Roll-to-Roll Advanced Materials Manufacturing DOE Laboratory Consortium

Project period: 1/1/2016 – 12/31/2018

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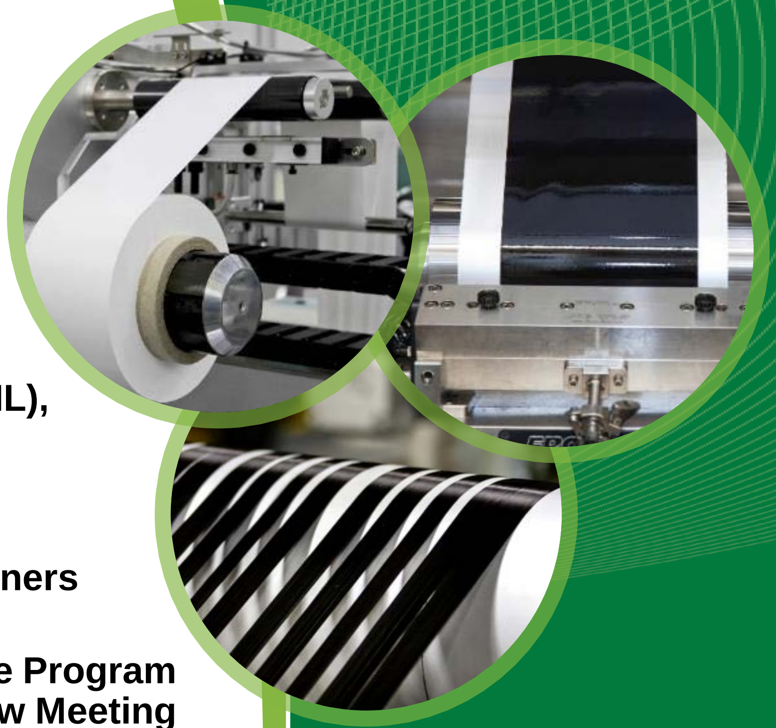


Co-Principal Investigators/Lab Leads:
R2R Core: Gregory Krumdick (ANL), David Wood (ORNL), Ravi Prasher (LBNL), Michael Ulsh (NREL)
Water: Yupo Lin (ANL)
Functional Materials: Venkat Srinivasan (ANL)
Industry partners: Matt Fronk (Kodak) and CRADA partners

U.S. DOE Advanced Manufacturing Office Program Review Meeting
Washington, D.C.
July 17-19, 2018

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

- **Timeline**
  - Project start date: January 2016
  - Projected end date:
    - Core lab work: December 2018
    - CRADAs: April 2019
  - Project completion
    - Core lab work: 80%
    - CRADA work: 10%
- **FY 18 Budget**
  - Core lab work: $2,278K
  - CRADA work: $1,150K plus $1,150K non-federal cost share
- **Barriers**
  - Continuous processing
  - Registration and alignment challenges
  - Materials compatibility
  - Stoichiometry control
  - Availability of materials data
- **Partners**
  - ORNL, ANL, LBNL, NREL
  - Kodak Eastman Business Park (EBP)
  - Navitas Systems
  - Fisker, Inc.
  - SolarWindow Technologies, Inc.
  - Proton OnSite

Project Objectives

- MYPP Target 8.1: Develop technologies to reduce the cost per manufactured throughput of continuous R2R manufacturing processes for selected products by 50% concurrent with a 10X production capacity increase compared to 2015 typical technology.
  - Doubling battery electrode thickness with no loss of power for lithium ion batteries
  - Eliminate need for multi-layered gas diffusion electrode assembly and enable a single coating step with comparable performance to catalyst coated membranes for fuel cells
- MYPP Target 8.2: Develop in-line instrumentation tools that will evaluate the quality of single and multi-layer materials in-process with respect to final product performance and functionality against performance specifications at a 100% level.
  - Developing in-line quality control technologies and methodologies for real-time identification of defects and expected product properties “in-use/application” during continuous processing
- Transfer technology through collaborative research and development agreements with industry.

Technical Innovation

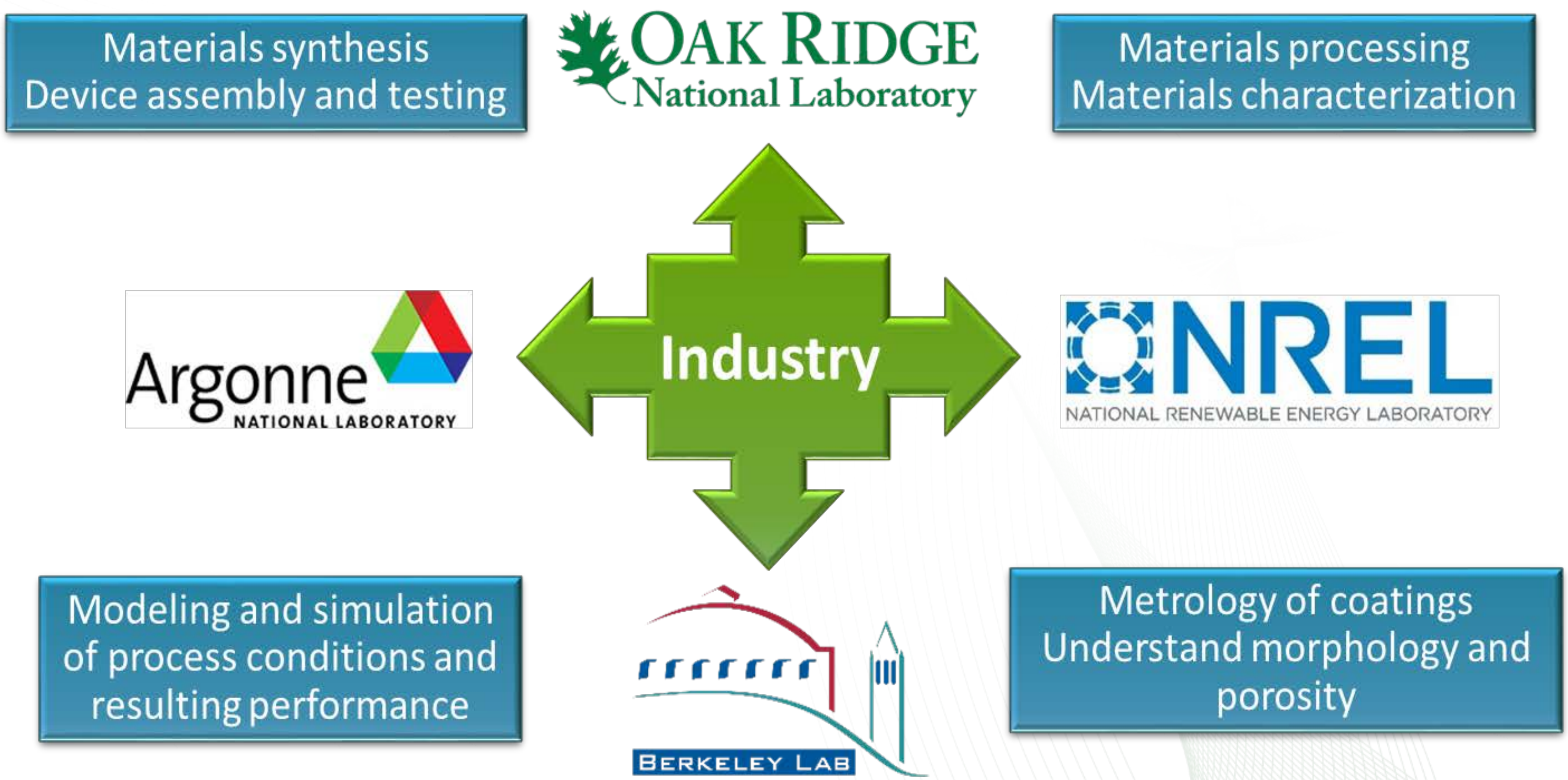
- Materials currently made using time-consuming, inefficient batch processes can be manufactured at significantly lower costs (as much as 80%) using a continuous roll-to-roll process.

