peak at just above 20^{o} 2θ is associated with the β phase.



Consistent with the literature, a broad peak at 20^{o} gives way to smaller, sharper peaks at 18, 18.5 and 20^{o} as the temperature at which the film was dried increases.

Technical Accomplishments

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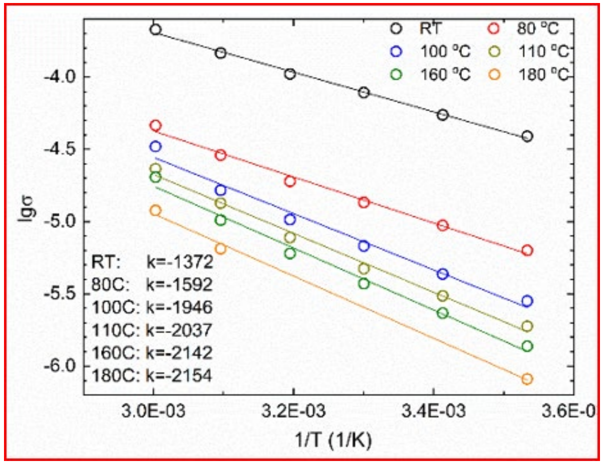
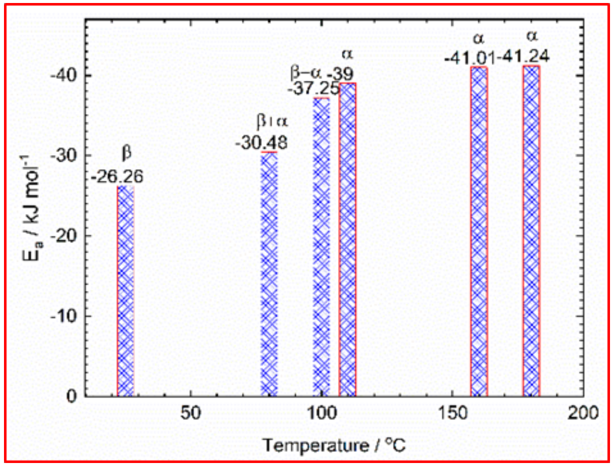
To determine the impact on performance, several films were cast and put in cells with blocking electrodes and the conductivity measured using a high frequency impedance instrument.





The films showed significant decreases in ionic conductivity and increasing activation energies (increases in the magnitude of the slope of data, left, translated to energy, right) with increases in drying temperature.

Technical Accomplishments

With this information in hand, we began to rethink our processing methods, starting from mixing.

Brief overview of battery electrodes:

- Electrode films consist of three components: active material, conductive additive, and binder.
- Ideally, the conductive additive will promote charge transfer at the active material interface and an electronic pathway through the electrode. The binder should hold all of the material together through its life.
- To accomplish this, the three materials must be combined such that their final distribution leads to optimum performance.

Technical Accomplishments

Overview of electrode processing:

- In mixing, we need to intimately combine three components: active material, carbon black and polymer binder.
  - The easiest way to do this is in a solvent using a high shear mixer that can break-up any agglomerated particles to their basic units which, for carbon black, is sub 100 nm and can bring the materials within a few microns of each other through the mixing blades.
- They could be combined in several ways:

I. Add the three materials together as solids then add solvent (NMP) and mix them together.

II. Mix the carbon and active material together in solvent, then add solubilized binder. (In previous research referred to as the Solids Process.)

III. Mix the carbon and solubilized binder together, then add the active material. (In previous research referred to as the Glue Process.)

IV. Mix the active material and solubilized binder together, then add the carbon.

V. Mix active material and part of the carbon together, mix the rest of the carbon with the solubilized binder, then mix those two solutions together (Hybrid Process).

Technical Accomplishments

Overview of electrode processing (cont.):

There is one caveat to electrode mixing:

- It is easier to make thick electrodes using a high molecular weight binder (~1e6 g/mol).
- It takes about 10 hours to fully dissolve high molecular weight binder in NMP.
- If you wait longer than a few hours after mixing, the active material will settle out.

