

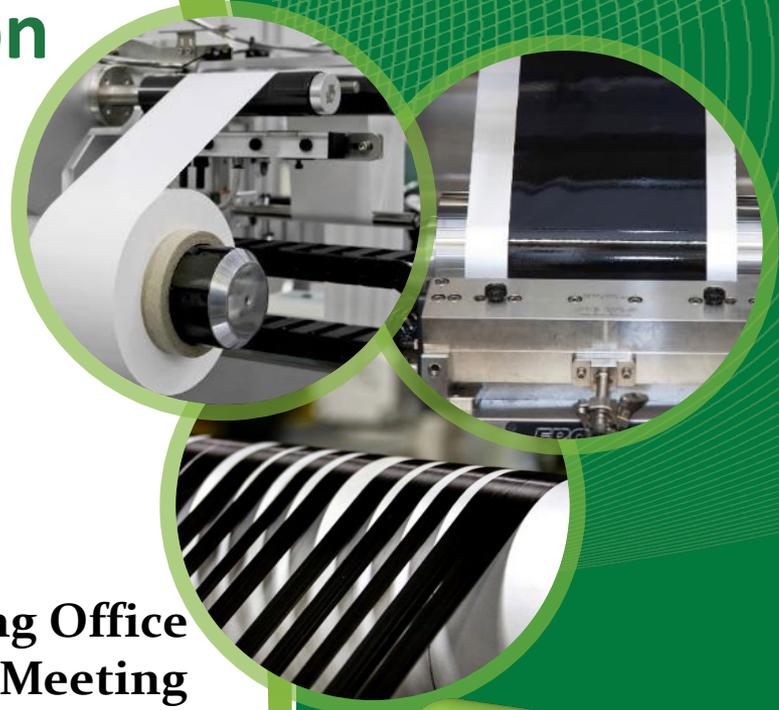
Roll-to-Roll Advanced Materials Manufacturing (R2R AMM) DOE Laboratory Collaboration

Claus Daniel, Collaboration Lead, Presenter

Co-Principal Investigators/Lab Leads:

David Wood (ORNL), Gregory Krumdick (ANL),
Michael Ulsh (NREL), Vince Battaglia (LBNL),
Randy Schunk (SNL)

U.S. DOE Advanced Manufacturing Office
2019 Annual Peer Review Meeting
Arlington, VA
June 12, 2019



For more
details see
posters in
Tuesday poster
session:
6, 20, 21



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Overview

Timeline

- Project start date: October 2019
- Projected end date:
 - Core Projects: September 2021
 - CRADAs: October 2019*
- Project completion for FY19
 - Core Projects: 30%
 - CRADA Projects: ~80%

FY 19 Budget

- Core lab work: \$3,000K per year
- 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

* AMO MYPP for FY 2017-2021, June 2017 draft, section 3.1.8

Partners

- ORNL, ANL, NREL, LBNL, SNL
- Navitas Systems
- Fisker, Inc.
- SolarWindow Technologies, Inc.
- Proton OnSite*

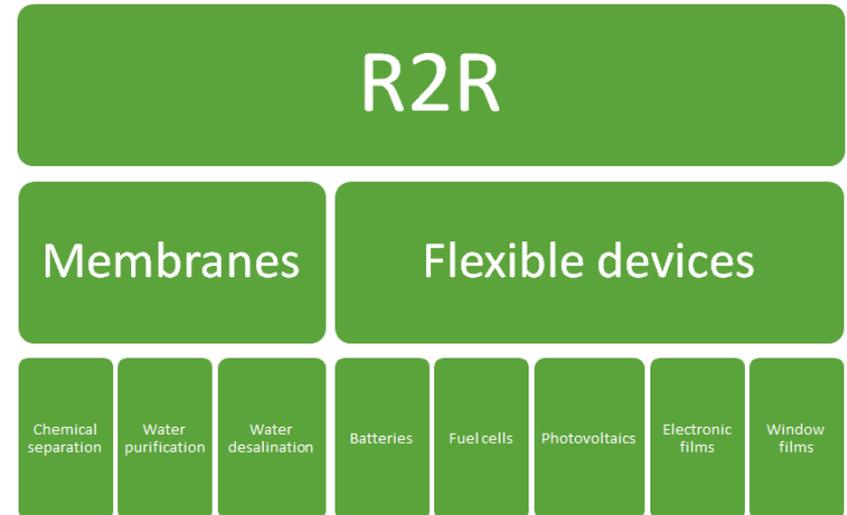
* Pending contract award

Project Objectives

- AMO 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.
 - Develop in-line multilayer coating technology with yields greater than 95% for a wide-range of applications.
 - Technological focus areas are the process science on multi-layered coating deposition and drying/curing, its associated fundamental kinetics, modeling and simulation, and metrology to understand quality and defects.
- AMO 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.
 - Develop in-line quality control technologies and methodologies for real-time identification of defects and expected product properties “in-use/application” during continuous processing.
- Complete the technology transfer of continuing collaborative research and development agreements (CRADAs) with industry.

