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

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LBNL

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Project ID # **bat232**

Overview

Timeline

- Project start date: 10/1/2018
- Project end date: 9/31/2021
- Percent complete: 50%

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:
  - $350 k (1.25 FTEs)

Partners

- Interactions / collaborations
  - Arkema
  - Umicore
  - Daikin America
  - LBNL
    - G. Liu (LBNL)
    - D. Parkinsen (LBNL)

Relevance: Objectives and Impact

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Project Objective:

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

- Work this year (from Apr. ’19 to Feb. ’20):
  - 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 high performance cells for *Battery 500* or *Extreme Fast Charging* or *automotive applications* should be aware of the effects of mixing order and drying time and temperature on the morphology of the polymer and its ramifications in the fabrication of thick electrodes. Only by fully understanding all of the ramifications of electrode fabrication can a company or organization begin to start asking the right questions and make suggestions for improvements in cell performance.

Impact:

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

Issues of Thick Electrodes

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General Question

- Today's batteries are limited in thickness (50 to 70 μm) as a result of manufacturing capability

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

  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 (> 4.5 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 high loading electrodes in order to modify the materials or process conditions to optimize electrode fabrication and performance.

Technical Approach/Strategy

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Assess the construction of thick electrodes from the ground up by investigating the polymer morphology as a function of drying temperature, the impact of carbon additive on the structure, and trying to understand how mixing order impacts the structure.

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

Umicore

Arkema

Daikin-America

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 five 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

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Date	Milestones and Go/No-go Decisions	Status
December 2019	Use xray and FTIR to assess crystallinity of polymer films dried from NMP at different temperatures.	Met
March 2020	Fabricate and assess mechanical and electrochemical performance of electrodes produced through Process IV.	Met
June 2020	Perform cycle life testing and in depth analysis of capacity fade and impedance rise of cells produced by process V.	On schedule
September 2020	Perform comprehensive evaluation of electrodes produced by a hybrid mixing process VI.	On schedule

Technical Accomplishments

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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 superior to previous supplier.

2. Assessed electrode casting conditions
   - Casting speed good to our maximum rate of 10 cm/s
   - Height of doctor blade – up to 500 microns

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

(All work to this point conducted under one mixing condition.)

Technical Accomplishments

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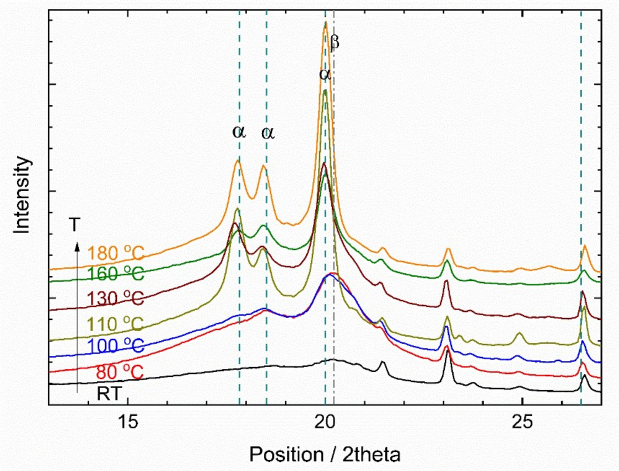
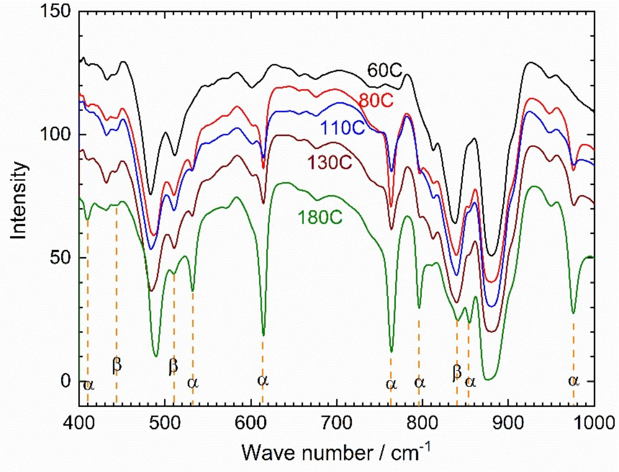
Last Year