- Because of this, we did not see the value of pursuing process I. because mixing all three together for 10 hours where most of the time was spent waiting for the binder to dissolve appeared impractical. (Here after, all binder was first solubilized in NMP before adding it to the other materials.)
- Mixing the active material and binder together as in IV, appeared to be a mute point since the active material is large enough that it easily mixes with binder solution but would likely impede the breaking up of the agglomerated carbon. For this reason, we did not pursue IV.
- Process V. is essentially a combination of II and III, which we therefore delayed until after reviewing the results of II and III.

Technical Accomplishments

Experimental

1. Electrode fabrication for Processes II and III.
    - Mixer: homogenizer set at 3k rpm, 1 hour duration
    - Doctor blade coated on Al foil; blade set at 500 microns.
    - Films dried in forced air convectional oven at different temperatures
        - 80,110, 130, 150, and 180°C.

2. Electrodes calendered to 40% porosity.

3. Cross-sectioned to perform SEM and EDS.

4. Electrochemically evaluated in single layer pouch cells of 12 cm^2 superficial area.

Technical Accomplishments

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Process II:

(Solids Processing)


Drying t: ~ 7 min.
Oven T: ~130 °C


Drying t: ~ 4.5 min.
Oven T: ~145 °C

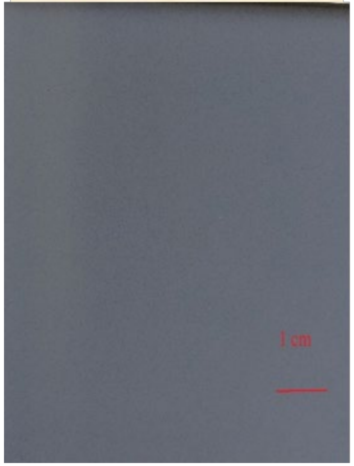

Drying t: < 4 min.
Oven T: ~170°C

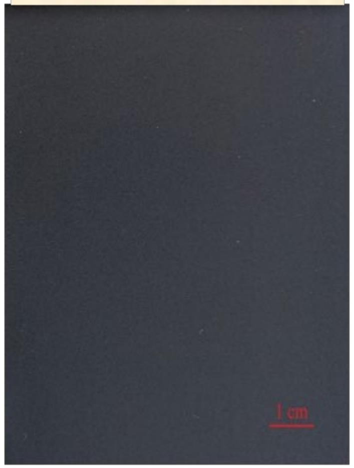
Observations:

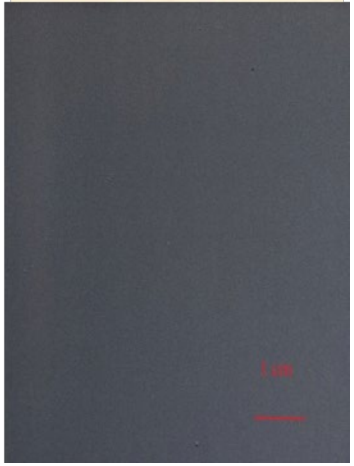
- Faster drying times
- Cracking above 145°C.

Process III:

(Glue Processing)


Drying t: ~ 20 min.
Oven T: ~130 °C


Drying t: ~ 15 min.
Oven T: ~150 °C


Drying t: ~ 12 min.
Oven T: ~180 °C

Observations:

- Slower drying times
- No cracking, even at 180°C.

Results suggest that carbon/binder configuration greatly influences drying time; and that cracking is more dependent on drying time than drying temperature.