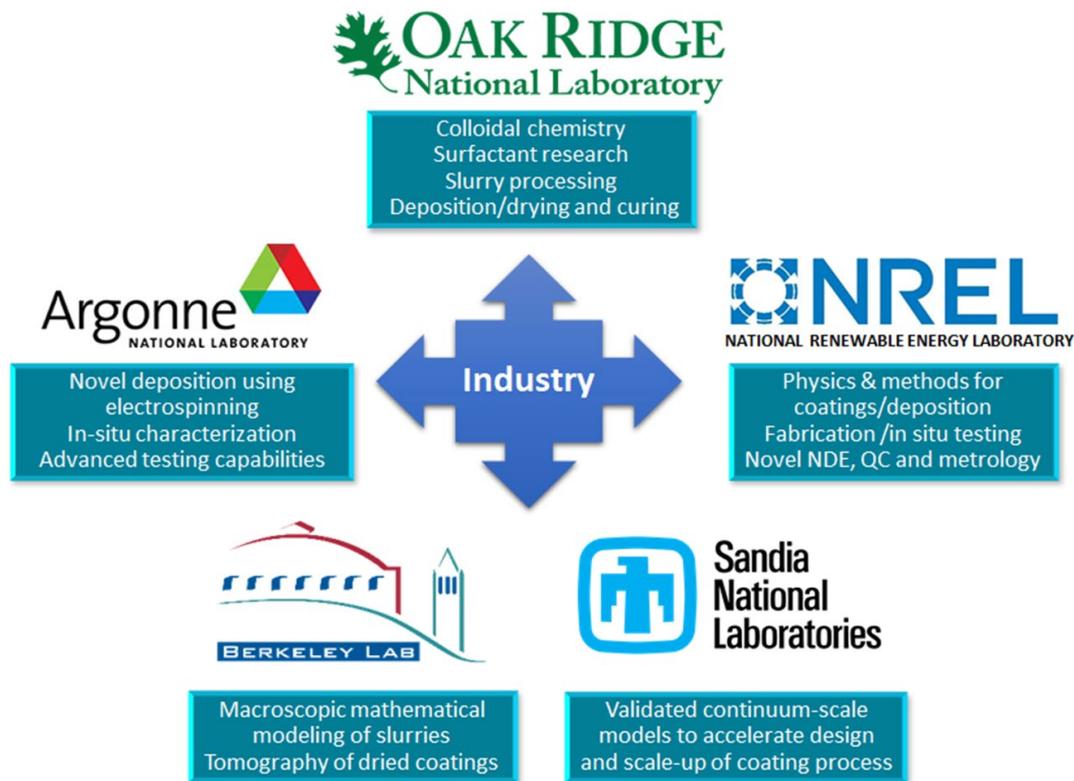
Technical Innovation

- 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. Applications are:
 - functional coatings
 - filtration applications
 - flow batteries for grid applications
 - fuel cell membranes
 - platinum group metal-free catalysts
 - electrodes for electrochemical CO₂ reduction concepts
 - water filtration and purification
- 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”.

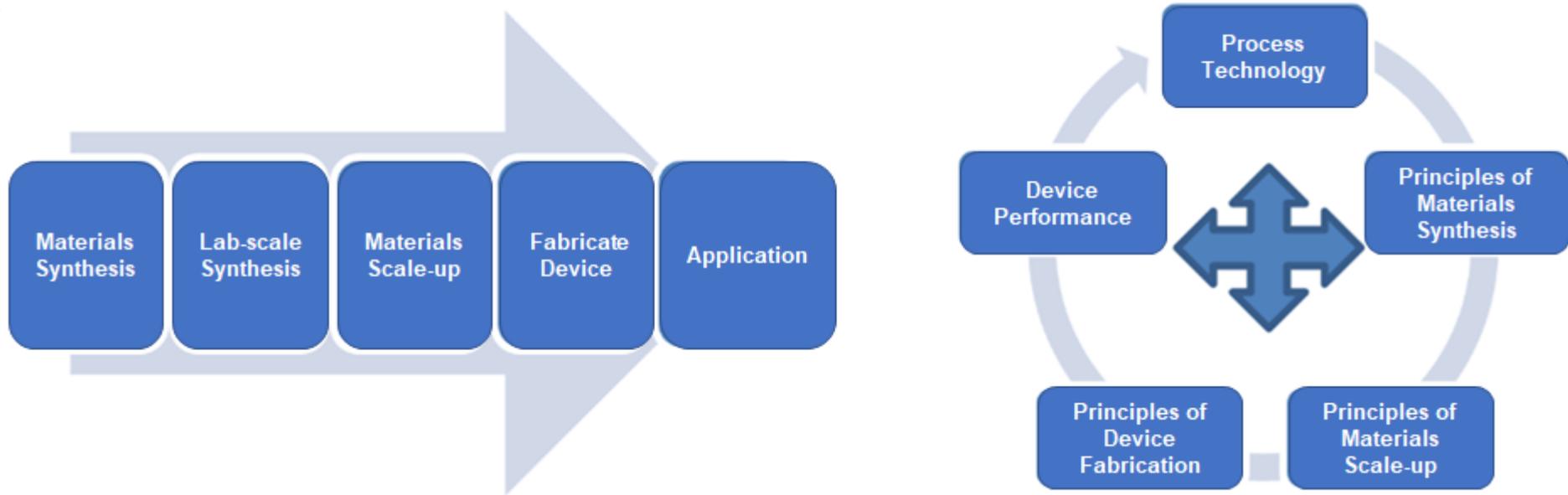


Project / Technical Approach

A collaboration of five DOE labs and industry partners that address challenges in colloidal chemistry, slurry processing, novel deposition, *in situ* characterization and testing, physics and methods of coatings, novel NDE-QC-metrology techniques, macroscopic mathematical modeling of slurries, tomography of coatings, and continuum-scale models to accelerated the design and scale-up of coating processes for continuous roll-to-roll manufacturing