- Successful energy-efficient, cost-effective production of novel technologies will be facilitated through a collaborative effort involving multiple DOE laboratories with unique capabilities and an industry partner with a pre-production roll-to-roll facility. Applications include:
  - solid-state batteries achieving targets of $80/kWh, 500 Wh/kg, and 10-min charging;
  - a LIB separator that could reduce LIB cost by 6-10%; and
  - advanced electrolysis electrodes for low-cost hydrogen production that could reduce the manufacturing labor for a membrane electrode assembly by a factor of 15-20 and the overall cost of the assembly by over 60%.

- Developing roll-to roll manufacturing capabilities that are energy efficient, have low environmental impact, ultra-low cost and are employed to manufacture technologies for energy saving applications will have a “global impact”.

Project / Technical Approach

A collaboration of 4 DOE labs and industry partners that addresses challenges in material synthesis, materials processing, material properties and metrology using modeling and simulation of fabrication processes and product performance to facilitate production with a continuous roll-to-roll manufacturing process

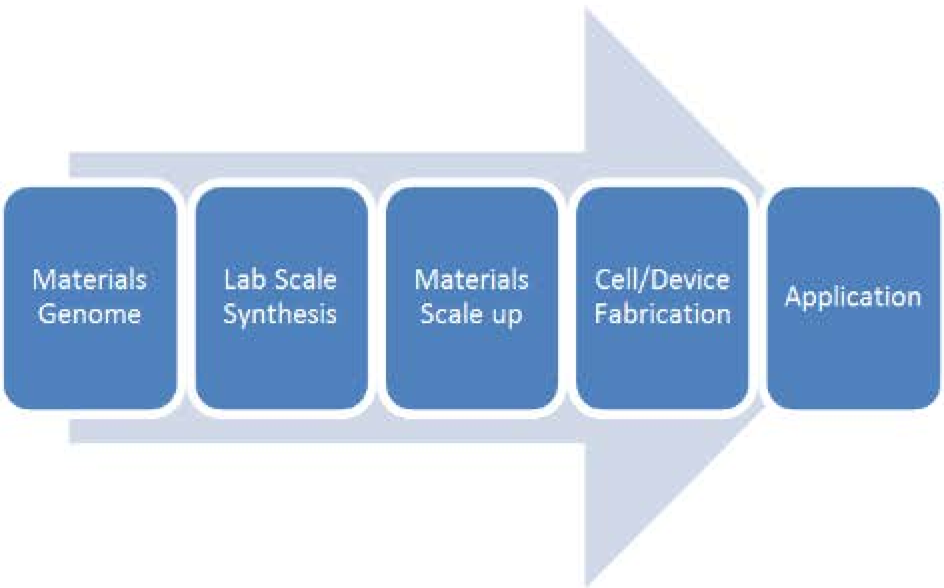


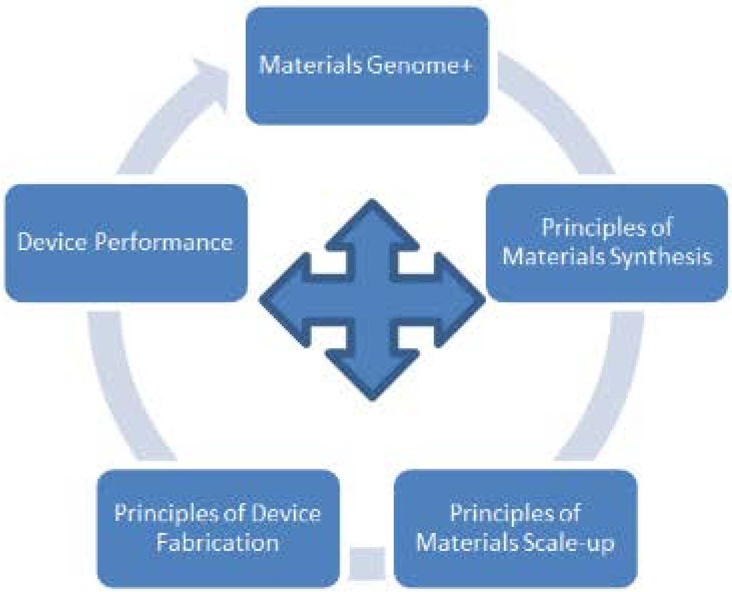
Lab-industry partnership started with ORNL-Kodak MOU and is spanning the network to assist commercialization

EASTMAN BUSINESS PARK – FROM POC TO COMMERCIAL SCALE

- Extensive suite of tools to assist small companies
- Key set of development apparatus to conduct early and mid-stage pilot work.
- Technical resources in IP friendly manner
- Scale-up through full manufacturing

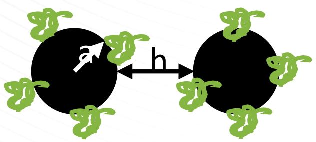
4-lab consortium changes linear approach to AMM-type approach for process development