Characterization of pure PVdF films dried at temperatures from RT to 180^{o}C using XRD and FTIR

XRD



FTIR

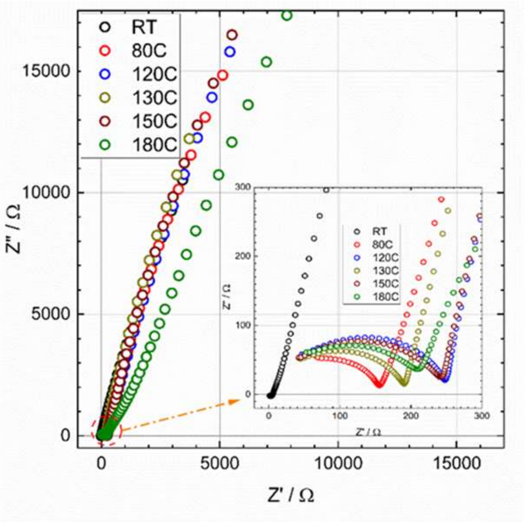


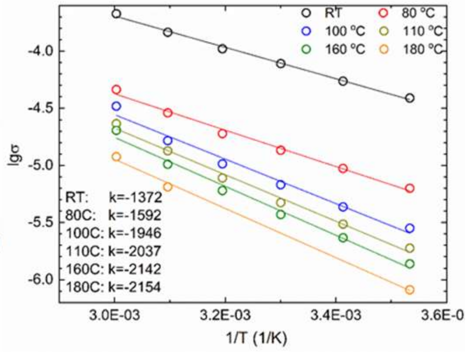
As the temperature of drying increases,
the polymer becomes more crystalline as it shifts from
broad β peaks to sharp α peaks.

Technical Accomplishments

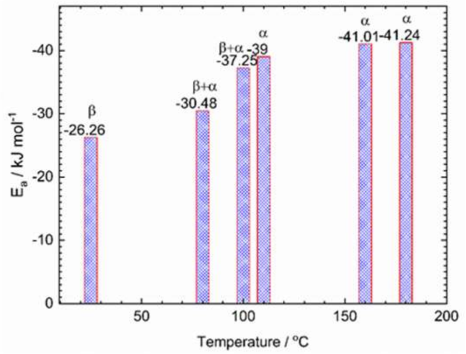
Impedance data of pure PVdF dried at temperatures from RT to 180^{o}C

EIS of electrolyte soaked film taken between two inert electrodes





Conductance decreases with increase
in drying temperature / crystallinity



Activation energy of conductance increases with increase
in drying temperature / crystallinity

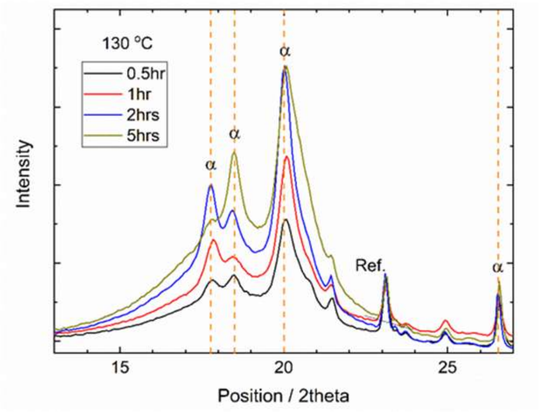
This is a significant problem because thick electrodes will require high temperatures to dry in the same amount of time as it takes thin electrodes.

