AMM-R2R - Roll-to-Roll Manufacturing Science and Applications: Accelerate R2R Materials Manufacture for Energy Storage and Generation

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This presentation does not contain any proprietary, confidential, or otherwise restricted information.
1. Implement high-speed, low-cost R2R manufacturing methods for reaching ultimate lithium ion cell cost targets
2. Link electrode slurry processing parameters to cell performance
3. Develop optimized electrode architecture layering approaches common to many existing and emerging applications
4. Develop in-line metrology and non-destructive evaluation (NDE) for determining effect of coating defects on cell performance

- Combination of graded electrode lithium-ion battery architectures with novel processing, process modeling and novel in-line process modeling to solve known problem of thick electrode mass-transport limitations.
- Understanding the rheological properties of electrode slurries is highly desirable for optimizing and reducing the cost of lithium ion battery manufacturing and achieving bilayer/multilayer electrode architectures.
### Technical Approach

#### Pouch Cell Testing Matrix

<table>
<thead>
<tr>
<th><strong>Cathodes</strong></th>
<th><strong>Anodes</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode #1: All Small Particles</td>
<td>Anode #1: All Small Particles</td>
</tr>
<tr>
<td>Cathode #3: Dual-Pass: Large Bottom/Small Top</td>
<td>Anode #2: Mixed Particles</td>
</tr>
<tr>
<td>Cathode #3: Dual-Pass: Large Bottom/Small Top</td>
<td>Anode #3: Dual-Pass Large Bottom/Small Top</td>
</tr>
<tr>
<td>Cathode #3: Dual-Pass: Large Bottom/Small Top</td>
<td>Anode #4: Dual-Pass Small Bottom/Large Top</td>
</tr>
<tr>
<td>Cathode #3: Dual-Pass: Large Bottom/Small Top</td>
<td>Anode #5: Single-Pass: Large Bottom/Small Top</td>
</tr>
<tr>
<td>Cathode #3: Dual-Pass: Large Bottom/Small Top</td>
<td>Anode #6: Single-Pass Small Bottom/Large Top</td>
</tr>
<tr>
<td>Cathode #3: Dual-Pass: Large Bottom/Small Top</td>
<td>Anode #7: All Large Particles</td>
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</table>

- Fabricate and test all combinations of 2 cathodes and 6 anodes
Accomplishments and Progress: Dual-Pass Electrodes Generally Outperform Single-Pass (Dual Slot-Die)

- SEM cross-sections verified that electrode structures were similar for single-pass and dual-pass coatings.
- Two graded configurations outperformed the all-small-particle cathode baseline.
- All-large-particle cathode baseline was one of the worst performers.
- Generally good agreement between the rate capacity results and the cycle-life results.
Accomplishments and Progress
Excellent Capacity Retention Under Extended USABC Cycling at 0.33C/-0.33C Charge/Discharge Rates

Cycle Life Comparison (C/2 Discharge)

Specific Capacity (mAh/g)

Cycle No

C1: All Small / A7: All Large
C3: Dual-Pass Large Bottom / A7: All Large
C5: Single-Pass Large Bottom / A7: All Large
C7: All Large / A7: All Large
C7: All Large / A1: All Small
C7: All Large / A5: Single-Pass Large Bottom
C1: All Small / A4: Dual-Pass Small Bottom
C3: Dual-Pass Large Bottom / A2: Mixed
C2: Mixed / A7: All Large
C4: Dual-Pass Small Bottom / A7: All Large
C6: Single-Pass Small Bottom / A7: All Large
C1: All Small / A1: All Small
C3: Dual-Pass Large Bottom / A4: Dual-Pass Small Bottom
C1: All Small / A2: Mixed
C2: Mixed / A4: Dual-Pass Small Bottom
C4: Dual-Pass Small Bottom / A2: Mixed

4 mAh/cm²

C/2 Charge, C/2 Discharge
Accomplishments and Progress
Particle Size and Porosity Grading Both Make a Substantial Difference in Capacity Retention at 2C Discharge Rates (Accelerated Durability Testing)

- Best long-term performer was a mixed particle cathode with a dual-pass, small-particle bottom layer.
- Worst performer was the all-large particle cathode paired with a single-pass, large-particle bottom layer.
- Worse performance for single-pass (dual slot-die coating) cases is likely due to unoptimized drying protocol.
Fisker/LBNL/ORNL CRADA project: Freeze Tape Casting of LLZO Electrodes

- **Purpose:** Development of novel high-energy-density solid-state lithium batteries based on Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) electrolyte and high-capacity cathode active materials.