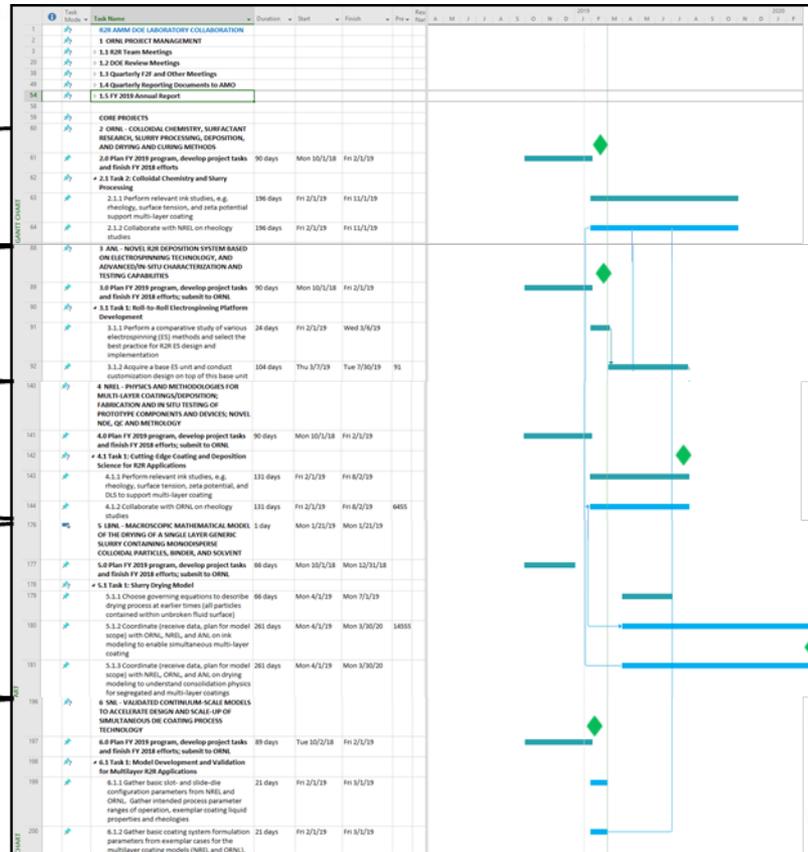


Change from a Linear Approach to An Advanced Materials Manufacturing Approach



Project Tasks and Milestones

- Bi-weekly team meetings are held to review progress on each task.
- DOE Technical Managers attend every other team meeting to receive updates.

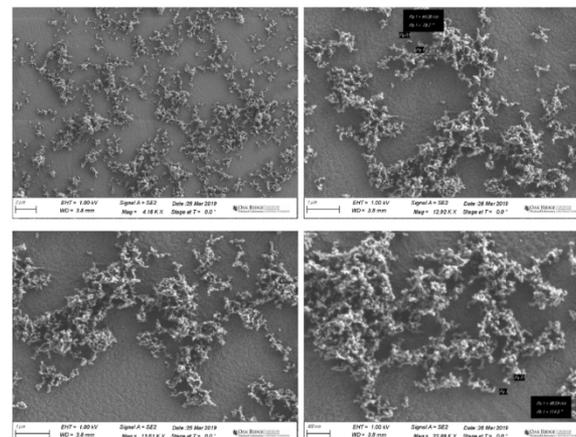


Vertical lines represent connected collaborative efforts between the 5 labs where materials and/or data are exchanged

Note: Chart truncated for illustrative purposes

Results and Accomplishments – Colloidal Chemistry and Slurry Processing

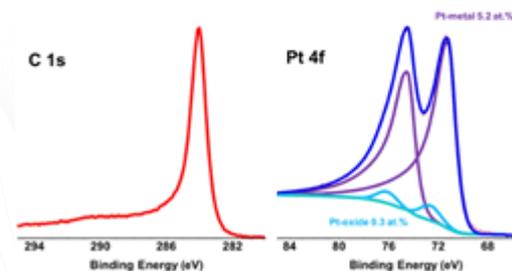
- Surface chemistry for Pt/C particles was assessed using EDS and XPS and the average carbon primary particle size was determined to be approximately 50 nm.
- Elemental analysis showed a uniform distribution of platinum on the surface of the carbon particles.
- Zeta potential measurements were performed on colloidal suspensions of Pt/C particles dispersed in water, isopropyl alcohol, and Nafion D2020. Zeta potential decreases when the isopropyl alcohol content is increased.



SEM images of the carbon particles coated with Pt catalyst; C primary particle size is approximately 50 nm

Surface Composition (at.%)

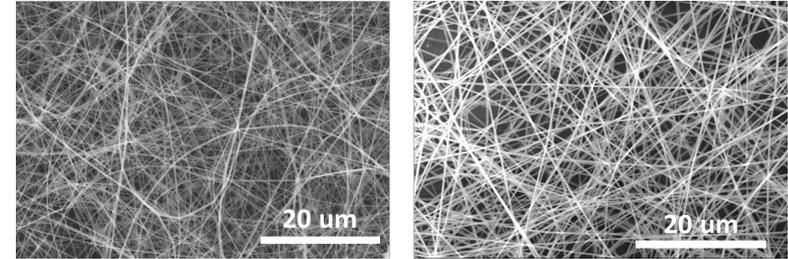
	C	O	Pt	N
C-Pt	87.8	6.7	5.5	trace



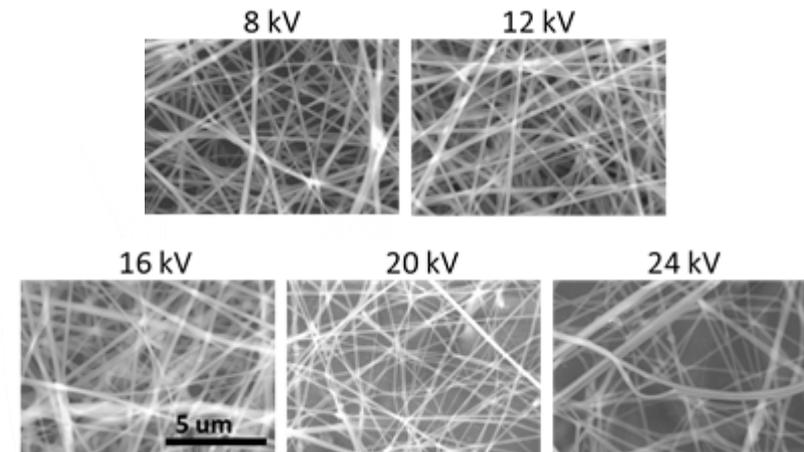
XPS core data analysis and the element at% on the surface of the particles