Technical Accomplishments

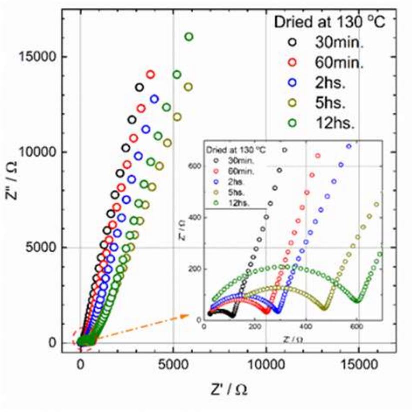
Effect of prolonged drying

Cells allowed to dry at 130^{o}C for: 0.5, 1, 2, 5, and 12 hrs

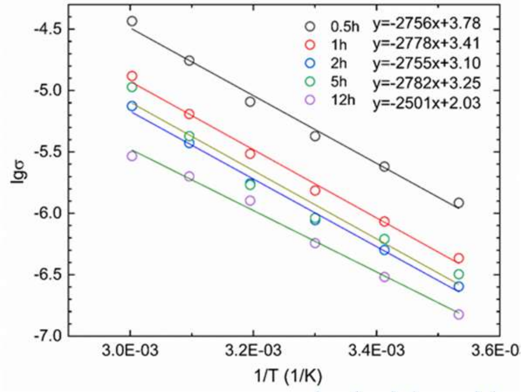
XRD



EIS



Conductance *vs* 1/T



electrolyte added

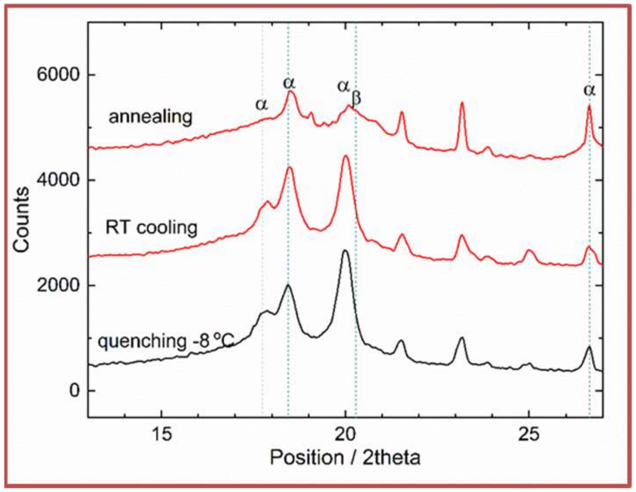
As the binder remains longer at a high drying temperature, the level of crystallinity increases and conductance decreases.

Technical Accomplishments

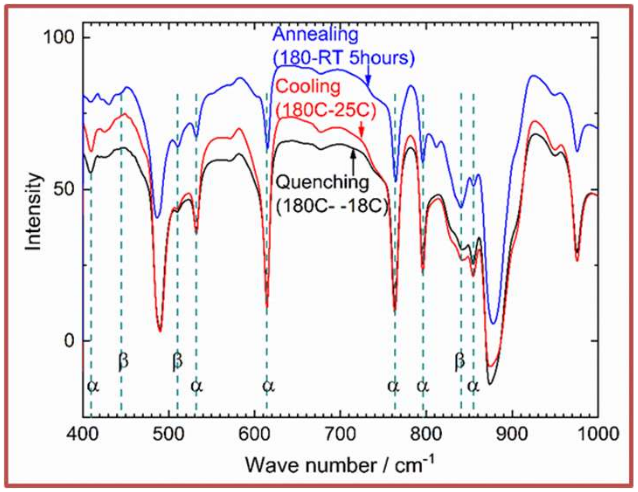
Effect of cooling rate

1. Annealing (5-hour controlled cooling)
2. Natural cooling at RT
3. Quenching to -8^{o}C

XRD



FTIR



It appears that the crystallinity formed at 180^{o}C can be reduced if followed by a slow annealing step.