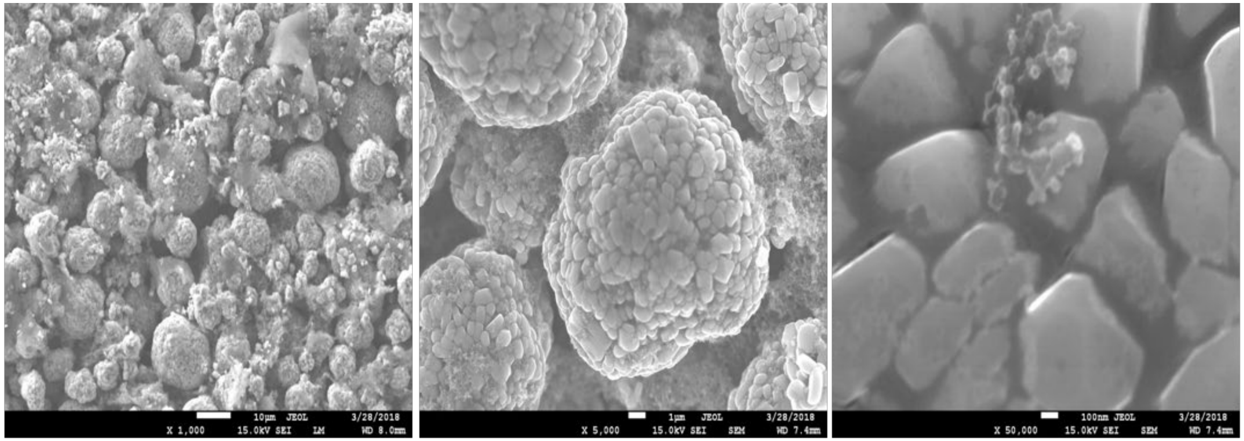
If we are to get drying times down to 3 min, will need something that mostly resembles II.

Technical Accomplishments

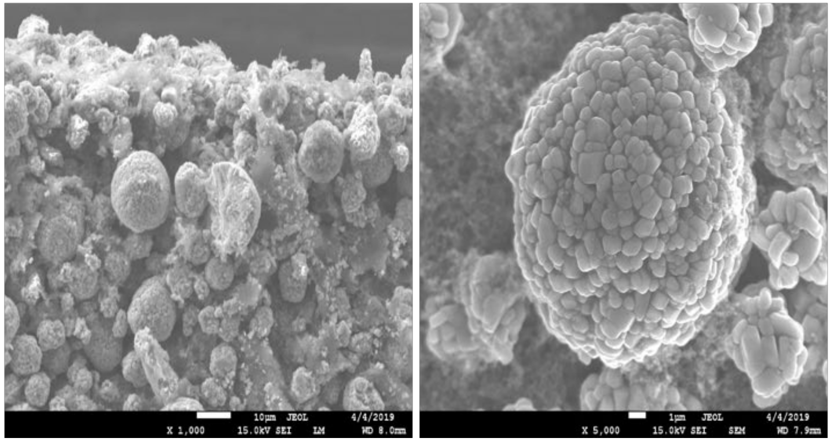
SEMS

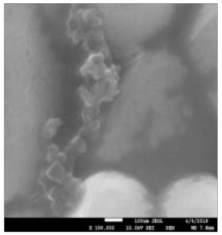
Electrode cross-section | **Cathode particles** | **Carbon black**

II*



III*





Observation:

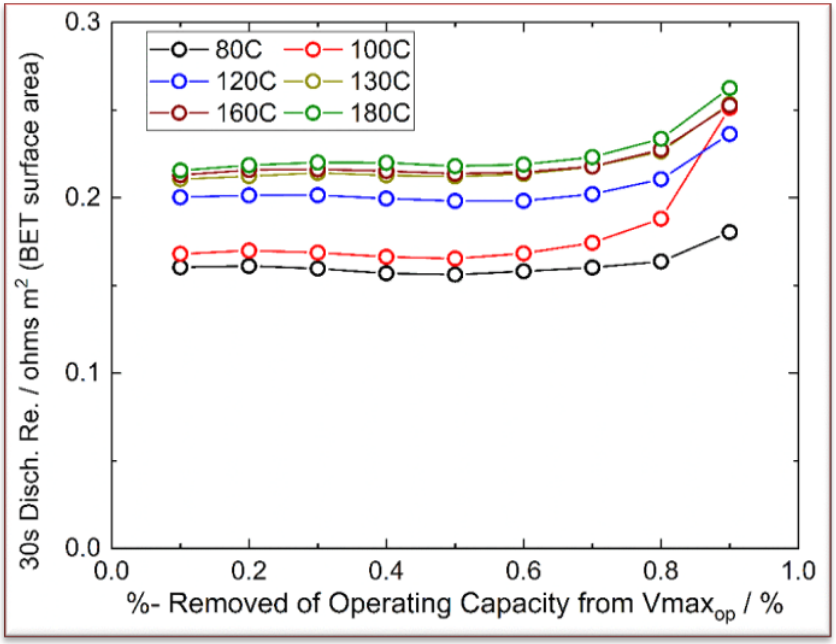
It appears that mixing the polymer with the carbon black first (III. <u>Glue</u> Process) results in larger agglomerates of carbon black and binder between particles that require more time to remove the absorbed binder from.