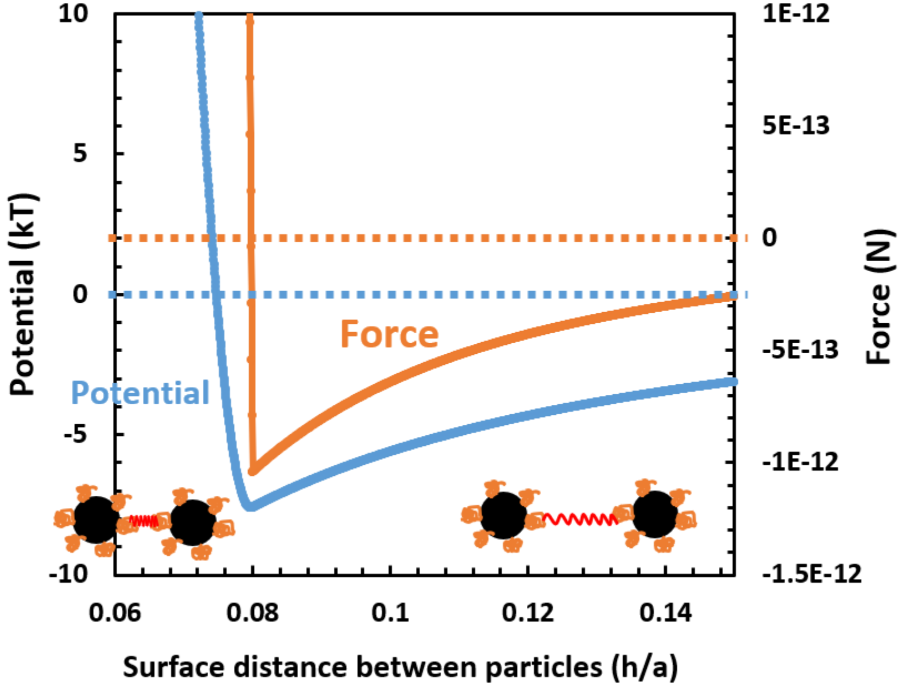


Viscoelastic model of anode slurry

Colloidal Interactions



- Van der Waals
- Double layer
- Polymer steric
- Depletion

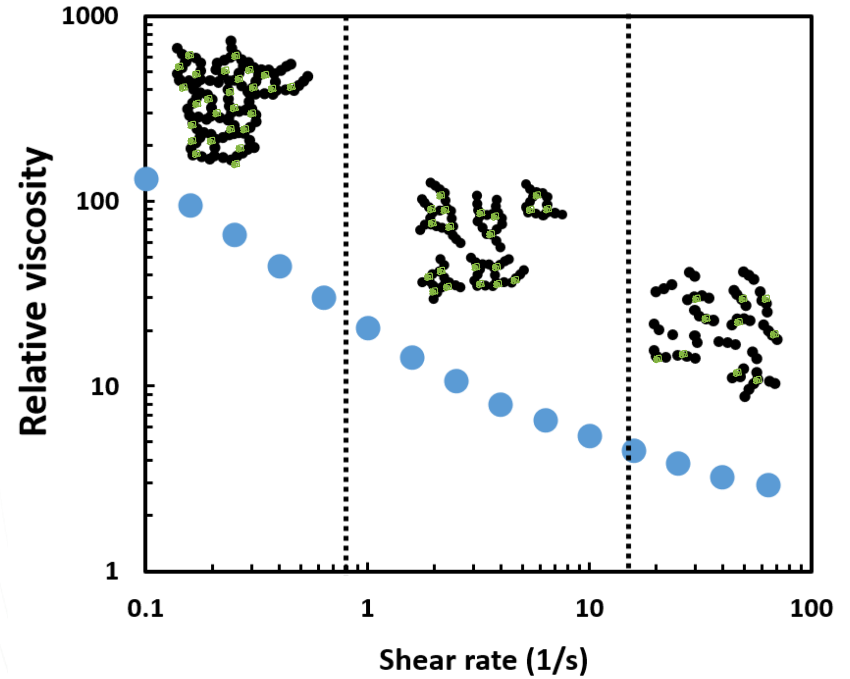


Rheology

$$\eta_{total} = \eta_{struct} + \eta_{hydr}$$

structural | hydrodynamic

1.2% carbon black slurry



Functional Materials: Understanding Material Synthesis

Achievement

- Demonstrated the first-known studies for tracking, *in situ*, particle growth during synthesis.
- Developed the first known model that links process conditions to growth morphology.

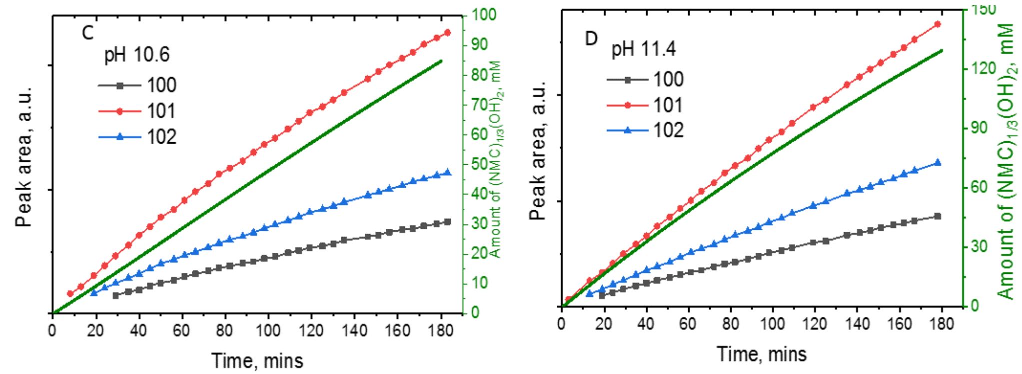
Significance and impact

Control over morphology during particle synthesis rooted in empirical trial-and-error. This project has demonstrated that a science-based approach can be developed to predict the morphology of the particle when changing process conditions. By developing *in situ* synchrotron-based methods to “watch” growth and combining them with growth models, this project brings science to empiricism and accelerates the time to develop new process conditions.

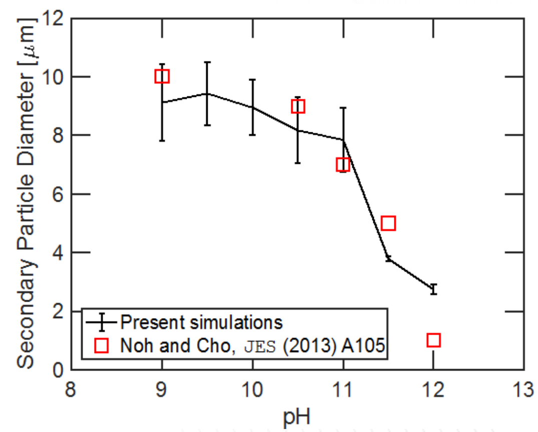
Details and next steps

– Compare the experimental growth dynamics to the mathematical model

– While the present effort is on co-precipitation, the model will be expanded to describe calcination of particles.