Technical Accomplishments

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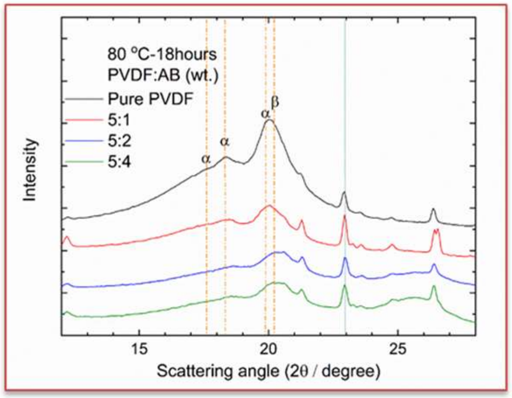
Effect of carbon black on crystalinity

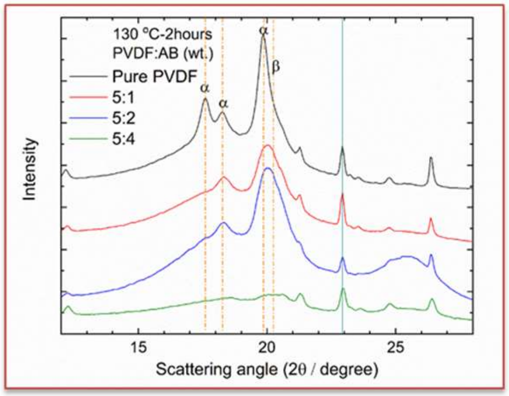
Films of 4 carbon black contents dried at three temperatures:

- Polymer:Carbon = 5:0, 5:1, 5:2, and 5:4

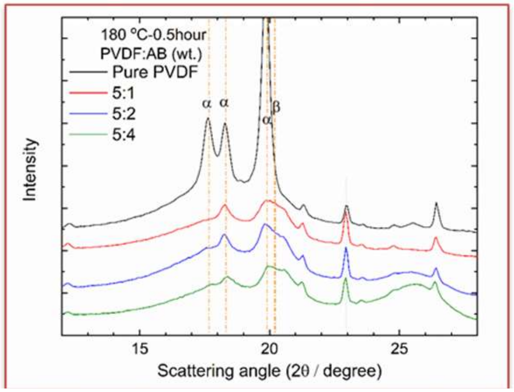
Dried at 80°C



Dried at 130°C



Dried at 180°C



The crystallinity is greatly reduced by all levels of carbon addition at all temperatures.

Technical Accomplishments

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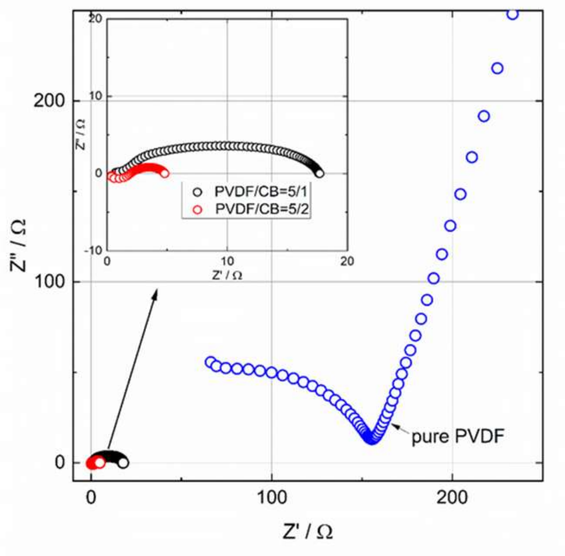
Consideration of lower carbon content

Up until now we have been using a binder to carbon ratio of 5:4, but we have found, especially when carbon is added directly to the polymer before the active material that a lot of carbon can lead to excessive agglomeration of carbon and binder which can reduce the rate of drying.

The previous results indicate that a small fraction of carbon can reduce the crystallinity, but can it provide conductivity?



This graph shows that the electronic conductivity of the polymer is greatly reduced even when the carbon is 1/6th the weight fraction, *i.e*. a lot of carbon is not needed in the polymer to make it conductive.