(*both electrodes dried at 130°C)

Technical Accomplishments

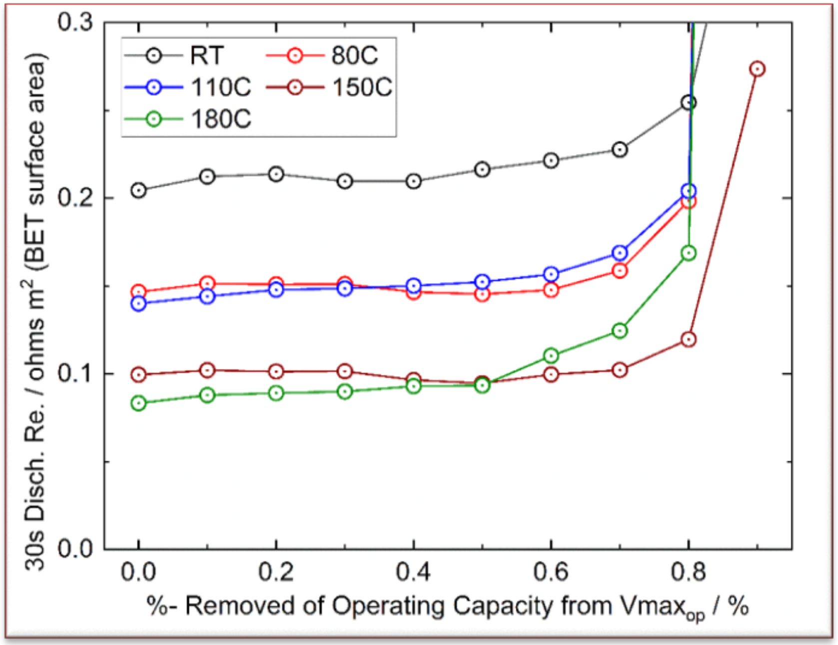
30-sec discharge pulse resistance as a function of DOD (based on BET area of active material)

II.



Electrode impedance *increases* as the drying temperature increases

III.



Electrode impedance *decreases* as drying temperature increases.

Could indicate that uniform coating on active materials is inhibiting ion transport. May suggest a path forward and potential benefit of hybrid mixing (Process **V**).

Responses to Previous Year Reviewers' Comments

…address 1-3 significant questions/criticisms/recommendations from the previous year's reviewers' comments… We will focus here on the criticisms (all from the same reviewer).

1. "… the approaches and evaluations of work used are standard to the industry, which is acceptable, but does not introduce anything novel to justify the project funding."
   - This is hard to believe. No company is capable of making thick electrodes with today's production equipment – if they could, they would. The reason they can't is because line speeds would need to be drastically modified to simultaneously meet drawdown requirements (that may require fast speeds to take advantage of shear thinning physics) and drying requirements (that require slow speeds to effectively remove all of the solvent). Our goal is to understand these limitations to allow for the production of high speed, thick electrodes on today's production lines.

2. "… binder-solvent systems that do not "mud-crack," yet yield thick, high-density films need to be considered."
   - Investigating different binders for Li-ion batteries was never the intended scope of this project. Starting from highly processible, highly stable PVdF is the goal. Producing thick films with something short of these properties would be a project of entirely different scope and approach.

3. "… the project team has reached out to industrial partners. However, it appears the project team has not taken advantage of efforts and accomplishments at other national laboratories.."
   - Each lab is given resources to conduct research in different areas. Ours was to investigate the limits of today's technologies and processing capabilities. Our lab was not expected to move to different processing equipment or technologies as conducted by other labs.