In situ Wide Angle x-ray scattering (APS) to track growth morphology

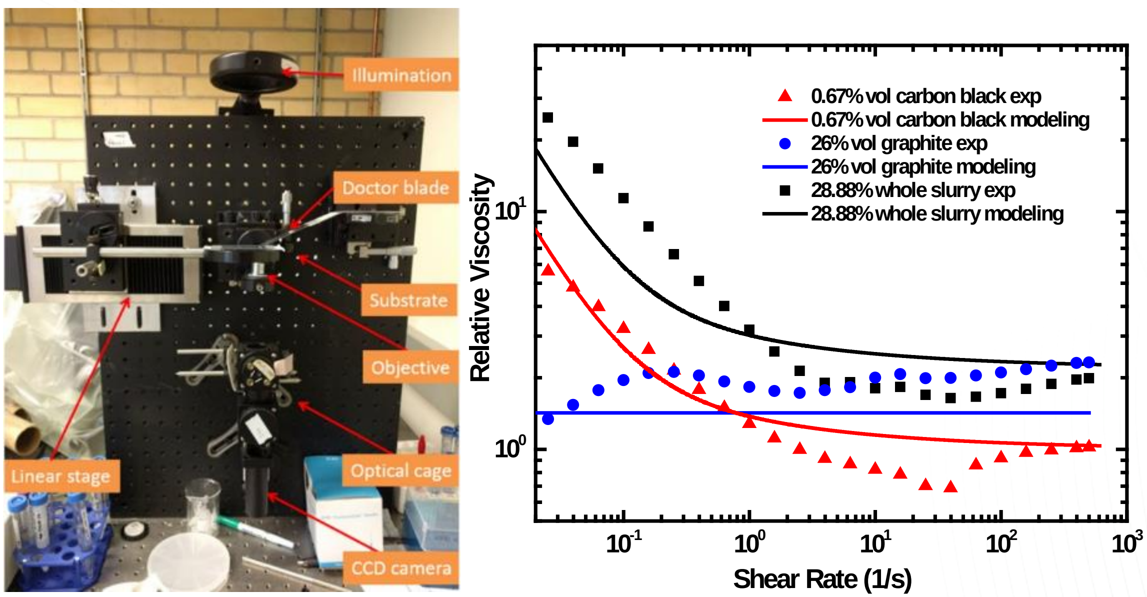


Growth model showing excellent prediction of size with process conditions

Fundamental Understanding of Anode Fabrication from Colloid Science

Achievement

- A better understanding of the anode coating process was obtained using a in-situ optical microscopy.
- The rheological properties of anode slurry were well predicted by a viscoelastic model based on inter-particle colloidal interactions.



Anode slurry coating, in-situ visualization, and rheology modeling

Significance and impact

The viscoelastic model successfully related the colloidal interactions between graphite, carbon black, and polymer binders to the rheological properties of anode slurry. It revealed the importance of correlated networks of carbon black to the stability of the slurry. This rheological model provides a powerful method to formulate anode slurry in a cost-effective and scientific way.

Details and next steps

- Continue the rheological modeling of anode slurries during the drying process.
- Extend the rheological model to account the effect of mixing sequence on rheology of anode slurry.
- Summarize the rheology modeling data and submit a manuscript to *Journal of the Electrochemical Society.*
- Build in-situ equipment to investigate the dynamic processes of mixing and drying.

Structured Lithium-Ion Battery (LIB) Electrodes Boost High-Rate Discharge Capacity

Achievement

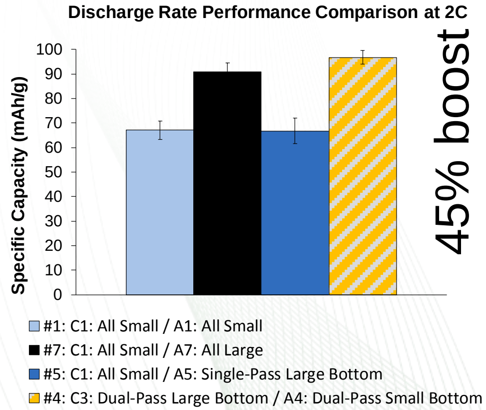
AMO R2R AMM DOE Lab Consortium achieves significant rate capacity, power density, and energy density improvement when structuring ***both*** the LIB anode and cathode.

Significance and impact

When a simple particle-size modification was made and combined with a thick (4 mAh/cm2) bilayer approach, with an emphasis on materials processing and coating deposition methodology (dual slot-die and dual-pass), substantial improvements were realized in rated capacity at 2C discharge rates. This technology enables simultaneous high energy and power density.

Details and next steps

- Finish discharge rate performance and capacity fade testing (high/low rates).
- Data will be summarized and submitted for publication in Advanced Energy Materials.
- Follow-up paper is planned in 2018 on long-term-cycling results for submission to JPS.
- Leverage findings with VTO XFC and advanced electrode architecture projects.



"C1/A1" = Cathode/Anode Baseline Structure

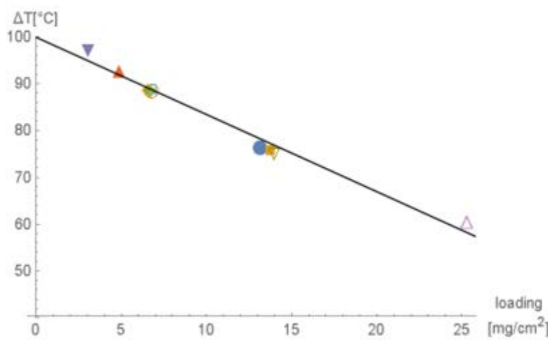
In-line Porosity Measurement for Battery Electrodes

Achievement

NREL and ORNL jointly developed and demonstrated a real-time in-line measurement for battery electrode porosity

Significance and impact

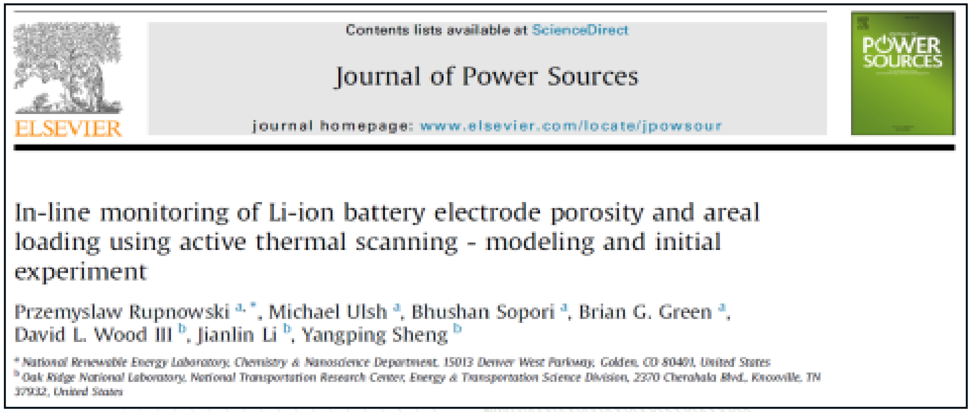
Technique enables critical quality inspection for high performance battery electrode manufacturing. Created and validated transient heat transfer model of electrode layer linking porosity with thermal measurement. Validated measurement on cathodes coated on ORNL R2R coating line.



Correlation of thermal model and measured thermal responses to actual loading of coated electrodes; measurement setup on web-line

Details and next steps

- Published joint (NREL-ORNL) publication in Journal of Power Sources.
- Submitted joint patent application ("Batch and Continuous Methods for Evaluating the Physical and Thermal Properties of Thin Films," U.S. Patent Application 15/554,551).
- Second paper being drafted.