Technical Accomplishments

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Numeration of slurry preparation methods:

- In mixing, we need to intimately combine three components: active material, carbon black, and polymer binder.
  - We considered the following mixing sequences

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 carbon with 75% of binder; mix active material with remaining 25% of the binder; then mix the two together. (Hybrid: III + IV)

VI. Mix active material and fraction of the carbon together; mix the rest of the carbon with the solubilized binder, then mix those two solutions together (Hybrid Process: II + III).

Technical Accomplishments

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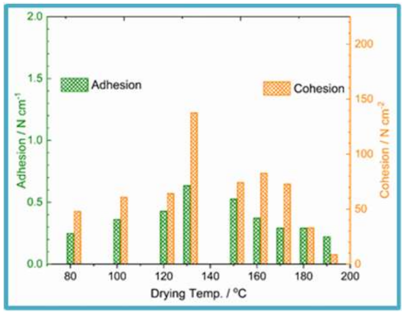
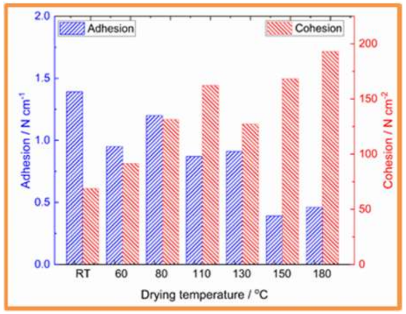
Mechnical properties of electrodes from 4 slurry processes

Results of Peel Tests, Pull Tests, and HPPC testing to Measure Adhesion, Cohesion, and Resistance *vs*. Drying Temperature

Process No. II



III



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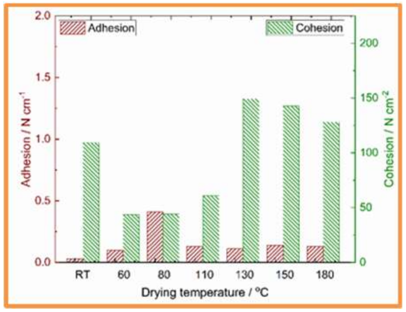
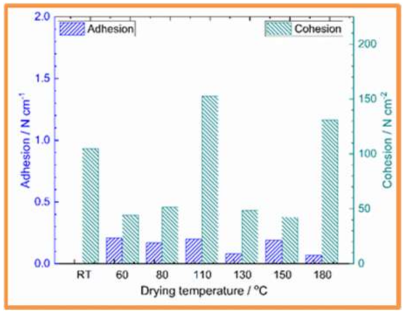


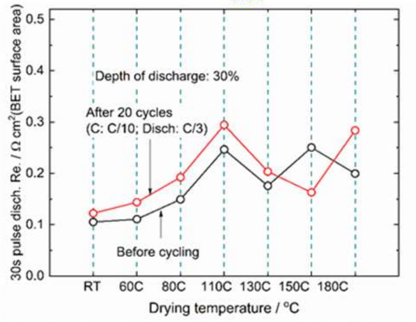
V



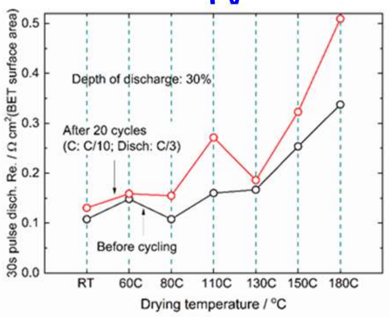
II

Data not yet collected

III



IV



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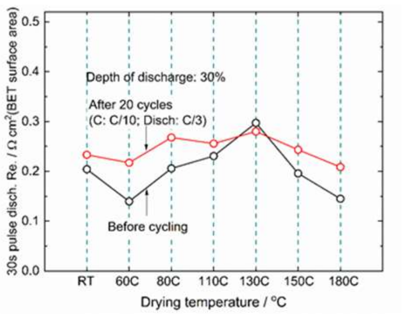

Technical Accomplishments

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Points of interest:

In general, we expect resistance to rise with drying temperature unless carbon can break up the crystallinity.