Collaboration and Coordination

Partnerships / Collaborations	
Arkema	Provides binders of PVdF of different molecular weights, some blends, and some experimental binders. More importantly, discussions with bring new insights.
Umicore	Provided baseline active material.
Black Diamond Structures	Provides a conductive carbon additive that enhances the cohesive strength of the laminate.
Daikin-America	Provides battery-grade electrolyte.
BYU (Wheeler)	Provides separators and performs calculations of the drying configurations of particles in electrodes.
HydroQuebec	Provides current collectors, other cell parts, equipment for making cells, and expertise on cell manufacturing.
LBNL	Colleagues provide capabilities in macroscopic modeling and characterization of laminates using the techniques at the ALS and NCEM.

Remaining Challenges and Barriers

What we have learned:

- Polymer morphology is critical to electrode performance
  - Crystallinity and distribution
- High drying temperatures result in a crystal structure that reduces ionic mobility.
- Low drying temperatures require too much time for drying (which leads to longer production times and increases in cost – not acceptable).
- Coatings of polymer on the active material appears to reduce the rate of Li-ion transport into and out of the cathode material.
- Large agglomerations of carbon black and polymer slow down the drying time to unacceptable levels, even at high temperatures; however, these electrodes when dried at higher temperatures show the lowest levels of electrode impedance and no cracking.
- We need to measure the impact of total polymer content on drying speed.

Challenges:

- If a combination of mixing processes is possible, and the goal is to minimize the inactive material content and maximize the loading and do so at today's drying rates of 30 m/min (and less than 3 min total), what should that combination be?

Proposed Future Work

LBNL

Six months remaining

Complete present investigation of processes II and III

- **Investigate the effect of polymer content on speed of drying and temperature limit before cracking**
- Establish relationship between polymer morphology and mechanical properties
  - Measure the adhesion and cohesion of polymer films produced at various temperatures
  - Measure the adhesion and cohesion of electrodes produced at various temperatures
  - Assess crystal structure of polymer in electrodes being tested
- Allow the electrodes to cycle to end-of-life
  - Look for relationship between mechanical properties and cycle life

Fabricate electrodes via process V.

- Optimization required in:
  - The ratio of two slurries: carbon mixed with polymer and carbon and active material mixed with polymer
  - Drying temperature schedule for performance and drying time
- Preliminary work suggests the following considerations
  - Binder is necessary for providing mechanical integrity to a free standing film
  - Binder covering the cathode surface blocks ion transport but improves mechanical strength
  - Large binder and carbon agglomerations slow down drying but eliminates cracking and reduces impedance
  - By breaking the polymer and carbon into two slurries (one-with and one-without active material) may allow us to minimize the total amount of binder.
  - Minimizing drying time leads to less crystallization which correlates to higher ionic conductivities
  - Films dried at 80°C results in β-phase that leads to better ionic conductivity.
  - *Since polymer crystallinity and mud cracking both depend on drying temperature, if the temperature is a variable, at what fraction of solvent is it important that the slurry be at a particular temperature*?
    - *i.e.* **can we remove most of the solvent at high temperature, reduce the temperature to a preferred temperature for polymer crystalization, then crank the temperature back up to complete the drying?**

Any proposed future work is subject to change based on funding levels.

Summary

Relevance

- The work is focused on getting at the fundamental principles to producing high energy density electrodes, a top VTO priority. Advancements in this area should result in faster routes to producing high energy density cells.

Approach

- Scope out the effects of each process of cell manufacturing on the final properties of the electrode.
- Use bench scale techniques consistent with large scale manufacturing
- Measure critical properties as a function of temperature and solvent content
- Use standard and advanced diagnostics to provide understanding between materials, processing, and electrode quality.

Major Technical Accomplishments

- A methodology for fabricating thick electrodes that allows us to study casting speeds and drying temperatures independently.
- PVdF crystallizes into different structures depending on drying temperature that affects ion transport.
- Different mixing orders result in electrodes of different morphologies and different dependencies on drying temperature.

Future Work

- Complete characterization of films produced by two different mixing sequences to assess polymer content and morphology on mechanical properties and cycling capabilities.
- Investigate combinations of mixing processes (that minimize polymer content) and combinations of drying temperatures to produce highly functional, high loading Li-ion cathodes.
- Work with battery manufacturers in sharing results.