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POWER SOURCES

In-line monitoring of Li-ion battery electrode porosity and areal loading using active thermal scanning - modeling and initial experiment

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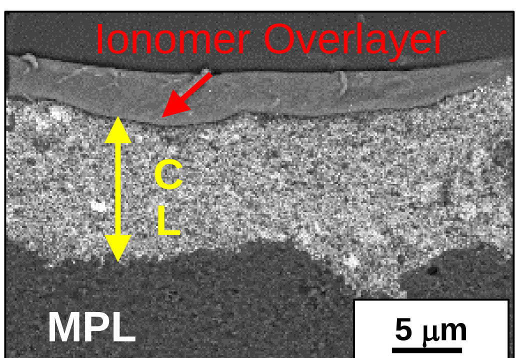
Kodak Argonne NATIONAL LABORATORY BERKELEY LAB NREL NATIONAL RENEWABLE ENERGY LABORATORY OAK RIDGE National Laboratory | NATIONAL TRANSPORTATION RESEARCH CENTER | MANUFACTURING DEMONSTRATION FACILITY

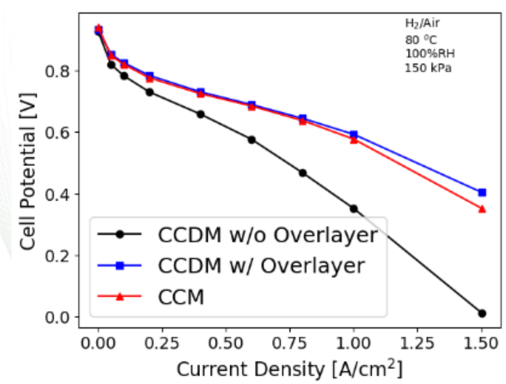
Technical Approach: Fuel Cell Core Lab Project

- Current standard manufacturing practice for most PEM MEAs is by fabricating catalyst-coated membranes (CCM)
  - The electrodes are coated onto separate transfer liners and then hot-pressed onto the membrane, or
  - The electrodes are directly coated onto the membrane
- Limits to CCM production
  - The former method entails multiple additional steps and materials, due to the use of a transfer liner
  - The latter is very difficult due to swelling of the membrane during solvent- or aqueous-coating of the electrodes
- Gas diffusion electrodes (GDE) are recently becoming of more interest in the industry as a pathway for MEAs
  - The different structure of GDEs may provide improved performance and lifetime under some operating conditions
  - GDEs may also be easier to fabricate
  - Deposition onto the low-strength, highly liquid sensitive (hygroscopic) membrane is eliminated
  - Use of transfer liners is eliminated
- However, it appears that an over-layer of ionomer is required for GDEs to achieve performance comparable to CCMs
- The goal of this project is to explore, understand and optimize material and process parameters for single-process (no extra ionomer over-layer) R2R manufacturing of GDEs with comparable performance to CCMs



TEM of spray-coated GDE with ionomer over-layer

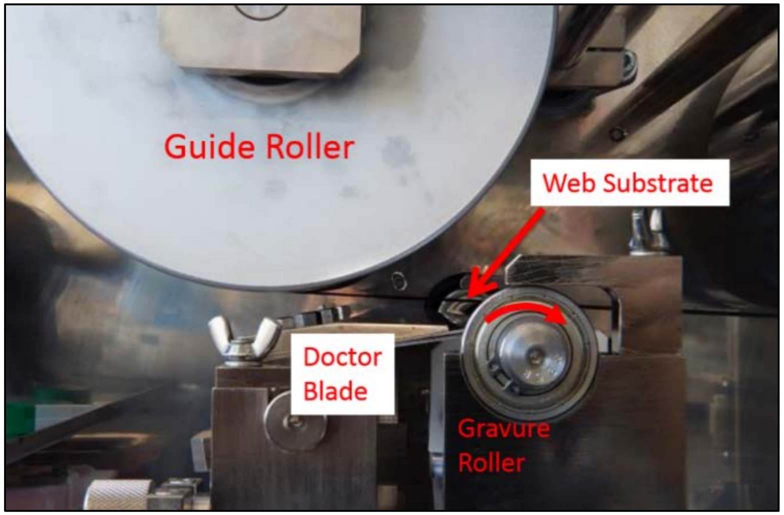
Performance comparison between lab-scale spray-coated CCM baseline and GDEs with and without over-layer

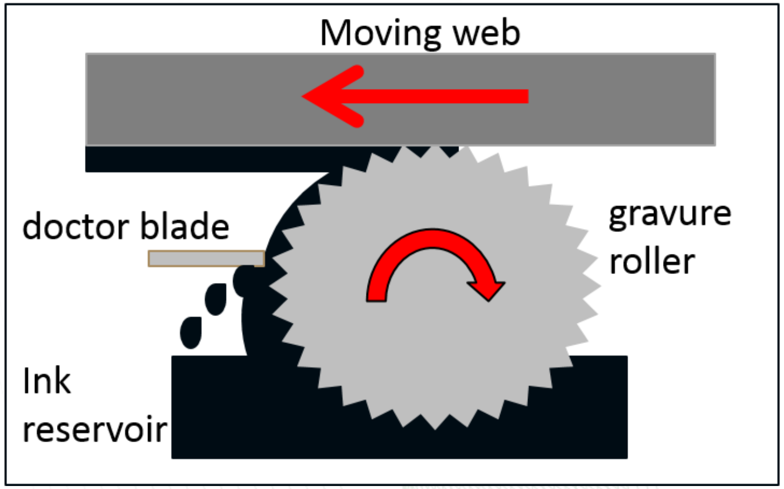


Results and Accomplishments

R2R Coating of Ionomer Gradient Electrodes

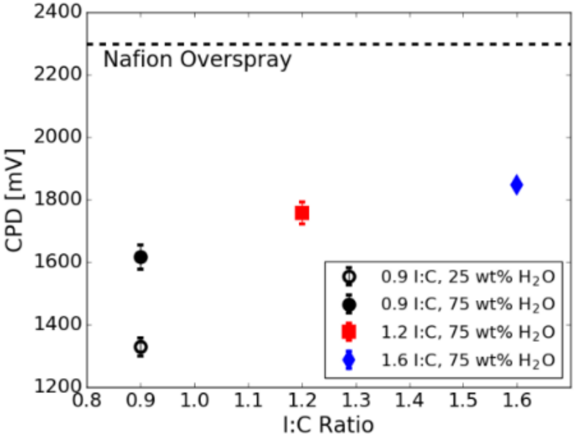
- Down-selection from rod-coating screening experiment to demonstrate successful R2R coating
- Inks – Coated 2 m each
  - 0.9 I:C, 25 wt% H_2O
  - 0.9 I:C, 75 wt% H_2O
  - 1.2 I:C, 75 wt% H_2O
  - 1.6 I:C, 75 wt% H_2O
- Solvents: water and 1-propanol
- Catalyst: 50 wt% Pt/HSC
  - Loading: 0.1 ± 0.1 for all coatings
- Ionomer: Nafion 1000 EW
- Substrate: SGL 29BC
- Oven Temp: 80 ˚C
- Web Speed: 1 m/min