- Process II – Active material mixed with carbon:
  - Active material and carbon coated together with binder
  - Adhesion and cohesion rise to 130ºC and then fall together with drying temperature (cracking of material seen at 140ºC.)
  - Resistance rises with temperature to 130oC and then levels out
  - (No aging data for these cells)
- Process III – Carbon mixed with binder:
  - Adhesion and cohesion the best; adhesion declines with temperature, cohesion increases.
  - Carbon and binder promotes adhesion and cohesion.
  - Resistance rises with temperature to 130ºC and levels off.
  - The resistance is comparable after 20 cycles.
- Process IV – Active material mixed with binder:
  - The cohesion jumps up at 130ºC. Adhesion is generally poor.
  - Again, if binder is with active material, binding is poor.
  - The impedance is low and stable at low temperature but increases with high temperature and is much worse after 20 cycles. Coating of binder on active material leads to a resistice barrier.
- Process V – Active material with binder and carbon black with binder
  - The carbon has 10x more surface area than the active material but only 75% of the binder; this electrode should look more like Process IV.
  - Again, binder associated primarily with active material results in poor adhesion.
  - Resistance is somewhat independent of drying temperature up to 130ºC then begins to drop, similar to process IV. Mixing some carbon with the binder helps with the resistivity at high temperature drying.

Responses to Previous Year Reviewers' Comments

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…address 1-3 significant questions/criticisms/recommendations from the previous year's reviewers' comments…

No review found of poster presentation for 2019.

Collaboration and Coordination

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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 <u>expertise on cell manufacturing</u>.
LBNL	Colleagues provide capabilities in macroscopic modeling and characterization of laminates using the techniques at the ALS and NCEM.

Remaining Challenges and Barriers

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What we have learned:

- If industry is to move to thick electrodes, it needs to figure out how to dry them as fast as thin electrodes; this will require high temperature drying.
- Carbon black is added to electrodes to improve charge transfer kinetics at the active material interface and to provide electronic conductivity between particles.
- When dried at high temperatures, the binder crystallinity is such that ionic mobility is inhibited.
- The addition of high surface area carbon to binder appears to breakup the crystallinity of the binder
- Some polymer associated with the active material appears to improve adhesion.
- If a large fraction of the binder is associated with the active material, the electrode resistance is high and the maximum temperature before “mud cracking” during drying is low.
- If a large fraction of the binder is associated with the carbon, than the agglomeration of carbon and binder is excessive and the drying is prolonged.

The method of addition of carbon to the slurry greatly impacts drying conditions and electrode performance

Proposed Future Work

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Investigate hybrid mixing scenarios V *and* VI*.*

- For process V, we want to repeat this effort with a carbon surface area to active material surface area equivalent to the distribution of polymer between the two.
- For process VI, we want to test a distribution of carbon added to the active material such that the surface area is equivalent, with the rest mixed in a separate solution with binder.

Mixing speed.

- The fact that these electrodes made of the same fraction of materials but differ only by mixing order suggests that they are in a metastable state. We would like to determine at what mixing speed do the electrodes behave the same independent of mixing order.
  - Does this occur prior to breakdown of the polymer, active material, or carbon?
  - Does this mixing speed result in best overall performance or does one of the metastable mixing conditions lead to better overall performance?

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

Summary

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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 mixing order
- Use standard and advanced diagnostics to provide understanding between materials, processing, and electrode quality.

Major Technical Accomplishments

- Polymer crystallinity as a function of drying temperature
- Ionic conductivity as a function of drying temperature
- Effect of prolonged drying
- Effect of cooling conditions after drying conditions
- Impact of carbon content on crystallinity
- Impact of mixing order and temperature on electrode performance for 4 conditions.

Future Work

- Assess hybrid mixing conditions of electrode performance
- Investigate high mixing speeds of electrode performance