Results and Accomplishments – Electrospinning Recipe, Materials and Platform Development

- Demonstrated that water and acetic acid provided structurally-sound electrospinning (ES) nanofibers and organic solvents resulted in thicker fibers with the fiber diameter being dependent on the feed rate
- Conducted studies of various ES methods and steady-shear rheology for ES ionomer/catalyst slurries
- Developed optimum ES recipes and demonstrated LLZO and LSCF precursor nanofibers
- Developed sintering path to convert LLZO precursor nanofibers to ceramic nanofibers with desirable crystal structure
- Correlated agglomerate size changes of a catalyst to cell performance by combining the x-ray scattering data with TEM and in-situ electrochemical testing



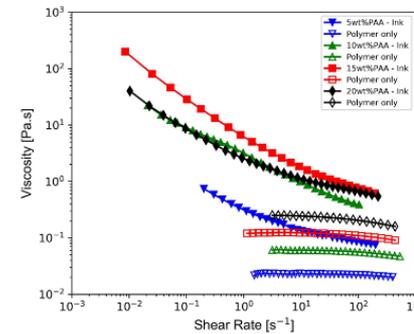
SEM images of as-spun polymer precursor nanofibers of LLZO (left) and LSCF (right)



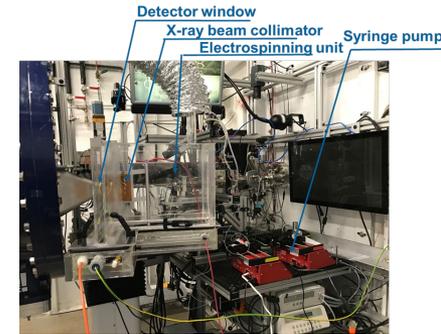
SEM images of the as-spun LLZO polymer precursor nanofibers that were synthesized under different voltages

Results and Accomplishments – Fabrication & In Situ Testing of Prototype Devices

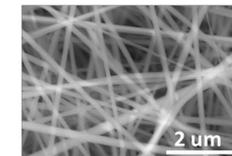
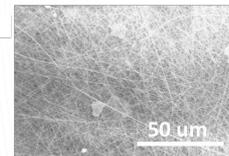
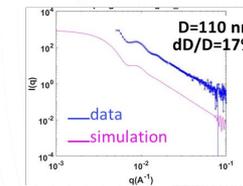
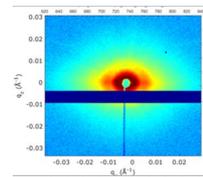
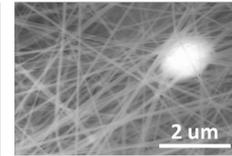
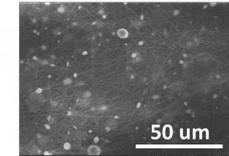
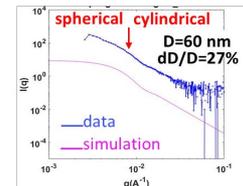
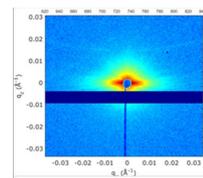
- Performed initial rheology studies of ES slurries using polyacrylic acid (PAA) as the carrier polymer demonstrating the ionomer/PAA slurries are all Newtonian across the range of PAA solids loadings and the ionomer/particle/PAA slurries are all shear-thinning
- Demonstrated SAXS to be capable of capturing electrospun nanofiber morphology features. The fiber diameters derived from SAXS data gave good consistency with SEM characterization.
- Demonstrated USAXS-SAXS-WAXS to be a powerful in-situ technique to study the dispersion of fuel cell catalyst inks



Steady-shear rheology of ionomer/PAA and ionomer/particle/PAA slurries



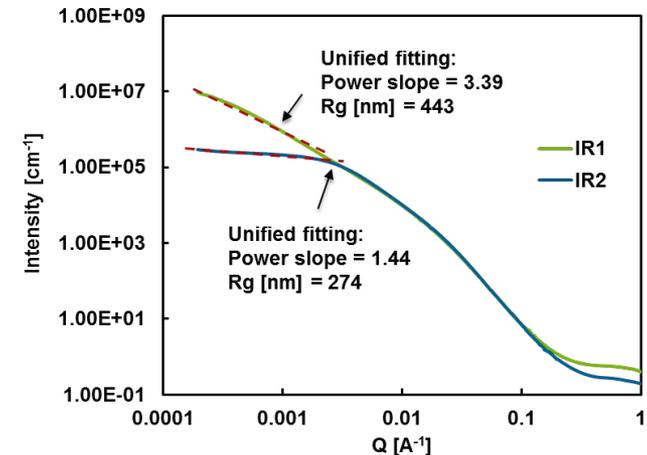
ES unit mounted at 12-ID-B beamline of APS for in-situ SAXS study of ES process



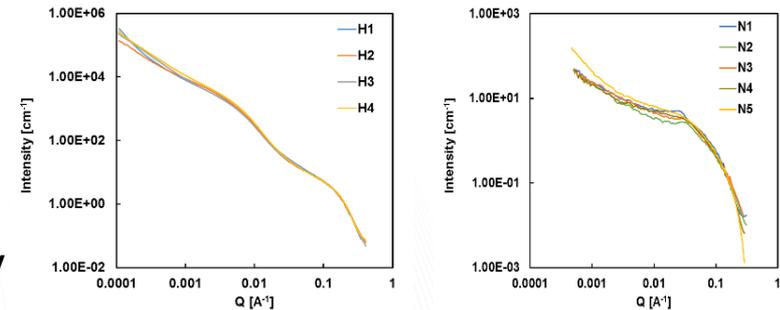
2D-SAXS data (left), intensity profile (middle), SEM images (right) of two LLZO nanofiber samples with different morphologies and diameters