- **Technical Innovation:** Application of freeze tape casting to make thin dense LLZO electrolyte layers and vertically porous cathode scaffolds with LLZO.

- **Technical Approach**
  - Freeze tape casting of LLZO electrolyte bilayers
  - Novel freeze drying and sintering protocols to obtain LLZO cubic phase
  - Infiltration of cathode active material into LLZO scaffold pores
  - Evaluation of hybrid coin cells with liquid electrolyte added to cathode

- **Accomplishments and Progress**
  - Developed a novel formulation protocol for LLZO slurries
  - Successful freeze tape casting of LLZO bilayers
  - High ionic conductivity obtained after sintering to LLZO cubic phase
  - Successful assembly of hybrid coin cells and rate capability testing

- **Next steps**
  - Increase freeze tape casting coating length
  - Apply Li anode to LLZO/cathode bilayer via evaporation
  - Assemble full pouch cell and test for rate capability and cycle life

![Diagram of hybrid coin cell setup]
Navitas Systems/ORNL/NREL CRADA project: LIB Separator Coatings

- **Purpose:** Improve the stability and lifetime of LIB separators
- **Technical Innovation:** Explore ceramic separator coatings to improve properties
- **Technical Approach**
  - Identify ceramic materials to provide improved thermal and mechanical stability
  - Develop ceramic slurries and characterize properties
  - Perform uniform and patterned coatings
  - Test cells to understand improvements
- **Accomplishments and Progress**
  - Characterized slurries by TGA, SEM, XRD
  - Performed uniform coatings
  - Performed patterned spray coatings
- **Next steps**
  - Make interdigitated spray coatings
  - Test cells
  - Demonstrate R2R pattern-coating
Relevance

- R2R is the only manufacturing process platform that will meet cost and volume targets for MEAs.
- All DOE-sponsored cost analyses for high volume production of MEAs/cells assume R2R processing.
- Cost reduction need: 60 cents/mile in 2013 to 13 cents/mile in 2025.

Objective

- Develop single-step coating process for direct coating of electrodes.

<table>
<thead>
<tr>
<th>Task 1: Membrane Electrode Assemblies</th>
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<tbody>
<tr>
<td>1.2 Develop processes for direct coating of electrodes on membranes or gas diffusion media.</td>
</tr>
<tr>
<td>1.3 Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste.</td>
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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

Limitations 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

<table>
<thead>
<tr>
<th>Production Volume (sys/yr)</th>
<th>1000</th>
<th>10,000</th>
<th>20,000</th>
<th>50,000</th>
<th>100,000</th>
<th>500,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>m² active area/yr</td>
<td>7,470</td>
<td>74,702</td>
<td>149,404</td>
<td>373,511</td>
<td>747,022</td>
<td>3,735,111</td>
</tr>
<tr>
<td>Slot die coating process ($/m²) - Direct or Decal</td>
<td>$52.59</td>
<td>$9.14</td>
<td>$4.92</td>
<td>$4.00</td>
<td>$2.93</td>
<td>$1.30</td>
</tr>
<tr>
<td>Total Additional Cost for Decal Transfer ($/m²)</td>
<td>$9.19</td>
<td>$4.03</td>
<td>$3.63</td>
<td>$3.51</td>
<td>$2.26</td>
<td>$2.17</td>
</tr>
<tr>
<td>Total Cost of Catalyst Application with Decal Transfer ($/m²)</td>
<td>$61.77</td>
<td>$13.17</td>
<td>$8.55</td>
<td>$7.51</td>
<td>$5.19</td>
<td>$3.47</td>
</tr>
<tr>
<td>Additional Decal Transfer Cost (% of Coating Cost)</td>
<td>17%</td>
<td>44%</td>
<td>74%</td>
<td>88%</td>
<td>77%</td>
<td>167%</td>
</tr>
</tbody>
</table>

At high volumes, direct electrode coating would provide significant cost reduction for electrode production
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 direct-coated GDEs with comparable performance to CCMs

- 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 (liner + hot pressing process = 63% of process cost for decal-based CCM)
- However, it appears that an over-layer of ionomer is required for GDEs to achieve performance comparable to CCMs

Impact

- Developing a direct-coating pathway will enable faster, simpler, cheaper manufacturing of fuel cell electrodes