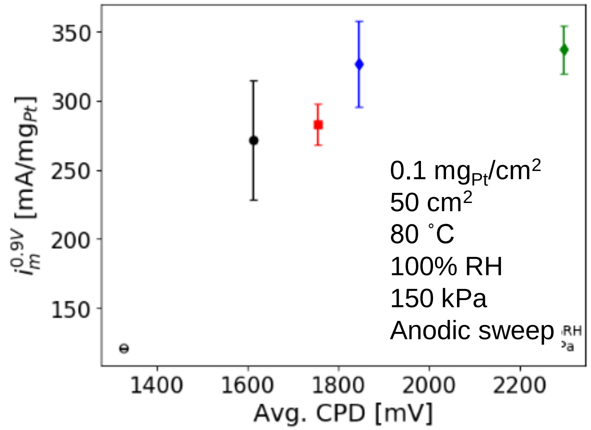


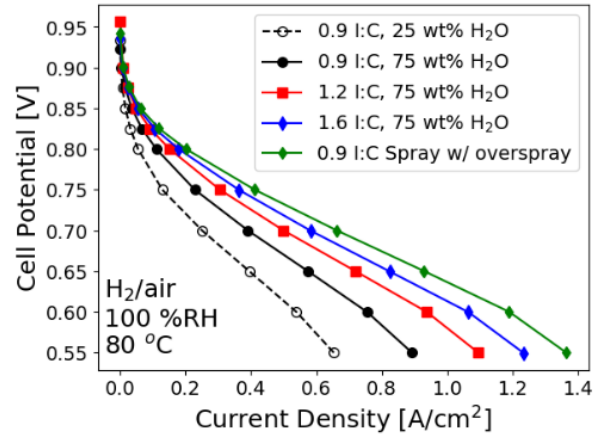


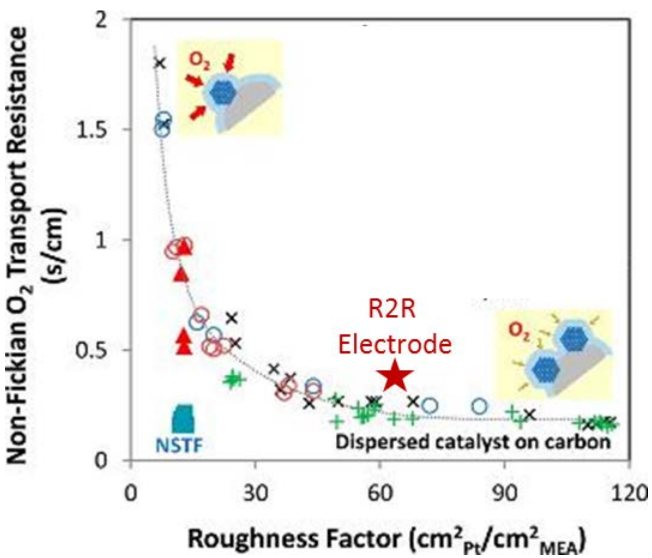
Results and Accomplishments

R2R Electrodes Achieved Equivalent Mass Activity to Spray-Coated Electrodes









Published in: Anusorn Kongkanand; Mark F. Mathias; *J. Phys. Chem. Lett.* **2016,** 7, 1127-1137.

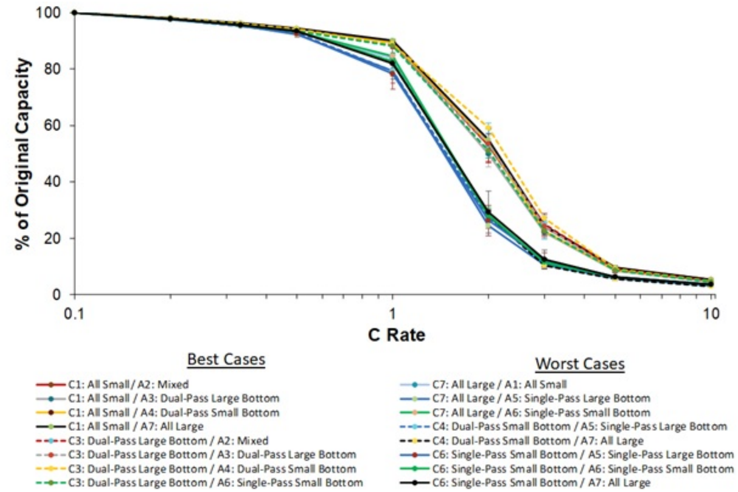
- Confirmed that R2R electrodes show the same trends as Mayer-rod electrodes
- Demonstrated R2R electrodes without ionomer overlayer produce equivalent mass activity to spray-coated electrodes with ionomer overlayer
- Utilized O_2 limiting current measurements to show oxygen mass transport can be further optimized

Transition: Information dissemination (FY17-18)