Results and Accomplishments - Advanced Ink and Membrane Characterization

- Performed USAXS data on iridium oxohydroxide (IrO_x) catalyst-ionomer inks with different dispersion formulations and solvent compositions
- Demonstrated a lower population of agglomerates as the aggregates are uniformly distributed in the catalyst ink indicating a reduction in the agglomerate size with the addition of ionomer, which correlates with known rheological behavior showing that the unsupported catalyst ink is stabilized against agglomeration by ionomer
- Investigated ink formulations for the effect of solvent and ionomer on the structure-rheology correlation of Pt/Vulcan and Pt/HSC inks.



USAXS profiles and fitting results for IrO_x inks with and without ionomer



USAXS profiles of Pt/Vulcan or Pt/HSC ionomer inks using various solvent ratios and ionomer contents

Results and Accomplishments - Cutting-Edge Coating & Deposition Science

- Developed an empirical ink/coating model for multi-layer slide die coating
 - Conducted a process window analysis for a two-layer construction (i.e. membrane + one electrode)
 - Model predicts that the target total thickness is achievable
- Performed blade coating of single-layer membranes to understand the efficacy of coated ionomer layers with respect to membrane functionality (precursor study to multilayer coating)
 - Cast membrane thicknesses were within the intended range for several electrochemical applications
 - Conductivities were comparable to a commercially available comparator (Nafion)

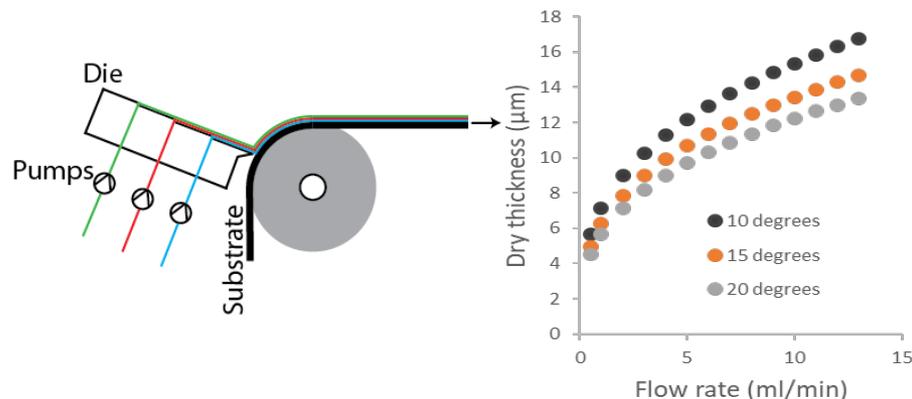
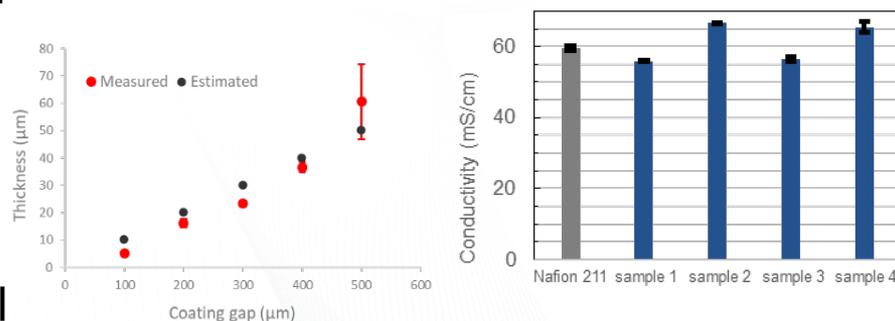


Diagram of a three-layer slide die flow (left) and results of empirical process window model for total dry thickness of a two-layer slide die coating as a function of flow rate (right)



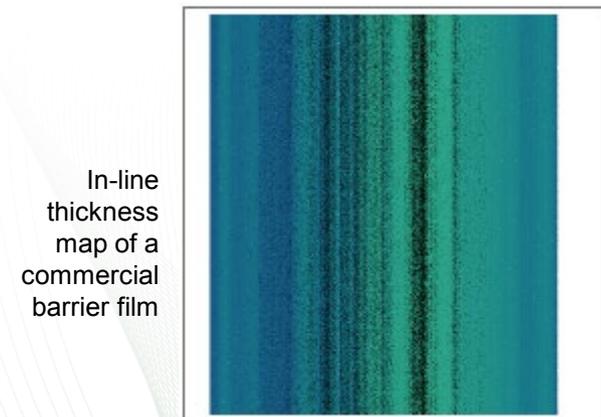
Cast membrane thickness as a function of coating gap (left) and proton conductivity of the cast membranes compared to a commercially available membrane (right)

Results and Accomplishments - Novel NDE, QC, and Metrology Methods

- Continued to study multi-spectral techniques for in-line real-time imaging of thickness of commercially available, proprietary, and experimental polymer films for various applications, including barrier films and energy conversion
 - Performed UV-Vis and near-IR fast spectroscopy (single-point) to establish feasibility of the method on a range of membrane materials and structures
 - One output is that membranes thicker than $\sim 50 \mu\text{m}$ (required for many applications) will require a higher wavelength range than our current imager
 - Performed thickness imaging in-line on a 100+ meter roll with several membrane materials