TEM of spray-coated GDE with ionomer over-layer (left);
Performance comparison between lab-scale spray-coated CCM baseline and GDEs with and without over-layer (right)
Technical Approach

- Through exploring a combination of ink formulation, cell materials, and processing, develop a method for fabricating high-performance GDEs

- Gas diffusion electrode studies
  - Gravure, slot die, and dual-slot coating (NREL, ORNL)
  - Coating consolidation modeling (LBNL)
  - XCT, Electron Microscopy, Kelvin Probe and XRF characterization (ANL, ORNL, NREL)

- Ink studies
  - Formulation, mixing and rheology (NREL, ORNL)
  - USAXS characterization (ANL)
  - Rheological modeling (LBNL)

- MEA fabrication and testing (NREL)
- QC development (NREL, ORNL)
Accomplishments and Progress Determined Function of Ionomer Overlayer

- **Function:** Ionomer overlayer AND hot pressing needed to adhere GDE and membrane and create good interface.
- Ionomer overlayer is thin: approx. 100-200 nm.
- Good interface needed for best performance.
Accomplishments and Progress Determined Influence of MPL Roughness

Stylus Profilometry

SGL 29BC - Rough

H23C8 - Smooth

MEA Cross-Section

EIS Modeling

Smoother MPL leads to:
• Less ionomer needed in overlayer
• Lower catalyst layer proton resistance \( (R_{CL}) \)
• Expected to be better for R2R GDEs
We achieved single-process (no extra ionomer over-layer) R2R manufacturing of GDEs with comparable performance to CCMs.

R2R Coated GDEs
Slot die (2019), Gravure (2018)
1 m/min x 9 cm
Cathode loading: 0.12 mgPt/cm²
Pt/HSC – Nafion (0.9 I/C)
Coating speed: 1 m/min

2018 vs 2019
• Switch to smooth MPL
• Switched from gravure to slot-die coating (see TA008)
• Reduced I:C (1.6 → 0.9)

Keys to High Performance R2R GDEs
• Water-rich catalyst ink
• GDL with smooth MPL
• Slot die coating vs ultrasonic spray
Many technologies (e.g. water filtration membranes, fuel cell and electrolyzers, photovoltaics, batteries, and barrier films) are multilayer constructions that are coated through a series of coating and drying steps.

Multilayer coating processes enable the co-deposition of multiple layers, reducing capital and process costs and increasing throughput.

Multilayer coating presents a challenge as the properties of each layer must be tuned relative to the adjacent layers to enable stable flows and coatings while simultaneously achieving the requisite thickness and functional properties.

Multilayer coating may also enable new device constructions or manufacturing pathways that are not currently accessible with sequential, single layer coatings.
Technical Approach – Ink Formulation

- Slide coating requires ink properties to be tuned to enable stable flows
- Many aspect of an ink can be adjusted to affect a specific property
- Design of Experiments (DOE) methods being used to determine correlations between ink formulation and properties and reduce number of experiments
- Future work will couple flow modeling with ink formulation and coating to validate models and produce high-quality coatings

**DOE Experimental Matrix**

**FFD**
- Full Factorial Design
- Design Points
- $N = p^k$
- $p \in N$
- Numbers of experiments

**BBD**
- Box-Behnken Design
- Tabulated design
- $p = 3$

27 cases (FFD) → 15 cases (BBD)

**Contour Plot of Catalyst Ink Density**

Technical Approach - Multilayer Slide Coating

- Technology developed by photographic film industry but there are few reports in technical literature and it has not been applied to DOE-funded technologies.
- The properties of each layer (density, viscosity, surface tension) must be tuned to prevent flow instabilities.
- Flow modeling provides guidance on stable flow regimes and can guide ink formulation.

Impact of Viscosity Ratios and Layer Thickness on Stability

Accomplishments and Progress
Ink Characterization (Zeta Potential)

- Nafion and 1-propanol are effective at stabilizing the surface charge of Pt/C particle dispersions.

<table>
<thead>
<tr>
<th>wt. fraction (D2020)</th>
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<tbody>
<tr>
<td>Nafion</td>
<td>0.2</td>
</tr>
<tr>
<td>1-propanol</td>
<td>0.46</td>
</tr>
<tr>
<td>Water</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Pt/C Particles in H₂O

Pt/C Particles in Nafion D2020 – KNO₃
Nafion D2020: 500× diluted
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 ~50 µm (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.