- Two extensive public annual reports on OSTI
- Daniel, C. D. “Roll-to-Roll Advanced Materials Manufacturing Lab Consortium Project ID: MN018.” 2017. Presented at the U.S. Department of Energy's (DOE's) 2017 Annual Merit Review and Peer Evaluation Meeting for the Hydrogen and Fuel Cells Program and the Vehicle Technologies Office, Washington, DC (June) https://www.hydrogen.energy.gov/annual_review17_manufacturing.html
- Daniel, C. D. “Roll-to-Roll Advanced Materials Manufacturing Lab Consortium Project Period: FY 2016/17.” 2017. Presented at the Advanced Manufacturing Office Peer Review, Arlington, VA (June) https://energy.gov/eere/amo/downloads/amo-2017-technical-resources-forum-presentations
- Daniel, C. D.; Wood, D.; Ulsh, M; Krumdick, G.; Prasher, R. “AMO Roll-to-roll Advanced Materials Manufacturing Laboratory Consortium.” 2017. Presented at the TechConnect World Innovation Conference & Expo (May). http://www.techconnectworld.com/World2017/sym/Advanced_Manufacturing_Innovation.html
- Du, Z.; Rollag, K.M.; Li, J.; An, S.J.; Wood, D.L. 2017. “Enabling aqueous processing for crack-free thick electrodes”. *Journal of Power Sources*, 354, (June): 200-206
- Higa, K.; Zhao, H.; Parkinson, D.; Barnard, H.; Ling, M.; Liu, G.; Srinivasan, V. “Electrode Slurry Particle Density Mapping Using X-ray Radiography.” 2017. Journal of the Electrochemical Society, 164(2), A380-A388.
- Khandavalli, S.; Mauger, S.; Stickel, J. J.; Hurst, K.; Neyerlin, K. C.; Ulsh, M. 2017. “Rheological properties and interparticle interactions of fuel cell catalyst dispersions,” poster presentation at the Society of Rheology Meeting; Denver, CO (October).
- Krumdick, G.; Dunlop, A.; Trask, S.; Polzin, B.; Jansen, A.; Wood, D.; Wood, M.; Li, J.; Daniel, C.; Ulsh, M.; Rupnowski, P.; Prasher, R.; Ma, F. 2017. “Structured Cathodes and Anodes for High-Energy and High-Power Lithium-Ion Batteries (LIBs).” poster presentation at the Advanced Manufacturing Office Peer Review; Arlington, VA (June).
- Ma, F; Battaglia, V.; Prasher, R. “Viscoelastic Modeling of Anode Slurry.” 2018. *Journal of the Electrochemical Society,* (forthcoming).
- Mauger, S.; Khandavalli, S.; Neyerlin, K.C.; Stickel, J.; Hurst, K.; Ulsh, M. 2017. “Rheological characterization of interparticle interactions in fuel cell catalyst dispersions,” oral presentation IO1A-1382 at the Fall Electrochemical Society Meeting; National Harbor, MD; (October).
- Mauger, S.; Neyerlin, K.C.; Yang-Neyerlin, A.C.; Bender, G.; Ulsh, M.; Green, B.; More, K. 2017. “Material-process-performance relationships for roll-to-roll coated fuel cell electrodes,” oral presentation IO1B-1441 at the Fall Electrochemical Society Meeting; National Harbor, MD (October).
- ORNL Invention Disclosure 201303063, “Transformational Thick Cathode having Hierarchical Pore Structure”
- Rupnowski, P.; Ulsh, M.; Sopori, B.; Green, B.; Wood III, DL.; Li, J.; Sheng, Y. 2017. “In-line monitoring of Li-ion battery electrode porosity and areal loading using active thermal scanning – modeling and initial experiment.” *Journal of Power Sources*, in press: 11 pages https://doi.org/10.1016/j.jpowsour.2017.07.084
- Seong Jin An, Jianlin Li, and David L. Wood. 2017. Addendum to “Fast formation cycling for lithium ion batteries” [*J. Power Sources* 342 (2017) 846–852], *Journal of Power Sources*, 350, (May), Page 152
- Sopori, B.; Ulsh, M.; Rupnowski, P.; Bender, G.; Penev, M.; Li, J.; Daniel, C.; Wood III, D.L. “Batch and Continuous Methods for Evaluating the Physical and Thermal Properties of Films.” Filed March 8th, 2016, U.S. Patent Application No. 16/051,314 (Alliance for Sustainable Energy, LLC).
- Ulsh, M.; Mauger, S.; Neyerlin, K.C. 2017. “Material-process-performance relationships for roll-to-roll coated PEM electrodes,” poster presentation at the Hydrogen and Fuel Cells/Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Washington, DC (June).
- Ulsh, M.; Mauger, S.; Neyerlin, K. C.; Wood, D.; Li, J.; Wood, M.; More, K.; Myers, D.; Kariuki, N.; Park, J.; Cetinbas, C. F.; Ahluwalia, R.; Krumdick, G.; Weber, A.; Ma, F.; Prasher, R. 2017. “PEM Fuel Cell Gas-diffusion Electrodes with Ionomer-rich Surface Layer.” poster presentation at the Advanced Manufacturing Office Peer Review; Arlington, VA (June).
- Ulsh, M. “DOE Advanced Materials Manufacturing/Roll-To-Roll Consortium.” 2017. Presented at the AIMCAL R2R Conference (October). http://www.aimcal.org/
- Wood, M.; Li, J.; David L. Wood, D.L.; Daniel, C.; Krumdick, G.; Jansen, A.; Polzin, B. “Evaluation of Thick Graded-Porosity Cathode Architectures as a Means of Improving Energy Density and Battery Performance”. Submitted to the *Journal of Power Sources,* forthcoming

Transition (beyond DOE assistance)

Results of experimentation and computational modeling will be made available to commercial and industrial organizations through open sources.



Experimental data and computational models will be shared with the Kodak EBP R2R Pre-Production Facility, as requested, for use with any customers with similar technologies.

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CRADA Projects

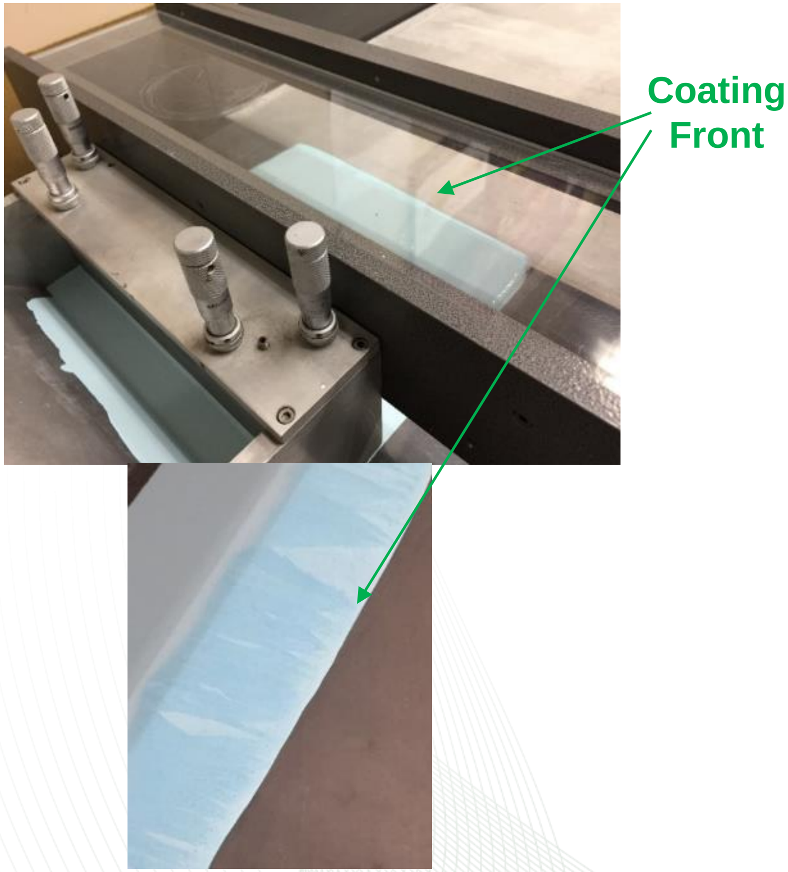
Fisker/LBNL/ORNL: Three-Party CRADA Begins to Demonstrate All-Solid-State LIB Processing

Achievement

Within the framework of the AMO R2R AMM Consortium, Fisker, Inc. has partnered with LBNL and ORNL to demonstrate all-solid-state batteries based on LLZO separators and cathode scaffolds, and scaled the freeze casting process to the pilot level at ORNL.

Significance and impact

The freeze casting process will be used to enable the high-volume manufacturing of all-solid-state LIBs based on the LLZO electrolyte. These types of LIBs utilize ultra-high-energy-density Li metal anodes, low-cost solid electrolytes, and high-voltage composite cathodes. High-speed scaling of this methodology will assist in achieving the DOE ultimate targets of $80/kWh, 500 Wh/kg, and 10-min charging.