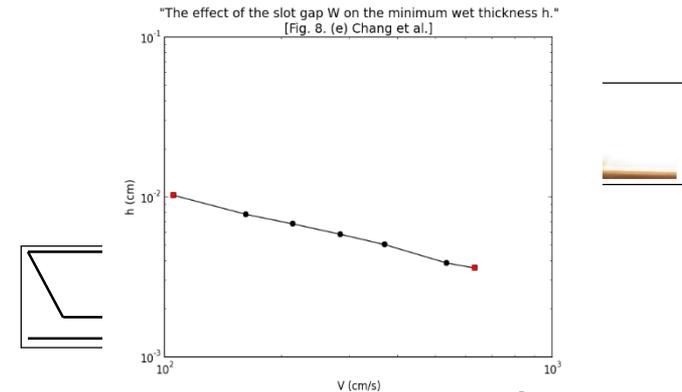
NREL metrology web-line with multi-spectral imager, multiple light source, and membrane web path (below) in a reflectance configuration for thickness imaging



In-line thickness map of a commercial barrier film

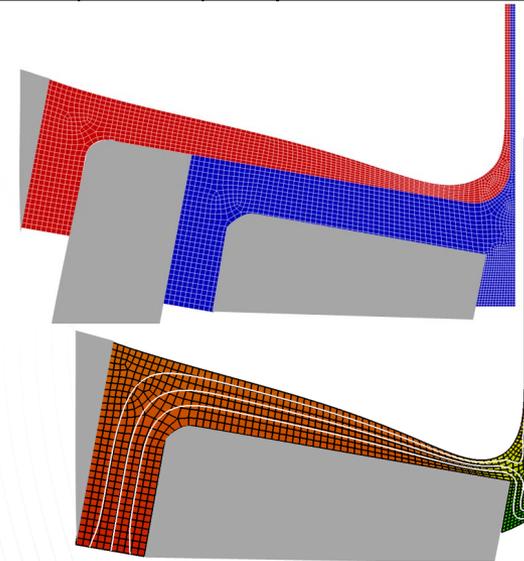
Results and Accomplishments – Model Development & Validation for Multilayer R2R Applications

- *Purpose:* Validated models and user-friendly workflows for multilayer slide- and slot-coating processes. Models will provide valuable design tool for ink-tuning/selection, process parameter space understanding, and process operating window prediction.
- *Results:* Completed initial single-layer slot-die model and workflow and single- and two-layer slide-die process models.
- *Next steps:* Guide ink-design work of NREL slide-coating exemplar with single layer model (rheologies, process parameters). Demonstrate/validate two-layer slot-die deposition model with ORNL coating trials. Begin work on multilayer drying models for dry/cure/oven process design



Chang et al. (2007)

Single-layer slot-die deposition model validation: Pattern of streamlines (lower left) and published flow visualization



Slide coating: two-layer and single-layer predicted pattern of flow and free surface shape

CRADA Projects

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ORNL Development Assistance Opportunity for Roll-to-Roll (R2R) Advanced Energy Materials Manufacturing

Solicitation Number: ORNL-R2RAMM-2017-02-02
Agency: Department of Energy
Office: Oak Ridge National Laboratory - UT Battelle LLC (DOE Contractor)
Location: Oak Ridge National Laboratory

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Special Notice
Feb 02, 2017
2:31 pm
- [Changes](#)
Feb 03, 2017
12:16 pm

Solicitation Number: ORNL-R2RAMM-2017-02-02
Notice Type: Special Notice

Synopsis:
Added: Feb 02, 2017 2:31 pm Modified: Feb 03, 2017 12:15 pm [Track](#)

[Changes](#)

Description

UT-Battelle, LLC, acting under its Prime Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy (DOE) for the management and operation of the Oak Ridge National Laboratory (ORNL), conducts research and development (R&D) in support of the DOE Advanced Manufacturing Office (AMO) and Fuel Cell Technologies Office (FCTO) in conjunction with its R2R Advanced Materials Manufacturing (AMM) Consortium partners Argonne National Laboratory (ANL), Lawrence Berkeley National Laboratory (LBNL), the National Renewable Energy Laboratory (NREL), and the Eastman Kodak Company. The AMO AMM Consortium's mission is to assist U.S. manufacturers in the areas of energy storage and conversion, flexible electronics and displays, energy efficiency, and water purification, and develop a robust associated domestic materials and components supply chain. Only projects that have a strong likelihood of creating jobs domestically, reducing air pollutants, petroleum use, and greenhouse gas (GHG) emissions, and boosting system and device energy efficiency are of interest. The selected projects will be conducted under joint Cooperative Research and Development Agreements (CRADAs) between ORNL, ANL, LBNL, NREL, and the industrial partners.

Projects shall focus on advanced materials and component development, synthesis and processing methods, and quality control and metrology in the specific areas of:

ALL FILES

- [Printable Notice of Opportunity](#)
Feb 02, 2017
[AMO-AMM CRADA-Solici...](#)
- [CRADA Template](#)
Feb 02, 2017
[Roll to roll consord...](#)
- [Roll to Roll Consortium Fast Sheet](#)
Feb 02, 2017
[R2R AMM DOE Lab Cons...](#)

GENERAL INFORMATION

Notice Type: Special Notice

Original Posted Date: February 2, 2017

Posted Date: February 3, 2017

Response Date: -

Original Response Date: -

Archiving Policy: Manual Archive

Original Archive Date: -

Archive Date: -

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

Achievement

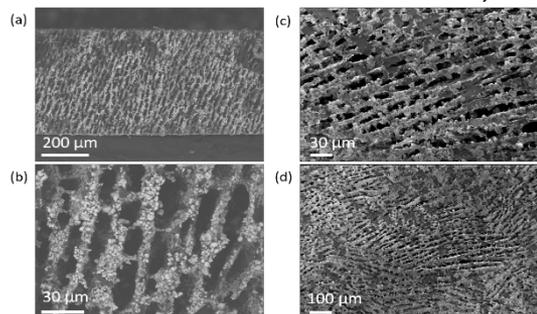
Within the framework of the AMO R2R AMM Collaboration, Fisker, Inc. has partnered with LBNL and ORNL to demonstrate all-solid-state batteries based on LLZO separators and cathode scaffolds, and scaled the freeze casting process to the pilot level at ORNL.

Significance and impact

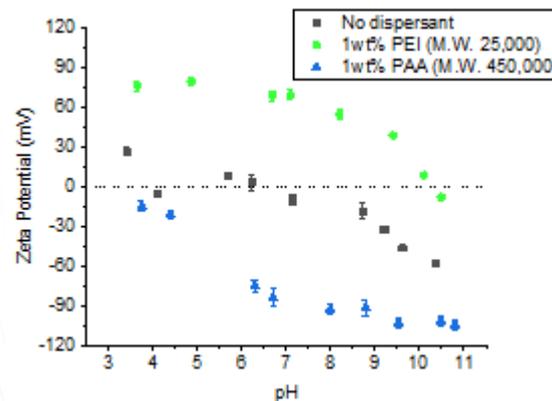
The freeze casting process will be used to enable the high-volume manufacturing of all-solid-state LIBs based on the LLZO electrolyte. These types of LIBs utilize ultra-high-energy-density Li metal anodes, low-cost solid electrolytes, and high-voltage composite cathodes. High-speed scaling of this methodology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

Details and next steps

- Fabricated small-scale slurries at LBNL and ORNL to produce freeze tape cast 2-3 inch porous layers.
- Assessed slurry stability visually and characterized the final pore structure via SEM.
- Measured the surface charge of LLZO particles with and without the presence of dispersants via zeta potential measurements.
- Sputter LiPON interlayers and Li metal anodes.



Freeze tape cast LLZO green tapes. (a),(b), fracture surface SEM images of green tapes produced at LBNL. (c),(d), surface SEM images of green tapes



Zeta potential of LLZO (from NEI) in the presence/absence of dispersants

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

Achievement

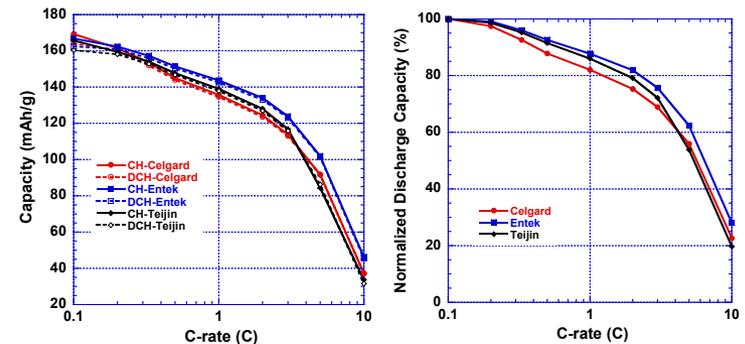
Within the framework of the AMO R2R AMM Collaboration, Navitas Systems, Inc. has partnered with ORNL and NREL to demonstrate R2R production of advanced separator for lithium ion batteries.

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. A 10% increase in electrified powertrains will reduce U.S. oil consumption by 3%, total U.S. energy use by 1%.

Details and next steps

- Completed rate performance testing of the two separators in full coin cells consisting of NMC622 and graphite.
- Prepared 3 formulations of slurries with a binder (PVDF-HFP, CMC, or a combination of the two) in a solvent (NMP, DI-H₂O or a mixture of the two) and dispersed a ceramic (Al₂O₃) in the binder solution. PVDF-HFP in NMP solvent had no significant agglomeration.
- Developed inks of suitable viscosity for spraying and NREL performed initial ink formulation with the ORNL recipe.
- Preparing for patterned spray coating of the separator substrate.



Rate performance comparison with three separators
a) capacity vs C-rate and b) normalized discharge capacity vs C-rate



Ceramic coating on separator with various binders

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 Collaboration, 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

- Selected the NREL metrology line as the system for integration of the R2R Multiplex Scribing Technology, obtained approval of the laser enclosure and begin building and aligning the scribing optics system.
- Optimized P1 scribing and initiated P2 scribing optimization and used R2R deposition to coat approximately six meters of material with several layers. Initial results confirmed the P1 scribes effective with complete removal of the conductive oxide layers.



Front of the laser safety enclosure built onto the NREL diagnostic roll-to-roll system

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

Achievement

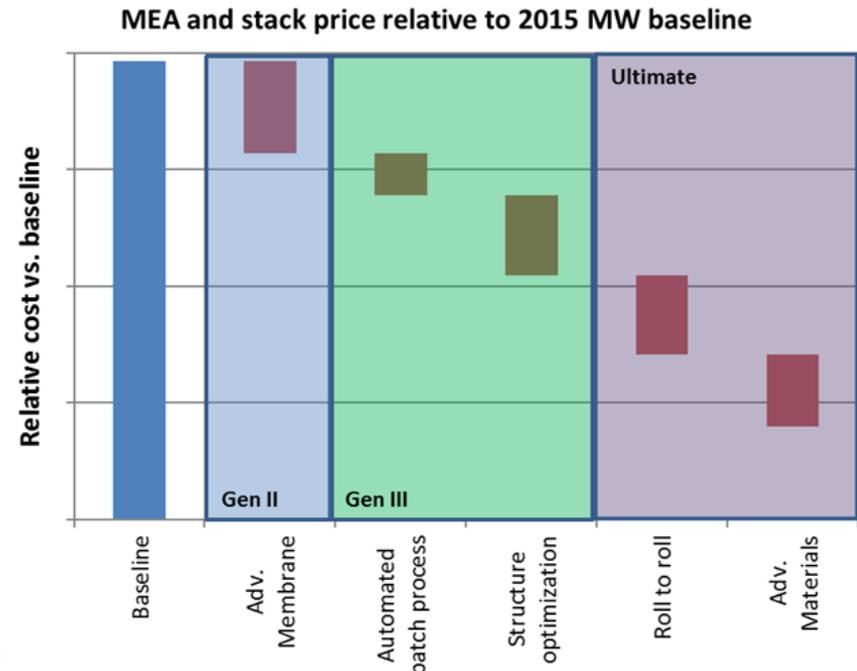
Within the framework of the AMO R2R AMM Consortium, Proton OnSite has partnered with NREL, ORNL, and ANL to research R2R manufacturing of advanced (low loading and directly coated onto membrane) electrolysis electrodes for low-cost hydrogen production.