Details and next steps

- Signing of CRADA was January 5, 2018.
- Feasibility of pilot-scale freeze-casting coating line was completed March 14, 2018 at Montana State Univ. (see figures at right).
- Initial recommendations have been provided to Fisker on how the freeze casting process could be industrially scaled.

Navitas/ORNL/NREL: Three-Party CRADA Begins to Demonstrate R2R Production of Advanced Separator and Lithium Ion Batteries

Achievement

Within the framework of the AMO R2R AMM Consortium, Navitas Systems, Inc. has partnered with ORNL and NREL to demonstrate R2R production of advanced separator for lithium ion batteries.

Significance and impact

A R2R method will be developed to fabricate the separator, which replaces the conventional discrete operations and enables superior safety, high throughput and low manufacturing cost. According to BatPac, the separator accounts for 6-10% of LIB cost. The cost benefits from this CRADA would boost EV market share. A 10% increase in electrified powertrains will reduce U.S. oil consumption by 3%, total U.S. energy use by 1%, and total US CO_2 emissions by 1%.

Details and next steps

– Signing of CRADA was December 22, 2017.

– First teleconference took place on April 11 with progress updates from Navitas. Navitas has down-selected the separator for the CRADA. Navitas has also started some trial operations handling the separator in a R2R manner at their product site.

– A site visit to Navitas occurred on May 10 to allow ORNL and NREL to see the actual operation and discuss project plan.

SolarWindow Technologies/NREL/ANL: Three-Party CRADA Begins to Demonstrate Diffractive Multiplexing for High-Throughput Roll-to-Roll Laser Patterning of Flexible Organic Photovoltaic Modules

Achievement

Within the framework of the AMO R2R AMM Consortium, SolarWindow technologies inc. has partnered with NREL and ANL to demonstrate diffractive multiplexing for high-throughput R2R laser patterning of flexible organic photovoltaic modules

Significance and impact

Multiplexing for R2R laser scribing based on a diffractive optical element will be developed to:

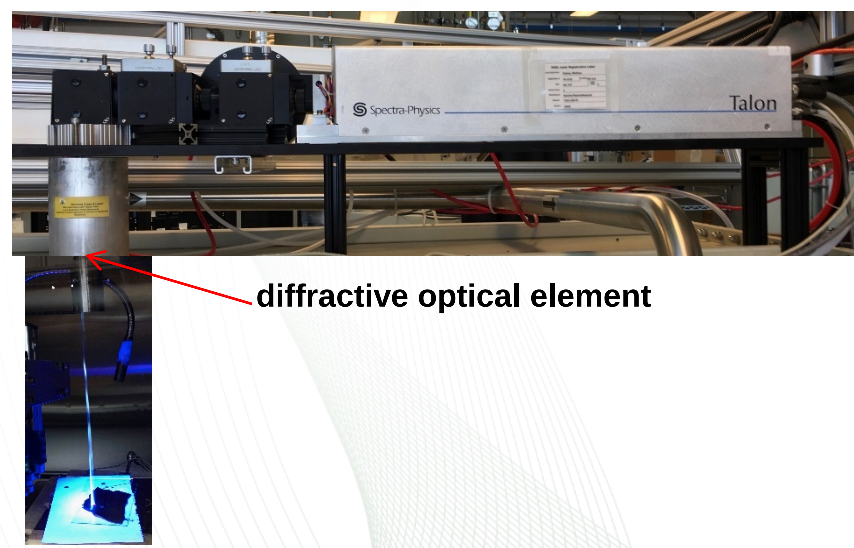
1) Drastically reduce up-front capital and on-going operational costs vs. many-laser/optics systems, and
2) Dramatically increase process speeds over galvanometer step-and-scan systems

Details and next steps

– Signing of CRADA was March 13, 2018.

– SolarWindow Technologies has an employee at the NREL site and discussions to modify NREL's R2R metrology line to demonstrate the technology have been started. Demonstration will occur at a 300-mm web width with 25+ scribes simultaneously. In order to create appropriate materials the project will also use NREL's R2R coating line and NREL/ANL metrology capability to analyze the scribe quality.

– First optics for testing have arrived at NREL.



Proton OnSite/NREL/ORNL/ANL: Four-Party CRADA Begins to Research R2R Manufacturing of Electrolysis Electrodes

Achievement

Within the framework of the AMO R2R AMM Consortium, Proton OnSite has partnered with NREL, ORNL, and ANL to research R2R manufacturing of advanced (low loading and directly coated onto membrane) electrolysis electrodes for low-cost hydrogen production.

Significance and impact

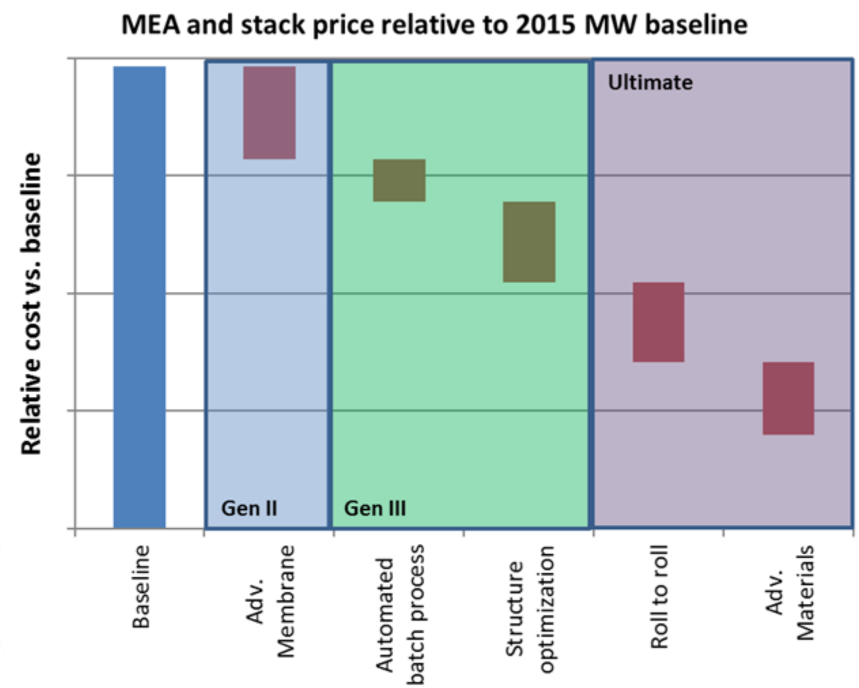
Ink characterization and optimization, R2R coating, advanced electrode characterization, and metrology development capabilities of the Consortium will be brought to bear. Overall goals of this development effort are to reduce the manufacturing labor for the membrane electrode assembly (MEA) by a factor of 15-20 and the overall cost of the MEA by over 60%. A secondary goal is to enable integration of thinner membranes due to the improved uniformity in electrode thickness.

Details and next steps

– Currently finalizing multi-lab statement of work.

– Final work plan to be approved by AMO & FCTO.

– CRADA to be approved and executed.



Proton MEA cost waterfall chart

Questions?

Acknowledgments

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