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

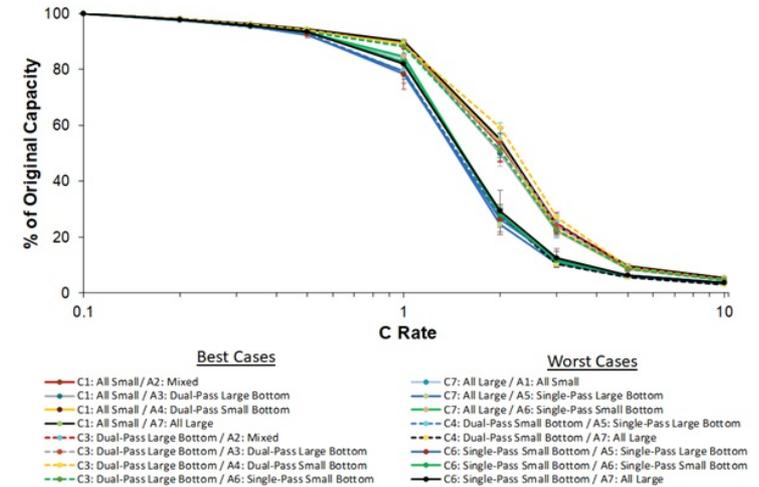
- CRADA to be approved and executed.



Proton MEA cost waterfall chart

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 industry partners, as requested, and in open publications for use by any companies with similar technologies.



Transition: Information dissemination (FY19)

- Batch and Continuous Methods for Evaluating the Physical and Thermal Properties of Films, Bhushan Lal Sopori, Michael Joseph Ulsh, Przemyslaw Rupnowski, Guido Bender, Michael Mihaylov Penev, Jianlin Li, David L Wood III, Claus Daniel, US Patent App. 15/554,551, 2018
- Park, J., N. Kariuki, D. J. Myers, S. A. Mauger, K. C. Neyerlin, and M. Ulsh, “In Situ X-Ray Scattering Characterization of PEMFC Catalyst Ink Microstructure during Ink Processing”, 233rd Electro Chemical Society Meeting, , MA2018-01 1794, 2018.
- Rupnowski, P., M. Ulsh, B. Sopori, B.G. Green, D.L. Wood III, J. Li, Y. Sheng. “In-line monitoring of Li-ion battery electrode porosity and areal loading using active thermal scanning – modeling and initial experiment.” *J. Power Sources*, 375, p.138-148, 2018.
- Zhange Feng, Pallab Barai, Jihyeon Gim, Ke Yuan, Yimin A. Wu, Yuanyuan Xie, Yuzi Liu, and Venkat Srinivasan, “In Situ Monitoring of the Growth of Nickel, Manganese, and Cobalt Hydroxide Precursors during Co-Precipitation Synthesis of Li-Ion Cathode Materials”. *Journal of The Electrochemical Society*, 165 (13) A3077-A3083 (2018)
- Daniel, Claus; Wood III, David; Krumdick, Gregory; Ulsh, Michael; Battaglia, Vince; Crowson, Fred “Roll-to-Roll Advanced Materials Manufacturing DOE Laboratory Collaboration - FY2018 Final Report”, ORNL/SPR-2019/1066, January 2019. DOI: 10.2172/1502542
- Barai, P.; Feng, Z.; Kondo, H.; Srinivasan, V. “Multiscale Computational Model for Particle Size Evolution during Coprecipitation of Li-Ion Battery Cathode Precursors, *J. Phys. Chem. B*, March 19, 2019, 123 (15), pp 3291–3303, DOI: 10.1021/acs.jpcc.8b12004
- S.A. Mauger, C.F. Cetinbas, J.H. Park, K.C. Neyerlin, R.K. Ahluwalia, D.J. Myers, S. Khandavalli, L. Hu, S. Litster, M. Ulsh, “Control of Ionomer Distribution and Porosity in Roll-to-Roll Coated Fuel Cell Catalyst Layers”, 2018 Fuel Cell GRC, 2018
- S.A. Mauger, C.F. Cetinbas, J.H. Park, K.C. Neyerlin, R.K. Ahluwalia, D.J. Myers, S. Khandavalli, L. Hu, S. Litster, M. Ulsh, “Control of Ionomer Distribution in Roll-to-Roll Coated Fuel Cell Catalyst Layers”, 19th International Coating Science and Technology Symposium, 2018.

For more details see our posters

- Tuesday poster session – 5-7 pm

21	Roll to Roll Manufacturing	AMM-R2R - Roll-to-Roll Manufacturing Science and Applications: From Ideal Materials to Real-World Devices	Gregory Krumdick
20		AMM-R2R - Roll-to-Roll Manufacturing Science and Applications: Accelerate R2R Materials Manufacture for Energy Storage and Generation	Mike Ulsh
6		AMM-R2R - Applied Materials Genome Initiative - From Ideal Materials to Real-World Devices	Vince Battaglia

Questions?

Acknowledgments

Sponsors

AMO: Valri Lightner, Isaac Chan, Brian Valentine, Bob Gemmer

FCTO: Sunita Satyapal, Nancy Garland, Shukhan Chan

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